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Performance of structural materials for the DEMO divertor

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A mis padres

*When we look up at night and view the stars,
everything we see is shining
because of distant nuclear fusion*

Carl Sagan

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*Elena
Madrid, 2017*

Motivation of the work

The energy economy of the future is likely to be very different to that seen today, and probably our society and economic model as well. Nowadays, a large part of this energy is made available from power stations using combustible fuels. However, the limitation of these resources and the worldwide recognition that the production of greenhouse gas affects the human safety are the driving force of the change in the energy sources. Among the alternatives proposed, nuclear fusion offers an excellent opportunity to produce a significant amount of energy intrinsically safe while consuming a small amount of fuel and without contaminating emissions.

The viability of commercial fusion is still under assessment through the International Thermonuclear Experimental Reactor (ITER) whose construction is ongoing. The last step before building a real industrial reactor is called DEMO (Demonstration Power Plant), will be the prototype of the fusion reactor built in a power plant. The final design of DEMO will depend on the results obtained from the exploitation of ITER and other fusion experiments. However, it should be robust enough to withstand the operating environment for an acceptable minimum time without failure. Thus, the selection of materials that could resist these extreme operating conditions is a critical issue in the future of nuclear fusion.

Fusion plasma leads to heat fluxes to the plasma facing materials of 15-20 MW/m² in the divertor region. Hence, only tungsten presents appropriate resistance to ion and charge-exchange particle erosion in comparison with other materials. However, the mechanical properties of commercially available W are not yet adequate for structural purposes due to its intrinsic brittleness at relatively low temperatures, thus limiting the operating temperatures of the reactor. However, this temperature bound is incompatible with the actual design concept of the water-cooled divertor. It is based on a structure consisting of W armour joined to a CuCrZr alloy heat sink. But the thermal stresses generated at the interface (because of the mismatch of thermal expansion coefficient and elastic modulus between both elements, together with the loss of strength and creep of CuCrZr at temperatures above 300 °C) make it necessary the development of new materials.

While several solutions have been proposed for this target, none of them has fulfilled all the requirements. Therefore, the aim of this investigation is the analysis of the mechanical behaviour, microstructure, fractography as well as the thermal characterization of novel materials for the armour and heat sink of the DEMO divertor, based on the actual design of ITER. These materials include tungsten alloys and composites (W-Ti, W-TiC, and W-Ta) for the armour and Cu-based composites (WC-Cu, W-Cu and W-CuCrZr) for heat sink applications, and a special focus has been placed on the tensile and fracture properties of W-Cu composites. Where a novel methodology has been developed.

Abstract

One of the most critical issues to the development of nuclear fusion, as a viable and sustainable source of energy, is the design of structural materials that can withstand the harsh operating conditions inside the reactor.

These conditions are especially hostile for the components that line the vacuum vessel and are exposed directly to the plasma (PFM, Plasma Facing Materials) in the divertor. They should work in particularly extreme conditions (both mechanical, thermal and electrical) while subjected to high particle and neutron flux. Furthermore, the joint between these PFMs and the proposed cooling systems of the reactor is an issue that has not been solved yet. The difference between the coefficients of thermal expansion and conductivity of the materials under research: tungsten base alloys as PFM and copper or CuCrZr pipes through which the cooling fluid will circulate, make it necessary the development and characterization of novel materials.

Therefore, the scope of this thesis is to study the thermo-mechanical performance of novel tungsten-based alloys for future fusion reactors, for use both as PFM, in heat sinks (Heat Sink Materials) or as thermal barriers. The limited amount of available material (as they are in the laboratory stage), as well as the focus on simulating the operation conditions of pressure and temperature, made it essential to develop new techniques for mechanical characterization. Thus, it has been possible to examine the fracture behaviour of these materials, obtaining relevant variables such as the R-curve as a function of temperature. This is something entirely new due to the characteristics of the materials under study.

With the aim of improving the ductility of tungsten, for its use as PFM, several alloys have been studied (W 2 wt% Ti, W-1 wt% TiC, W 5 wt% TiC, W 5 wt% Ta and W 15 wt % Ta). These were produced by powder metallurgy and consolidated by hot isostatic pressing (HIP). The effect of the different alloying elements (Ti, TiC and Ta) and their percentage, as well as the processing parameters (grinding and milling time), were analysed through flexural and fracture tests in the temperature range between 25 °C and 1200 °C, both in air and under high vacuum atmospheres. Additionally, the micro-mechanisms of failure were identified by scanning electron microscopy. Thus, the processing parameters to achieve the optimal densification and microstructure were identified. However, despite of this, the results revealed brittle mechanical behaviour in almost the entire temperature range for the alloys, with no improvement in the ductile to brittle transition temperature, as compared to

pure tungsten. Metal matrix composites produced by melt infiltration of copper and CuCrZr in a porous preform of tungsten have also been characterized up to 800 °C temperature and under high vacuum, for their use as heat sinks.

In addition, it is worth highlighting the development and implementation of an experimental setup to perform tensile tests in this environment through digital image correlation. Accordingly, the mechanical and thermal properties (coefficients of thermal expansion and conductivity) of these materials have been obtained, and they are superior to those of the current commercial products. Furthermore, thermal properties can be tailored by controlling the porosity of the initial W preform, hence the composition of the final product.

In order to increase the operating temperature of the reactor, without compromising the joint between the PFM and the cooling system, it is necessary to develop materials that act as a thermal barrier. For this purpose, WC-Cu base cermets with different compositions (25, 50 and 75 vol% Cu) have also been studied. The mechanical and microstructural analysis was performed up to 800 °C, which is higher than the service temperature. The fracture surfaces of the test specimens revealed two predominant fracture mechanisms: (i) intragranular fracture by cleavage of WC grains; and ii) ductile rupture of the copper phase, whose effect on mechanical properties is more evident as its content in the cermet increases. Moreover, it has been shown that a small proportion of Cu in the cermet can considerably reduce the high difference between the thermal expansion coefficients of W and CuCrZr, used as PFM and cooling system, respectively, without significantly increasing its thermal conductivity. In the overall, a comprehensive characterization of the mechanical behaviour as a function of temperature of three groups of materials, with complementary tasks in the future fusion reactors ITER and DEMO, has been achieved. Furthermore, the understanding of fracture behaviour of tungsten-based materials has been broadened and improved. To achieve it, new characterization techniques and a novel methodology for obtaining the R-curve at high temperature, have been developed.

Resumen

Uno de los condicionamientos críticos para el desarrollo de la fusión nuclear como fuente viable y sostenible de energía es el diseño de materiales estructurales que puedan soportar las condiciones extremas de operación que tienen lugar en el interior de un reactor de fusión.

El problema de los materiales es especialmente complejo para los componentes de la vasija que interactúan directamente con el plasma (PFM, *Plasma Facing Materials*). Estos materiales tienen que trabajar en condiciones extremas (tanto mecánicas, térmicas como eléctricas) e incluso llegar a soportar el impacto directo del plasma. Del mismo modo, la unión entre estos PFM y los sistemas de refrigeración propuestos para el reactor es un tema que aún no ha sido resuelto. La diferencia entre los coeficientes de expansión térmica, así como la conductividad de los materiales en juego: aleaciones de base wolframio como PFM y tuberías de cobre o CuCrZr por las que circulará el fluido refrigerante, hacen necesario el desarrollo y la caracterización de nuevos materiales.

Por este motivo, el objetivo fundamental de esta tesis es estudiar el comportamiento mecánico de nuevas aleaciones de base wolframio para los futuros reactores de fusión, tanto para su aplicación como PFM, en disipadores de calor (Heat Sink Materials) o en barreras térmicas. La limitada cantidad de material disponible (ya que se encuentra en fase de desarrollo en laboratorio), así como el esfuerzo por simular las condiciones de presión y temperatura en operación de estos materiales, ha requerido el desarrollo de nuevas técnicas de caracterización mecánica. Gracias a ellas ha sido posible ahondar en el comportamiento a fractura de estos materiales, permitiendo obtener variables tan interesantes como la curva R en función de la temperatura, algo completamente novedoso dadas las características particulares de los materiales objeto de este estudio.

Con el objetivo de mejorar la ductilidad del wolframio, para su uso como PFM, se han estudiado diversas aleaciones (W-2Ti, W-1TiC, W-5TiC, W-5Ta y W-15Ta, todas las composiciones expresadas en porcentajes en masa) procesadas por ruta pulvimetalúrgica y consolidadas mediante prensado isostático en caliente (HIP, Hot Isostatic Pressing). El efecto de los distintos elementos, ya sean aleantes, como el Ti o el Ta, o fase reforzante cerámica dispersa, como el TiC, y su porcentaje, así como las condiciones de producción (tiempo de molienda y prensado), han sido analizados mediante ensayos de flexión y fractura en el intervalo de temperaturas entre 25 °C y 1200 °C, en aire y en alto vacío.

Adicionalmente, los micro-mecanismos de rotura fueron identificados mediante microscopía electrónica de barrido. Los resultados obtenidos permitieron determinar los parámetros óptimos de procesado, en términos de densificación y microestructura obtenida. Sin embargo, casi todas las aleaciones estudiadas mostraron un comportamiento mecánico frágil, en casi todo el intervalo de temperaturas, sin lograrse una optimización de la temperatura de transición dúctil-frágil, en comparación con el wolframio puro.

Por otro lado, también se han caracterizado, en atmósfera inerte hasta 800 °C de temperatura, materiales compuestos producidos mediante infiltración de cobre y CuCrZr en una preforma porosa de wolframio. El principal uso de estos materiales es como disipadores de calor.

Además, cabe destacar el desarrollo e implementación de un sistema experimental para realizar ensayos de tracción en este entorno mediante correlación digital de imágenes. Con él, ha sido posible determinar que las propiedades mecánicas y térmicas (coeficientes de conductividad y dilatación térmicos) de estos materiales son superiores a las de los productos comerciales actuales, pudiéndose optimizar estos parámetros mediante el control de la porosidad en la preforma inicial.

Con el fin de aumentar la temperatura de operación del reactor, sin comprometer la unión entre el PFM y el sistema de refrigeración, es necesario el desarrollo de materiales que actúen como barrera térmica. Es por ello que se han estudiado, además, cermetes de base WC-Cu con distintos porcentajes de cobre (25, 50 y 75 vol% Cu). El análisis mecánico y microestructural se ha realizado hasta 800 °C, temperatura superior a la prevista a alcanzar en servicio. Las superficies de fractura de las probetas ensayadas revelaron dos mecanismos de fractura predominantes: i) fractura intragranular por clivaje de los granos de WC; y ii) la ruptura dúctil de la fase de cobre, cuyo efecto en las propiedades mecánicas es más evidente conforme su contenido en el cermet aumenta. Es más, se ha demostrado que una pequeña proporción de Cu en el cermet puede reducir considerablemente la elevada diferencia entre los coeficientes de expansión térmica del W y del CuCrZr, usados como PFM y sistema de refrigeración, respectivamente, sin aumentar significativamente su conductividad térmica.

En definitiva, se ha conseguido una caracterización exhaustiva del comportamiento mecánico en función de la temperatura de tres grupos de materiales, con aplicaciones complementarias en los futuros reactores de fusión ITER y DEMO. Se ha ampliado y mejorado el conocimiento del comportamiento a fractura de materiales de base wolframio, para lo que ha sido necesario desarrollar nuevas técnicas de caracterización mecánica y una nueva metodología de obtención de la curva R en condiciones de alta temperatura.

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List of Acronyms

The following table describes the significance of various abbreviations and acronyms used throughout the document. Standard acronyms, such as chemical elements or compounds, are not in this list.

ASTM	American Society for Testing and Materials
BSE	Backscattered electrons
CFC	Carbon-fibre reinforced carbon
CTE	Coefficient of thermal expansion
CTOD	Crack tip opening displacement
D	Deuterium
DBTT	Ductile to brittle transition temperature
DENT	Double-edge notch tension test (fracture test configuration)
EDX	Energy dispersive X-ray spectroscopy
EEC	Equivalent Elastic Crack (elastic-plastic fracture model)
EUROFER 97	Reduced activation ferritic/martensitic steel, 9CrWVTa steel
FEA	Finite element analysis
FPB	Four-point bending (flexure test configuration)
FPZ	Fracture plastic zone
HHF	High heat flux
HIP	Hot isostatic pressing
HIP	Hot isostatic pressing
HTXRD	High temperature X-ray diffraction
ITER	International Thermonuclear Experimental Reactor
JET	Joint European Torus
LEFM	Linear Elastic Fracture Mechanics
LVDT	Linear variable differential transformer (displacement sensor)

LFA	Laser flash analysis
MA	Mechanical alloying
MMC	Metal matrix composite
ODS	Oxides dispersion strengthened
OFHC	Oxygen free high conductivity Cu
PFC	Plasma facing component
PFM	Plasma facing material
RAFM	Reduced activation ferritic martensitic steel
RFA	Resonant frequency analysis
RT	Room temperature
SE	Secondary electrons
SELNB	Single edge laser notched beam (fracture test configuration)
SEM	Scanning electron microscopy or microscope
SiC	Silicon carbide
SPD	Severe plastic deformation
T	Tritium
TB	Thermal Barrier
TBR	Tritium breeding ratio
TC	Thermal conductivity
TPB	Three point bending (flexure test configuration)
UFG	Ultrafine grained
WHA	Tungsten heavy alloys
XRD	X-ray diffraction

List of Symbols

a	crack length
a_0	initial crack length
A_0	original cross-sectional area in tensile testing
at. %	atomic weight fraction
B	width of prismatic samples for bending and tensile tests
d_{hkl}	interatomic space distance in the unit cell
E	elastic modulus
E'	generalized elastic modulus
E_{IET}	elastic modulus measured via impulse excitation technique
E_{th}	theoretical elastic modulus obtained via mixtures law
$f(Q), Q$	energy amplification factor in nuclear fusion technology
$f, vol. \%$	volume fraction
G	elastic strain energy release rate in fracture mechanics
$g(Q)$	reaction rate in nuclear fusion technology
G_c	critical fracture energy
H	hardness
K_I	mode-I stress intensity factor
K_{IC}	fracture toughness, Mode I stress intensity factor under plane strain
L, L_s	rollers spans in bending testing
l_0	original length in tensile testing
l_i	instantaneous length in tensile testing
M	bending moment for fracture bending tests
n	particle density in nuclear fusion technology
P	applied force in bending and tensile testing
P_{max}	maximum load for fracture bending tests
P_Q	critical load for fracture bending tests

P_s	“secant” load for fracture bending tests
r_p	second-order estimate of the fracture zone in fracture mechanics
r_y	first-order estimate of the fracture zone in fracture mechanics
s	dimensionless spread factor for the estimation of the coefficient of thermal expansion
T	temperature
W	thickness of prismatic samples for bending and tensile tests
$wt. \%$	weight fraction
$Y, F(a/W)$	geometrical factor in fracture mechanics

α , CTE	coefficient of thermal expansion
δ	deflection of the bending beam for bending testing
Δa_p	visually measured physical crack extension in fracture mechanics
Δa_s	inferred effective crack extension in fracture mechanics
ε	strain
ε_s	true strain in tensile testing
θ	diffraction angle in HTXRD
λ	wavelength of the X-ray incident beam in HTXRD
ν	Poisson’s ratio
ρ	density
ρ_{exp}	experimental density measured via Archimedes immersion principle
ρ_r	relative density
ρ_{th}	theoretical density
ρ_x	element’s density
σ	stress
σ_f	flexural strength
σ_s	true stress in tensile testing
σ_{YS}	yield strength
τ_E	energy confinement time in nuclear fusion technology

Chapter 1

Introduction

1.1. The need for nuclear fusion

The history of humankind has been, and is, conditioned by the use of energy. Furthermore, throughout our history as a species, the use of energy has conditioned our technological development, the current economic model and, ultimately, our social structure. But the energy economy of the future is likely to be very different to that seen today, and probably our society and economic model. While population is one of the key drivers of energy consumption, technology has become one of the primary drivers of economic and social development. Since most technologies run on electricity, its demand is increasing rapidly, faster than total primary energy supply (Council 2016).

A large part of this energy is made available from power stations using combustible fuels (such as natural gas, coal, and oil) which as of 2011 supplied 82 % of the world energy (see Fig. 1.1). For 2020, studies predict a 6 % drop in fossil fuels contribution (World Energy Council 2013). The limitation of these resources and the worldwide recognition that the production of greenhouse gas impacts on the human safety are the drivers of this change in the consumption of energy resources. Hence, in the long term, there will be only three alternative ways to supply energy: nuclear fission, renewables energies, and nuclear fusion, as it is unlikely that one of them will be sufficient on its own (Neu 2003).

1. Introduction

Fig. 1.1. Total Primary Energy Supply by resource 1993, 2011 and 2013 Source: WEC Survey of Energy Resources 1995, World Energy Resources 2013 and WEC World Energy Scenarios to 2050. Used by permission of the World Energy Council

In particular, the relative importance of renewable energy sources grew a 5 %, and more than 11 % in the case of the European Union where it grew between 2004 and 2014 from 13.5 % to 24.9 % (Eurostat 2016). These high growth rates are caused mainly by the continuous improvement in the conversion efficiency of PV cells, even achieving “grid parity” in many countries. Technology is continually improving, and new technologies such as Eolic energy, concentrating solar power or Perovskite3 cells are potential emerging technologies.

However, their cyclical nature, energy storage problems, both on a daily and seasonal time scale, are key factors in the integration of these technologies in the global electricity market. Furthermore, the energy that they produce is still more expensive than traditional fossil-fuel based technologies and are only currently economically viable due to policy and regulatory incentives, though some of them start to be competitive and others will get it soon.

Nuclear fission is the lowest-cost baseload electricity supply option in many markets since Uranium costs account for only about 5% of total generating costs, plant operators are protected against resource price volatility. But the nuclear fission has persistent fears associated with the safety of the reactors themselves, especially after the Fukushima Daiichi accident in March 2011. It resulted in a developmental break and a nuclear retreat in some countries. Thus, in December 2015, only China, Korea, India, and Russia accounted for forty of the sixty five reactors that the International Atomic Energy Agency recorded as under construction. Besides, there are also similar concerns over the storage and disposals of the high-level waste.

In contrast, nuclear fusion presents an excellent opportunity to produce a significant amount of energy intrinsically safe while consuming a small amount of fuel and avoiding

greenhouse gasses emissions. Furthermore, the fuels i.e. deuterium and lithium, are economical and abundantly available. And the only radioactive product (tritium) will be produced at the plant, limiting its transportation outside the facility, which will reduce the cost and hazards associated with fuel processing and handling (Ciampichetti et al. 2002). Further, the safety prospects of a fusion reactor are quite favourable due to the inherently self-limiting fusion process, the limited radiologic toxicity and the passive cooling property.

The technical viability of fusion is still under assessment through the International Thermonuclear Experimental Reactor (ITER) whose construction is ongoing. While ITER is being built, the conceptual design and engineering design of the first Demonstration power plant (DEMO) are current activities to be completed by 2030 (Cabal et al. 2017).

1.1.1. Fusion Basics

Nuclear fusion is the process where two light atomic nuclei gather to form one heavier and more stable nucleus, releasing energy. In that conversion, a tiny amount of mass is transformed into energy as quantified by Einstein's equation, $E=mc^2$.

This reaction happens naturally in the sun and most stars in the universe, however, producing power from fusion here on Earth is much more challenging than in the sun. There, the conditions necessary for fusion regarding temperature, density, and confinement time are maintained by gravity, but this solution is impossible to implement on Earth (Magaud et al. 2004).

Despite the many research works performed in the whole world since 1950's, no industrial application of fusion for energy production has been achieved, apart from nuclear weapon where the power of the reaction is not restrained.

- *Thermonuclear burn criteria*

The most accessible fusion reaction in the fusion reactors is that involving two isotopes of hydrogen: deuterium (D), with an "extra" neutron, and tritium (T), with two "extra" neutrons

In the D-T reaction, a deuterium and tritium atom combines, or fuses, to form an intermediate nucleus consisting of two protons and three neutrons. This nucleus splits immediately into a neutron of 14.4 MeV energy and an α -particle (a helium atom) of 3.5 MeV (Van Oost & Rebhan 2008).

Fig. 1.2. D-T nuclear fusion reaction and tritium breeding system primary reaction

To obtain this fusion reaction, a certain amount of energy is necessary to overcome the natural tendency of the two nuclei to repel each other. The probability of overcoming this barrier is quantified as the “cross section” of the reaction and represented in Fig. 1.3.

Fig. 1.3. Cross section of main fusion reactions (Magaud et al. 2004)

Although the most efficient reaction is the one between D and T, reactions between deuterium isotopes can also happen, thus the cross section is slightly lower. This reaction may have two results with 50 % probability:

Deuterium is abundant in seawater but tritium exists in only trace amounts, so it needs to be produced using nuclear reactions with lithium, which is also abundant in the earth's crust. This fusion reaction has the advantage that the fuel resources are virtually unlimited. However, for the self-ignition of the capsule, only the energy contained in the charged particles (D-T) is available (Pfalzner 2006)

Releasing fusion as an energy source requires not only the temperature to be sufficiently high, but other conditions must also be met. As a hot gas, plasma should be isolated or confined, and particle density should be high enough for the reaction to be energetically viable and maintained. This condition is known as ignition, and the requirements for it to happen were firstly formulated by Lawson in 1957, known as Lawson Criteria (Lawson 1957).

$$n \cdot \tau_E > g(T) \cdot f(Q) \quad (1.6)$$

According to it, for the fusion reaction to be energetically viable, the product of the energy confinement time (τ_E) and particle density (n) should be lower than the variation of the reaction rate with temperature, referred as $g(T)$ and the energy amplification factor, referred as $f(Q)$. This latter is the relation between the power generated and the external power coupled to it.

The “break-even” point is achieved when $Q = 1$, hence the power produces by the plasma is equal to the power supplied. In the D-T reaction, for a thermonuclear temperature of 10^8 K, the Lawson criterion is:

$$n \cdot \tau_E \approx 10^{20} \text{ (m}^{-3}\text{s)} \quad (1.7)$$

Two different approaches to achieve energy break-even are being pursued: small values of confinement time with high particle densities, or longer confinement times with moderate densities (Stacey 2012).

In the first approach, known as Inertial confinement, a pellet of D-T fuel is heated to thermonuclear temperatures and compressed to densities of 10^{27} - 10^{28} m^{-3} by pulsed energy

sources (e.g. laser beam or X-ray) for a short period (10-100 ns), with the aim of obtaining the highest number of fusion reactions before the plasma disperses.

The United States of America (USA) is arguably the world leader in the inertial confinement approach to fusion. In early 2014, the US National Ignition Facility achieved fusion fuel gains exceeding unity using a “high-foot” implosion method, which is a manipulation of the laser pulse shape to reduce hydrodynamic instability in the implosion (Hurricane et al. 2014).

The second approach is based on the fact that plasma can be confined by applying a suitable magnetic field. Submerged in it, charged particles follow helical orbits winding around field lines and forced to move along the field. Particle movement perpendicular to the field lines is restricted while the particle moves freely in the longitudinal direction, to avoid the escape of the plasma at the extremities of it, the magnetic fields have a ring-shape or toric topology. Densities of 10^{20} - 10^{22} m⁻³ are achieved during 10^{-1} - 10^1 s while heated to thermonuclear temperatures by external sources.

Despite the recent advances in inertial confinement, magnetic fusion is the most advanced concept for energy-generating fusion reactors, since near break-even was firstly achieved in 1990 in the Joint European Torus (JET) reactor. Moreover, European fusion research is focused on this technology.

1.1.2. Magnetic plasma confinement and the tokamak

Many conceptual schemes for achieving magnetic confinement have been proposed. However, research is concentrated on two types of machines, the tokamak, and the stellarator. The tokamak is the only device that has produced significant fusion, on JET and the Tokamak Fusion Test Reactor (TFTR) in the US (Smith & Cowley 2010).

The difference among the reactors lies in the method implemented to generate the second magnetic field. This additional field, known as “poloidal” field in contrast to the primary toric or “toroidal” field, is necessary to avoid the split of the plasma produced by the centrifugal force and the lack of homogeneity of the field in the torus.

In a tokamak, this field is produced as a result of an axial current circulating in the plasma itself. This poloidal magnetic field adds a vertical component to the magnetic field, which has the effect of giving the magnetic field throughout the vessel a twist.

The stellarator is also based on a torus-shaped vessel but relies entirely on external coils to generate the helically shaped magnetic field required to contain the plasma. This configuration is lagging behind the development of the tokamak configuration due to its complexity. However, it does feature a significant advantage, since there is no need for a plasma current, it can be suitable for continuous operation, whereas tokamaks, without auxiliary facilities, can only work in pulsed mode (EUROfusion Consortium n.d.).

The progress of fusion research in achieving breakeven point ($Q = 1$) through the years is shown in Fig. 1.4, measured by the triple product of the Lawson criteria ($n \cdot \tau_E$ vs temperature) as an indication of the performance of a fusion plasma. It indicates the

substantial progress towards power station conditions that have been achieved in recent decades.

The advances achieved in JET, in terms of optimizing plasma stability and confinement, led to the design of the next step tokamak device, ITER. It will be capable of producing 500 MW of fusion power ($Q=10$). In comparison, in 1997 JET produced 16 MW of fusion power from a total input power of 24 MW ($Q=0.67$), that is $\sim 70\%$ of the energy needed to heat the plasma. The mission of ITER is intricate and detailed, but it can be summarized in the following goals (IAEA 2001):

- Achieve extended reaction in inductively-driven D-T plasma operation with $Q \geq 10$, not precluding ignition, with an inductive burn duration between 300 and 500 s
- Demonstrate steady state operation using the non-inductive current drive with $Q \geq 5$
- Confirm availability and integration of essential fusion technologies
- Test components for a future reactor
- Test tritium breeding module concepts; with a 14 MeV-neutron power load on the first wall $\geq 0.5 \text{ MW/m}^2$ and fluence $\geq 0.3 \text{ Mwa/m}^2$

Fig. 1.4. Triple product achieved on different fusion facilities plotted against the centre plasma temperature for the last three decades. The solid symbols correspond to experiments with deuterium plasmas and the open symbols to plasmas of a mixture of deuterium and tritium. The temperature one keV is equivalent to 11 Mio. K., Please note the logarithmic scale on the vertical axis (Mlynář 2007)¹

ITER operation will evolve through several stages. First, a period of hydrogen and helium operation will be used to commission all tokamak and auxiliary systems by the end of 2025 (ITER Organization 2016). It will be followed by a short period of deuterium operation to get closer to thermonuclear conditions and to phase gradually into full D-T operation in

¹ Public use release on p. 207 of (Mlynář 2007).

1. Introduction

2035, which will then provide access to significant levels of fusion power and α -particle heating (Campbell 2016)

The last step before building a real industrial reactor is called DEMO and would be the prototype of the fusion reactor built in a power plant. The final design of DEMO will depend to a large extent on the results obtained from the exploitation of ITER and other fusion experiments. This research relates to materials addressed for the DEMO reactor and beyond, as the total service time in ITER will be short enough for conventional materials to be used.

1.2. The fusion reactor

The conceptual layout of a tokamak fusion power station can be observed in Fig. 1.5. Fusion power plants will be similar to existing thermal power stations, but with a different furnace and fuel.

Fig. 1.5. Cutaway view of a tokamak fusion reactor: (A) vacuum chamber; (B) plasma reaction; (C) plasma radiation; (D) blanket; (E) electricity production (Magaud, Marbach, and Cook 2004)

In summary, the reactor core is arranged in different layers like an onion: the vacuum chamber encloses the space where the plasma is reacting, surrounded by the first wall, i.e. the first element encountered by the plasma heat load, and the blanket. The first wall, blanket, and vacuum chamber are cooled down by a heat extraction system. The heat is used to generate steam that supplies a conventional turbine and alternator electricity generating system. Outside the vacuum chamber, the coils for the magnetic field are located and, as the magnets are superconductors and operate at very low temperatures, the whole core is inside a cryostat (Hamacher & Bradshaw 2001).

During the D-T operation phase, the D-T fuel will be injected at the bottom of the vacuum chamber in the form of a frozen pellet so that it penetrates deeply into the centre. Once

inside, it is heated and magnetically confined to produce the plasma with a volume of approximately 2000 m³. This D-T fusion reaction releases neutrons at high energy and α -particles (helium nuclei).

The hot plasma is thermally insulated from the material surroundings by magnetic confinement, known as plasma facing materials (PFMs). However, as neutrons are unaffected by this confinement, the kinetic energy (~80 % of the total energy for a D-T plasma) produced by their impact on the walls will generate the heat. The heat is then removed by flowing coolant fluids in the heat sink which in turn provide conventional electrical energy. A small fraction is used to supply electricity to the various components in the plant itself. Electrical power is required mainly for the plasma heating systems and the cryo-system which produce low-temperature helium for the superconducting magnets, the current in the magnets and the current drive.

The majority of the plasma-facing surface (620 m²) will be situated in the blanket system (Fig. 1.5E). This component will define the plasma boundaries providing a plasma facing surface compatible with the performance requirements (heat loads and impurity influx). Besides, as the neutrons produced during the D-T reaction will be mostly absorbed by its walls, it will provide shielding to the following external components (e.g., vacuum chamber and magnetic system), thus releasing heat for electricity production and the tritium breeding system. This system will contain lithium in the walls in a solid (ceramic) or a liquid form (metallic alloy), depending on the blanket design implemented. Lithium presence in these walls causes reactions ((1.4)(1.3)) and ((1.5)). Though most of the tritium is produced by the reaction with ⁶Li (Eq. (1.4)). With the presence of beryllium as a multiplier² Of the reaction, the fusion reactor would virtually produce unlimited tritium for its own use, plus a small surplus to start up new plants. For radioactive reasons, the tritium inventory should be kept low, so it should be removed from the blanket regularly.

Whereas the neutrons easily penetrate the walls, the α -particles are confined by the magnetic field. As they collide with the D-T plasma, the heat produced (~700 MW) sustains the plasma temperature against leakage of energy. However, the excess of helium "ash," should be exhausted from the plasma to maintain the concentration and to avoid the losses though radiation associated with it. The *divertor* is the device designed for it.

1.2.1. The ITER divertor

Situated at the bottom of the vacuum vessel, the primary function of the divertor is to extract the power coming from the plasma via conduction, convection, and radiation while maintaining the plasma purity.

² Note that D-T reaction (1.1) produces only one neutron and the reaction (1.4) between this neutron and lithium releases only one atom of tritium, hence the tritium breeding ratio (TBR) would be 1. Since neutron losses are inevitable (due to absorption in structural materials, geometric losses through divertor and diagnosis voids in the blanket), endothermic reactions with Pb or preferably Be are suited for neutron multiplication in the blanket (TPB>1) (Maki 1988)

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Fig. 1.6. ITER divertor design. Retrieved January 2017, from <https://www.iter.org/mach/Divertor>

The ITER divertor itself consists of an assembly of fifty for cassettes (Fig. 1.6). Each divertor cassette has a supporting stainless steel structure that holds three plasma facing components (PFCs), namely the inner and outer targets and the dome. The cassette assemblies also host numerous diagnostic components for plasma control and physics evaluation and optimization (Janeschitz et al. 1995).

Fig. 1.7. Design of the components of the ITER divertor targets: (a) W monoblocks with CuCrZr coolant channel for inner and outer vertical targets; (b) Flat tile design with hypervapotron cooling channel for the dome (Hirai et al. 2016)

The inner and outer vertical targets are positioned at the intersection of magnetic field lines where heat fluxes are estimated at 10 MWm^{-2} in steady state and 20 MWm^{-2} during slow transients. As the high-energy plasma particles strike the vertical targets, their kinetic energy is transformed into heat, and the heat is removed by active cooling. The inner and outer vertical targets consist of monoblocks with swirl tape in the coolant channel (Fig. 1.7a), whereas, the dome consist of flat tiles with hypervapotron cooling circuit as it is

exposed to lower heat fluxes (Fig. 1.7b). The divertor plates will have (due to erosion) a limited lifetime and will occasionally be exchanged. A too large replacing frequency would impair however also the availability of the plant (Samm 2006).

In the reference ITER divertor design, carbon-based materials (carbon fibre reinforced carbon, CFC) were selected for the HHF regions of the lower part of the vertical targets throughout the non-active (H and He) phases of plasma operation (Pitts et al. 2009). Since recent research in a plasma environment, like that expected for ITER, suggests that first wall will be subjected to erosion. The eroded carbon would eventually redeposit in the form of amorphous hydrocarbon films with high fractions of tritium. Thus leading to a rapid build-up of a high tritium inventory (Hirai et al. 2010), this divertor should be switched to a full tungsten (W) armoured design before the start of the D-D and D-T operations, namely after just 3–4 years of service.

To reduce the costs and guarantee the survival of it during the nuclear phase, ITER Organization proposed to start reactor operations with full W divertor (Hirai et al. 2013), incorporating it to the baseline at the end of 2013 (Hirai et al. 2015).

The HHF test requirements for this W divertor were defined to be 5000 cycles at 10 MW/m² and three hundred cycles at 20 MW/m² for the small-scale mock-ups and straight part of full-scale prototype PFCs (Pitts et al. 2009). Furthermore, the plasma facing material (PFM) requires high thermal conductivity, excellent thermal shock resistance, low activation, low erosion by plasma particles and good connection with the heat sink material for active cooling (Zinkle & Busby 2009).

Fig. 1.8. Elements of the outer vertical target shaping design of ITER divertor. Monoblock design. (Pitts et al. 2013)

1. Introduction

This heat sink material will be made of a Cu alloy (CuCrZr) with an integrated high-pressure coolant tube to remove the heat efficiently. Different design options for the attachment of the PFM to the heat sink have been developed, manufactured and tested (Scheerer et al. 2001). For the inner and vertical targets, the reference design for the PFCs of the divertor is the monoblock (Fig. 1.7a and Fig. 1.8). As compared to the flat tile concept it was shown to have higher defect tolerances and better thermal fatigue behaviour even after neutron irradiations (Schlosser et al. 2005). What is more, the joint between the heat sink and the PFM can be reliably tested through non-destructive testing via ultrasonic technique (Visca et al. 2011). Nonetheless, flat tile design will be kept for the dome (Pitts et al. 2013).

Chapter 2

The next step: DEMO

2.1. Introduction

In comparison to the ITER design ($Q=10$), the requirements of electricity generation and tritium self-sufficiency in DEMO and beyond lead to significant challenges in the selection of the materials. DEMO will have significantly higher values of fusion power, plasma density, temperature across the whole profile, fuelling rate and core radiation fraction (Wenninger et al. 2015). One of the biggest problems in this context is the real lack of capability to reliably predict the behaviour of the divertor of future devices since it will be subjected to a unique environment where the knowledge of its true performance is still uncertain.

At present, the European DEMO reactor design has not been formally selected, and the detailed operational requirements are not yet available. (Federici et al. 2014). However, the different model's proposed cluster around a vessel radius of around 7.5 m and fusion power of almost 1 MW (2-3 MW theoretical), determined by the energy confinement and divertor protection. And by internal electrical power needed to run the plant (He pumping, current drive systems), respectively (Zohm 2014). In comparison, ITER's "R" measures 6.2 m and that of the largest tokamak in operation, JET, measures half that, and the fusion power of ITER will be 0.5 MW.

In addition, the following technological challenges have been identified:

- The diagnosis and control technologies of DEMO should have highest availability, reliability, and efficiency.
- Tritium self-sufficiency should be guaranteed, thus DEMO is no longer an experiment, and the industry should be involved in it.
- Materials will have to cope with a tougher environment (i.e. much higher fluencies and neutron damage) for a longer lifetime.

2.2. Materials issues for the DEMO Divertor: status and needs

Both the blanket system and the divertor are among the most challenging components of the machine. Indeed, they will cover an area of about 830 m² in ITER and even larger in DEMO. As the first wall, they will be subjected to high heat fluxes (HHF) of plasma particles and electromagnetic radiation. Furthermore, there are other conflicting project requirements such as shielding, assembly, remote handling and integration with other in-vessel components that have to be solved (Merola et al. 2014).

Since they should resist this harsh reactor environment during several years of operation, materials selection and design of plasma-facing components (PFCs) remain significant challenges in the safe and reliable operation of the nuclear reactors. For ITER, as exposed previously, both components went through its final design review in 2013 and the primary materials selected are the following (Barabash 2013):

- Beryllium and Tungsten (W) for the PFCs of the blanket and divertor, respectively.
- Precipitation hardened copper alloy CuCrZr as heat sink material
- EUROFER 97, reduced activation ferritic/martensitic steel, 9CrWVTa alloy, as structural materials for the blanket module

In the case of the structural materials for the blanket, the main issues are related to the structural stability at high temperature and under 14 MeV neutron bombardment, since selected EUROFER steel can withstand these conditions only up to 550 °C due to its ductile-brittle transition temperature (DBTT). Research is now focused on vanadium alloys (V-Cr-Ti system) for high-temperature operation in combination with a liquid lithium breeder system) and SiC/SiC composites (Giancarli et al. 2012). However, reduced activated ferritic/martensitic (RAFM) steels are the furthest developed technology due to their superior embrittlement properties around 300 °C (Gorley 2015). Hence RAFM steels are, up to his date, the baseline materials for structural purposes.

For this reason, the components of the divertor, which are of interest to this study, are armour targets and the heat sink. The object of this study is to determine the performance of different materials for these applications.

2.2.1. Plasma facing materials

Careful selection of the materials for the first wall minimizes radioactivity induced by neutron activation. To reduce the radioactive waste footprint from fusion, materials in the core reactor should meet the criteria of low activation, i.e. all materials used in the reactor should be suitable for recycling or disposal in non-active landfills one hundred years after removal from the reactor (El-Guebaly et al. 2007). In this regard, engineering materials are limited to C, Si, Fe, Mn, V, Cr, W, Be and Ta. Of these, beryllium will cover the major part of the blanket plasma-facing wall in ITER, but it will not be a suitable option for an economical fusion reactor concept. The radioactivity of these elements after exposure to neutron irradiation can be observed in Fig. 2.1 as a function of the time.

Fig. 2.1. Radioactivity of low/reduced activation elements versus time after exposure to a neutron irradiation dose of 20 MW/m², outboard first wall (Zinkle 2013)

Considering low activation criteria and the requisites of a relatively high fracture toughness ($>30 \text{ MPa m}^{1/2}$) with low creep strength ($>150 \text{ MPa}$, $\sim 1\%$ in 1000 hours) and chemical compatibility among them, only the following compounds come into question:

- Reduced activation ferritic/martensitic steels
- Oxide dispersion strengthened steels
- Refractory metals and alloys
- Vanadium alloys
- SiC/SiC ceramic composites

The temperature window of these materials for first wall applications (RT-800 °C or 300-1100 °C depending on the heat sink design) can be observed in Fig. 2.2.

2. The next step: DEMO

Fig. 2.2. Temperature window of the low activation materials proposed for first wall applications. Data retrieved from (Baluc n.d.)

Among the remaining options, tungsten is uniquely suitable for the armour due to its high melting point (3410 °C), high threshold energy for sputtering (around 100-200 eV for H isotopes) and retention of tritium, and relatively high thermal conductivity at room temperature (174 Wm⁻¹K⁻¹). For these reasons, it is the baseline material for the state-of-the-art plasma-facing component technology (D. Stork et al. 2014)

However, several risks are associated with the use of tungsten. Tungsten has a body-centred cubic (BCC) crystal structure so there are few slip planes and a propensity for brittle fracture as its DBTT is around 400 °C, even in an unirradiated state. As a structural material, both the DBTT and the fracture toughness are key issues. The fracture toughness of polycrystalline tungsten at room temperature is quite low, in the region of 10 MPa m^{1/2}. To serve as a comparison, copper alloys for the use in the ITER blanket can have fracture toughness reaching 168 MPa m^{1/2} (Alenxander et al. n.d.). In addition, W shows a strong tendency to recrystallization at temperatures well below its melting point (Palacios et al. 2015). Furthermore, it has been reported that crack formation and recrystallization can occur in a W monoblock due to the cyclic heat load relevant to ITER (Budaev et al. 2015), these cracks can result in the brittle destruction which is a hazard for the full tungsten divertor. As a result, the temperature window of W is between 500 °C and 1200 °C, for radiation embrittlement and recrystallization respectively.

Another drawback of tungsten is its strong reactivity in air (Cifuentes et al. 2012), potential oxidation/deflagration could occur in a loss of coolant accident with simultaneous air ingress into the vacuum vessel. This accident would involve temperatures of the components above 1000 °C because of the decay heat. To mitigate the risk, self-passivating tungsten alloys have been developed in the last years, and considerable progress has been made in this regard with W–Cr–Y alloys (Calvo et al. 2016).

In DEMO, neutron irradiation will be more critical for materials than in ITER. Radiation generates lattice defects and He bubble production by transmutation in the PFM leading to embrittlement and reduced thermal conductivity. Moreover, there is an actual lack of radiation embrittlement data for tungsten due to the absence of an irradiation facility with a fusion-relevant neutron spectrum (Linke 2008).

There are as well limits related to the heat flux density of the first wall together with the thermal and mechanical performance limits of available structural materials. These limits are estimated to be 1.5 MWm^{-2} for water cooling concept and 1.0 MWm^{-2} for He cooling. A critical parameter to this issue is the coolant exit temperature, which is chosen considerably higher in DEMO (compared to ITER) to allow efficient power generation and to exceed the elevated ductile to brittle transition temperature for the intended materials (Wenninger et al. 2015). Nevertheless, in general, water-cooled systems can reach much higher heat transfer values than gas-cooled systems. Hence the baseline of the near-term concept DEMO is the water-cooled design, as the He concepts are at a much lower level of development (Derek Stork et al. 2014).

Considering these shortcomings, further enhancements of the properties of W are essential before its commercial use.

2.2.2. Heat sink materials

There is such an extensive list of materials requirement for DEMO heat sink. However, a thermal conductivity of at least $50 \text{ W.m}^{-1}\text{K}^{-1}$ combined with acceptable mechanical properties are the key parameters for the selection of these materials, considering that the heat sink should assume as well structural functions (J. H. You 2015). However, this choice will depend primarily on the divertor concept design, helium cooled or water-cooled.

Ag 429	Cu 401	Au 317	Al 237	Be 201	Ca 201	W 174	Mg 156	Rh 150	Si 149		Melting point <500 °C
Ir 147	Na 141	Mo 138	C 129	Ru 117	Zn 116	K 102	Co 100	Cd 97	Cr 94		Activation/H solubility
Ni 91	Os 88	Li 85	In 82	Fe 80	Pd 72	Pt 72	Sn 67	Ge 60	Rb 58		Availability/Cost
Ta 58	Th 54	Nb 54	Tc 51	As 50							Strength
											Ductility
											Water corrosion

Fig. 2.3. Elements with a thermal conductivity higher than $50 \text{ Wm}^{-1}\text{K}^{-1}$, values of thermal conductivity are given in each box. The legend on the right indicates not satisfied criteria. Data retrieved from (J.-H. You 2015)

Ideally, only Cu, Fe and Ta can fulfil most of the requirements, as observed in Fig. 2.3, where a selection of the elements with the thermal conductivity higher than $50 \text{ Wm}^{-1}\text{K}^{-1}$ (arrayed in ascending order of thermal conductivity indicated in the box) is depicted. Colour boxes indicate not satisfied criteria by each element according to the given legend; thus, only the white ones are left.

- Water cooled divertor

Copper alloys are recommended as the material for the HHF heat sinks in the water cooled divertor design of DEMO, due to the unrivalled heat conduction of copper, and the existing tungsten-copper alloy design for ITER. Tantalum and iron (ferritic steel) exhibit brittle behaviour low temperatures so their use should be limited.

2. The next step: DEMO

The selection of a precipitation hardened alloy (CuCrZr) as heat sink material is due to its good weldability, reduced He production and its better mechanical performance, mainly fracture toughness and reduced swelling, as compared to other copper alloys.

However, despite the above-listed properties, the analysis of the main factors of radiation damage available indicates that precipitation hardened alloys, such as CuCrZr, are only suitable for structural applications within the narrow temperature range of 180 °C to 280 °C. At irradiation temperatures above 300 °C, pronounced softening occurs in the alloy due to radiation-enhanced precipitate coarsening, dislocation recovery and recrystallization processes (Fabritsiev et al. 1996). Thus, it is not compatible with the high coolant temperatures required in a fusion reactor. Under irradiation at temperatures below 180 °C copper alloys suffer a rapid loss of ductility. In DEMO and beyond, the divertor operation temperatures threshold should be higher to increase the efficiency of the reactor.

Fig. 2.4. Schematic cut view of the water-cooled W-CuCrZr monoblock design. (a) Temperature field predicted for the heat flux load of 15 MW m⁻² and water temperature of 150°C. (b) Finite element analysis (FEA) simulations of the thermal stresses in the component. (J.-H. You 2015)

In addition, PFCs include various combinations of joints between armour and Cu alloy heat sink materials. The joining technology of the PFM to CuCrZr has been tested up to stationary surface heat loads of 20 MW/m² (D. Stork et al. 2014). Brazing, Hot Isostatic Pressing (HIP), electron beam welding or diffusion bonding have been developed and applied successfully in previous tokamaks and stellarators (Linke et al. 2004). Though, these joints must withstand the thermal, mechanical and neutron loads and the cyclic mode of operation and operate under vacuum, while providing an acceptable design lifetime and high reliability (Barabash et al. 2000). Besides, the stresses induced by the mismatch in the coefficients of thermal expansion and temperature gradient at the PFM and the CuCrZr interface could cause the detachment of the component. The thermal stresses at the interface were simulated by (J.-H. You 2015) using by FEA for a coolant temperature of 150 °C, with expected heat load of 15 MW.m⁻² in the PFM and represented in Fig. 2.4.

- He-cooled divertor

The benefits of the helium coolant are its chemical inertness, as it is compatible both with PFM in the divertor and with the blankets systems that contain beryllium, where water

cooling would lead to considerable safety concerns about the steam-beryllium reaction with H production. Another advantage of the use of helium coolant is that helium gas allows for relatively high operation temperatures (600 °C with pressures of ~10-14 MPa), above the DBTT of tungsten PFC, hence a high thermal efficiency of the power conversion system (Wang et al. 2012).

On the contrary, the drawbacks of He-cooled divertor concept, are the heat removal capacity of He (up to 10 MW/m², as compared to 20 MW/m² of liquid water) and the higher costs associated with the gas technology (pumping power, larger tubes size...) (Norajitra et al. 2007). Due to the temperature boundaries, the selected materials for the He-cooled divertor are W and ODS-EUROFER steel for the heat sink and structural components (Norajitra et al. 2011), in this regard, the limitations exposed previously for W due to its brittleness are even more pronounced. Therefore, the preferred divertor design for mid-term fusion reactors is the water-cooled concept.

2.3. Recent trends to enhance the performance of armour and heat sink materials

To solve the issues as mentioned earlier, the development of a range of advanced ductile or strengthened W compounds for the target and the heat sink armour of the water-cooled divertor are crucial issues for the development of a commercial fusion reactor.

While the real effect of neutron irradiation is still uncertain; the research activities carried out worldwide are making steady progress (Battabyal et al. 2013). Several fusion experiments are currently running with the goal of understanding the underlying physical principles and, more importantly, to address the materials behaviour under this harsh environment, i.e. ASDEX-Upgrade tokamak in Garching (Association EURATOM, Germany) or JET in Culham (United Kingdom).

2.3.1. Improving ductility and toughness of W

Since the mechanical properties of W are a function of the production history, alloying elements, purities, and thermomechanical treatment, various strategies have been followed for its modification and improvement. Further details of the underlying physical, mechanical and corrosion properties of W, together with details of main processing routes are extensively reviewed in the book by Lassner and Schubert (Lassner & Schubert 1999). To summarize, the main ductilisation strategies are: (i) alloying to promote solid solution, (ii) maintenance of a refine or worked microstructure and (iii) producing composite materials with inert dispersoids (Rieth et al. 2013).

It has been found that the addition of certain elements, such as rhenium, technetium, titanium or cobalt (Mutoh et al. 1995) can improve the ductility of W thereby reducing the DBTT of the alloy. Research by (Luo et al. 1991) observed a decay of the DBTT when iridium was added in solid solution, but cost limitations inhibit their use in the reactor. Rhenium is known to enhance the ductility of W. The addition of ~5 wt.% Re by solid solution reduces

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the DBTT of W by ~ 300 °C (Mutoh et al. 1995), but its use for fusion applications is excluded because of neutron activation issues, cost, reduced thermal conductivity, and radiation-induced intermetallic phases, that produce hardening and embrittlement. Re atoms in the W crystal structure result in a transition to an asymmetric dislocation core and a reduction of the Peierls stress (Rowcliffe n.d.), though similar effects could be obtained by alloying with tantalum, vanadium, molybdenum or titanium since they also form solid solution with W

On the other hand, materials with an ultrafine-grained (UFG) microstructure usually exhibit enhanced ductility. Besides, it would be expected that a UFG microstructure improves the irradiation resistance of W, as grain boundaries can be strong sinks for the radiation-induced defects. The improvement of the fracture toughness through grain size engineering has been investigated extensively. W-doped with potassium or W-La₂O₃ produced via severe plastic deformation (SPD) with grain sizes ~ 300 nm showed an increase in fracture resistance at low temperatures (Faleschini et al. 2007) and (Fan et al. 2014), but they are not suitable for producing industrial-scale semi-finished products. Hence powder metallurgical routes, i.e. mechanical alloying and hot isostatic pressing (HIP) are the preferred ways. However, in spite of their small grain sizes, research by (Palacios et al. 2013) and (Aguirre et al. 2011) of HIP alloys with Y₂O₃, La₂O₃, or TiC particles demonstrated to enhance the brittleness at moderate temperatures.

The last strategy is currently focused on W composites, with enhanced fracture toughness by reinforcing with W fibres (dispersion of W ductile fibres in W by mechanical synthesis) (Riesch et al. 2016), but despite the promising results, the production of industrial scale pieces is still distant. Further solutions are described elsewhere (Waseem & Ryu 2016).

Among all of these solutions, W-based composites and alloys have demonstrated to lower the DBTT considerably while enhancing the fracture toughness as compared to pure commercial W (Rieth et al. 2011).

2.3.2. Improving the thermo-performance of Cu-based materials

In contrast to the observed for armour materials, the strategies proposed to solve the issues related to heat sink applications are utterly linked to the production of Cu metal matrix composites (MMCs) since they make use of the very high thermal conductivity of copper. Due to the low-activation requirement, research is exclusively focused on W and SiC as strengthening reinforcements.

Several authors have reported the use of SiC fibre reinforced Cu MMCs in the interface between W and CuCrZr to increase the creep resistance of the component up to 300 °C (Kimmig, Allen, et al. 2013) (Kimmig, Elgeti, et al. 2013). Though tungsten-copper MMCs, with W wires or W particles as reinforcement, seem to have the biggest potential from both the fabrication and the design point of view (J. H. You 2015).

2.4. Scope

However, although the design of DEMO divertor has yet to be formally confirmed, it should be robust enough to withstand the operating environment for an acceptable minimum time without failure. While several solutions have been proposed for this target (see section 2.3), none of them has fulfilled all the requirements.

Therefore, the scope of this study is to examine the thermo-mechanical performance of divertor armour, heat sink and thermal barrier materials, based on the actual design of ITER. These materials include: tungsten alloys (W-Ti and W-Ta), W composites (W-TiC and W-Ta), Cu-based MMC (W-Cu and W-CuCrZr) and WC-Cu cermets, respectively.

Chapter 3

Characterization Techniques

Characterization is one focus of this work and serves as a basis for the validation process of the different concepts. All relevant characterization techniques applied in this work are briefly itemized. However, since many of them are standard analytical techniques (i.e. metallographic preparation or electron microscopy), a full description of its fundamentals will not be given here.

The analysed materials were supplied for characterization by different European Research groups. These materials were cut by refrigerated electro-discharge machining to prismatic specimens of non-standard dimensions (due to the limitation of material) for bending tests and to dogbone shape specimens for tensile tests.

3.1. Microstructure analysis

Microstructure analysis was performed on polished and etched samples. The first step in samples preparation was to embed the specimen in an epoxy resin since samples dimensions are too small to be held in the automated polishing system. Specimens were then ground with SiC papers (400, 600, 1200 grit), under continuous water cooling and polished with 9, 6 and 3 μm diamond suspension while lubricating with alcohol based emollient. Finally, to eliminate completely any deformation or scratches, Vibromet 2 (BUEHLER, Lake Bluff, Illinois, USA) vibratory polishing machine was used with 1 μm diamond paste to obtain highest quality surfaces.

To reveal the true metallographic microstructure of the samples, i.e. grain boundaries and higher contrast between the constituents, samples were previously etched with Murakami's reagent (100 ml water, 10 g NaOH and 10 g $\text{K}_3\text{Fe}(\text{CN})_6$) for 10 s to reveal W grains. Also, materials containing Cu, i.e. WC-Cu and W-Cu/CuCrZr (Chapters 5 and 6), were also etched with a specific Cu etchant (60 ml Ethanol, 15 ml HCl and 5 g FeCl_3) for 5 s.

3.1.1. Optical and electron microscopy

The morphology and grain topography of the materials under study were investigated with optical and scanning electron microscopy

An optical microscope Axiovert 100 Optical Microscope (Zeiss, Oberkochen, Germany) was used for surface analysis with resolutions of up to 0.5 μm . For higher magnification and fractography examination of post-mortem specimens, a Field Emission Scanning Electron Microscope (FESEM) from Auriga Series (Zeiss, Oberkochen, Germany), with detectors for Secondary Electrons³ (SE), Backscattered Electrons⁴ (BSE) and Energy Dispersive X-ray Spectroscopy (EDXS), was used. This latter was performed with a coupled Bruker X-Ray detector and QUANTAX-Spirit software (Bruker Corporation, Billerica, MA, USA). In the SEM and FESEM, the area to be analysed is irradiated with a focused electron beam (beam size 1 - 10 nm) accelerated by a cathode voltage between 1-30 kV in the vacuum, which is swept across the surface of the specimen to form the image. This picture is formed from the secondary electron and backscattered electrons emission. The three-dimensional appearance of the pictures is due to the large depth of field of the scanning electron microscope (3-10nm) while the intensity of the corresponding pixel displayed in the image comes from the detected current of the SE or BSE. The diffracted backscattered electrons provide information on the crystalline orientation of the sample while the characteristic X-rays (EDXS) on its chemical composition. Detailed descriptions of the working principles of the SEM can be found in (Amelinckx et al. 1997).

3.1.2. X-ray Diffraction

X-ray diffraction analysis gives information on the crystallographic phase, texture and stress state of crystalline materials. In the crystal lattice, atoms are arranged in a regular pattern, known as the unit cell, i.e. the smallest volume element that by repetition in three dimensions describes the crystal. The structure may be thought of as repeating planar arrays (h,k,l) of atoms spaced a from one another by a distance d_{hkl} , determined by the shape of the unit cell.

The geometry of the peaks is related fundamentally to positions of those atoms with little regard to what those atoms are. Intensity, on the contrary, is connected to the composition since the intensity of scattering is related to atomic scattering

The diffraction effects are observed when a monochromatic X-ray beam with wavelength λ impacts on this periodic structure at an angle θ , diffraction occurs barely when the distance travelled by the rays reflected from successive planes differs by an integer multiple of λ . We can express this relationship mathematically in Bragg's law (3.1). By changing the X-ray incidence angle θ , the d_{eal} , spacing of a polycrystalline material can be obtained, and the scattering angle will be 2θ .

³ Secondary electrons are those electrons re-emitted by the specimen under irradiation by the incident electron beam.

⁴ Backscattered electrons are incident electrons which have been scattered through angles approaching 180° within the sample and, consequently, leave the sample again.

$$2d_{hkl}\sin\theta = n\lambda \quad (3.1)$$

The diffraction spectrum consists of a plot of reflected intensities versus the scattered angle 2θ . The intensities of the reflections are determined by the distribution of the electrons in the unit cell. The highest electron density is found around atoms. Therefore, the intensities depend on what kind of atoms we have and where in the unit cell they are located, hence they can be compared with a known crystal structure to be identified. In the case of multiple phases, the resulting diffractogram is formed by the addition of the individual patterns.

Through the analysis of these peaks, the mean crystallite size of the material can be obtained as well. For a diffraction peak at angle θ , the crystallite size broadening (β_τ) of a peak can usually be related to the mean crystallite dimension (τ) by the Scherrer equation⁵:

$$\tau = \frac{K\lambda}{\beta_\tau \cos\theta} \quad (3.2)$$

Where β_τ is the line broadening in radians at the half-intensity maximum and K is the shape factor which typically has a value of about 0.9 (Connolly 2012).

In this work, pure commercial tungsten and two W-based composites, W-30Cu and W-30CuCrZr (Chapter 6), were analysed with the multipurpose diffractometer X'Pert PRO MPD (PANalytical, Almelo, The Netherlands) with a $\text{CuK}\alpha$ ($\lambda=0.15405$ nm) radiation source and provided with an oven Anton Paar HTK1200 (Anton Paar GmbH, Ashland, VA, USA). Data were taken for the 2θ range of 20 to 90 degrees with a step of 0.001 degrees. Indexing process of powder diffraction pattern was done, and Miller Indices ($h\ k\ l$) to each peak were assigned in first step.

In order to study the evolution of the composites with thermal exposure, the diffractograms were measured at different temperatures from 25 °C to 800 °C with 15 °C/min ramp and 10 min dwell time, until stable conditions were achieved. The measurements time for each diffractogram was about 32 minutes. All the measurements were acquired under vacuum conditions at a pressure lower than 10^{-5} mbar to avoid the oxidation of the samples, Once the last measured was obtained, the sample was cooled down in vacuum to room temperature.

3.1.3. Density measurement

Experimental densities (ρ_{exp}) of the materials were determined via the Archimedes method using high purity ethanol at room temperature. Additionally, theoretical densities (ρ_{th}) were calculated using the density of each component and the rule of mixtures, which in the case of two components has the following form:

⁵ Note that particle size broadening is not significant at sizes above 10.000 Å (1 µm), and it is trivial to un-measurable at sizes as small as 0.1 µm if equipment parameters are unknown.

$$\rho_{th} = \frac{\rho_1 \rho_2}{(100 - x)\rho_2 + x\rho_1} 100 \quad (3.3)$$

Where ρ_1 represent the density of pure tungsten ($\rho_w=19.25 \text{ g/cm}^3$ (Lassner & Schubert 1999)) or tungsten carbide (only for Chapter 5, $\rho_{WC}=15.63 \text{ g/cm}^3$ (Kurlov & Gusev 2013)); while x and ρ_2 correspond to the weight percent and density of the alloying or reinforcement element: titanium carbide ($\rho_{TiC}=4.93 \text{ g/cm}^3$), titanium ($\rho_{Ti}=4.54 \text{ g/cm}^3$), tantalum ($\rho_{Ta}=16.65 \text{ g/cm}^3$) and copper ($\rho_{Cu}=8.96 \text{ g/cm}^3$) from reference values (ASM International. Handbook Committee. n.d.).

Based on these two results, experimental and theoretical densities, relative density (ρ_r) was determined to obtain the porosity of the materials.

3.2. Mechanical characterization

3.2.1. Bending tests

The ultimate strength of the materials was measured in bending, i. e. flexural strength, in three-point bending/flexure (TPB) configuration, where the specimen was loaded at a location midway between two support bearings, following the scheme proposed in Fig. 3.1. When tested in three-point bending, the sample is subjected in its upper part to compression stresses and in its lower part to tensile stress.

Fig. 3.1. Schematic illustration of the setup for three-point bending test, with B the sample width, W the sample thickness or depth, L_s the length of the support span and P is the applied load

Although four-point flexure (FPB) is recommended in the ASTM C1161 (ASTM Standard C1161-13 2008), three-point flexure has been selected for the present work, since it has advantages over FPB for small specimens and in high temperature conditions: it uses simpler test fixtures; it reduces frictions and bonding points between supports and specimen at high temperature and for fracture toughness testing; and it is sometimes helpful in Weibull statistical studies.

The flexure stress is computed based on simple beam theory under the assumptions that the material is isotropic and homogeneous, the moduli of elasticity in tension and compression are identical, and the material is linearly elastic.

The output of such a tensile test is recorded as load or force versus elongation. These load–deformation characteristics are dependent on the specimen size. To minimize these geometrical factors, load and elongation are normalized to the respective parameters of stress and strain. The standard formula for the strength of a beam in three-point flexure is as follows:

$$\sigma_f = \frac{3PL_s}{2BW^2} \quad (3.4)$$

Where P is the break force, L_s the outer (support) span, B is the specimen width and W the specimen thickness. Linear strain ε is defined as

$$\varepsilon = \frac{6\delta W}{L_s^2} \quad (3.5)$$

Where ε is the strain, and δ the deflection of the bending beam.

However, this method is restricted to the elastic bending regime. When the DBTT is exceeded, and plastic deformation occurs, yield strength σ_y as determined using the 0.002 strain offset method, was represented in the graphs.

TPB tests were performed on smooth bar bars in vacuum and air (oxidation atmosphere) atmospheres. Vacuum atmosphere tests have been performed inside a vacuum camera furnace with W heating resistances fully refrigerated, coupled (Sigmatest Materialprüftechnik GmbH, Wedel, Germany) to an Instron 8501 Universal testing machine (Instron, High Wycombe, United Kingdom) with alumina bars for bending/compression testing. It was operated at pressures of about 10^{-6} mbar, and between 400 and 1200 °C of temperature. The heating rate was also 30 °C/min and once the set point was reached the heating was held during 10 min for the thermal stabilization of the system before testing. Load and displacement of the load point were continuously monitored during testing using a 1 kN (10 kN in the case of Chapter 5 and 6 materials) load cell and a linear variable differential transformer induction transducer, respectively.

Tungsten based armour materials (Chapter 4) were also tested in an air atmosphere in the temperature range between 25 °C and 1000 °C, in 200 °C steps. A small silicon carbide furnace with Eurotherm MTS 653 controller (MTS Systems Corporation, Eden Prairie, MN, USA), mounted inside the loading zone of an Instron 3369 servomechanical universal testing machine (Instron, High Wycombe, United Kingdom), was used for heating the specimens at 30 °C/ and testing them at high temperature. Two thermocouples were attached close to the opposite ends of the samples to control the temperature of both specimens and furnace in the oxidizing atmosphere environment. Since the thermal mass of the furnace was much higher than specimens' one, no noteworthy temperature gradients were reported.

Test conditions, i.e. loading rate, specimen dimensions and testing temperatures, were individually set for each material. Hence, these parameters are properly included in each Chapter. In any case, two to three samples were used for each material and each temperature to ensure test repeatability.

3.2.2. Fracture toughness measurement⁶

Bending test configuration was also used to determine the fracture toughness in the plane (K_{IC}) of the specimens, i.e. the resistance of material to the propagation of a crack. The fracture toughness is measured by loading a sample containing a deliberately-introduced crack of length a (Fig. 3.2) and recording the stress at which the crack propagates. The main test configuration used was the Single-Edge Laser Notched Beam (SELNB), Fig. 3.2a, where samples are tested under bending. However, two types of W-Cu composites⁷ (Chapter 6) have also been tested under monotonic tensile load in quasi-static condition with Double-Edge Notched Tension (DENT) test configuration (Fig. 3.2b) at three different temperatures, to investigate the sensitivity of this property to specimen geometry. Thus, results demonstrated a high incidence of both sample's geometry and loading symmetry, so SELNB is the preferred configuration for the calculation of fracture toughness.

Fig. 3.2. Schematic illustration of the setup for the measurement of fracture toughness in a) SELNB test configuration and b) DENT test configuration

Cracks were introduced using a femto-second laser in the bottom of the bars in SELNB configuration, as explained by Palacios (Palacios & Pastor 2015). When samples width (W) was too large, a previous disc notch was machined. Thus, the laser notch was introduced in the bottom of it, as presented in Fig. 3.3b and c. In the case of DENT specimens, two symmetrical edge cracks were introduced on both sides of the samples (Fig. 3.3a), primary with a diamond disc and secondly through femto-second laser. Although these laser notches are very short cracks emanating from a round/ellipse (disc notch) opening, the ratio between its length and radius is too low, so local stresses are governed by the general principles of stress gradients, and the stress concentration effect of an elliptical cut-out can be neglected⁸ (Shukla 2005).

⁶ Further details on fracture mechanics and its application to the study of cracking of tungsten materials can be found in Chapter 7.

⁷ The amount of the material consolidated by HIP, i.e. W armour materials and thermal barriers (Chapter 4 and 5, respectively) was too limited to machine DENT specimens.

⁸ Note that the stress intensity factor for crack emanating from the tip of an elliptical or rounded notch is different from that of an edge crack.

Fig. 3.3. Scanning electron micrograph of (a) W-40 wt% Cu specimen in DENT test configuration and (b) W-15 wt% Ta specimen in SELNB test configuration. (a) Disc and (c) laser notch in the bottom

With the laser technique, real cracks types with no melted layer (or heat affected layer) in the surrounding of the notch, have been obtained. Overall notch lengths were measured under the scanning electron microscope; yielding mean tip radius between 1-50 nm and laser notches of around 250 μm .

Load computed for the determination of fracture toughness was selected following the guidelines of the ASTM 5% secant method⁹ (ASTM Standard E1820-11 2009). A secant line, with a slope equal to 95 % of the initial elastic loading slope of the load-deflection curve, was used to determine the critical load (P_Q), with the objective of defining the stress intensity factor at the 2 % or less crack extension.

The ratio P_{max}/P_Q , where P_{max} is the maximum load that the specimen was able to sustain, defines the validity of the tests regarding linearity. If this ratio exceeds 1.10, then K_{Ic} is not size-independent, and it would be necessary to use larger specimens to determine K_{Ic} and the use of a fracture theory approach different from the Linear Elastic Fracture Mechanics (LEFM). Even though non-standard size specimens were tested in this work, some of the ASTM Standard considerations have been appraised during the experimental campaign.

Among the materials analysed in the present work, only those containing a high proportion of copper showed values of P_{max}/P_Q above 1.10. Namely, such tests are not valid for determining LEFM parameters. This restriction is quite demanding for materials containing copper, and it is difficult to be accomplished. For this reason, these values have been reported in terms of comparison of materials behaviour trends rather than for the

⁹ Further details on the estimation and importance of P_Q can be found in Chapter 7.

certification of this property. Nevertheless, the reader is referred to Chapter 7 for a deeper analysis on the cracking of ductile tungsten materials.

The critical stress intensity factor, for mode I stress in SELNV specimens was then computed from the critical load, P_Q , and the beam section using the equations proposed by Pastor and Guinea (Pastor et al. 1995)(Guinea et al. 1998).

$$K_{Ic} = \frac{3PL\sqrt{a}A - \frac{a}{W}B + \left(\frac{a}{W}\right)^2 C - \left(\frac{a}{W}\right)^3 D + \left(\frac{a}{W}\right)^4 E}{2W^2 \left(1 - \frac{a}{W}\right)^{\frac{3}{2}} \left(1 + \frac{2a}{W}\right)} \quad (3.6)$$

Where a , is the notch length, P the maximum or critical load, and W , width or thickness, L , span distance, and:

$$A = 1.989 - 0.356 \frac{W}{L} \quad (3.7)$$

$$B = 1.217 - 0.315 \frac{W}{L} \quad (3.8)$$

$$C = 3.212 - 0.705 \frac{W}{L} \quad (3.9)$$

$$D = 3.222 - 0.020 \frac{W}{L} \quad (3.10)$$

$$E = 1.226 - 0.015 \frac{W}{L} \quad (3.11)$$

Fracture toughness in tension was measured using the expression proposed by Bowie (Bowie 1964) and by Tada (Tada et al. 2000) for DENT test specimens (Fig. 3.2b). The most recent expression proposed by Janssen (Janssen et al. 2006) has also been tested for the calculation of the stress intensity factor, however, since its values are similar to those obtained with Bowie' equation, this analysis will not be included in the present work. Alternatively, Tada's values are on average 12 % lower than those obtained with the other methods, for this reason, ASTM (ASTM Standard STP410 1966) recommends Bowie empirical formula for the calculation of fracture toughness in DENT specimens, therefore, this expression is the one included here:

$$K_{IC} = Y \frac{P\sqrt{a}}{BW} \quad (3.12)$$

Where Y is the geometrical factor (also known as $F(a/W)$) defined by:

$$Y = 1.98 - 0.36 \frac{2a}{W} + 2.12 \left(\frac{2a}{W} \right)^2 - 3.42 \left(\frac{2a}{W} \right)^3 \quad (3.13)$$

Values of sample width, W , thickness, b , and average notch length, a , of the specimens tested under this configuration are: (9.44 ± 0.04) mm, (2.71 ± 0.09) mm and (3.150 ± 0.001) mm, respectively.

Fig. 3.4. Geometry parameter, Y , versus (a/W) for single and double edge notch tension tests configurations

Despite the fact that manufacturing perfect symmetrical laser notches is not a trivial issue, double-edge notch configuration was chosen over single-edge-notch specimen due to the lack of symmetry of the latter during loading, which implies a degree of bending in line with the crack opening. Besides, a significant disadvantage of the asymmetric specimen configuration is the high gradient of the stress intensity factor (dK/da). Y and, therefore K_{IC} , increases much faster with (a/w) for the single edge crack plate, as compared with the double edge crack plate (Fig. 3.4). Furthermore, one of the main requirements for quasi-static tests is the slow stable crack growth (Fatemi n.d.).

3.2.3. Tensile tests and the development of a new experimental setup

The tension test is the commonly used test for determining quasi-static properties of materials. The uniaxial loading condition results in a uniform stress distribution across the cross section of the test specimen, for this purpose, a universal joint is needed. Hence, residual bending stresses are avoided.

3. Characterization Techniques

Tensile tests were performed on dumbbell or dogbone-shaped samples (ASTM Standard E8/E8M-16a 2016) where the size of the narrow portion of it was $2.0 \text{ mm} \times 2.5 \text{ mm} \times 17.0 \text{ mm}$. This dogbone specimen configuration was chosen so that, during testing, deformation is confined to the narrow centre and, also, to reduce the likelihood of fracture at the ends of the specimen (Callister 2007). Before testing, a small mechanical load was applied to verify the symmetry of specimen and the uniaxial response of it.

The output of the tensile tests was recorded as load versus displacement of the frame; these were then normalized to engineering stress and engineering strain as defined by

$$\sigma = \frac{P}{A_0} \quad (3.14)$$

$$\epsilon = \frac{l - l_0}{l_0} = \frac{\Delta l}{l_0} \quad (3.15)$$

in which P is the instantaneous load applied perpendicular to the specimen cross section, A_0 is the original cross-sectional area, l_0 is the original length before any load is applied, and l_i is the instantaneous length.

True stress-strain (Fig. 3.5b) were calculated as the load P divided by the instantaneous cross-sectional area (A_i) over which deformation is occurring, defined by

$$\sigma_T = \frac{P}{A_i} \quad (3.16)$$

$$\epsilon_T = \ln \frac{l_i}{l_0} \quad (3.17)$$

Fig. 3.5. Scale tensile specimen with plane cross section and schematic stress-strain curve with the nomenclature used during this work

In order to obtain the instantaneous cross-sectional area, it was necessary to develop a new experimental setup for the recording of the tests. It is important to highlight the limitations of it. Tests were performed inside a high vacuum chamber of significant size (50 cm x 40 cm x 30 cm), operating at temperatures above 800 °C in tension and up to 1200 °C in compression/bending, so any recording system should be outside the chamber and far away from the testing sample. Furthermore, specimens were millimetric, so mounting directly to them conventional extensometers, such as strain gages or LVDT (linear variable differential transformer), is a burdensome task. In addition, painting speckle patterns on the sample surface to facilitate the measurement was insufficient and even useless when testing above 500 °C. So the strain measurements were conducted through the window on the back side of the chamber as validated previously by Zhang (Zhang et al. 2012) on polymeric foam cored sandwich structures, however, the maximum testing temperature achieved by them was 90 °C, which is far below the 800 °C achieved during this work.

The instantaneous cross-sectional area was then obtained through the non-contact optical full-field Digital Image Correlation (DIC) method. DIC uses image registration algorithms to track the relative displacements of material points between a reference (typically, the undeformed) image and a current (typically, the deformed) image (Peters & Ranson 1982). The concept of correlation is used to calculate the strains from the deformation of the specimen. Berfield et al. (Berfield et al. 2007) defined the theory underneath by assuming a locally homogeneous deformation over a small subset of the sample. The deformed coordinates (x_q' , y_q') of a material point q in the neighbourhood of a point p , at undeformed location (x_p , y_p), are given by

$$x'_q = x_q + u_p + \frac{\partial u_p}{\partial x} \Delta x_q + \frac{\partial u_p}{\partial y} \Delta y_q \quad (3.18)$$

$$y'_q = y_q + v_p + \frac{\partial v_p}{\partial y} \Delta y_q + \frac{\partial v_p}{\partial x} \Delta x_q$$

where u_p and v_p are the x and y components of the displacement vector of point p , respectively, x_q and y_q are the undeformed coordinates of point q , $\Delta x_q = x_q - x_p$ and $\Delta y_q = y_q - y_p$

The displacement of p can be obtained by least-square or cross-correlation of the grayscale intensity value before and after deformation, over a small locally homogeneous square subset S centred on p . Since the grayscale intensity of a point is assumed to be invariant with deformation, the correlation depends on the original position of point p and the parameters describing its deformation, therefore, changes introduced to the grayscale intensity of the pattern, such as fluctuations of the light source, will affect the accuracy of the correlation. At high-temperature testing, both sample and heating system radiates, so the successful analysis of the images is even more challenging.

Fig. 3.6. A typical load-time curve of W-40 wt% Cu composite during tensile tests at 550 °C. Insets are test frames that show the different phases of the test

In this study, every test was recorded with a frame rate at 10 fps (frames per second) at low temperature and 5 fps at higher temperatures. Selected frames of a tensile test can be presented in Fig. 3.6. Afterward, an open source 2D DIC MATLAB program called Ncorr (Blaber et al. 2015) was used for the processing of the recorded displacement fields. Once displacement field is obtained, a virtual extensometer was computed in MATLAB to get the instantaneous length, l_i and, thus, instantaneous area, A_i , and true strain, ϵ_T from Ncorr records. Fig. 3.7 illustrates an example of the results obtained after the analysis of a W-30Cu sample tested at 500 °C. Both strain and displacement mapping fields of a selected group of pixels can be observed.

Fig. 3.7. DIC strain and displacement pixels' fields obtained with Ncorr software for W-30 wt% Cu composite tested at 550 °C in vacuum

For the performance of the tensile tests a new experimental setup was developed (Fig. 3.9). Alumina bars of the INSTRON 8501 universal testing machine used for bending tests were replaced by nickel-base alloy ones (Bohler Alloy 75, Böhler-Uddeholm, Viena, Austria) with suitable connection and universal joints, manufactured in our mechanic's workshop. The loading frame displacement was recorded for calculating engineering strain curve (Fig. 3.5) while the DIC system, with a high-resolution camera (3840 px x 2748 px) coupled with an adequate light source, was set in front of the sample on a stable tripod to obtain true strain over the loading area. Constant volume was assumed during the tensile tests. Hence 2D deformation setup was required, and only one camera was needed. However, as tests were performed at elevated temperatures and under high vacuum (30 °C/min heating rate and 10 min dwell time under 10^{-6} mbar pressure), the DIC measurements were conducted through the window on the back side of the chamber. With this setup, it was possible to obtain resolutions higher than 10 $\mu\text{m}/\text{pixel}$.

Random speckle patterns were painted on the sample surface with a permanent marker to facilitate the DIC measurement at low temperatures. However, at temperatures above 500 °C only surface roughness, with its characteristic grayscale pattern, was used to calculate the displacement fields, as observed in Fig. 3.6 and Fig. 3.7.

Fig. 3.8. Experimental setup for tensile test with DIC system

3.3. Elastic modulus measurement

Elastic constants can be determined by static and by dynamic techniques (Bunshah 1971). Static techniques are based on the measurement of stresses and strains during mechanical tests (tensile and flexural stresses in this investigation), and Young's moduli are determined from the slope of the linear region of the stress-strain curve (Fig. 3.5). Nanoindentation techniques are a popular static method for the measurement of elastic constants when the volume of material available is limited (Radovic et al. 2004) but, though this technique has been widely studied by the student (see Appendix A), it will not be included in this document.

On the contrary, dynamic methods are non-destructive techniques that provide the advantage of ease specimen preparation, a wide variety of specimen shapes and sizes. Elastic materials possess specific mechanical resonant frequencies that are determined by the elastic modulus, mass, and geometry of the test specimen. The dynamic elastic properties of a material can, therefore, be computed if the geometry, mass, and mechanical resonant frequencies of a suitable (rectangular or cylindrical geometry) test specimen of that material can be measured. The material must be considered homogeneous¹⁰ and isotropic¹¹ for this measurement.

¹⁰ Homogeneous (according to the norm ASTM E1876-01): the condition of a specimen such that the composition and density are uniform, so that any smaller specimen taken from the original is representative of the whole. Practically, as long as the geometrical dimensions of the test specimen are large for the size of individual grains, crystals, components, pores, or microcracks, the body can be considered homogeneous.

¹¹ Isotropic (according to the norm ASTM E1876-01): the condition of a specimen such that the values of the elastic properties are the same in all directions in the material. Materials are considered isotropic on a macroscopic scale if they are homogeneous and there is a random distribution and orientation of phases, crystallites, components, pores, or microcracks.

Fig. 3.9. Schematic of support setup for impulse excitation technique for flexural mode of vibration

In principle, resonant methods measure the fundamental resonant frequency of tests specimens of suitable geometry by exciting them mechanically by a singular elastic strike with an impulse tool (see the scheme of Fig. 3.9). A transducer senses the resulting mechanical vibrations of the specimen and transforms them into electric signals. Specimen supports, impulse locations, and signal pick-up points are selected to induce and measure specific modes of the transient vibrations. The signals are detected, and the fundamental resonant frequency is isolated and measured by the signal analyser, which provides a digital reading of the frequency of the specimen vibration. The appropriate fundamental resonant frequencies, dimensions, and mass of the specimen are used to calculate dynamic Young's modulus, dynamic shear modulus, and Poisson's ratio. For this, GrindoSonic (J.W. Lemmens N.V, Belgium) and the GENEMOD software has been used following the calculations suggested in the ASTM E1876-09 standard (ASTM Standard E1876-01 2005).

In this work, the elastic properties of the materials under study have been determined by dynamic and static techniques, with the Impulse Excitation (IE) method, also known as Resonant Frequency Analysis (RFA) at room temperature and through the load-deflection curves of the bending tests, up to 1200 °C in some cases.

3.3.1. Elastic modulus and thermal expansion coefficient of composite materials

Chapters 5 and 6 are devoted to the characterization of composites for heat sink applications, WC-Cu and W-Cu/CuCrZr, respectively. A broad study of the evolution of the elastic modulus with temperature and composition was made following this procedure.

Load-deflection curves of the bending tests were analysed to calculate the modulus of elasticity by drawing a tangent to the steepest initial straight-line portion of it (Fig. 3.5). These data were then compared with values measured using RFA at RT. Additionally, the evolution of elastic modulus with temperature was estimated with three micromechanical models: Voigt (Voigt 1889), Reuss (Reuss 1929) and Hill (Hill 1952). Voigt model is also known as the rule of mixtures or the iso-strain model, i.e. an arithmetic average of the modulus of the two components, while the Reuss model is known as the inverse rule of mixture model or the iso-stress model, i.e. the harmonic mean (Younes et al. 2012). Alternatively, the Hill approach (Voigt-Reuss-Hill model, VRH) is an average of the two previous, where the loading is intermediate between the two extreme cases. Hence, the relations between volume fraction and modulus of elasticity, denoted by f and E , respectively, are the following:

Voigt model:
$$E_{Comp}^V = f_1 E_1 + f_2 E_2 \quad (3.19)$$

Reuss model:
$$E_{Comp}^R = \frac{E_1 E_2}{f_2 E_1 + f_1 E_2} \quad (3.20)$$

Hill model:
$$E_{Comp}^H = \frac{E_{Comp}^V + E_{Comp}^R}{2} \quad (3.21)$$

Where $f_2 = 1 - f_1$

Where the suffix Comp indicates the calculated properties of the composite, either W-Cu/CuCrZr or WC-Cu, while the numbers, 1 and 2, represent the elastic modulus and volume fraction of each component, i.e. W, WC or Cu.

Fig. 3.10. Linear thermal expansion, α , against Young's modulus, E . The contours show the thermal stress generated, per $^{\circ}\text{C}$ temperature change, in a constrained sample (Ashby 2009)

From the above results, it was also possible to estimate the uniaxial Thermal Expansion Coefficient (α , CTE) of the composites, which is a critical parameter for the structural design of the elements. It is well known that both properties, thermal expansion, and elastic constants, are related intimately to lattice vibration and so, to the nonlinear terms in the

interatomic force laws. This general trend is observed in the α - E chart (Fig. 3.10) where all classes of materials are considered.

The expansion of materials as their temperature is increased can be explained by the increased average spacing between atoms as they vibrate with greater amplitude at higher temperatures. Fig. 3.11 shows schematically the potential energy of bonded atoms, known as the Lennard-Jones potential or Energy well. The continuous line corresponds to a more rigid material since it shows a deeper potential. The average distance between atoms shifts towards the right-hand side of Fig. 3.11. Thus, materials are expected to expand when they are heated. Here, we do not consider any phase changes which either yield contraction or expansion (Le Bourhis 2007).

Fig. 3.11. Potential energy as a function of inter-atomic distance for materials with weak (dashed line) and strong (continuous line) bonds

The stiffness (Young's modulus) depends on the restoring force when atoms are forced apart (or together), which is the gradient of the plot. Materials with strong inter-atomic forces such as ceramics, i.e. a narrow energy well, tend to have low thermal expansion coefficients and high stiffness. In contrast, polymers, which in general have weak inter-atomic forces, tend to have high expansivities and low stiffness, i.e. a broad, shallow well. Metals are usually intermediate between these two cases (Cambridge 2015). Comparison of these effects of the shape of the energy well thus indicates a general inverse relationship between elastic modulus and thermal expansion coefficient.

Research performed by Barker (Barker et al. 1963) found that a large number of polycrystalline and amorphous materials obey the relation (3.22) at normal temperatures, where s is a dimensionless spread factor ($0.5 < s < 2$) and E is the elastic modulus.

$$E\alpha^s = 15 \text{ [Nm}^{-2}\text{K}^{-2}] \quad (3.22)$$

A later review by Arenz (Arenz 2005b), based on the energy well proposed the following empirical relation for a series of isotropic hard solids, W, WC, and Cu included.

$$E = 4.5\alpha^{-2.3} \quad (3.23)$$

Where E is the elastic modulus measured by the bending tests. Here, Energy Well theory and thermodynamic analysis were employed to obtain the qualitative relationship. The thermal expansion coefficient of the composites was then calculated as a function of temperature and composition with the equation mentioned above.

Chapter 4

Tungsten materials for armour applications

Tungsten has been selected as the armour for the ITER divertor because of its exceptional resistance to ion and charge-exchange particle erosion in comparison with other materials (Davis et al. 1998). However, the mechanical properties of commercially available W are not yet adequate for structural purposes due to its intrinsic brittleness at relatively low temperatures. DBTT occurs close to $0.15 T_m$, thus limiting the operating temperatures of the reactor.

The most successful approach towards reducing the brittleness of W at low temperatures is alloying to promote solution softening. In addition, the maintenance of a UFG microstructure, with the dispersion of hard particles such as La_2O_3 , Y_2O_3 or TiC may have the capability of inhibiting grain growth increasing the recrystallization temperature. Further details are extensively described in Chapter 2.

Tungsten materials are usually fabricated by powder metallurgy routes, where the mechanical milling is a critical step for alloying and developing nanostructured materials. Final consolidation is performed by hot isostatic pressing (HIP), although the achievement of fully dense materials is complicated due to the elevated melting point of W. In this regard, several research works have shown that Ti is a sintering activator for the W alloys (Aguirre et al. 2010). As observed in the W-Ti phase diagram (Fig. 4.1), Ti solubility in W is total while Ti content is below 10 wt.%. Furthermore, it has been reported that Ti addition might alter the core structure of the screw dislocations and their slip mechanism, increasing W ductility (Li et al. 2012).

4. Tungsten materials for armour applications

Fig. 4.1. W-Ti binary phase diagram(Jonsson 1996)

Similar approach could be applied to Ta additions, this element also forms a solid solution with W, does not produce new phases after transmutation and it has been widely used to alloy low activation ferritic-martensitic steels to reduce their DBTT (Cottrell et al. 2007). In particular, the addition of other refractory metals could lead to an improved W product for divertor applications, as the high melting point, high thermal conductivity and high resistance to sputtering and erosion are shared (Baluc et al. 2007).

Therefore, this chapter is focused on the influence of both microstructure and chemical composition on the fracture behaviour of W materials consolidated by HIP¹². In particular, W-2 wt% Ti, W-1/5 wt% TiC, W-5/15 wt% Ta have been studied. In an effort to better evaluate the influence of the processing parameters; those were modified for each material with the following aims:

- For W-2Ti, the goal was to achieve the proper Ti alloying in W, while maintaining a refined microstructure. To achieve it, two W-2Ti products were produced with different milling times: 20 h and 75 h.
- For W-1TiC and W-5TiC the purpose was to achieve a good dispersion of the TiC nanoparticles in the W matrix, inhibiting the grain growth.
- For W-5Ta alloy and W-15Ta composite, the objective was to analyse the effect of Ta on the mechanical behaviour of W, both in solid solution or in a second phase as a composite.

The characterization of the materials has been carried out through three-point bending and fracture toughness tests in the temperature interval from 25 °C to 1200 °C, as well as a basic physical characterization.

¹² Partial content of this Chapter has been published by the author in (Tejado et al. 2015) and (Muñoz et al. 2014). Further details can be found in the corresponding Appendix A.

4.1. Materials processing and preparation

W alloys studied were manufactured at the *Departamento de Física* of the Carlos III University, Leganés, Spain, while W-15Ta composite was produced at the *Instituto de Plasmas e Fusão Nuclear* of the Technical University of Lisbon, Portugal. Even through the manufacturing process was not directly included in this study, it deserves mentioning because it affects strongly many of the properties to be explored.

Two main products can be depicted: W-alloys (W-2Ti and W-5Ta) and W-composites (W-TiC, W-5TiC and W-15Ta), although the alloys can be considered also as composites because elements additions are not totally dissolved in the W substrate during HIP.

Fig. 4.2. Materials processing scheme

The manufacturing process of the W-alloys consisted of:

1. Blend of the W powder (99.95 % purity, median particle size 1 μm) with the alloying element in a Tubular T2F mixer for 4 h;
2. Mixing/grinding of the blends was performed at 150 rpm in a high-energy planetary ball mill under a high purity Ar atmosphere. Tungsten carbide (WC) balls of Ø 10 mm with a 4:3 ball-to-powder ratio inside a WC container were used as grinding media. The milling time was set for each composition varying from 4 h in the case of the W-15Ta composite to 75 h for the W-2Ti alloy, as presented in Table 4.1.
3. Encapsulation in a steel container and degassing for 24 h at 400 °C in MPa in low vacuum ($\sim 2 \times 10^{-3}$ mbar).
4. Consolidation by HIP for 2 h at 1200 °C and 195 MPa with high purity Ar.

4. Tungsten materials for armour applications

Table 4.1. Main processing parameters of the W-based materials studied: composition, properties of the starting powders and milling time

Material	Composition		Starting powders		Mechanical alloying
	Addition	(wt.%)	Purity (%)	Avg. Particle size (μm)	Milling time (h)
W-2Ti	Ti	2	99.9	<100	20
					75
W-1TiC	TiC	1	99	0.04	50
W-5TiC		5	99.9	<2	70
W-5Ta	Ta	5	99.9	<2	50
W-15Ta		14.8	99.95	<75	4

Alternatively, W-15Ta for W-15 wt% Ta (W-15Ta), W powder (99.95 % purity, median particle size 1 μm) was mixed with Ta powder (99.95 % purity, median particle size 75 μm) in a Retsch PM400MA planetary ball mill (Retsch, Haan, Germany) during four hours under high purity Ar atmosphere mill to obtain the W-15 wt.% Ta material. Consolidation was performed by HIP under the same conditions. Further details of the production and microstructural characterization of W-15Ta can be found in the literature (Dias et al. 2015)

Cylindrical bullets of 30 mm in diameter and 50 mm in length were obtained after consolidation by HIP. Miniaturized bend specimens (nominal dimensions $1.7 \times 1.7 \times 25 \text{ mm}^3$) and small discs with a diameter of 15.7 mm and a height of 2 mm were produced by refrigerated electro-discharge machining to comply with the needs of mechanical and thermal diffusivity testing, respectively. Results have been compared with pure tungsten, processed by the same group and metallurgical route, as a reference material (Palacios et al. 2014)

The mechanical behaviour of the HIP materials was evaluated. Mechanical strength, yield strength, and fracture toughness were obtained by performing non-standard three-point bending tests. The tests were conducted in both oxidizing and vacuum atmospheres and at a temperature range between 25 °C and 1200 °C. The target of the research was to evaluate how the mechanical behaviour of pure tungsten is improved by the additions of Ti (W-2Ti), Ta (W-5Ta and W-15Ta) and TiC (W-5TiC), especially at very high temperatures when the material suffers strong thermal degradation.

4.2. Solid solution materials: W-2Ti

Two W-Ti products have been characterized in this chapter. The scope was to determine the optimal processing conditions to achieve the proper alloying of Ti in W, maintaining a UFG microstructure. Hence, mechanical alloying (MA) times were set in 20 h and 75 h.

4.2.1. Microstructure

The samples were etched with Murakami reagent to reveal the grain boundaries, however, the presence of a solid solution surrounding the tungsten particles impeded to obtain micrographs with good contrast. Thus, the estimation of grain size could be made by observation of the fracture surfaces after testing at room temperature (Fig. 4.3b). In these images, the role of the milling time on the morphology and grain size can be easily evaluated. Fig. 4.3a revealed the presence of large tungsten particles that may not have been totally ground, as starting particle size is $\sim 12\ \mu\text{m}$. These polyhedral coarse W grains are surrounded by nanometric rounded grains of the $\beta(\text{W-Ti})$ solid solution, as observed in Fig. 4.3b where a higher magnification SEM image is presented. $\beta(\text{W-Ti})$ solid solution was produced because of Ti diffusion along the grain boundaries of W during sintering, revealing a bimodal grain morphology.

On the other hand, the microstructure observed in Fig. 4.3c is more homogeneous, as faster grain refinement has been obtained after 75 hours of MA. Sparse W grains of 250-500 nm can still be spotted, though $\beta(\text{W-Ti})$ solid solution is the predominant phase.

Fig. 4.3. SEM fracture morphologies of W-2Ti with (a) and (b) 20 h milling time and (c) 75 h milling time, both tested at 25 °C

In contrast to the observed for W-4 wt% Ti materials (W-4 wt% Ti and W-4 wt% Ti-0.5 wt% Y2O3) manufactured by the same metallurgical route (Aguirre et al. 2011), Ti seems to be totally dissolved in the $\beta(\text{W-Ti})$ phase. Aguirre reported the presence of elongated lagoons of titanium, where no tungsten atoms diffusion was observed. The author suggested that the consolidation HIP treatment might produce the segregation of Ti into

large pools sparsely distributed in the corresponding alloy, even though the solubility of Ti in W is much higher, as observed in the corresponding phase diagram (Fig. 4.1).

However, a later study performed by Jahangiri (Jahangiri & Öveçoğlu 2016) on the effects of MA and Ti content on the effective lattice parameter, crystallite size and lattice strain of W with different fractions of Ti, proved that Ti-phase was still present for alloys containing 4 wt% Ti, as the calculated solubility of Ti for this alloy was 1.78 wt% (6.5 at%) after 10 h milling time. Furthermore, they observed that with the increase of MA duration, so does the solubility of Ti. However, despite the advantages of increasing the MA time, it should be noted that these effects are narrowed by the oxygen contamination of the alloy. Fig. 4.4a illustrates the oxygen content in the powders as a function of the milling time.

Fig. 4.4. (a) Oxygen content versus milling time for W-2Ti blends; (b) Effect of milling time on the average crystallite size and internal strain of the W-2Ti powders (Savoini et al. 2013)

Although the powder handling and milling were carried out under a high purity Ar atmosphere, the presence of oxygen in the powders was evident. Fig. 4.4a shows a continuous increase of the O content with the milling time determined using an LECO TC500 analyser. After 20 h of milling, the oxygen content of the W-2Ti blend was 0.35 wt.%, while it reached 0.7 wt% after 75 h. However, it should be highlighted that the initial O₂ content of the elemental W and Ti powders was 0.037 % and 0.069 %, respectively.

The milling effect on the XRD patterns, i.e. of the average crystallite size and lattice strain, is shown in Fig. 4.4b. The cumulative grain refinement for W-2Ti is in accordance to the observed in the SEM fractographic images (Fig. 4.3). It indicates that at least 50 h of milling, at the present conditions, are required for getting grain refinement with average crystallite size of ~20 nm for W-2Ti. Consequently, a compromise milling time for constraining the O₂ contamination, while achieving the suitable homogenization and refinement, should be stated.

4.2.2. Mechanical properties

The density of the samples was measured using Archimedes' immersion method with high purity ethanol. The results can be observed in Table 4.2. Contrary to expectations, with the increase in milling time and the homogenization, so does the porosity. The elastic modulus follows the same trend. Since the content of O₂ has been doubled during the MA, this contamination could be the responsible for it.

Table 4.2. Densities, experimental (ρ_{exp}) and theoretical (ρ_{th}) measured for the samples along with the relative density (ρ_r) calculated from them and the estimated porosity and elastic modulus measured via IET (E_{IET}) and theoretically calculated (E_{th})

Material	Milling time (h)	Density				Elastic modulus	
		ρ_{exp} (g/cm ³)	ρ_{th} (g/cm ³)	ρ_r (%)	Porosity (%)	E_{IET} (GPa)	E_{th} (GPa)
W-2Ti	20	17.98±0.04	18.08	99.45	0.55	371±8	378
	75	17.60±0.03		97.34	2.66	381±1	

- Flexural strength

The TPB test results for the flexural strength of both materials showed that the alloyed behaviour was linearly elastic until fracture at almost all studied temperatures. However, at 1200 °C under vacuum, the samples exhibited plastic deformation without breaking. In this case, the 0.2 % yield strength offset was represented using dashed lines (Fig. 4.5).

Fig. 4.5. Average flexural strength versus test temperature for the W-2Ti alloys and pure W in air and under vacuum. The dashed lines represented the yield strength at 0.2 % when the materials exhibited a ductile behaviour

Increasing the milling time increased as well the flexural strength across the entire temperature range. Moreover, results for W-2Ti after 75 h MA are $\sim 40\%$ higher than for W-2Ti after 20 h MA, and even 4 times greater than those of reference pure W. The evolution of the bending strength with temperature is quite similar for the three materials represented: strength is almost constant with temperature, with no clear influence of the atmosphere. Above 800°C values decreased due to thermal degradation. At 1200°C , the properties had completely degraded even under a vacuum atmosphere, most likely due to the porosity decreasing the alloy cohesion. The DBTT was defined as when the σ - ϵ curves changed their behaviour from linearly elastic to plastic. An improvement was observed upon the refinement of the grain size, as the DBTT of W-2Ti after 75 h MA, was above 800°C . This alloy appears to exhibit better bending strengths at low temperature than corresponding strengths reported for the W-4Ti alloy, which did not show plastic deformation up to 1000°C (Aguirre et al. 2009).

- Fracture toughness

The fracture toughness tests showed brittle behaviour in all the temperature range tested for both atmospheres (Fig. 4.6). The addition of Ti in the tungsten matrix promotes the toughening of the alloy for all the temperatures studied, showing approximately an improvement of 3 and $1\text{ MPa m}^{1/2}$, after 75 h and 20 h MA respectively, as compared to pure W. The homogenization and refinement of the microstructure lead to higher values of K_{IC} since defects, i.e. large non-milled W particles, may act as stress concentrators for the fracture.

Values obtained at ambient atmosphere are slightly higher than those obtained in vacuum. However, this improvement of the values was attributed to the possible blunting of the surface defects due to superficial oxide formation.

Fig. 4.6. Nominal fracture toughness of W-2Ti alloys and pure W tested as a function of temperature. The error bars correspond to the standard deviation of the experimental data.

Both materials presented brittle intergranular fracture, due to the decohesion among β (W-Ti) particles, and cleavage of large W particles, typical of BCC metals. These results supported the brittle behaviour observed during the fracture tests and maintained up to temperatures below 800 °C.

Fig. 4.7. SEM Fractography of W-2Ti alloys tested at (a) 25 °C (20 h MA), (b) 200 °C (20 h MA), (c) 400 °C (75 h MA) and (d) 600 °C (20 h MA) in TPB configuration and under ambient atmosphere

Regarding the testing atmosphere, no passivation effect can be attributed to Ti alloying, neither after 20 h nor 75 h MA. At 400 °C oxidation is clearly visible on the fracture surfaces of both alloys (Fig. 4.7b) and at 600 °C samples are entirely covered by a tungsten oxide layer (Fig. 4.7c).

4.2.3. Conclusions

It has been reported that the addition of Ti can moderately enhance the strength and fracture toughness of W in all the temperature range tested. However, these results did not show an apparent decrease of the DBTT as compared to pure W. Even although the present processing conditions appear to develop a particle dispersion and fine grain structure, especially after 75 h milling time. This result could be associated with Ti segregation at the grain boundaries. Furthermore, a non-negligible O₂ concentration is also present in the alloys, which may also be segregated at the grain boundaries forming complex oxides. These phases segregated would assist a high concentration of internal stresses at grain boundaries, promoting grain boundary decohesion and the brittleness of the alloys, as it occurs in Mo

alloys (Liu et al. 2013). Furthermore, the performance of these alloys under a possible loss of vacuum inside the reactor is quite similar to the exhibited by pure tungsten.

4.3. Strengthened/stabilized materials: W-1TiC and W-5TiC

This section focusses on the strengthening effect of dispersed carbide particles (TiC) on the mechanical performance of W. The presence of second-phase particles, such as TiC, dispersed in the W matrix can effectively reduce its DBTT. They induce grain refinement, and they could even act as sinks to capture radiation-induced defects, thereby improving radiation resistance as well (Tan et al. 2016). Furthermore, second-phase particles can inhibit recrystallization because of their improved high-temperature strength and creep resistance by hindering the sliding of grain boundary and stabilizing the microstructure at higher temperatures (Fukuda et al. 2013).

The goal was to achieve a good dispersion of the nanoparticles in the W matrix, inhibiting the grain growth and stabilizing the microstructure at high temperature. Two alloys with different amount of TiC dispersoids have been chosen for detailed analyses: W-1wt% TiC and W-5 wt% TiC. Processing parameters, i.e. 50 and 70 h of MA for W-1TiC and W-5TiC, respectively, were set following to the observations reported in 4.2.

4.3.1. Microstructure

Fig. 4.8. Scanning electron micrographs of a polished section of (a) W-1TiC and (b) W-5TiC showing the details of the microstructure. Grey areas indicate W-rich phase while black ones indicate TiC rich areas after 50 and 70 h of MA, respectively

Fig. 4.8 presents the surface morphology of W-TiC alloys. The results show that strengthening particles, mostly existing at grain boundaries (black areas), inhibit the growth of tungsten grains (grey areas) during the sintering process. Therefore, the refinement of the microstructure is higher for W-5TiC. In both materials, but especially in W-5TiC, W phase exhibits roughly bimodal grain size: large grains of several microns as well as areas with submicron grains. Besides, TiC aggregates can be observed in both microstructures. The aggregation probability of TiC particles is relatively high due to their covalence chemical

bond characteristics, therefore, the accumulation of TiC particles at W grain boundaries occurs (Chen et al. 2008).

The densification achieved for both materials is summarized in Table 4.3. It can be observed that addition of TiC decreases density since the density of TiC (4.93 g/cm³) is lower than that of tungsten (19.2 g/cm³). According to this table, the relative density of W-TiC materials also increases with increasing TiC content. It indicates that TiC is beneficial to sintering and densification of composites to a certain extent, up to this percentage, TiC particles tend to aggregate, lowering the densification (Chen et al. 2008). However, the increased MA time could be co-responsible of this densification.

Table 4.3. Experimental (ρ_{exp}) and theoretical (ρ_{th}) densities measured for the samples along with the relative density (ρ_r) calculated from them and the estimated porosity. Elastic modulus, measured through the Impulse excitation technique (IET) is also included

Material	Milling time (h)	Density				Elastic modulus	
		ρ_{exp} (g/cm ³)	ρ_{th} (g/cm ³)	ρ_r (%)	Porosity (%)	E_{IET} (GPa)	E_{th} (GPa)
W-1TiC	50	17.23±0.05	18,19	94.69	5,31	354±2	403
W-5TiC	70	16.15±0.04	16,81	96.10	3,90	381±4	407

The elastic modulus increases as well with the increase in TiC content, hence the addition of TiC improves the elastic modulus and hardness of the composites. This increase in elastic modulus is indeed due to the direct contribution of the high elastic modulus of TiC as compared to the one of pure tungsten.

4.3.2. Mechanical properties

This section of the Chapter analyses the effect of the addition of 1 and 5 wt% TiC on the thermomechanical performance of W. When adding this compound, the mechanical behaviour has been enhanced for all temperatures under test, as it can be observed in Fig. 4.9 and Fig. 4.11.

- Fracture toughness

The toughness of the two alloys as a function of temperature was assessed from three-point bending on notched bars. They are plotted in Fig. 4.9, together with the results corresponding to the pure W. For W-1TiC, the load–displacement curves were linear until fracture in the whole temperature range. W-5TiC exhibited this performance up to 1000 °C when slight plastic behaviour was observed (represented as dashed lines in the graph). Thus, the stress intensity factor loses its validity with increasing ductile behaviour and the calculated values give only a lower bound of fracture toughness. The evolution of K_{IC} with temperature for W-1TiC is comparable with that observed for pure W in air atmosphere as it shows better performance in air than in vacuum. This is probably due to the growth of superficial oxidation that contributes to the blunting of the superficial defects causing an apparent increase in the values. On the contrary, no such differences can be extracted from

W-5TiC performance, since its values are overlapped in all the temperature range. Thus, it seems that TiC may act as oxidation inhibitor; this effect will be explained with more details in the fractographical analysis.

Fig. 4.9. Fracture toughness versus temperature for W-1TiC and W-5TiC alloys and pure W. The error bars correspond to the standard deviation of the experimental data. The dashed lines indicate the region where linear elastic fracture mechanics is no longer valid

- *Flexural strength*

Fig. 4.10 shows the temperature effect on the bending behaviour of the alloys. The stress-strain curves for W-1TiC reveal plastic deformation only at 1200 °C and completely brittle behaviour at lower temperatures. The W-5TiC alloy exhibits plastic deformation at 1000 °C and an entirely brittle behaviour at $T \leq 1000$ °C. The yield strength values at 0.2 % of plastic strain and the ultimate bending strength when brittle performance was observed, as shown in Fig. 4.11.

Fig. 4.10. Stress versus strain curves after TPB tests for (a) W-1TiC alloy and (b) W-TiC alloy. Dashed lines indicate tests performed under a high vacuum atmosphere

When comparing pure tungsten with W-TiC alloys average bending strength, it can be perceived that the flexural strength exhibited an increase over room temperature levels as the test temperature increased, except in the pure W sample, as shown in Fig. 4.11. Strength decreased with further increasing test temperature from 800 to 1200 °C. On the contrary, the strength of pure W always decreased with increasing temperature. W-5TiC possessed the highest strength value of ~900 MPa at 800 °C. However, DBTT is still up to 1000 °C.

The addition of TiC particles to tungsten matrix is beneficial to mechanical properties of W. These secondary phase particles mostly remained at the grain boundaries. Usually, because of their high modulus, the strengthening particles will bear more stress than tungsten matrix when suffering the same strain, since they have good interface joint with adjacent tungsten matrices. This assures the load transferring to TiC particles when loading. The load transferring mechanism is an important strengthening mechanism.

These results are in good agreement with the ones reported by Song (Song et al. 2003) for TiC particle-reinforced tungsten based composites but slightly lower than those reported by (Chong et al. 2010) of 1065 MPa for an alloy containing 1 wt% TiC processed by MA as well.

4. Tungsten materials for armour applications

Fig. 4.11. Flexural strength versus temperature for W-1TiC and W-5TiC alloys and pure W. The error bars correspond to the standard deviation of the experimental data. The dashed lines indicate the region where ductile behaviour was observed, hence 0.2 % yield strength is represented.

Furthermore, it should be noted that the bending strength at 1100 °C for other W alloys processed by the same route is noticeably lower: around 300 MPa for pure W and around 350 MPa for ODS W-2Ti-0.5Y2O3 and W-4Ti-0.5Y2O3 (Palacios et al. 2013) (Aguirre et al. 2010). Therefore, it can be stated that small amounts of TiC can enhance the thermomechanical performance of pure W.

- Fractographical analysis

Morphological features of the fracture surfaces of W-TiC materials tested at room temperature are shown in Fig. 4.12. It can be checked that the size of W grains in the W-5TiC material is significantly smaller than that of W-1TiC. This is due to a high amount of TiC particles, which restricts the grain growth of W grains during the sintering process.

Fig. 4.12. Fracture surfaces of (a) W-1TiC and (b) W-5TiC tested at 25 °C in TPB

However, with higher content of TiC and MA times, small grains alignment has been observed (Fig. 4.13a), while large W grains remain un-milled (Fig. 4.13b).

Fig. 4.13. Fracture surfaces of W-5TiC tested at 400 °C in vacuum atmosphere. Alignment of small grains (a) and large W particles (b) can be appreciated

Morphologies of fracture surface of both materials are similar: the fracture surface displays a typical brittle fracture mixing of intergranular rupture of small grains with transgranular cleavage fracture on larger W grains. Even with the addition of strengthening particles, grain boundaries are weaker than the grain interior and this effect is maintained at higher temperatures as observed in Fig. 4.14 for W-1TiC tested at 800 °C. However, the high density of grain boundaries contributes to the crack deflection. It might result from the secondary strengthening particles. These particles, with high hardness and modulus, will deflect the crack propagation path. The more flexuous the crack propagation path, the higher the fracture toughness due to energy consumption during deflection.

Fig. 4.14. Fracture surface of W-1TiC tested at 800 °C under vacuum atmosphere

Although the melting point of both W and TiC is over 3000 °C, strong degradation of the materials can be observed after testing at 1200 °C. Affinity of W with carbon is very high hence WC compounds may be sintered during the heating process (Davis 1995).

Fig. 4.15. Fracture surface of W-5TiC tested at 1200 °C under vacuum atmosphere

As shown in test results, the primary benefit of adding 5 wt% TiC is the increase in the values of flexural strength and fracture toughness of the alloy. However, a secondary benefit can be attributed to the addition of TiC: oxide formation is inhibited up to 600 °C, as shown in the fracture surfaces of W-1TiC after testing at 400, 600 and 800 °C in air (Fig. 4.16a, b, and c, respectively). With regards to the latter, it should be mentioned again that at 400 °C W-2Ti alloys (Fig. 4.7) and pure W (Palacios et al. 2014) are covered by an oxidation layer.

Fig. 4.16. SEM fractographic surfaces of W-1TiC material tested in TPB at a) 400 °C, b) 600 °C and c) 800 °C, tested in air

4.3.3. Conclusions

The results show that strengthening particles mostly existing at grain boundaries inhibit the growth of tungsten grains in the sintering process. The W-TiC composites have an average nanometric grain size, and the fine grains are helpful to improve the strength and toughness of composites. The maximum of flexural strength and fracture toughness are 900 MPa and 8.5 MPa.m^{1/2}, respectively corresponding to the alloy W-1TiC at 800 °C, although similar results were presented by W-5TiC.

However, per values obtained from the TPB tests, these W-1TiC and W-5TiC alloys have the ductile–brittle transition above 1000 °C, which is higher than that of pure W. TiC hard

particles strongly constrain the plastic behaviour of the W matrix by hindering dislocation movement. Ishijima (Ishijima et al. 2005) attributed the detrimental effect on the ductility to the following three microstructural factors: (1) precipitation of the brittle W_2C phase, (2) heterogeneity in grain size and particle distributions and (3) significant loss of carbon necessary for the formation of finely dispersed particles of transition metal carbides.

4.4. Solid solution and composite materials: W-Ta

The microstructure and mechanical properties of the two W-Ta materials containing 5 wt% Ta (5.12 at %) and approximately 15 wt% Ta (14.8 wt% and 15 at%) are presented in the following chapter. Emphasis has been placed on these materials in light of their thermo-mechanical performance.

Table 4.4 summarizes materials densities: experimental, theoretical and relative, as well as the calculated porosity. Densification was determined to lie between 91.81 % of the theoretical value for W-5Ta and 92.96 % for W-15Ta, while the relative density of reference pure tungsten was 91.64 %. It indicates an increase in the densification with Ta content, even after an extended milling time for W-5Ta material. In consequence, no clear correlation of the densification after HIP with the manufacturing conditions can be deduced from these results. Nevertheless, porosity could be attributed to the Kirkendall effect¹³ (Smigelskas & Kirkendall 1947), as the maximum temperature reached during the HIP process was 1573 K, which represents only 0.43 T_{hom} for Ta and just 0.39 T_{hom} for W.

Table 4.4. Density of reference pure tungsten, W-5Ta and W-15Ta materials

Alloy	Experimental (g/cm ³)	Theoretical (g/cm ³)	Relative (%)	Porosity (%)
Pure W ¹⁴	17.64 ± 0.02	19.25	91.64	8.36
W-5 wt% Ta	17.54 ± 0.01	19.10	91.81	8.19
W-15 wt% Ta	17.49 ± 0.12	18.82	92.96	7.04

4.4.1. Microstructure

Secondary electron images and EDX spectroscopy maps of the sintered materials are presented in Fig. 4.17 and Fig. 4.18. The study of W-5Ta microstructure via metallography and etching with Murakami reagent shows three different phases: i) lagoons of tantalum, ii) large tungsten grains and iii) Ta(W) solid solution surrounding the W grains, as shown in Fig. 4.17.

¹³ The Kirkendall effect assumes that diffusion is a vacancy mechanism so that the flow of matter is matched by an equal and opposite flow of vacancies. The atoms of the two solids don't change places directly; rather diffusion occurs where voids open, making room for atoms to move.

¹⁴ Reference values for pure tungsten were obtained from Palacios et al. (Palacios et al. 2014)

Fig. 4.17. Scanning electron micrograph of a W-5Ta sample after etching with Murakami reagent. EDS analysis revealed that dark grey particles correspond to Ta pools, observing the diffusion of W from the Ta(W) solid solution

Scanning electron micrograph of a W-5Ta sample after etching with Murakami reagent. EDS analysis revealed that dark grey particles correspond to Ta pools, observing the diffusion of W from the Ta(W) solid solution.

Due to the long milling time during manufacturing, around 50 h, nanometric grains were produced and are difficult to appreciate in SEM images. Nevertheless, as observed in the fractographical analysis (shown in Fig. 4.22 and Fig. 4.23) the faceted fracture surfaces revealed an average grain size of 50 nm for this Ta(W) phase with coarser grains of W and Ta over several microns. These heterogeneities may stem from the inner core of the powder particles after MA, revealing that although a very effective partial reduction in particle size was observed, the system had not yet achieved steady-state.

Fig. 4.18. Scanning electron micrograph of a polished section of W-15Ta showing size and distribution of W and Ta phases. (a) Secondary electrons image. (b) EDS mapping of W (red) and Ta (green) in (a). The dark spots correspond to residual porosity

In contrast to that observed for W-5Ta, two distinct phases (distinguishable by colour/pattern contrast) can be identified from the backscattered SEM images of the W-15Ta composite presented in Fig. 4.18. The EDS map confirms that the grey pattern phase and the solid phase are that of a W-rich phase and a Ta-rich phase, respectively, both

composed of smaller grains, with average sizes smaller than 30 μm . This observation can be better appreciated in the fractographical analysis presented in Fig. 4.22 and Fig. 4.23.

4.4.2. Mechanical properties

- Fracture Toughness

The variation of fracture toughness with temperature for the two materials is shown in Fig. 4.19. At all temperatures, both in air and vacuum, the fracture toughness increases with increasing Ta content. However, the increase in fracture toughness with temperature is significantly higher (over 3.5 times greater than the reference W at RT) for W-15Ta even at the highest temperatures tested. Those values are in reasonably good agreement with data reported in the literature (Wurster et al. 2011) for tests conducted on W-Ta alloys of nominally 1, 5 and 10 wt % of tantalum. Even while their investigations were carried out on forged specimens, similar conclusions are reached when considering samples with the crack plane parallel to the forging direction. Those authors also reported the increase in fracture toughness with temperature, until a change in fracture behaviour and a drop in global fracture toughness was observed. This maximum value of K_{IC} can also be seen in Fig. 4.21 at 800 °C and was explained (Rupp & Weygand 2010) as the onset of yielding, i.e. BDTT of the intergranular fracture mode. At low temperatures, specimens fail by brittle fracture with cracks propagating easily through the grain boundaries. On the other hand, at higher temperatures, materials are ductile so that only blunting of the notch tip occurs. This effect is also more visible in air experiments, where the oxides on the surface of the notch could lead to unrealistic higher K_{IC} values.

Fig. 4.19. Nominal fracture toughness of W-5Ta, W-15Ta and pure W tested as a function of temperature. The error bars correspond to the standard deviation of the experimental data. The dashed lines indicate the region where linear elastic fracture mechanics is no longer valid

- *Flexural strength*

The TPB testing produced load-displacement data spanning a temperature range of 25-1000 °C in air and 400-1200 °C in an inert/vacuum atmosphere. These data have been converted to stress-strain and are presented in Fig. 4.20 for both materials. Furthermore, ultimate flexural strength values have been summarized and are presented in Fig. 4.21 as a function of temperature.

Fig. 4.20. Stress-strain curves from non-standard three-point bending tests on (a) W-5Ta and (b) W-15Ta at different temperatures. Dashed lines represent tests performed under vacuum atmosphere

As opposed to the observations for fracture toughness, the W-5Ta alloy exhibits a significantly higher strength as well as a higher DBTT – around 1100 °C – than the W-15Ta material. The W-5Ta specimens failed by brittle fracture at low temperatures. Its transition from brittle to ductile fracture behaviour can be observed with increasing temperature, marked by a steep increase of flexural strength at 1200 °C. Up to this temperature, the degradation of the material is visible even under a vacuum atmosphere, probably owing to the porosity decreasing the alloy cohesion.

Fig. 4.21. Ultimate flexural strength versus test temperature for W-5Ta, W-15Ta, and W in air and vacuum. The open symbols and dashed lines represented the yield strength at 0.2 % when the materials exhibited a ductile behaviour

While this alloy has a very abrupt DBTT in the range 1000-1100 °C, W-15Ta exhibits a smooth transition from brittle to ductile fracture, starting at about 400 °C in vacuum but being fully visible over 800 °C. Moreover, although the average ultimate flexural strength of this alloy is approximately 1.5 times lower than that observed for W-5Ta (but almost twice as high than for the reference W), the effect of the atmosphere is less detrimental, as its behaviour is similar up to 1000 °C when the material is thoroughly oxidized. Given this data, we could establish that the increase in Ta content may inhibit the oxidation of W.

- Fractographical analysis

The dominant failure mechanisms at ambient temperature were similar in both materials: intergranular cracking as well as fracture by cleavage of microstructural heterogeneities, i.e. large W and Ta grains, especially for W-5Ta (Fig. 4.22 and Fig. 4.23).

Because of the sub-granular structure of the W-5Ta alloy, with grains smaller than 50 nm, many small facets can be observed on the fracture surface. Moreover, partially pulled-out grains could be regularly found, as well as the presence of many small pores mainly on the grain boundaries. These brittle fracture mechanisms are responsible for the low toughness of the materials as shown in Fig. 4.19.

Fig. 4.22. Fracture surface of W-5Ta specimen tested at room temperature. As the grains possess subgrains with a size smaller than 1 μm, the micrographs show strongly faceted fracture surfaces, cleavage of coarse grains, aligned W grains, and visible porosity

Additionally, Fig. 4.23 of a post-mortem specimen illustrates that W particles of similar size tend to bring into line in a precise way. The influence on the mechanical properties and the DBTT of W-5Ta has been previously reported with commercially forged materials (Rieth et al. 2013). These tests also reported an intergranular fracture mode in this system, with the crack propagating straight through the sample and failing in a brittle intergranular manner.

Fig. 4.23. Fracture surface of W-5Ta specimen tested at room temperature

As opposed to observations for W-5Ta, W-15Ta specimens show a much greater amount of trans-crystalline fracture and plastic deformation of grain boundaries (see Fig. 4.24 and Fig. 4.25), especially at high temperatures. Therefore, the amount of trans-crystalline fracture seems to be correlated with the fracture toughness of the samples, as K_{Ic} is about

twice as high. For this material, the crack is triggered within the large and linked-up W/Ta regions as it cannot propagate easily over long distances within the more brittle phase.

Fig. 4.24. Fracture surface of W-15Ta tested at 1200 °C in vacuum atmosphere showing intergranular fracture and cleavage of W grains

In addition to the fracture behaviour, fractography analysis also revealed the presence of nanometric grains, but stick together into larger conglomerates of nearly 100 μm (Fig. 4.25).

Fig. 4.25. Fracture surface of W-15Ta specimen tested at room temperature

4.4.3. Conclusions

Two W-Ta materials were manufactured by hot isostatic pressing using standard powder metallurgy techniques. After HIPing a density around 92 % was achieved for both systems. A very fine microstructure, consisting of grains of Ta(W) solid solution in the submicron range, surrounding Ta pools and non-milled W grains, was found in the case of W-5Ta. By

contrast, the W-15Ta material presented a biphasic microstructure composed of both W-rich and Ta-rich phases.

Their mechanical properties (strength and toughness) were measured through three-point bending tests on smooth and notched specimens from 25 °C up to 1000 °C in air and to 1200 °C in high vacuum. The thermos-mechanical properties of the W-5Ta material are dominated by the refined microstructure; it shows a sharp ductile-to-brittle transition in the range 1000 °C to 1100 °C but, by contrast, with very modest fracture toughness, due to decohesion of those small grains.

In the case of the W-15Ta system, it exhibits significantly higher fracture toughness and lower DBTT –around 400 °C– than the W-5Ta material. Therefore, the improvement in toughness of the W-15Ta system could be attributed to a change in the fracture initiation mechanisms, as the DBTT of this material is lower.

To conclude, it has been determined that the addition of Ta enhance the mechanical performance of pure W. However, it has a detrimental effect on the DBTT, more noticeable with lower percentages of Ta. Nevertheless, a possible way to solve this issue has already been proposed for other tungsten alloys (Eck & Pink 1992)(López-Ruiz et al. 2013). It consists of the performance of a thermo-mechanical treatment at higher temperatures. Further investigations into the effect of milling time and chemistry are currently on-going, but it appears that tantalum has no beneficial effects on the DBTT of tungsten after the proposed milling-HIP processing.

4.5. Summary

The main requirements of tungsten materials for structural divertor applications comprise properties like high thermal conductivity, high-temperature strength and stability, high recrystallization temperature, and enough ductility for an operation period of about two years under massive neutron load (Rieth et al. 2013). However, the brittleness of tungsten commercial tungsten products is still the principal problem for their use in structural applications.

In the present chapter, three ductilisation strategies have been followed: (1) alloying to produce a solid solution with Ti and Ta; (2) maintaining a UFG microstructure adding TiC dispersed particles; and (3) producing composite materials with Ta.

The processing parameters, i.e. MA duration, were optimized to obtain UFG microstructures. Increasing the milling time led to a decrease and homogenization of the grain size. However, this effect was narrowed by the O₂ contamination during the process.

It has been reported that strength and recrystallization control can be improved with dispersed TiC particles which inhibits the grain growth. The intrinsic brittleness of tungsten, however, cannot be enhanced by particle dispersion or solid solution with Ti or Ta, nor even with W-15Ta composites. On the contrary, intergranular rupture is enhanced even more, and the DBTT is even higher than that of pure W.

Chapter 5

Thermal Barrier Materials

5.1. Introduction¹⁵

Carbide cermets have historically been developed to provide protection against corrosion and erosion for applications in oil and gas industry, but also against heat as Thermal Barrier (TBs) to control the heat flow and retard rapid chilling. For instance, TBs have the capability to improve the durability of engines by reducing the surface temperature of the underlying components (Fauchais & Vardelle 2012). This aspect could be of great importance for future fusion power plants, where the adequate control of the heat exhaust is presently being explored (Turnyanskiy et al. 2015).

The future divertor design will probably include several joints between the armour and components where heat transferred is not desired. For this purpose, new thermal barriers should be developed.

In addition, as exposed earlier, the actual design model of the divertor is based on a structure consisting of W armour and CuCrZr alloy heat sink. But the thermal expansion mismatch between these materials, together with the loss of strength and creep of CuCrZr at temperatures above 300 °C, limit the operation temperature window of the reactor (J.-H. You 2015). The use of TBs, along with internal cooling of the underlying PFCs, could enable the reactor to operate at higher temperatures thus achieving a remarkable increase in the efficiency and performance of the fusion plant. Furthermore, the problems exposed in the previous chapter (Chapter 4), associated to the high DBTT of W, could be solved by increasing the operational temperature of the whole system.

In both cases, these TBs should withstand the harsh environment coupled with high temperature, large temperature gradient, complex stress condition and radiation (Xu & Guo 2011) while being chemically compatible with the PFC. No single component can satisfy

¹⁵ Contents of this Chapter are partially included in (Tejado et al. 2017)

these multifunctional requirements. Nevertheless, WC-based cermets can fulfil most of the requests by the reinforcement of a metal matrix like copper. Research performed by (Dias et al. 2017) has found that the thermal diffusivity of Cu can be reduced by a factor of three with the addition of just 25 vol. % WC, being lower than for pure copper or tungsten, as desirable for thermal barrier materials. Therefore, the thermophysical and strength properties of these materials are of great importance to assess their feasibility as TBs.

For this purpose, the present Chapter presents the results on the mechanical characterization of these novel WC-Cu cermets. The focus is placed on the temperature effect and composition dependence, as the volume fraction of Cu varies from 25 to 50 and 75 %.

5.2. Materials

The cermets characterized in the present investigation were produced by tubular blending (1h) of commercially pure WC powder (diameter of 1 μm and 99.9 % nominal purity) with Cu powder (diameter <37 μm and 99.99 % nominal purity) for variable volume fraction of Cu (25 %, 50 % and 75 %), subsequently consolidating the mixtures by hot pressing. Furthermore, to obtain the highest densification, processing parameters (Temperature, Pressure and Time) were individually set for each composition, as presented in Table 5.1.

Table 5.1. Main processing parameters and densification achieved for the consolidated cermets

Processing parameters	WC-25Cu	WC-50Cu	WC-75Cu
Temperature ($^{\circ}\text{C}$)	1150	1050	900
Pressure (MPa)	47	37	22
Time (min)	6	5	5
Densification (%)	95	92	91

Through this manufacturing route, it was possible to achieve densifications above 90 %. WC-25Cu sample reached the highest value, which could be due to the combination of high pressure and temperature as compared to the rest of the material.

5.2.1. Microstructure

In Fig. 5.1, Fig. 5.2 and Fig. 5.3¹⁶ it is presented the microstructure of the consolidated cermets: particles of WC dispersed in a binder matrix of copper. Coalescence of small WC grains can be observed, with larger aggregates of 20 to 30 μm , especially in WC-25Cu (Fig. 5.1). The application of a high pressure during the consolidation particles sliding and rearrangement of small grains into a denser configuration (Kingery et al. 1963).

However, it can be appreciated that WC particles are arranged forming a network with interpenetrated Cu, caused by the optimal blending process and the small grain size of

¹⁶ Images courtesy of T.Palacios

starting WC powders. Even for the cermet with lower WC content, there is a continuum three-dimensional WC structure with a double network of Cu and WC.

Fig. 5.1. SEM images of (a) Microstructure of the WC-25Cu cermets and the EDX maps of (b) W, (c) Cu and (d) W + Cu elements. Corresponding X-ray EDS maps for Cu-K α , and W-M α .

Fig. 5.2. SEM images of (a) Microstructure of the WC-50Cu cermets and the EDX maps of (b) W, (c) Cu and (d) W + Cu elements. Corresponding X-ray EDS maps for Cu-K α , and W-M α

Fig. 5.3. SEM images of (a) Microstructure of the WC-75Cu cermets and the EDX maps of (b) W, (c) Cu and (d) W + Cu elements. Corresponding X-ray EDS maps for Cu-K α , and W-M α .

5.3. Results and discussion

5.3.1. Flexural strength

The flexural strength was tested in three-point bending configuration on 27.0 mm x 3.5 mm x 1.3 mm bars with a crosshead speed of 100 $\mu\text{m}/\text{min}$. The reported flexural strength was the average of at least two measurements. This test configuration was also used to determine the fracture toughness of the cermets by introducing a femto-second laser notch in the bottom of the bars in SELNB configuration. Both properties were conducted at room temperature (RT), 425, 550 and 80 $^{\circ}\text{C}$ using inductive heating at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under very high vacuum atmosphere (10^{-6} mBar). The upper limit for test temperatures was set in 675 $^{\circ}\text{C}$ for samples containing 50 vol% Cu and 75 vol% Cu due to softening of Cu at higher temperatures.

Fig. 5.4. Flexural strength of WC-Cu cermets as a function of composition and temperature. Mean values and standard error. Square symbols and dashed lines illustrate brittle behaviour and hence, ultimate flexural strength instead of yield strength

Fig. 5.4 shows the flexural strength of the WC-Cu composites at 0.2 % plastic strain, i.e. yield strength. When fracture strain was limited to the linear elastic regime, ultimate flexural strength was reported with square symbols and dashed lines. The flexural strength, both ultimate and yield, increases with WC content and reaches a maximum of about 800 MPa at 425 $^{\circ}\text{C}$ when Cu content is just 25 %. Furthermore, the tensile behaviour of all three kinds of the composites exhibit almost the same trend. It reaches a maximum at 425 $^{\circ}\text{C}$ and decreases slowly up to 675/800 $^{\circ}\text{C}$, with a slight recovery of the values at 675 $^{\circ}\text{C}$. Above this temperature, the softening of the metal phase leads to acutely low values of flexural strength, so only WC-rich composite (25 vol% Cu) was tested under this condition.

It is noticeable that the addition of Cu leads to a significant increase in ductility. This rise can be better observed in Fig. 5.5, where the tensile stress-strain curves of the cermets are

plotted. WC-25Cu composite exhibits elastic behaviour up to fracture at all temperatures, though slight plastic yield takes place at 675 °C, which indicates that fracture is dominated by the brittle WC phase. On the contrary, the Cu-rich cermet (75 vol% Cu) exhibits ductile behaviour from RT (Fig. 5.5 c). At this temperature, the elongation is indeed one order of magnitude higher than the one exhibited by WC-25Cu. However, the rupture strength at all temperatures was considerably lower compared to the latter (700 MPa against 175 MPa at 675 °C for WC-25Cu and WC-75Cu, respectively).

Fig. 5.5. Tensile curves of a) WC-25Cu, b) WC-50Cu and c) WC-75Cu, at four testing temperatures: 25 °C, 425 °C, 550 °C and 675 °C

In Fig. 5.5 (b) the tensile curves of WC-50Cu are presented. It exhibits an intermediate behaviour; while rupture strains are much lower than for the Cu-rich cermet, both yield and ultimate strength values are around 30 % higher. Nevertheless, the increase in flexural elongation as compared to WC-25Cu is only evident up to 425 °C, since both cermets present similar values of rupture strain below this temperature (< 0.3 %).

5.3.2. Elastic modulus

Load-deflection curves of the bending tests were used to calculate the modulus of elasticity by drawing a tangent to the steepest initial straight-line portion of it. Those data were then compared with values measured using resonance frequency analysis (RFA), also known as Impulse excitation method at RT. Additionally, the evolution of elastic modulus with temperature was estimated with the *Voigt*, *Reuss* and *Hill* micromechanical models. Materials data for the modulus of elasticity of WC and Cu were taken from (Wheeler & Michler 2013) and (Davis & ASM International 2001), respectively.

Fig. 5.6. Elastic modulus of (a)WC-25Cu, (b)WC-50Cu and (c)WC-75Cu as a function of temperature, mean and standard error. Values were measured from the tensile curves and by Resonant Frequency Analysis. Upper and lower bounds were estimated with the Voigt and the Reuss models, respectively, while the Hill model is the average of them

The elastic modulus values are plotted in Fig. 5.6 as a function of temperature and Cu content. The data were measured from the bending curves up to 675-800 °C and,

additionally, at RT through RFA. The elastic modulus data measured for all the cermetes are located within the boundaries established by Voigt and Reuss, calculated with Equations (3.19) and (3.20), Hill average modulus (Equation 3.21) is also shown.

The Voigt method clearly overestimates the stiffness while the Reuss method slightly underestimates it. In all cases, the experimental values lie between Hill average and Reuss bound which seems to be a good approximation for the macroscopic constant of the cermetes. However, for WC-75Cu, the results approximate Reuss values at all temperatures. This deviation of the elastic modulus to the lower bound has already been observed in particle-reinforced metallic composites, such as Cu-W (Weidmann et al. 1990) or Al-Cr. It is due to a certain amount of hydrostatic stress generated in the composite when the softer matrix phase is restrained from deformation by the hard particles (Totten & MacKenzie 2003).

To include the effects due to porosity differences in the elastic modulus estimations, the Voigt and Reuss boundaries were corrected with the measured porosity values. Hence, no overestimation of the elastic constants has been done.

Elastic modulus values obtained from RFA are significantly higher than those measured by TPB for each cermet sample. The difference found between the stiffness achieved with dynamic and the static methods is a frequent observation and, indeed, it has been previously studied by other authors reporting this mismatch (Ledbetter 1993) (Radovic et al. 2004). It is caused mainly by the fact that the dynamic modulus was derived on the basis of the material being ideal on the macroscopic level, i.e. isotropic, homogeneous and elastic. However, Cu presents a significant crystallographic anisotropy in Young's modulus (Armstrong et al. 2009) and small inhomogeneities, i.e. pores or microcracks, could be neglected by the sensor. Furthermore, this technique is very sensitive to variations in dimensions of the samples (Quinn & Swab 2000). Thus, a non-prismatic shape or a rough surface would lead to incorrect values of the elastic constants.

Fig. 5.7. Flexural elastic modulus from the TPB tests of the WC–Cu cermetes as a function of composition and temperature. Mean values and standard error

To discriminate the effect of Cu content, the static elastic modulus is also plotted in Fig. 5.7 as a function of temperature and composition. Measured stiffness is in good agreement with theoretical values, while data obtained for WC-75Cu and WC-25Cu composites follows the same trend, WC-50Cu elastic properties remain nearly constant in the temperature range tested.

5.3.3. Fracture toughness

The fracture toughness results of WC-Cu cermets as a function of temperature and composition are summarized in Fig. 5.8. At temperatures above 550 °C for WC-50Cu and WC-75Cu, the ratio P_{max}/P_Q overcomes the limit 1.10 encompassed by the ASTM standard (ASTM Standard E1820-11 2009), so LEFM can no longer be applied¹⁷. However, these values provide a lower bound of fracture toughness, so they have been reported with the goal of comparing materials behaviour trends.

Fig. 5.8. Fracture toughness of the cermets as a function of temperature and composition. Mean values and standard error. Apparent values of K_{IC} are plotted when LEFM is no longer valid

It can be observed that there is an improvement in the fracture toughness when the WC volume fraction increases from 25 vol% to 75 vol%. Moreover, a clear trend with temperature can be inferred from it. At RT, where little plastic deformation is observed, both WC-25Cu and WC-50Cu composites exhibit toughness around 8 MPa.m^{1/2}. On the contrary, when temperature increases, the effect of the high concentration of WC is more evident, showing the highest value of toughness, ~ 9 MPa.m^{1/2}, at 425 °C for WC-25Cu. This effect has

¹⁷ The ratio P_{max}/P_Q , where P_Q is the critical load obtained with the 5 % secant method and P_{max} is the maximum load that the specimen can sustain, defines the validity of the tests regarding linearity. If this ratio exceeds 1.10, then K_{IC} is not size-independent. It would be necessary to use larger specimens to determine K_{IC} and the use of a nonlinear fracture theory approach instead of the Linear Elastic Fracture Mechanics (LEFM). For further details the reader is directed to Chapter 7.

already been observed for W-based materials (Tejado et al. 2015), and it is due to a softening of the grain boundaries and explained by the blunting of the crack tip (Salem et al. 2002). Up to this temperature, Cu ductile phase controls the fracture and, hence, the degradation of the cermet.

Fig. 5.9. SEM fracture surfaces of the WC-Cu cermets tested at 25 °C: a) WC-25Cu, b) WC-50Cu, and c) WC-75Cu

The difference in properties of the three materials is evident upon viewing their fracture surfaces. Fig. 5.9a shows a micrograph of the WC-rich cermet (25 vol% Cu) that justifies the macroscopic brittle fracture at all the temperatures tested. The carbide particles evidence flat, cleaved planes, while the microstructural ductile nature of the Cu phase results in the elongation of the metal around the carbide particles. This effect is more pronounced when the Cu content in the cermets is increased. Fig. 5.9b and Fig. 5.9c show the residual porosity present after material processing. Nevertheless, despite the thermal mismatch and the weak bond between WC and Cu, no decohesion was observed between both phases.

The fracture behaviour is a combination between the transgranular fracture of WC particles and plastic deformation of Cu matrix. For WC-25Cu, the number of fracture dimples is relatively low (see Fig. 5.9a) and increases gradually with the Cu volume fraction in the WC-Cu system. Transgranular fracture of WC particles can be explained by the existence of cracks that can be propagated from stress concentrators, i.e. pores and defects observed in Fig. 5.9a, along with the crystal planes during fracture process.

Fig. 5.10. SEM fracture surface of WC-75Cu cermet tested at 675 °C in vacuum.

The degradation of the tensile performance up to 425 °C can be explained through Fig. 5.10. It shows the fracture surface of a WC-rich (75 vol% Cu) sample tested at 675 °C. While WC particles remain practically unaltered, Cu phase is apparently degraded because of the temperature increase. This image illustrates as well several inhomogeneities in the grain size of WC particles, which could be the reason of the no so high performance of WC-25Cu composite as expected.

5.3.4. Coefficient of thermal expansion

From the elastic modulus results, it was also possible to estimate the uniaxial thermal expansion coefficient, α , of the cermets, which is indeed a relevant parameter for structural design of elements. The empirical relation, $E=4.5\alpha^{-2.3}$, proposed by Arenz (Arenz 2005a) has been used to obtain the thermal expansion coefficient of the cermets, as exposed in Chapter 3.

Fig. 5.11. Coefficient of thermal expansion of the WC-Cu cermets as a function of composition and temperature. Literature values for CuCrZr (Birol 2010) and W (Hidnert & Sweeney 1925) are also presented

Fig. 5.11 shows the coefficient of thermal expansion of the WC-Cu composites between RT and 800 °C. It can be observed that an increase in Cu leads to an increase in this factor. Furthermore, this effect is more evident at higher temperatures. These data have been obtained from the empirical relation $E=4.5\alpha^{-2.3}$, where E is the elastic modulus measured by the bending tests (see Fig. 5.7.), thus, the same trend is followed. To analyse their suitability as thermal barriers for fusion applications, literature values of W and CuCrZr have been represented as well in Fig. 5.11. It can be observed that, with just a small percent of Cu, these cermets can reduce the thermal expansion coefficients mismatch between W and CuCrZr, which, undoubtedly, one of the main concerns regarding the joint between the PFM and the heat sink. In addition, their value as thermal barriers was validated by Dias (Dias et al. 2017), who measured their thermal diffusivity (Fig. 5.12).

They observed that it was lower than for that of pure copper or tungsten, as desirable for thermal barrier materials. What is more, the thermal diffusivity of copper can be reduced by a factor of three with the addition of just 25 vol% WC, and the results are not very different than for WC-50Cu. Thus, thermal diffusivity is below the expected with the rules of mixture. These values could be associated with a percolation effect due to the microstructure of these cermets.

Fig. 5.12. Thermal diffusivity of the WC-Cu cermets as a function of composition and temperature. Literature values for W, WC and Cu are also presented

According to percolation models, below percolation threshold the thermal diffusivity of the cermets should be almost the value of the reference material, i.e. copper. Over the percolation threshold, the thermal diffusivity of the cermets should be reduced very quickly up to saturation. The limit, in this case, is the thermal diffusivity of the pure WC. This hypothesis may be justified by the presence of a 3D WC network as “percolation channels” controlling the heat transport in the material. Fig. 5.1 to Fig. 5.3 revealed a WC network interpenetrating the copper matrix in all cermets, as a consequence of the excellent blending process and the small grain size of the starting WC powders. Even for WC-25Cu it is clear that there is indeed a continuum three-dimensional WC structure with a double network (Cu and WC) that percolates the whole material.

5.4. Conclusions

The effect of different contents of Cu on the thermal and mechanical properties of WC-Cu cermets was studied. Three compositions (25, 50 and 75 vol% Cu) were tested up to 800 °C (WC-75Cu) and 675 °C (WC-50Cu and WC-25Cu) both under vacuum atmosphere.

Fracture surfaces of WC-Cu composites revealed two kinds of fracture mechanisms: transgranular cleavage of WC particles and ductility of Cu phase. The dominant fracture mechanism depends strongly on the content of Cu and temperature; thus, macroscopic ductile behaviour and high rupture strains were observed for Cu-rich cermet (75 vol% Cu).

On the contrary, the tensile behaviour of WC-25Cu was brittle up to fracture and up to 675 °C, where slight plastic yield appears. Besides, the high concentration of WC resulted in the highest values of tensile strength at 425 °C, 800 MPa. The behaviour of WC-50Cu cermet is in-between the observed for the above materials, with brittle to ductile transition temperature at 425 °C.

5. Thermal Barrier Materials

The measured elastic properties and the estimated thermal expansion coefficient fit well the analytical models for composite materials, with values between the theoretic boundaries for all cases. However, the thermal diffusivity of the cermets is lower than expected by these rules. Thus, this is a beneficial effect of the microstructure presented, a continuum three-dimensional WC structure with a double network (Cu and WC) that percolates the whole material. Consequently, a slight percent of Cu (25 vol% Cu) can reduce significantly the large difference in thermal expansion between W and CuCrZr as armour component and heat sink, respectively.

The thermal performance of these materials, together with their mechanical properties could indeed reduce the heat transfer from the PFM to the underlying element while supporting the high thermal stresses of the joint. Though, high heat flux tests should be performed in advance to verify their performance under peak heat loads. This component could be either a heat sink with a low melting point, such as Cu or CuCrZr alloy, or any other element of the reactor where heat transfer is not required. Furthermore, the presence of these cermets could allow the reactor to operate at higher temperatures, even above the DBTT of W, without compromising the underlying materials.

Chapter 6

Heat Sink Materials

6.1. Introduction

Many design concepts for next-generation fusion devices include W based materials joined to a Cu or CuCrZr heat sink. However, the lifetime of the joints is compromised by the high thermal stresses at the interface that results from mismatch of the coefficient of thermal expansion (CTE) and the elastic modulus between both elements (Pintsuk et al. 2003). Additionally, W–Cu system has no mutual solubility hence the bonding strength at the interface is quite poor.

To overcome this problem, an interlayer material is needed. For this purpose, a metal matrix composite (MMC) between W and Cu could tailor the CTE by controlling the composition and thus reducing the thermal mismatch. The interest in these MMC composites is two-fold: the W matrix provides the necessary composite strength at high temperatures, while Cu and its alloys provide the required high thermal conductivity towards efficient heat removal in the cooling system.

Notwithstanding, the production of perfectly dense W–Cu MMCs is not a trivial issue. It is not only due to these properties mismatches but also due to the significant difference between the melting points of W (approximately 3400 °C) and Cu (about 1083 °C). This makes it difficult to produce a conventional alloy. To solve this problem, several authors have reported the beneficial effects of cobalt during the sintering process (Joo et al. 1994) and (Moon et al. 1998). The addition of cobalt powder increases the wettability of W particles by Cu, forming an intermetallic compound, Co_7W_6 , that reduces the overall porosity and improves the mechanical properties of the final product (Daneshjou & Ahmadi 2006). Nonetheless, radioprotection requirements limit the presence of cobalt inside the reactor (Barabash 2013).

Of the preferred methods for producing fully dense W–Cu composites, laser (Elsayed et al. 2015) and plasma sintering (Tang et al. 2014) have gathered much attention in the last few decades. However, these processes are complex, and the problem of an adequate electrical conductivity of the powders and the achievement of homogeneous temperature distribution is particularly acute (Suarez et al. 2013). Furthermore, homogeneous and dense

W-rich composites (>60 wt% W) can only be produced by the melt infiltration technique (Hamidi et al. 2011).

In this synthesis route, a W rigid skeleton with proper relative density is produced via powder metallurgy and then, compacted and sintered before molten copper is infiltrated into the open pores of the W structure (Johnson et al. 2005) (Liang et al. 2015). An extra sintering treatment is needed to obtain higher densifications (Xu et al. 2014).

In this Chapter, four MMC with compositions of W-15/30/40 wt% Cu and W-30 wt% CuCrZr were produced by melt infiltration. Their thermophysical and strength properties were investigated and measured to assess their feasibility as a component of next-generation fusion reactors. Thus, a graded structure could be developed with these composites, tailoring the properties mismatch between the W-PFM and the Cu-based cooling tubes.

In a first batch, composites with 30 wt% Cu (W-30Cu) and 30 wt% CuCrZr (W-30CuCrZr) were manufactured and tested. Secondly, once the successful processing route was validated, the above technique was applied to produce composites with 15 and 40 wt% Cu (W-15Cu and W-40Cu). Results have been compared with those obtained for W-30Cu composite to accurately determine the effect of Cu content on the thermomechanical properties. Therefore, this Chapter is split into two sections: first, W-30Cu and W-30CuCrZr have been tested and compared; secondly, the effect of Cu content has been duly studied via W-15Cu, W-30Cu, and W-40Cu materials.

6.1.1. Materials processing

Materials were manufactured by *Louis Renner GMBH* Company (Amtsgericht Stuttgart, Germany) and supplied to UPM by our EUROfusion partner IPP (Max Planck Institute of Plasma Physics, Garching bei München, Germany), based on the following processing route.

The W skeleton was produced with commercial powders of tungsten with 8 μm size, consolidated by uniaxial cold pressing. The green specimens were sintered at 1150 $^{\circ}\text{C}$ for 2 h under high purity hydrogen atmosphere. Sintered skeletons with desirable density values, i.e. 85 %, 70 % and 60 % (36 %, 52 % and 76 % pore volume fraction), were infiltrated by oxygen free molten copper/CuCrZr. Infiltration was done at 1150 $^{\circ}\text{C}$ in a hydrogen atmosphere for 2 h. Finally, specimens were machined into plates (3 mm x 30 mm x 150 mm) for later characterization. From the composite materials, the bend-test (2.8 x 2.8 x 30 mm) and tensile-test (dogbone-shaped, 2.0 x 2.5 x 17.0 mm of the narrow portion) specimens were cut.

Four different compositions were produced with this technique: W-15wt% Cu, W-30 wt% Cu and W-40 wt% Cu. Densification achieved can be observed in Table 4.3.

Table 6.1. Experimental (ρ_{exp}) and theoretical (ρ_{th}) densities measured for the samples along with the relative density (ρ_r) calculated from them and the estimated porosity

Material		Density			
Notation	wt% Cu/CuCrZr	ρ_{exp} (g/cm ³)	ρ_{th} (g/cm ³)	ρ_r (%)	Porosity (%)
W-15Cu	15	15,01±0.01	16.42	91.40	8.60
W-30Cu	30	13.77±0.05	14.32	96.22	3.78
W-40Cu	40	12.43±0.01	13.19	94.24	5.76
W-30CuCrZr	30	13.73±0.01	14.32	95.92	4.08

6.2. Materials W-30Cu and W-30CuCrZr

6.2.1. Microstructure

The microstructure of W-30Cu and W-30CuCrZr after metallographic preparation can be observed in Fig. 6.1 and Fig. 6.2. Samples were previously etched with W¹⁸ and Cu¹⁹ specifics etchants to reveal the real metallographic microstructure, i.e. grain boundaries and higher contrast between the constituents.

Fig. 6.1. Scanning electron microscope images of (a) W-30Cu and (b) W-30CuCrZr composites after metallographic preparation and etching

¹⁸ W etchant for 10 s: Murakami's reagent, 100 ml water, 10 g NaOH and 10 g K₃Fe(CN)₆

¹⁹ Cu etchant for 5 s: 60 ml ethanol, 15 ml HCl and 5 g FeCl₃

Fig. 6.2. SEM images with EDX map of (a) W-30Cu and (b) W-30CuCrZr composites after metallographic preparation and etching

From the above pictures, it can be observed that the average grain size of W varies from several microns to dozens, while Cu forms an interconnected network structure around W particles, and the same observation is made in W-30CuCrZr. The interface between W and Cu or CuCrZr appears tight, without any interspace or porosity which is consistent with the high relative density ($\sim 96\%$ for both composites) that was measured.

Additionally, the microstructure of these two MMCs was also investigated by High-Temperature X-ray Diffraction (HTXRD) with a PANalytical X'Pert PRO MPD diffractometer with a $\text{CuK}\alpha$ ($\lambda=0.15405\text{ nm}$) radiation source. Data were taken for the 2θ range of 20° - 90° with a step of 0.001° . The powder diffraction pattern indexing process was used, and Miller Indices ($h\ k\ l$) were assigned to each peak in the first step. With a view to studying the evolution of the composites with thermal exposure, the diffractograms were measured at different temperatures from 25°C to 800°C with $15^\circ\text{C}/\text{min}$ ramp, and 10 min dwell time until stable conditions were achieved. All the measurements were acquired under vacuum conditions at $<10^{-5}$ mbar pressure.

Diffraction spectra of the samples were measured under conditions corresponding to testing temperatures, from 25°C to 800°C , and the typical XRD patterns for the composites are shown in Fig. 6.3.

Fig. 6.3. XRD diffraction patterns of (a) W-30Cu and (b) W-30CuCrZr from 25 °C to 800 °C

For W-30Cu, only metallic W (JCPDS: 4-0806) and Cu (JCPDS: 04-0836) diffraction peaks were identified despite the variation in temperature. The absence of oxides indicates the success of manufacturing the materials under preferable vacuum conditions. While the intensity and width of W reflections remain constant for all the temperature range, the peak intensity of the Cu (111) reflection at 43.29° strongly depended on the testing temperature, and it was raised nearly three times from 9000 to 25000 counts per second (cps) for 25 °C and 800 °C, respectively. It indicated a higher crystalline quality and/or orientation alignment for Cu at higher temperatures (Pranevičius et al. n.d.). However, the average crystallite size, calculated using Scherrer formula from the linewidth of their respective XRD peaks, did not reveal grain growth for any of the components. Hence, results are not included in the present work. Those results are in agreement with the reported recrystallization temperature of bulk W between 900 °C and 1400 °C (Palacios et al. 2015).

The XRD pattern of W-30CuCrZr also exhibited diffraction peaks at diffraction angles matching only with those of metallic W and Cu, with no evidence of precipitate phases. These results suggest that the precipitate phases are too tiny or sparse. In contrast to W-30Cu, the Cu(111) diffraction peak in W-30CuCrZr is weaker at all temperatures, which suggests the solution of Cr or Zr is present in the Cu matrix, resulting in Cu lattice shrinkage as observed by (Zhang et al. 20115) for CuCrZr alloys.

Thus, from the HTXRD, it can be assessed that no additional phases, i.e. interfacial reaction between W and Cu or CuCrZr, are induced by thermal exposure. Additionally, optimization of the manufacturing processes in an industrial environment has been assessed.

6.2.2. Mechanical properties

Both flexural strength and fracture toughness (K_{IC}) were tested in three-point bending configuration on 2.8 mm×2.8 mm×25.0 mm bars. K_{IC} was determined by introducing a femto-second laser notch in the bottom of the bars. The stress intensity factor for mode I

stress was then computed from the critical load (P_Q) and the beam section using the equation proposed by Guinea et al. (Guinea et al. 1998). The ASTM 5 % secant method (ASTM Standard E1820-11 2009), i.e. a secant line with a slope equal to 95 % of the initial elastic loading slope of the tangent line, was used to determine P_Q .

- Fracture toughness

At RT curves were perfectly elastic up to fracture²⁰, however, on increasing temperature the stress intensity factor loses its validity with increasing ductile behaviour. Thus, the values plotted in Fig. 6.4 are apparent ones, giving only a lower bound approximation of the fracture properties. For a deeper analysis of the fracture behaviour of these composites, the reader is referred to Chapter 7. A complete study of the application of the fracture mechanics to W-based composited was implemented there.

With the aim of providing a first insight on the fracture properties of both composites, Fig. 6.4 shows the variation of apparent fracture toughness as a function of temperature. For W-30Cu, the fracture toughness decreased rapidly from 17.5 MPa.m^{1/2} at 25 °C to 4 MPa.m^{1/2} at 800 °C. The absolute fracture values are on average 25 % higher for W-30CuCrZr than for W-30Cu, but the latter exhibits a plateau region between 300 °C and 550 °C. Up to this temperature, the decrease is nearly constant. The local morphological configuration of the phases plays an important role in triggering the fracture and subsequent failure.

Fig. 6.4. Apparent fracture toughness of the composites as a function of temperature and composition. Mean values and standard error

²⁰ Load vs. deflection diagrams and crack growth resistance curves of W-30Cu and W-30CuCrZr composites, calculated with the novel equivalent elastic crack approach, are presented in Chapter 7, Fig. 7.13.

- *Flexural strength*

Fig. 6.5 shows the flexural strength of the WC-Cu composites at 0.2 % plastic strain, i.e. yield strength.

The flexural strength of the two composites exhibits the same trend: at 25 °C both present values higher than 550 MPa but it decreases slowly up to 800 °C. However, a slight recovery of the values is observed at 550 °C for W-30Cu, but the error bars at this point are also higher. Additionally, the material with a composition of W-30CuCrZr showed a yield flexural strength that was 50 % greater than W-30Cu over the entire temperature range.

Fig. 6.5. Yield flexural strength of the composites as a function of composition and temperature. Mean values and standard error

- *Tensile strength*

Fig. 6.6 depicts the variation of yield and rupture strength of the composites after tensile testing. It is noticeable that for both materials the tensile strength decreases as the measurement temperature increases from 20 °C to 800 °C. While values of yield and rupture strength follow the same trend for W-30CuCrZr, this behaviour was different in the W-30Cu composite. Thus, the softening and degradation of the Cu phase leads to relatively low rupture strength values.

Fig. 6.6. (a)Yield and (b) Maximum tensile strength of the composites as a function of composition and temperature. Mean values and standard error

The test flow curves were obtained at constant crosshead speed of 100 $\mu\text{m}/\text{min}$ for W-30Cu and W-30CuCrZr, and they are shown in Fig. 6.7a and b, respectively. True stress-strain curves were obtained through the DIC technique as explained in Chapter 3.

Fig. 6.7. True stress-strain curves for (a) W-30Cu and (b) W-30CuCrZr composites at different temperatures

Addition of Cu leads to a significant increase in maximum elongation at 425 °C. At this temperature both materials exhibit the highest values of rupture strain. However, the loss of strength in the W 30CuCrZr composite is not as prominent at temperatures below 550 °C. In addition, as observed for the TPB tests, this material exhibits higher values of rupture stress and uniform elongation in tension. Up to 550 °C, both composites show relatively flat tensile stress-strain curves without any maximum, indicating an extensive plastic

deformation and crack tip blunting without apparent crack extension, i.e., the CuCrZr base alloy has relatively high fracture toughness.

These results are considerably better than those obtained by Zivelonghi and You (Zivelonghi & You 2014) for a W-CuCrZr composite with 30 vol% CuCrZr. They reported a maximum strength at 300 °C of around 350 MPa and close to 200 MPa at 550 °C. These researchers stated that the thermal stress caused by the thermal expansion mismatch between the constituents upon heating was responsible for this behaviour.

- Elastic Modulus

Fig. 6.8 shows the variation of the elastic modulus as a function of temperature by measuring the slope of the strength curves. The elastic modulus decreases slowly from 175 GPa and 150 GPa, for W-30Cu and W-30CuCrZr respectively, to 110 GPa at 800 °C, but the slope of W-30CuCrZr seems to be quite moderate as its value at 25 °C is lower. However, the absolute values of the elastic modulus are slightly higher for W-30Cu below 800 °C. As the testing temperature increases, so does the relative contribution of the W skeleton on the elastic properties. Thus, its degradation starts at higher temperatures. At higher temperatures, the effect of Cu or CuCrZr is residual, so they tend toward the same values.

Fig. 6.8. Elastic modulus of W-30Cu and W-30CuCrZr as a function of composition and temperature. Mean values and standard error

Additionally, elastic modulus data are shown separately for each composition in Fig. 6.9. Results obtained from the Strength Tests (ST) have been compared with those obtained at 25 °C with Resonant Frequency Analysis (RFA) and represented within the Voigt and the Reuss boundaries. The Hill average modulus is also shown. Furthermore, the residual porosity (4 %) has been considered to avoid the overestimation of the predicted elastic constants.

Fig. 6.9. Elastic modulus of a) W-30Cu and b) W-30CuCrZr as a function of temperature, mean, and standard error. Values were measured from the strength tests (ST) curves and using the resonant frequency analysis (RFA). Upper and lower bounds were estimated with the Voigt and the Reuss models, respectively, while the Hill model is the average of these two methods

The values obtained from the strength curves of W-30Cu and Hill model match closely, as expected for a no-fibres composite (Totten & MacKenzie 2003). However, the predicted bounds for W-30CuCrZr slightly overestimate the stiffness, although the observed trend is the same, i.e. the decreasing rate is lower up to 550 °C. The difference between measured and predicted values might be attributed to the selected reference constants, and thus published values that were reported for CuCrZr alloys differ significantly depending on the processing route and the thermal history of the alloy (Park et al. 2008). Metallurgical grade CuCrZr alloy is the reference selected for the grey area in Fig. 6.9b. However, Papastergiou (Papastergiou 1997) reported the material data for its use in the JET hyper-vaportrons from studies of (Tivey 1995), both in hardened and aged conditions. The value of the elastic modulus of the hardened material is on average 30 % higher than the data after aging (70 GPa to 100 GPa at RT). To obtain the hardened alloy, it was previously heated to 475 °C for several hours and then quickly quenched so that no new crystal phases appear, while its strength remains rather high. However, after operation at high temperatures, new crystal phases may appear in the grain boundaries. The aging of the material leads to its softening, thereby reducing the strength and elastic modulus while increasing the ultimate elongation. Aged CuCrZr alloy has also been selected as a reference for bounds calculations, and it is included in the green area in Fig. 6.9b. From the above studies, it can be assessed that the CuCrZr phase in the composite W-30CuCrZr seems to be in an intermediate condition. Thus, hardened constants overestimate the stiffness while aged condition slightly underestimates it.

Elastic modulus values obtained from RFA are significantly higher than those measured by ST for both composites. This mismatch has already been reported for Cu-based composited in Chapter 5, and attributed to the sensitivity of RFA technique to the specimens' dimensions and homogeneity.

- Thermal expansion coefficient

Research performed by Arenz (Arenz 2005b) found that a large number of polycrystalline and amorphous materials, W and Cu among them, obey the empirical relation $E=4.5\alpha^{2.3}$, where α is the uniaxial thermal expansion coefficient, and E is the elastic modulus. Both properties are related intimately to lattice vibration, so energy well theory and thermodynamic analysis can be used to obtain a qualitative relationship.

Fig. 6.10 depicts how the thermal expansion coefficient of the W-based composites varies with temperature. Published values for W and CuCrZr alloy are also presented for comparison. At each temperature, the thermal expansion coefficient monotonically increased with the increase in temperature. However, the relative rate of change in the coefficient is around $1.6 \cdot 10^{-3} \text{ } ^\circ\text{C}^{-1}$, which is closer to the temperature shown by W ($0.8 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$). In addition, there were not ample differences in the thermal expansion response of the two tested composites, and thus the skeleton structure of W determines the change in α , because its thermal expansion coefficient ($4.6 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$) is five times lower than that exhibits by Cu ($17.0 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$ (Kirby & Hahn 1969)) or CuCrZr ($14.0 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$). These results are consistent with those obtained by Duan (Duan et al. 2014) for W-Cu composites produced by infiltration of Cu into W fibre preforms and by You (You et al. 2013) for infiltrated W-CuCrZr composites, although their research was conducted up to lower temperatures.

Fig. 6.10. Coefficient of linear thermal expansion of W-30Cu and W-30CuCrZr as a function of composition and temperature. Published values for CuCrZr (Biol 2010) and W (Hidnert & Sweeney 1925) are also presented

Many design concepts for next fusion devices deal with W or W alloys joined to a Cu or CuCrZr heat sink. However, the lifetime of the components is compromised by the high thermal stresses at the interface because of the mismatch in the CTE and elastic modulus between those materials (Pintsuk et al. 2003). The metal matrix composites presented in

this chapter could efficiently dissipate heat while tailoring CTE through the control of W skeleton porosity. This is vitally important to enhance the performance, life cycle, and reliability of the component.

- *Fractographic analysis*

Fig. 6.11. Fracture surfaces for W-30Cu tested at 25 °C (top), 425 °C (middle) and 800 °C (bottom) in a vacuum atmosphere, and for W-30CuCrZr tested at 25 °C (top), 300 °C (middle) and 800 °C (bottom) in vacuum atmosphere

Fig. 6.11 shows the SEM images of the fracture surfaces after the strength tests. They clearly demonstrate the network of Cu formed throughout the W skeleton. During the infiltration stage, molten Cu flows around W particles forming a homogeneous microstructure while filling the voids of the W skeleton, resulting in a high densification.

Both materials exhibit similar fracture surfaces. At 25 °C, the dominant modes of fracture can be observed in left figures: transgranular fracture of W particles and plastic deformation of Cu matrix. This plastic behaviour can be illustrated by the number of fracture dimples: at room temperature, it is relatively low, but it increases gradually with temperature up to 425-550 °C where the composites reach the maximum elongation. The intrinsic brittleness of the W matrix can also be observed with the transgranular cleavage patterns of W particles at low temperatures, with the existence of cracks that are propagated along the crystal planes during fracture process.

The degradation of the tensile performance up to 425 °C can be explained through the figures on the right, where the one in the bottom shows the fracture surfaces of samples tested at 800 °C. While W particles remain practically unaltered, Cu phase is indeed degraded because of the temperature increase.

Fig. 6.12. EDX map of the fracture surfaces of W-30CuCrZr tested at (a) 25 °C and (b) 425 °C. For a better understanding of the surfaces, image of 425 °C test is shown with higher magnification

High magnification images with EDX of W-30CuCrZr at three testing temperatures, 25 °C, 425 °C and 800 °C, are shown in Fig. 6.12 and Fig. 6.13. The interfacial bonding between W and CuCrZr is quite strong, because the ductile fracture surfaces of CuCrZr fully cover the surfaces of W particles. Small particles of Cr can also be observed in Fig. 6.12, but the presence of them seems to be insignificant because no decomposition of CuCrZr alloy was observed in other images, i.e. Fig. 6.13. Upon viewing the following image, the thermal degradation of CuCrZr phase after testing at 800 °C is evident. The low values of tensile strength that is achieved by these materials at high temperature can be explained by the loss of resistance of the Cu phase and the subsequent loss of bonding to the W matrix. With the increase in temperature, the preferred fracture mode of W particles has shifted from transgranular to intergranular, because no brittle facets can be identified.

Fig. 6.13. Fracture surface of W-30CuCrZr tested at 800°C. SE image (left) and EDX map of composition (right)

6.2.3. Conclusions

Material system W-30Cu/30CuCrZr does not show any interfacial reaction or mutual solubility at operation temperatures. However, from the fracture surfaces, the interfacial bonding of W and Cu/CuCrZr was found to be strong even at high temperatures. These images also revealed two kinds of fracture mechanisms: transgranular cleavage of W particles and ductility of both the Cu and CuCrZr phases.

A remarkable temperature dependence can be assessed from the measured mechanical properties. The yield strength and fracture toughness of W-30CuCrZr are superior, but the elastic modulus and rupture strain are lower than the W-30Cu composite.

6.3. Materials W-15Cu, W-30Cu and W-40Cu

In the previous section, two MMCs were manufactured with compositions of 30 wt% Cu and 30 wt% CuCrZr with a homogeneous structure and high relative density through the infiltration technique. The results demonstrated that high densification and superior mechanical properties could be achieved through this manufacturing route.

In a second batch, the above technique was applied to produce composites with 15 and 40 wt% Cu. Results have been compared with those obtained for W-30 wt% Cu. The microstructure, thermal properties, and mechanical performance were analysed and discussed.

6.3.1. Microstructure

The relative densities of the sintered specimens, measured by Archimedes alcohol immersion method, revealed values of 91.4 %, 96.22 % and 94.24 % for W-15Cu, W-30Cu, and W-40Cu (Table 4.3), respectively. These results are in agreement with the ones published by other authors for W-Cu composites produced by the powder injection moulding method (relative density of 95.58 % with 20 % Cu content (Cheng et al. 2010)). But slightly lower than the ones obtained via microwave infiltration sintering method

(relative density of 98.87 % with 20 % Cu content) (Xu et al. 2014). However, most of researchers have reported the same tendency: with an increasing Cu fraction, internal pores infiltration and Cu migration become easier, which makes it easier to fill the pores inside the composite. This increases the density of the final product.

Fig. 6.14 shows the cross-section microstructure of polished and etched specimens of the W-Cu composites. The EDX mapping analysis shows that the green phase is W, while the surrounding red matrix is Cu. The microstructure indicates that polyhedral W grains are distributed in the liquid phase Cu matrix while the solidified liquid phase is intertwined through the solid phase as a network.

Fig. 6.14. SEM images with EDX detection of (a) W- 15 wt% Cu, (b) W-30 wt% Cu and (c) W-40 wt% Cu composites after metallographic preparation and etching

On the one hand, the difference among the microstructure observed for W-15Cu composite and the others is quite clear. Most of the grains detected at this magnification are W, and hence its average grain size is evidently larger than the observed for the other compounds. On the other hand, no apparent differences can be extracted from Fig. 1b and c, even though the vol% of Cu is slightly different, 48 vol% Cu and 64 vol% Cu, for W-30Cu and W-40Cu, respectively. In any case, these figures illustrate the continuity and connective between the W solids, while the Cu-phases are apparently isolated in the matrix of tungsten, though this is a continuous phase since it was produced by infiltration over the previous W scaffold. With increasing Cu content, the interconnection of the Cu-phases becomes much more frequent and, thus the W-W continuity decreases. Furthermore, the relative density measurements can be confirmed by the absence of visible pores in the Cu matrix.

6.3.2. Mechanical properties

- Fracture toughness

A detailed study on the fracture performance of these composites has been performed in Chapter 7. While W-15Cu and W-30Cu exhibited linear elastic load-displacement curves up to the crack onset at RT, the loss of linearity of W-40Cu curves was evident from room temperature and exhibited complex fracture behaviour at elevated temperatures. Since the stress intensity factor loses its validity with increasing ductile behaviour apparent fracture toughness values are given here (Fig. 6.15).

It can be observed that there is an improvement in the fracture toughness when the Cu content decreases from 40 wt% to 15 wt% (Cu is a weak phase). Besides, a clear trend with temperature can be inferred. The fracture behaviour of W-30Cu and W-40Cu are quite similar, with values constantly decreasing with temperature. However, W-30Cu exhibits values on average 30 % higher than W-40Cu (16 MPa.m^{1/2} versus 12 MPa.m^{1/2} at 25 °C). Nevertheless, this gap is narrower at high temperature because both composites exhibit almost the same value at 800 °C, 4.9 MPa.m^{1/2} and 6.0 MPa.m^{1/2}. On the contrary, when the temperature decreases, the effect of the low concentration of Cu (15 wt% Cu) is more evident because it reaches the highest value of fracture toughness at 425 °C, ~ 19 MPa.m^{1/2}. The softening of the W grain boundaries and the blunting of the crack tip may be the reason for this good mechanical behaviour (Kübier 2002). Up to this temperature, the Cu ductile phase controls the fracture and, therefore, the degradation of the composite. It shows values of around 9 MPa.m^{1/2}, which are much higher than the ones observed for the other materials tested. Finally, the difference in toughness between composites at 800 °C is controlled by the percentage of W in the original skeleton. The toughness increases as the percentage increases.

Fig. 6.15. Apparent fracture toughness of the composites as a function of temperature and composition. Mean values and standard error

Fracture toughness was also determined under tensile load with Double-Edge Notch Tension (DENT) specimen configuration to investigate the sensitivity of this property to the sample's geometry. Values of sample width, W , thickness, b , and average notch length, a , are (9.44 ± 0.04) mm, (2.71 ± 0.09) mm and (3.150 ± 0.001) mm, respectively.

Fracture toughness values were calculated with the most common geometrical factors, the pioneer proposed by Tada and the one developed by Bowie and included in the ASTM (ASTM Standard STP410 1966). They are comprised in Table 6.2 together with SELNB tests results for materials W-15Cu and W-40Cu at three testing temperatures, 25 °C, 550 °C and 800 °C.

Table 6.2. Fracture toughness values of W-15Cu and W-40Cu at 25 °C, 550 °C and 800°C measured with DENT (double edge notched tension) configuration (Tada and Bowie results) and SELNB (single edge laser notched beam) tests.

Material	Temperature (°C)	Fracture Toughness (MPa.m ^{1/2})		
		DENT		SELNB
		Bowie	Tada	
W-15Cu	25	10.4	9.1	18.1 ± 0.6
	550	10.0	8.9	15 ± 1
	800	5.3	4.7	8.8 ± 0.7
W-40Cu	25	16.9	14.9	12.2 ± 0.6
	550	9.4	8.2	7.45 ± 0.4

Before the analysis of the results, it should be however noted that due to the lack of material, only one test per temperature was made. Hence, average results may differ slightly from the ones reported here. Furthermore, Tada's values are on average 12 % lower than those obtained with Bowie expression for all temperatures and materials tested, which is consistent with ASTM observations.

In the case of W-15Cu, the relative rate of change in K_{Ic} with temperature is similar for both test configurations; the initial drop is quite moderate (on average 1 % lower), but it decreases rapidly to 50 % of the 25 °C fracture toughness value over 800 °C. SELNB values are considerably higher than those reported for tension tests with DENT specimens.

This wide mismatch is related to the loss of symmetry of the fracture process. During the test, the model assumes a stable and symmetrical crack growth emanating from both sides of the specimen. But in reality, this situation never happens; thus, it is common that one crack developpes earlier than the other and that it deflects above it, avoiding its fracture process zone and the stresses confined in it. When this happens, the stress condition in the sample is not uniaxial anymore, and a bending moment appears, so it should be considered in the stress intensity factor calculation. Furthermore, for the first time we know, this hypothesis is supported by experimental proofs, Fig. 6.16 (left column) illustrates a DENT sample containing W 15 wt% Cu that has been tested and recorded at 800 °C. These images can, therefore, explain that even though fracture toughness is a property of the material, different values of it are obtained when testing with various configurations, and this fact is even more pronounced at high temperature.

Fig. 6.16 (left column) illustrates the fracture process of a brittle specimen. Even though the initial notch lengths were the same, the crack on the right side of the specimen is growing faster than the opposite and, at the beginning, in the same plane. However, once it faces the crack-stress field ahead of the crack tip of the other, its path is deflected downwards until both cracks join and the specimen finally fails. This contributes to the loss of symmetry of the load system and the stress fields.

Fig. 6.16. Recorded frames of the fracture tests of (left) W-15 wt% Cu sample at 800 °C (one image each 60 s) and (b) W-40 wt% Cu sample tested at 550 °C (one image each 100 s)

On the other hand, for W-40Cu, both SELNB and DENT tests, reported a drop of fracture toughness of around 40 % with the increase of temperature, from 25 °C to 550 °C. The higher content of Cu in this composite leads to higher values of fracture toughness in tension than those obtained in bending. This effect has been widely studied for copper based metal sheets (Pardoen et al. 2004). The work required to fracture the ligament of a DENT specimen can be split into two components: the essential work of fracture and the one caused by necking. The stresses in the net ligament might be sufficiently high to cause yielding, so under tensile loads, and with high Cu content, the second term cannot be neglected. It tends to make the specimen fail by localized yielding and thus stress concentration due to the crack tip is subdued, which leads to necking formation at the crack tip and, thereby, it arrests the crack propagation (Shinde et al. 2012). The development of these plastic zones ahead the cracks can be observed in Fig. 6.16 (right column), though it is slightly larger for the right crack. When specimen finally splits the plastic deformation of the ligament can be observed, in contrast to the broken specimen shown in the left image.

However, it should be noted that small-scale yielding conditions break down when the plastic zone is not small compared to a characteristic dimension of a structure such as crack size or net ligament. Extensive plasticity occurs before failure when the original structural dimension is itself small, such in thin sections like ours, where plane stress conditions are more likely to apply than plane strain (Webster & Ainsworth 1994).

The images and results illustrated above clearly justify the selection of SELNB as the preferred testing configuration. In addition, SENB specimens require less machining than the others and with the selected geometrical factors, the influence of sample dimensions on K_{Ic} is not as strong as it is with a DENT configuration.

- Flexural strength

Fig. 6.17 shows the variation of flexural strength (0.2 % yield strength) as a function of temperature. The yield strength increases with W content, reaching a maximum of 920 MPa at 25 °C when the Cu content is just 15 wt%. Furthermore, the behaviour of the three materials is similar - bending strength constantly decreases with temperature with a relative rate of change between 0.55 MPa/°C and 0.70 MPa/°C from 25 °C to 800 °C: from 920 MPa to 340 MPa for W-15Cu and from 480 MPa to 120 MPa for W-40Cu. As observed for fracture toughness, the flexural strength of W-30Cu and W-40Cu match closely- especially at high temperatures.

Of note, our results for W-15Cu material are higher than the ones reported in the literature for a W-20 wt% Cu composite (Ibrahim et al. 2009), with a bending strength of almost 800 MPa at 25 °C. In addition, the sintering temperature of those materials, 1250 °C, which is beyond the value at 1150 °C for the ones in this study.

Fig. 6.17. Yield flexural strength as a function of temperature. Mean values and standard error

- *Tensile strength*

The Fracture behaviour of W-Cu composites can be better observed Fig. 6.18 where the true stress-strain curves of the tensile tests are represented. Real displacement as a function of temperature was obtained throw DIC analysis with resolutions above 10 $\mu\text{m}/\text{pixel}$. It should be, however, mentioned that the determination of the elastic displacements is complex and challenging, especially for Cu-rich samples where the necessary pre-load may cover this region. Thus, significant imprecisions are not unexpected.

Fig. 6.18. True stress-strain curves of tensile tests for (a) W-15Cu, (b) W-30Cu and (c) W-40Cu composites at different temperatures

It is noticeable that the addition of Cu leads to a significant increase in ductility, though all materials exhibit ductile behaviour at room temperature. The curves display a typical nonlinear behaviour up to fracture, after the initial linear region and the curve shows a strong nonlinear softening response until the fracture occurs. The tensile elongation of W-15Cu composite increases with increasing temperature, while decreasing the true rupture

stress, excepting for the 550 °C test. However, only one test has been represented for each temperature, but average values follow the general tendency observed at remaining temperatures. Zivelonghi (Zivelonghi & You 2014) explained this scattering in the final rupture strain as a consequence for the random nature of the microstructure of tungsten-reinforced copper composites.

On the contrary, both W-30Cu and W-40Cu exhibit utmost rupture strains at 425 °C. At this temperature, the elongation of W-30Cu are indeed twice that exhibited by W-15Cu (~5 % strain vs. 10 % strain) and three times higher in the case of W-40Cu (~15 % strain). However, the rupture strength at all temperatures were considerably lower compared to the latter (540 MPa, 380 MPa, and 320 MPa at 425 °C for W-15Cu, W-30Cu, and W-40Cu, respectively). The tensile strength values can be better observed in Fig. 6.19 where yield strength at 0.2 % strain and the maximum strength are plotted as a function of temperature and composition.

Fig. 6.19. (a) Yield and (b) Maximum tensile strength of the composites as a function of composition and temperature. Mean values and standard error

Both yield and maximum strength show a similar trend for the three composites under study. The highest values of tensile strength are obtained at room temperature (780 MPa, 560 MPa and 500 MPa for W-15Cu, W-30Cu, and W-40Cu, respectively) and almost stand at 300 °C. Above this temperature, they decrease uniformly down to 175 MPa for W-15Cu and to 80 MPa at 800 °C for W-30Cu and W-40Cu. However, the tensile performance of W-30Cu is on average 18 % higher than the observed for W-40Cu, but 40 % lower than for W-15Cu. Hence the effect of Cu content on the tensile behaviour is evident. However, these differences are slightly higher in the case of yield strength. The onset of plasticity observed at room temperature decreases from 600 MPa to 440 MPa and 335 MPa as the weight per cent of copper drops from 15 % to 30 % and to 40 %, respectively.

These results agree with the fracture surfaces of the specimens. W-30Cu fracture surfaces can be better observed in Fig. 6.11, where a detailed study was performed. Fig. 6.21

and Fig. 6.20 show the fracture surfaces of W-15Cu after testing at different temperatures. At low temperatures, i.e. 25 °C and 300 °C, predominantly transgranular cleavage of W grains indicates its brittle behaviour while minor deformation of the Cu phase can be detected. This is consistent with the rupture strains observed in tensile curves (Fig. 6.18a).

Fig. 6.20. SEM micrographs of the fractured surfaces of left: W-15Cu composite tested at (a) 25 °C, (b) 550 °C, and (c) 800 °C, and right: W-40Cu composite tested at (a) 25 °C, (b) 425 °C and (c) 800 °C

Furthermore, at 300 °C Fig. 6.21 depicts characteristic fan-shaped ridges coming from the origin of the crack inside the grain, thus illustrating the brittle transgranular fracture and cleavage planes inside the grain. At 550 °C, some large W residual grains remain; they

present a flat fracture surface with cleaved planes, while elongated Cu phase is around them. The effect of Cu on the macroscopic performance increases with temperature. At the maximum temperature under test, the degradation of the material is evident: while W grains are rounded and inter-granular fracture is the dominant mode of rupture in the W skeleton, the Cu phase is almost melted, and its contribution to the tensile performance is quite small. As published by Gaganidze (Gaganidze et al. 2014), with increasing the test temperature the transition from transgranular cleavage into intergranular fracture in the W skeleton is expected, thus, the fracture energy for the intergranular fracture is about one fourth of the fracture energy for the transgranular cleavage.

Fig. 6.21. Fracture surface of W-15Cu composite after tensile testing at 300 °C under vacuum atmosphere

The fracture surface of the material containing 40 wt% Cu is quite different, compared to the composites containing 15 wt% Cu -especially at 25 °C. Contiguity of W particles is rarely observable in contrast with the values observed in the previous composite. The deformation of the Cu phase is more prominent and particularly visible at 425 °C (Fig. 6.20b) with the characteristic dimples of a ductile fracture.

- Elastic modulus

Load-deflection curves of the tests were used to calculate the modulus of elasticity by drawing a tangent to the steepest initial portion of the straight line. Those data were also compared with literature values for W and Cu obtained from (Wheeler & Michler 2013) and (Davis & ASM International 2001), respectively (Fig. 6.22).

Fig. 6.22. Elastic modulus of W, Cu, and W–Cu composites as a function of composition and temperature. Mean values and standard error

The evolution of the elastic modulus with temperature for W-40Cu composite verges on the observed for pure Cu, with a slight relative rate of change. On the contrary, as Cu content decreases, the difference among the values obtained at RT, where they exhibit the highest, and at 800 °C increases. This is because all the data converge at the same point (~ 105 GPa). At higher temperatures, the main contribution to the system stiffness comes from the W porous phase because the Cu is already degraded.

Fig. 6.23. Elastic modulus at RT of W/Cu composites as a function of composition. Values were measured from the strength tests (ST) curves and by Resonant Frequency Analysis (RFA). Upper and lower bounds were estimated with the Voigt and the Reuss models, respectively, while the Hill model is the average of them

For a better understanding, the values obtained at RT from the strength tests have been compared with those obtained via RFA. Both represented within the bounds predicted by the rules of mixtures, i.e. the Voigt and the Reuss models, in Fig. 6.23.

It can be observed that, in all cases, the measured ST data are located between the area limited by the upper and lower bounds represented by the grey area. Furthermore, the data points are systematically closer to the lower bound, i.e. the Reuss model, because the Voigt limit clearly overestimates the stiffness. These data are in good agreement with observed by Hiraoka (Hiraoka et al. 2005) for W-Cu composites produced by different routes. Totten and MacKenzie (Totten & MacKenzie 2003) explained the Reuss approach of elastic modulus in metal matrix composites by the hydrostatic stresses generated in the composite when the softer matrix phase is restrained from deformation by the hard particles.

The elastic modulus values obtained from RFA are significantly higher than those measured from ST when Cu content is greater than 30 wt%.

- Thermal expansion coefficient

Arenz's empirical relation was used to estimate the coefficient of thermal expansion (CTE) of these composites as well. The CTEs versus temperature for pure tungsten, copper and W-Cu composites are illustrated in Fig. 6.24. One can notice that W-Cu composites, either W-15Cu or W-40Cu, show much lower CTE than that of pure copper and higher than that of pure tungsten. As expected, the CTE of W-Cu composites increases with increasing copper content. However, this difference becomes smaller as the temperature increases.

Fig. 6.24. Estimated coefficient of thermal expansion (CTE) versus temperature for investigated materials

At room temperature, Duan and co-workers (Duan et al. 2014) experimentally measured the CTE of W-Cu composites produced by a similar route. Their results agree well with the ones presented in Fig. 6.24. Furthermore, they treated the CTE of the composites as a weighted average of the thermal expansion of W and Cu in the sample, revealing that the

variation tendency of measured values of CTE is the same as that of the theoretical ones; hence the same approach can be made with materials presented in this Chapter.

In W-Cu composites, the high thermal expansion of Cu is constrained by the lower CTE of W particles, similar to the elastic modulus. Therefore, the CTE of the composite is affected by the Cu distribution as well as the W-skeleton. At higher temperatures, when Cu is apparently degraded, the CTE is entirely controlled by the W structure. Thus, all the materials tend to have the same value ($\sim 11.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$).

Fig. 6.25. Measured thermal conductivity versus temperature for investigated materials (Müller et al. 2017)

While it has been stated that the W skeleton determined the change in CTE, the Cu network structure benefits the increase of thermal conductivity, as reported by Müller (Müller et al. 2017) for these composites and included in Fig. 6.25. Thermal conductivity was measured by laser flash analysis (LFA). As expected, it increases with increasing Cu content, obtaining values of approximately 260 W/mK at room temperature for W-40Cu thus decreasing to values slightly below 240 W/mK at 1000 °C. Though W-15Cu composite presents similar values to pure tungsten at low temperatures, the thermal conductivity of the reference metal decreases significantly with temperature increase, while W-15Cu conductivity is steady. Anyhow, it can be stated that W-Cu composites exhibit indeed a considerably superior thermal conductivity compared to pure W and that this is nearly maintained in all the temperature range.

6.3.3. Conclusions

The mechanical properties of the W-Cu composites show an explicit dependency on the Cu content: the fracture mode transits from the dominance brittle fracture of W particles with constrained deformation of the Cu phase at low Cu content (W-15Cu) to the predominance of the ductile fracture of Cu when its ratio is higher (W-40Cu). With increasing temperature,

the contribution of the Cu phase to the rupture strain of the materials increases, but steady degradation is observed at 800 °C. Meanwhile, there is no visible growth of W particles.

6.4. Summary

W-Cu composites were fabricated via liquid Cu infiltration of open porous W preforms in an industrially viable production route. Four different compositions have been compared in this Chapter: W 15Cu, W 30Cu, W 40Cu and W 30CuCrZr. The resulting microstructure was optimal for heat sink and thermal management applications. The composites are highly dense and with a homogeneous distribution of W particles forming a continuous structure, while the Cu phase is located around it forming an interpenetrated network structure.

An extensive microstructural analysis has been made using both scanning electron microscopy (SE and EDX) and high-temperature X-Ray diffraction. Through this technique it was possible to assess that systems W 30Cu and W-30CuCrZr do not show any interfacial reaction or mutual solubility at operation temperatures, nor the presence of oxides or carbides impurities, determining as well the suitability and success of the processing route under vacuum conditions. Thus, the same assumption can be made for the remaining composites. However, fracture surfaces revealed that the interfacial bonding of W and Cu/CuCrZr is quite stable even at high temperatures.

Testing was performed up to 800 °C under a vacuum atmosphere (over this temperature, the performance of the materials is not relevant structurally), and values of fracture toughness, tensile and bending strength were obtained for all the composites. While the flexural strength and fracture toughness were already tested for the previous chapters' materials, tensile strength has also been characterised in these composites. However, the limitations of the testing environment (large high vacuum chamber operating at temperatures above 800 °C) and the specimens themselves (millimetric size samples situated far away from the recording and measuring system), led to the development of a new experimental setup for the acquisition of the real stress-strain curves. For this purpose, tests were recorded through the window on the back side of the chamber and analysed with a digital image correlation free software. Previous authors, such as Zhang (Zhang et al. 2012), already validated this procedure. However, the maximum testing temperature achieved by them was 90 °C, which is far below the 800 °C reached during this work.

This new setup allowed to explain visually the difference in fracture toughness values reported. The images obtained can, therefore, explain that even though fracture toughness is a property of the material, different values of it are obtained when different configurations are tested, and this fact is even more pronounced at high temperature. DENT tensile specimens of two composites with different yield strengths were tested and compared with the conventional SELNB values. When brittle behaviour is observed, their outcomes differ significantly because of the loss of symmetry of the fracture process. Since cracks do not develop at once, there is no symmetry in the stress condition. Thus, a bending moment should be included in the fracture equation. Furthermore, once a crack propagates, it tends to surround the stress field ahead of the opposite crack, and it contributes even more to this

asymmetrical condition. These results justify the selection of SELNB as the preferred testing configuration throughout this thesis.

On the contrary, when extensive plasticity is observed in the material, it tends to make the specimen fail by localised yielding, and thus, stress concentration due to the crack tip is subdued, which leads to necking formation at the crack tip and, thereby, it arrests the crack propagation. Consequently, the symmetry of the fracture process is maintained and results are close to those obtained with SELNB specimens. However, a further study of the fracture properties of these materials is included in the next chapter, where the limitations of linear elastic fracture mechanics have been analysed and partially solved.

Though mechanical properties are of great importance for the selection of these composites as heat sinks, they should indeed withstand high thermal stresses during operation, their thermal properties are critical. For this reason, CTE has been estimated from the elastic modulus in all the temperature range. From these data, it is apparent that the W skeleton determined the change in CTE, while the Cu network structure benefits increase in thermal conductivity. Furthermore, thermal properties can be tailored by controlling the porosity of the initial W preform, hence the composition of the final product.

To summarise, the metal matrix composites presented here would successfully drive away heat produced in the fusion chamber, avoiding the mismatch between materials by tailoring CTE and the thermal conductivity through the control of the porosity of the initial W skeleton. Furthermore, these materials exhibit improved mechanical properties at operation temperatures, i.e. below 350 °C, that can contribute to the structural support of the system. These facts are of vital importance for enhancing the performance, life cycle, and reliability of the heat sink components.

Chapter 7

Fracture mechanics and its application to the study of cracking of tungsten materials

7.1. Introduction

As described in Fig. 7.1, bulk commercial tungsten shows linear elastic behaviour almost up to the critical load and propagation occurs abruptly through the entire specimen, fracturing it. However, by introducing a high content of a ductile phase, such as copper, stable crack growth is achieved.

In order to characterize these composite materials, elastic-plastic fracture mechanics were used to describe the extensive plasticity before the initial crack propagation. In this chapter, the fracture tests on the W-Cu composites included in Chapter 6 were evaluated and the elastic-plastic fracture parameter (J-integral) was obtained.

Fig. 7.1 shows load-displacement curves of W-40 wt% Cu at different temperatures. They look different from a typical load-displacement curve of pure W introduced in Fig. 7.1a and even from that of W-15 wt% Cu (Fig. 7.1b). They clearly have absorbed a large amount of energy. Thus, it is reasonable to consider different fracture parameters such as energy terms rather than the stress term, i.e. the stress intensity factor (K_{IC}). Previously, an extensive description of the theory underneath is given in the following sections.

7. Fracture mechanics and its application to the study of cracking of tungsten materials

Fig. 7.1. Typical fracture behaviour of (a) pure W tested at RT, (b) W-15 wt% Cu tested at RT and (c) W-40 wt% Cu tested between 550 and 800 °C

7.2. Basic concepts for elastic and elastic-plastic fracture mechanics

Fracture toughness is a key engineering property of structural materials. Its values may also serve as a basis for material characterization, performance evaluation, and quality assurance for typical engineering structures, such as nuclear pressure vessels or aircraft structures (Zhu & Joyce 2012). It has been indeed a key parameter in the validation of the tungsten-based materials throughout this document.

The basic ideas leading to the start of modern fracture mechanics can be attributed to Griffith in 1921 (Griffith 1921). He proposed that the reduction in strain energy of a body when a crack propagates could be compared to the increase in surface energy due to the increase in the surface area of the body. The available energy per unit increase in crack surface area, G , is then given by:

$$G = \frac{\pi \sigma^2 a}{E'} \quad (7.1)$$

Where a is the crack length, σ the applied stress and E' is the generalized elastic modulus ($E'=E$ for plane stress, and $E'=E/(1-\nu^2)$ for plane strain).

In 1950s Irwin provided the extension of Griffith theory for an arbitrary crack and proposed the criteria for the growth of this crack (Irwin 1957). The condition was that the energy release rate, G , must be larger than the critical work, G_c , which is required to create a new unit crack area. Irwin also related the strain energy release rate to the stress field at the crack tip. The stress field around the crack tip is entirely determined by a quantity K called the stress intensity factor (Shukla 2005). Using the method of virtual work and Linear Elastic Fracture Mechanics (LEFM), Irwin presented a relationship between the energy release rate and the stress intensity factor as:

$$G = \frac{K^2}{E'} \quad (7.2)$$

Note that Eq. (7.2) is strictly valid for a through crack in an infinite plate in tension.

$$K = \sigma \sqrt{\pi a} F(a/W) \quad (7.3)$$

Where σ is the applied stress and $F(a/w)$ is a geometrical factor that depends on the crack and specimen geometry, a is the crack length, and W is the sample thickness. Fracture toughness, K_{IC} , is then the critical stress intensity factor at the crack tip needed to produce catastrophic failure under simple uniaxial loading (pure Mode I failure).

The theory predicts that the stresses in front of the crack tip will be higher than the applied stress (as a approaches zero), the stresses would indeed become infinite. But stresses in real materials are finite because the crack tip radius is finite. In addition, inelastic deformation, e.g., plasticity in metals, crazing in polymers or microcracks in concrete, results in further reduction of crack tip stresses, keeping them finite; thus, this stress singularity does not exist

7.2.1. Fracture process zone (FPZ)

The toughness or resistance to crack growth, of material is governed by the energy absorbed as the crack moves forward. In tough materials, fracture energy is associated with plastic flow near the crack tip. For a linear elastic solid, the plastic zone is confined to a small region near the crack tip (see Fig. 7.2), so the fracture energy given by Eq. (7.1) is constant. In many ductile materials, however, the fracture energy increases as the crack does. In such a case, the energy required for a unit advance of the crack is called the crack growth resistance R .

Fig. 7.2. Schematic model of Irwin approach for the plastic zone and the stresses ahead of the crack tip

As the stress intensity is increased, either by applying more stress or by crack growing, the plastic zone size will increase as well. However, the length of plastic flow is limited by the material's molecular or microstructural mobility; thus, the size of this region is limited. When the zone cannot grow anymore, the crack can no longer be constrained, and unstable propagation ensues (Roylance 1996).

Assuming a yield criterion, Irwin (Irwin 1960) (Irwin 1968) performed a rough estimate of the size of the first-order plastic zone, r_y , ahead of the crack tip, in a material with yield strength of σ_{ys} , to be

$$r_y = \frac{1}{n\pi} \left(\frac{K_I}{\sigma_{ys}} \right)^2 \quad (7.4)$$

Where $n=2$ for plane stress and $n=3$ for plane strain. Eq. (7.4) is correct only for perfectly elastic materials.

If plastic zone would be larger, a second-order estimate of the plastic zone r_p can be as twice as the first order estimate of the plastic zone size, i.e. $r_p=2r_y$. However, for quasi-brittle materials, such as concrete, whose fracture presents microcracks, curvilinear advances and softening by deformation, this coefficient may vary between 2 and 5 (Bazant & Planas 1998). In cementitious materials, the FPZ is the region where microcracking, causing strain softening, takes place. In ductile fracture under large scale yielding, it is the area of void initiation growth and coalescence. However, as the plastic zone becomes larger, LEFM breaks down, and plastic deformation has to be considered in detail (Cotterell 2002). Though there is not space for a discussion of these topics in this work, a brief description of them will be provided hereunder.

7.2.2. Elastic-plastic fracture mechanics approaches

When the fracture process zone is not confined to a small region surrounding the crack-tip, either by plasticity or microcracking, the problem becomes nonlinear. Besides, for LEFM to be applicable, the presence of an initial crack is needed, hence bodies with blunt notches - but no cracks-cannot be analysed using LEFM.

There are two general models for analysing elastic-plastic problems, effective or effective crack models, and cohesive models, depending on whether the FPZ is modelled implicit or explicit, and the size of this plastic zone.

The cohesive zone model is characterized by the properties of the bulk material, the crack initiation conditions, and its evolution, with the aid of a unique function of the Crack Tip Opening Displacement, CTOD²¹, called the softening function or softening curve (Elices et al. 2002). The cohesive crack model can explain and predict most of the experimental results of concrete and cementitious samples. Inside a range of common laboratory sizes and when the entire cohesive zone can be lumped in a single point ahead of the crack tip, LEFM can be applied, and cohesive crack models can be approximated by effective models with the R-curve (Elices & Planas 1996).

The effective models are applicable when the FPZ is minor compared to the sample dimensions. In this case, the FPZ is implicitly simulated evaluating the response of the sample away from the crack tip, by means of an Equivalent Elastic Crack approach (EEC)

²¹ CTOD is the displacement of the crack surfaces normal to the original (unloaded) crack plane at the tip of the pre-crack, a_0 . It serves as an engineering fracture parameter and can be equivalently used as K or J in practical applications.

with an associate R-curve²², $R-\Delta a_e$. EEC is an intermediate technique between the nonlinear structural analysis (cohesive material) and the linear analysis (linear elastic material). However, in contrast to cohesive and LEFM approaches, toughness is not constant so, in general, it is not a material property, and it depends on the geometry and specimen size (Elices & Planas 1993) (Planas et al. 1993).

For the sake of brevity, I will not elaborate any further in this regard. A detailed description of these parameters can be found in the textbooks written by Broek (Broek 1982). Erdogan (Erdogan 2000) or Anderson (Anderson 2005). While the primary elastic fracture mechanics concepts are compiled in the handbook by Elices (Elices 1998)

7.3. Determination of the stress intensity factor

K_{Ic} , measured as the plane-strain lower-bound toughness, is commonly obtained by loading a sample containing a deliberately-introduced crack of known length, a , and recording the stress at which the crack propagates. Testing is typically performed on single-edge notched (SEN) bend specimens loaded in three-point bending (Fig. 3.2.) and containing machined notched. The ASTM E1820 specifies that the specimen should be fatigued so that a sharp pre-crack is formed at the base of the notch. However, this is not a viable technique for W-based materials. Therefore, this pre-crack has been created through femto-second laser machining.

Fig. 7.3. Schematic illustration of the setup for the measurement of fracture toughness in SEN bend test configuration

For a three-point bending test specimen, the corresponding LEFM equations given by Strawley and Brown (Strawley & Brown 1965) and included in the stress intensity factor Handbook of Tada et al. (Tada et al. 2000) are:

$$K_I = \sigma \sqrt{\pi a} F(a/W) \quad \text{with} \quad \sigma = \frac{6M}{W^2} \left(M = \frac{PL}{4} \right) \quad (7.5)$$

²² R-curve is a plot of crack extension resistance as a function of either stable crack extension, Δa_p (a visually measured physical crack extension) or Δa_e (an inferred effective crack extension).

Where M is the bending moment in the central cross-section, a , is the notch length, P the maximum or critical load, W , the width or thickness, L the span distance and $F(a/W)$ is the shape function determined by:

$$F(a/W) = \frac{1}{\sqrt{\pi}} \frac{1.99 - a/W (1 - a/W) (2.15 - 3.93 a/W + 2.7 (a/W)^2)}{(1 + 2 a/W) (1 - a/W)^{3/2}} \quad (7.6)$$

The dimensions of standard size specimens used for fracture toughness testing are (250 x 50 x 25) mm for three-point bending (ASTM Standard E1820-11 2009), considering that Eq. (7.6) is only valid for values of $L/W=4$ and any a/W within 0.5 % accuracy. Furthermore, this expression overestimates the value of stress intensity factor for short cracks (Pastor et al. 1996).

However, testing specimens with span-to-depth ratios different from 4 is commonly required. In our case, materials volume available for thermo-mechanical testing was very limited. Furthermore, the dimensions of the environmental chamber and the foresight of analysing materials for first wall and blanket of fusion reactors, whose walls are only several millimetres thick, required the use of an evolved stress intensity factor.

Even though several authors have developed new analytical and computational solutions for stress intensity factors, for a variety of geometry and loading configurations (Murakami 1987) (Bakker 1995), these expressions do not cover the whole range of span-to-depth ratios. Hereof, Guinea and co-workers (Guinea et al. 1998) developed in 1998 a new simple and general expression for stress intensity factor for any span-to-depth ratio larger than 2.5, whose accuracy was equal or better than existing formulas.

The stress intensity factor for mode I stress in SENB specimens can be computed from the critical load and the beam section using the following equations:

$$K_{IC} = \frac{3PL\sqrt{a}}{2W^2} \frac{A - \frac{a}{W}B + \left(\frac{a}{W}\right)^2 C - \left(\frac{a}{W}\right)^3 D + \left(\frac{a}{W}\right)^4 E}{\left(1 - \frac{a}{W}\right)^{\frac{3}{2}} \left(1 + \frac{2a}{W}\right)} \quad (7.7)$$

Where:

$$A = 1.989 - 0.356 \frac{W}{L} \quad (7.8)$$

$$B = 1.217 - 0.315 \frac{W}{L} \quad (7.9)$$

$$C = 3.212 - 0.705 \frac{W}{L} \quad (7.10)$$

$$D = 3.222 - 0.020 \frac{W}{L} \quad (7.11)$$

$$E = 1.226 - 0.015 \frac{W}{L} \quad (7.12)$$

Therefore, the fracture toughness of the materials, characterized in this dissertation, was determined with specimens containing a single-edge deep crack subjected to slow bend loading and employing the above equations within the linear elastic regime. It should be however noted that if yielding occurs before fracture, the effects of crack tip plasticity would be significant, and the analysis of the fracture process zone should be performed (Folch & Burdekin 1999).

7.3.1. Limits to the validity of LEFM

As exposed in previous sections, several issues, regarding sample sizes and results obtained, should be considered for LEFM to be applied. These factors are well established for metals in the ASTM standards (ASTM Standard E1820-11 2009; ASTM 1997), however, for other materials, like polymers or composites, testing constraints are yet to be properly defined. Consequently, even though non-standard size specimens were tested in this work, some of these considerations have been appraised during the experimental campaign.

The fundamental criteria for the validity of the tests established in these standards are based on the application of LEFM. Therefore, it is necessary that the plastic zone, i.e. the FPZ, near the crack tip has a small size on sample dimensions and that the linearity of the load-displacement curve can be assessed.

- *Minimum sample dimensions*

Equation (7.3) provided the basis of the size effect phenomenon (nominal strength varies with the size of structure) (Bazant 2000; Bazant & Planas 1998). In the case of concrete materials, both the nominal strength and material brittleness always decrease with increasing element size under tension. Thus, concrete becomes perfectly brittle on a sufficiently large scale. The physical understanding of size effects is of major importance for structural analysis, since large structures are beyond the range of testing in laboratories (Tejchman & Bobiński 2013).

According to Bazant and Planas (Bazant & Planas 1998) the deterministic size effect is caused by the formation of the FPZ where the strain is intensely located. The strain location volume is not negligible to the cross-section dimensions and is large enough to cause significant stress redistribution in the structure and associated energy release. Thus, under plane strain conditions, and only for elastic-perfectly-plastic materials, the size of the first-order plastic zone, r_y , should be small enough compared with the dimensions of the specimen. The plastic zone size should not be as large as to interact with the sample's free boundaries or to destroy the essential nature of the singular stress distribution.

The ASTM E1820 standard provides the following guidelines concerning specimen size to obtain valid K_{IC} results in metals:

$$a, B, (W - a) \geq 2.5 \left(\frac{K_{IC}}{\sigma_{YS}} \right)^2 \quad (7.13)$$

Where a , B , W are the crack size, thickness, and width of the specimen, respectively. The depth requirement ensures nearly plane strain conditions and the condition on in-plane dimensions ensures that the nominal behaviour is predominantly linear elastic. This equation can be compared with (7.4) for the size of the first-order fracture process zone, r_y . The thickness of the specimens should be at least eight times the plastic zone, i.e. $B \geq 8r_y$, which corresponds to the 13 % of the sample thickness. Unfortunately, this requirement is impossible to be met by most of the materials supplied to us²³. Therefore, a careful treatment of the LEFM has been done throughout this work, giving apparent values of K_{IC} for the comparison of the materials.

- Linearity of the load-displacement curve

The records of the fracture tests may take any of the forms illustrated in Fig. 7.4. Brittle fracture behaviour (Type III) results in the development of rapid and unstable crack extension and can correspond to micro-ductile void growth fracture or cleavage fracture. The sudden drop in load is the point of crack initiation (P_{max} and P_Q in the graph)

On the contrary, ductile fracture behaviour (Type I) results in slow and stable crack extension by micro ductile void growth and coalescence which tends to absorb more energy. This macro mode of fracture has a continuous process of ductile tearing rather than a point fracture.

The critical load, P_Q , for the determination of K_{IC} is then obtained by drawing a secant line (OP_s , dashed line) with a slope equal to 95 % of the initial elastic loading slope of the test record (continuous line). The critical load is defined as follows: if the load at every point on the record that precedes P_s is lower than P_s , then P_s is P_Q (Fig. 7.4, Type I). If, however, there is a maximum load preceding P_s that exceeds it, then this maximum load is P_Q (Fig. 7.4, Types II and III).

²³ For W-40 wt% Cu samples tested at room temperature, $K_{IC} \sim 18 \text{ MPa.m}^{1/2}$ and $\sigma_{YS} \sim 400 \text{ MPa}$, specimens should be at least 5 mm thick.

Fig. 7.4. Principle types of load-displacement records during a fracture tests

The ratio $P_{\max}/P_Q$, where $P_{\max}$ is the maximum load that the specimen was able to sustain, defines the validity of the tests concerning linearity. If this ratio exceeds 1.10, then K_{Ic} is not size-independent, and it would be necessary to use larger specimens to determine K_{Ic} and the use of an elastic-plastic fracture theory approach instead of LEFM. Besides, ductile fracture should be defined with the J-integral curve

Among the materials analysed in the present work, only those containing a high proportion of copper (greater than 40 wt% Cu) showed values above 1.10. Namely, such tests are not valid for determining LEFM parameters. This restriction is quite demanding for materials containing copper, and it is challenging to be accomplished. As exposed in Chapter 3, these values have been reported in terms of comparison of materials behaviour trends rather than for the certification of this property.

7.4. The J-integral

The toughness can be measured as a point value or in a resistance curve format and is often characterized by the J-integral. Usually, a J-integral based resistance curve (i.e., a J-R curve) is used to describe a ductile material's resistance against crack initiation, stable growth and tearing instability. The J-integral is a measure of the amount of energy absorbed (due to both elastic and plastic responses) during the growth of a crack in the material of interest. It is a mathematical expression, a line or surface integral, which encloses the crack front from one crack surface to the other, used to characterize the local stress-strain field around the crack front. For elastic (linear or nonlinear) solids, the J-integral equals the crack extension force, G . Nevertheless, to arrive at a value of J_{Ic} , i.e. the elastic-plastic fracture toughness, the J-integral values must be plotted as a function of crack extension to form a so-called R-curve.

Stable crack growth results in a continuous fracture toughness versus crack extension relationship, the R-curve. For the definition of the R-curve, predominantly elastic conditions should exist throughout the test piece; hence the crack growth is stable. A typical point value

of ductile fracture toughness is defined near the onset of stable crack tearing and deduced from the R-curve near the transition from initial crack blunting to crack tearing, which is usually characterized by a distinct change in slope of the R-curve (as observed in Fig. 7.4, Type I). This result is referred to as fracture initiation toughness (Zhu & Joyce 2012).

Note that R-curve is a plot of crack extension resistance as a function of stable crack extension, either Δa_p , a visually measured physical crack extension, or Δa_e , an inferred effective crack extension. This latter is the fundamental parameter in the Equivalent Elastic Crack model developed for elastic-plastic materials. The R-curve for an ideally brittle material is flat because the surface energy is an invariant property. However, when nonlinear material behaviour accompanies fracture, the R curve can take on a variety of shapes.

7.4.1. Limitation on the application of W-based materials

The crack extension data may be collected using single-specimen or multiple-specimen techniques. The second procedure involves physical marking of the crack advance, and multiple specimens are used to develop a plot from which a single point initiation toughness value can be evaluated. Unfortunately, however, it is hard to determine the extent of crack growth accurately because of the diffuse nature of the crack front and the inherent difficulties of the testing environment (achieving testing conditions of temperature and vacuum is extremely time-consuming) and samples itself (millimetric sample sizes). Furthermore, this technique requires the use of at least nine specimens (ASM International. 2003), which in the case of high-temperature testing is materially prohibitive, since a modest amount of material was provided to us.

On the contrary, the single-specimen technique relies on the ability to determine the extent of crack growth while the specimen is loaded in the test frame. Crack growth is determined by an elastic compliance method or by an electrical resistance method, but this latter is restricted because of the limitations of the testing environment. In the elastic compliance technique, rather than letting the test run until the specimen is completely fractured, the sample is unloaded periodically during the test. At each unloading point, Δa is calculated as a function of the slope of the unload line, Young's modulus and specimen geometry. By using this method, the absence of remote yielding can be confirmed, because unloading should result in a return to the origin of the load-displacement diagram. However, due to samples dimensions, it is burdensome to determine the extent of crack growth and therefore a complete fracture is usually achieved.

In summary, it can be concluded that conventional techniques cannot be used in the determination of the crack growth for the materials under study, either by complications associated with the testing environment or to the materials amount limitations. Therefore, an advanced approach is required for the determination of the evolution of fracture toughness with temperature and composition, and the micro-mechanisms of failure associated with the process.

The following section is devoted to the definition of an elastic equivalent crack through the LEFM and the fundamentals of the compliance method. The main objective of the

following section is the investigation of the fracture mechanical properties of the W-Cu composites to study the influence of the copper content and the fabrication route on the fracture behaviour, thus, providing materials trends, rather than its numerical valuation.

7.5. New developed approach

In summary, in order to obtain the fracture behaviour of the W-Cu composites, the following issues have been addressed.

First, a real crack should be generated by means of fatigue testing. Since this is not feasible for our materials, femto-second laser was used to machine real cracks types. The benefits of this technique are manifold; No melted layer (or heat affected layer) in the surrounding of the notch is obtained, the overall tip radius are around 1 - 50 nm and, although it is quite expensive, preparation of samples and procedures are less time-consuming. Furthermore, in contrast to the observed for fatigue pre-cracks, no fracture process zone is generated prior testing and no additional cracks are generated because of the tensile-compression stress state induced during fatigue testing. SEM images of femto-second laser notches are depicted in Chapter 3, Fig. 3.3.

Secondly, if non-standard size specimens are to be tested, i.e. with span-to-depth ratios different from 4, conventional geometrical factors lose their validity, so a general expression for stress intensity factor for any span-to-depth ratio and for mode I stress in SENB specimens should be computed. In this regard, equations (7.7) to (7.12) by Guinea and co-workers (Guinea et al. 1998) provide an excellent solution.

Thirdly, for the definition of the R-curve, the crack extension, Δa , should be measured. Then, the coefficient (a/W) could be estimated during crack growth and with it, the fracture resistance, K_{IQ} . However, as exposed previously, the limitations of sample sizes, composition (very brittle material combined with a very ductile metal) and the testing environment make this task impossible. To solve this, an equivalent elastic crack has been calculated with and approximation of the Equivalent Elastic Crack approach proposed by Elices and Planas in 1993 (Elices & Planas 1993; Planas et al. 1993), but with the singularity that it can be used with small samples and with any span-to-depth ratio.

7.5.1. Experimental procedure

Fracture toughness samples were prepared with dimensions 2.8 mm×2.8 mm×30.0 mm, limited by the lab-scale size of the processing system. An initial notch was made in the middle of one side of the specimen using a diamond disc. From the notched end, a femto-second laser crack was machined, and its length and diameter were measured via SEM. Samples were then tested up to 800 °C under a high vacuum atmosphere, with 25 mm span and with a constant loading rate of 100 $\mu\text{m}/\text{min}$.

The output of the fracture tests was recorded as load versus displacement of the frame; this latter was then corrected to remove the system compliance and the uncertainties in the

load-displacement curve as explained in Appendix 7.A and Appendix 7.B, respectively. The compliance can be written as:

$$C_c = \frac{u}{P} \quad (7.14)$$

Where P is the applied load and u is its associated thermodynamically conjugate displacement deduced by Planas (Planas et al. 1994). In the latter approach, the total compliance, C_c , can be split into the compliance due to the crack $C_c(\alpha)$ existence and the one of the uncracked specimen C_0 . Where α is the crack-to-depth ratio (a/W). Substituting in Eq. (7.15):

$$C_c(\alpha) = \frac{u}{P} - C_0 \quad (7.15)$$

C_0 is inferred from the slope of a corrected load–displacement curve and is calculated as the ratio (du/dP) of specimen displacement to the load carried by the specimen during the test before crack propagates.

Guinea and co-workers (Guinea et al. 1998) deduced a general formula for the crack length as a function of the compliance based on the work by Broek (Broek 1982). Broek proposed a relation between the compliance and the elastic energy contained in the cracked specimen, U :

$$U = \frac{1}{2} C_c P^2 \quad (7.16)$$

By using the Griffith Energy criterion for fracture. The specific energy release rate, G , is then:

$$G = \frac{1}{2} \frac{P^2}{BW} \frac{dC_c}{d\alpha} \quad (7.17)$$

Which in terms can be related to K_I with Eq (7.2) where $G=K_I^2/E'$. After substituting Eq. (7.3) and (7.17) into this expression, and integrating it. The compliance as a function of α gets:

$$C_c(\alpha) = \frac{1}{E'B} [C_1(\alpha) + \beta C_2(\alpha) + \beta^2 C_3(\alpha)] \quad (7.18)$$

Where β is the span-to-depth ratio, W/L , and the factors $C_1(\alpha)$, $C_2(\alpha)$ and $C_3(\alpha)$ are, respectively:

$$C_1(\alpha) = -0.378\alpha^3 \ln(1 - \alpha) + \alpha^2 \frac{0.29 + 1.39\alpha - 1.6\alpha^2}{1 + 0.54\alpha - 0.84\alpha^2} \quad (7.19)$$

$$C_2(\alpha) = 1.1\alpha^3 \ln(1 - \alpha) + \alpha^2 \frac{-3.22 - 16.4\alpha + 28.1\alpha^2 - 11.4\alpha^3}{(1 - \alpha)(1 + 4.7\alpha - 4\alpha^2)} \quad (7.20)$$

$$C_3(\alpha) = -0.176\alpha^3 \ln(1 - \alpha) + \alpha^2 \frac{8.91 - 4.88\alpha - 0.435\alpha^2 + 0.26\alpha^3}{(1 - \alpha)^2(1 + 2.9\alpha)} \quad (7.21)$$

Through this procedure, Guinea et al. deduced the crack length as a function of the compliance by solving numerically Eq. (7.18) for any value of α :

$$\alpha = \frac{a}{W} = \frac{(C_c E' B)^{\frac{1}{2}}}{\left[(C_c E' B) + q_1(\beta)(C_c E' B)^{\frac{1}{2}} + q_2(\beta)(C_c E' B)^{\frac{1}{3}} + q_1(\beta) \right]^{\frac{1}{2}}} \quad (7.22)$$

Where:

$$q_1(\beta) = 0.98 + 3.77\beta \quad (7.23)$$

$$q_2(\beta) = -\frac{9.1 + 2.9\beta^2}{1 + 0.168\beta} \quad (7.24)$$

$$q_3(\beta) = -3.2\beta + 8.9\beta^2 \quad (7.25)$$

Finally, after substituting the equation (7.15) for C_c into Eq (7.22), we get an expression where the crack length is given with an accuracy better than one percent of the beam depth W , for any $(C_c E' W)$ and for the range of values $(2.5 \leq \beta \leq 16)$. Note that expressions (7.16) and (7.17) are only valid for linear elastic materials, therefore, when the plastic zone near the crack tip is developed, the equivalent elastic crack, a_{ee} should be defined instead conventional a .

The formula for the compliance provides values of a_{ee} , hence α , for every step of the test. Then, the equivalent stress intensity factor, K_{IQee} , may be sought having the expression (7.7) for any span-to-depth ratio larger than 2.5 and, from it, with Eq (7.2), the R-curve, i.e. the crack extension resistance curve, $G_{ee} - \Delta a_{ee}$, can be determined.

7.5.2. Experimental results

Before the R-curves are calculated, a comparative analysis has been carried out for energy values from two different methodologies. Firstly, LEFM has been used to obtain the values of the critical stress intensity factor, K_{IQ} , with Eq. (7.7) and the maximum load achieved during the tests. Then, the critical energy release rate, G_{IQ} , defined by Griffiths was estimated from the relationship $G_{IQ} = K_{IQ}^2 / E'$. On increasing temperature and copper content, the stress intensity factor loses its validity; thus, apparent values are given here.

Secondly, energy values G_F and G_{IC} were obtained with the work-of-fracture method recommended by RILEM (RILEM TCS 1985). The measured RILEM fracture energy (G_F) represents the average of the local fracture energy function over the ligament area. To avoid the energy dissipation sources identified by Elices et al. (Elices et al. 1992) that may influence the measurement of G_F , P-u curves where previously corrected as explained in the Appendix 7-A. Once the total work of fracture has been estimated, fracture energy of the materials can be calculated as:

$$G_F = \frac{\int_0^{u_{max}} P u_{max}}{b(W - a_o)} \quad (7.26)$$

Where the numerator defines the area W_F in Fig. 7.5. W_F represents the total work of fracture, both elastic and plastic, while the area under the maximum load, W_{IC} , accounts for the work necessary to create a unit free surface, i.e. the critical energy when cracking starts, thus, it should agree with G_{IQ} .

Fig. 7.5. Typical load-displacement curve with selected nomenclature for the Work-of-fracture method

Table 7.1 lists the average values of the fracture energy obtained from the three-point bend tests of W-15Cu, W-30Cu and W-40Cu specimens according to the exposed procedures. The notations used in the table are: the apparent fracture toughness (K_{IQ}) and energy release rate (G_{IQ}) measured with the maximum load (P_{max}) and with the LEFM equations, the RILEM fracture energy (G_F) measured from the total work of fracture (W_F) and the fracture energy (G_{IC}) measured from the work of fracture under maximum load (W_{IC}).

Apparent values of fracture toughness, K_{IQ} , were already presented in Chapter 6 (Fig. 6.15) though these were determined with the critical load (P_Q), with the objective of defining the stress intensity factor at the 2 % or less crack extension as defined in the ASTM (ASTM 1997). Despite the fact that this procedure was insufficient for characterising the complex fracture behaviour of these composites, a clear trend with temperature was inferred from it, i.e. there was an improvement in the fracture toughness when the Cu content decreases from 40 wt% to 15 wt% (Cu is a weak phase). However, if instead of computing P_Q in the stress intensity factor equation, P_{max} is considered, K_{IQ} and thus, G_{IQ} , are clearly overestimated, and no trend can be inferred from them. Consequently, an energy approach other than LEFM should be considered.

Values evaluated experimentally for RILEM fracture energy (G_F) are found to be in reasonable agreement with copper content. When increasing copper content so does the fracture energy released for all the temperature range. The higher values were exhibited by W-40Cu tested between 300 and 425 °C, around 47 and 44 kJ/m², respectively. These values are close to the ones observed for W-30Cu at the same temperatures, around 40 kJ/m², but much higher than those of W-15Cu composites, 19 kJ/m² at 425 °C. The upper values of G_F observed near 400 °C can be related to the DBTT of the tungsten skeleton, which determines the onset of ductile behaviour and shifts from a predominantly transgranular cleavage to an intergranular fracture, as observed by Gaganidze (Gaganidze et al. 2014).

7. Fracture mechanics and its application to the study of cracking of tungsten materials

Table 7.1. Fracture energy values for W-Cu/CuCrZr composites. Mean and standard error.
Average values of 3 to 4 tests

Cu content (W+wt.%Cu)	Temperature (°C)	Linear elastic fracture mechanics		Work of Fracture method (RILEM)	
		KIQ (MPa.m ^{1/2})	GIQ (kJ/m ²)	GF (kJ/m ²)	GIC (kJ/m ²)
15	25	17.6 ± 0.2	1.16 ± 0.03	3.1 ± 0.3	2.5 ± 0.4
	300	19.8 ± 0.8	1.6 ± 0.1	9.1 ± 0.6	2.7 ± 0.2
	425	20.0 ± 0.7	1.9 ± 0.1	19 ± 2	3.0 ± 0.2
	550	16 ± 1	1.5 ± 0.3	10.4 ± 0.2	2.3 ± 0.4
	675	11.6 ± 0.9	1.2 ± 0.2	7.2 ± 0.6	1.4 ± 0.2
	800	10.3 ± 0.6	0.9 ± 0.1	4.0 ± 0.6	1.1 ± 0.1
30	25	22.2 ± 0.9	2.8 ± 0.2	17.9 ± 0.8	6.3 ± 0.4
	300	21 ± 1	2.7 ± 0.3	39.8 ± 0.1	12 ± 1
	425	20 ± 2	3.1 ± 0.7	39 ± 1	9.7 ± 0.8
	550	14 ± 2	1.5 ± 0.5	25 ± 2	5.5 ± 0.6
	675	11 ± 1	1.0 ± 0.3	19 ± 3	3.9 ± 0.4
	800	5.8 ± 0.3	0.3 ± 0.1	10.9 ± 0.1	2.8 ± 0.1
40	25	18.9 ± 0.3	2.6 ± 0.1	22 ± 2	6.5 ± 0.3
	300	17.7 ± 0.2	2.31 ± 0.05	47 ± 2	8.3 ± 0.7
	425	15.8 ± 0.5	1.9 ± 0.1	44 ± 2	8.1 ± 0.5
	550	11.6 ± 0.1	1.06 ± 0.02	26 ± 1	5.5 ± 0.5
	675	8.1 ± 0.1	0.56 ± 0.02	20 ± 2	3.7 ± 0.2
	800	6.0 ± 0.2	0.36 ± 0.02	12.4 ± 0.6	1.6 ± 0.1
30 wt% CuCrZr	25	21.5 ± 0.3	3.1 ± 0.1	11 ± 1	4.9 ± 0.2
	300	22.9 ± 0.3	4.0 ± 0.2	26 ± 2	7 ± 1
	425	21 ± 1	3.6 ± 0.3	25.2 ± 0.6	8 ± 1
	550	20.1 ± 1	3.4 ± 0.3	23 ± 2	7.0 ± 0.1
	675	13.4 ± 0.3	1.55 ± 0.5	12.0 ± 0.6	3.50 ± 0.05
	800	9.40 ± 0.01	0.77 ± 0.01	11 ± 1	2.11 ± 0.02

If the materials would exhibit perfect elastic fracture behaviour, values determined experimentally for G_{IC} and G_{IQ} should be equal, but in our case, they are not. G_{IC} determines only the elastic energy dissipated in front of the notch to propagate until failure whereas G_F gives the total energy dissipated in the beam i.e. to propagate the notch, to create the FPZ in front of the notch and possible micro-cracks in beams, therefore, the difference in value. Furthermore, when a sudden drop in the loading capacity and unstable and fast crack propagation occurs, for example in room temperature tests of low copper content materials,

the P-u curves are incomplete. In most cases, the softening branch in the curves would reveal a positive slope (snap-back behaviour). However, since the controlling parameter was the central deflection instead of a monotonically increasing function of time, *i.e.* the crack mouth opening displacement, this part of the curve is not registered, and the work of fracture method does not provide reliable information.

There is as well an important size-effect, which is commonly observed in fracture toughness and energy measurements of many engineering materials including concrete, fibre reinforced composites and even coarse-grained ceramics, as explained earlier. The energy required to create a fresh crack decreases as the crack approaches the free boundary of the specimen, though there is a transition ligament length where the shift from the size-independent fracture energy (G_F) to the rapid decrease occurs. As deduced by Bazant (Bazant & Planas 1998), its length depends on the both the material properties and specimen size and shape. Hu and Wittmann (Hu & Wittmann 2000) argued that the size effect on fracture toughness and energy of a heterogeneous materials will be inevitable if this transition length is less than ten times the initial crack size. These studies essentially recognise that the local fracture energy is not constant over the FPZ. The newly developed methodology allows for this variation as a function of an equivalent elastic crack growth.

- *Crack growth resistance curves*

The model was applied to calculate the R-curves of the W-Cu composites defined in the previous Chapter, but to test the stability of the method, and for terms of comparison, pure commercial tungsten (Plansee SE, Reutte, Austria) was previously evaluated. Both the testing parameters (TPB configuration with the same span distance on two to three femto-second-laser machined samples) and the environmental conditions (high vacuum atmosphere) were similar as for W-Cu composites, though higher temperatures were achieved. The microstructure of the material was quite anisotropic, with shaped grains parallel to the base, therefore, two specimen configurations were tested: longitudinal (Longitudinal Orientation, L-O) and transversal (Transversal-Orientation, T-O), as arranged in the scheme shown in Fig. 7.6. A fracture surface of the material tested at 400 °C in longitudinal orientation is also shown. At this temperature, and as illustrated in Fig. 7.7a, the specimens failed by a brittle manner without a noticeable plastic deformation and transgranular cleavage can be clearly distinguished in the textured grains.

Fig. 7.6. Schematic specimen orientations selected and SEM micrograph of the fracture surface of a polycrystalline tungsten specimen tested in the longitudinal orientation at 400 °C

P-u curves and the evolution of fracture energy, G_{ee} , with temperature are plotted in Fig. 7.7. This latter was analysed just for samples where stable crack growth was registered, i.e. no sudden drop in the load is observed. At 25 °C all the specimens failed by a brittle manner, but at 400 °C slightly plastic deformation can be observed for the T-O. Thus, a primitive R-curve of these tests was obtained. For L-O samples, the load levels were always lower than for T-O, showing smooth and stable curves. On the other hand, at 400 °C, but especially at 600 °C, multiple steps in the loading curve for the T-O were observed. As explained by Gaganidze (Gaganidze et al. 2014) in a deeper analysis of the fracture behaviour of polycrystalline tungsten²⁴, this is a consequence of the change of fracture behaviour from transgranular cleavage to intergranular cleavage as the crack is deflected from the initial crack plane to an orthogonal one.

All specimens exhibited a rise in fracture energy with crack extension (i.e. rising R-curve). The curves were 'concave', showing increasing values of $dG_{ee}/d\Delta a_{ee}$ with crack growth. Furthermore, the increasing rate is much higher for T-O samples than for those with the crack parallel to the grains, because of the weak grain boundaries exhibited by pure tungsten at temperatures above its DBTT. The development of a crack perpendicular to the grains requires the supply of considerable energy as these grains are acting as crack arrestors. Thus, there is a continuous deflection of the crack path. Besides, the evolution of fracture energy for both orientations is also different, degradation of the properties starts at a lower temperature when L-O is chosen, i.e. as higher is the temperature lower is the fracture energy; while T-O specimens tested at 1000 °C did not show this evolution.

²⁴ Since the goal of this study is not the analysis of the fracture properties of pure tungsten, the reader is referred to the work by Gludovatz, (Gludovatz et al. 2009), Rupp (Rupp & Weygand 2010; Rupp et al. 2010) and Gaganidze (Gaganidze et al. 2014) for a deeper insight.

Fig. 7.7. Load vs. deflection diagrams and crack growth resistance curves of pure commercial tungsten tested in two orientations (a) and (c) Longitudinal direction; (b) and (d) Transversal direction

- Effect of copper content

Once the fracture energy behaviour of pure tungsten and therefore, of the W-skeleton, was obtained, the same study was performed on W-Cu composites. Three to four samples were analysed for each temperature and composition. Fig. 7.8 depicts the evolution of G_{ee} with equivalent elastic crack extension at different testing temperatures and for the three composites containing W and Cu, a)W-15Cu, b)W-30Cu and c)W-40Cu, respectively. The load-displacement curves have also been plotted as a function of temperature. Crack growth has been represented up to 1 mm, which corresponds to the 65 % of the initial ligament. Note that for W-15Cu composite tested at RT, linear elastic behaviour up to fracture is observed. Even though the data acquisition rate was selected to be quite high, 100 Hz, sudden crack growth make it impossible to fully register its development, so a reliable R-curve cannot be obtained.

As observed for pure tungsten, all specimens exhibited a rise in fracture energy with crack extension. It is evident, however, that the energy of the high Cu-content samples is greater than that of the low Cu-content samples. This increase in energy fracture can be quantified by the slope of the resistance curve. W-40Cu composite had a significantly higher growth fracture energy than W-15Cu, while the behaviour of W-30Cu material was intermediate. In addition, the shape of the curves depends as well on the Cu content, shifting from a simple growing curve to a clearly exponential one when its content is the highest.

It should be, however, remarked that at temperatures above 675 °C, the fracture energies exhibited by all the composites are quite low, as compared to pure tungsten. Up to this temperature, the Cu phase is extremely degraded. Hence, its contribution to the fracture resistance is quite low, and the opposition to the crack growth lies exclusively on the W-phase, which is essentially a foam with 15 to 40 % of pores.

The dependence of the calculated energy fracture values on test temperature is listed in Table 7.2 and can be described by the following exponential equation:

$$G_{IQee} = A * \exp(B\Delta a_{ee}) \quad (7.27)$$

Where the parameter A represents the crack-initiation energy, given by intercept on the ordinate axis at $\Delta a \rightarrow 0$. It is of the order 12 kJ/m² at RT and decreases with temperature to values around 5 kJ/m². It appears to follow the same tendency observed for G_F in each material, for example, W-30Cu exhibited the highest crack initiation energy at 425 °C. However, it was not possible to obtain an accurate extrapolation of the data for each sample, so further analysis of the initiation energy differences was not undertaken. Equally, the parameter B is quite similar for all materials and temperatures, though it is slightly higher as copper content is greater. Further research should be made to propose a reliable relation between composition, temperature and fracture energy.

Fig. 7.8. Load vs. deflection diagrams and crack growth resistance curves of (a) W-15Cu, (b) W-30Cu and (c) W-40Cu composites calculated with the equivalent elastic crack approach

7. Fracture mechanics and its application to the study of cracking of tungsten materials

Table 7.2. Crack growth resistance curve parameters for W-Cu composites. Mean and standard error.
Average values of 3 to 4 tests

Cu content (W+wt.%Cu)	Temperature (°C)	Crack-growth energy curves	
		Crack-initiation energy (A, kJ/m ²)	Exponential factor (B, mm ⁻¹)
15	300	9.7 ± 0.6	1.34 ± 0.01
	425	10.8 ± 0.6	1.6 ± 0.1
	550	6 ± 2	1.7 ± 0.2
	675	3.4 ± 0.6	1.9 ± 0.1
	800	4.7 ± 0.4	1.97 ± 0.01
30	25	12.3 ± 0.4	2.1 ± 0.1
	300	24 ± 2	1.70 ± 0.01
	425	29 ± 6	1.50 ± 0.01
	550	11.4 ± 3	1.8 ± 0.1
	675	2.6 ± 2	3 ± 1
	800	0.8 ± 0.1	2.60 ± 0.01
40	25	12.2 ± 0.4	2.07 ± 0.09
	300	10.1 ± 0.6	3.7 ± 0.7
	425	7 ± 2	2.7 ± 0.5
	550	4.7 ± 0.2	2.5 ± 0.2
	675	1 ± 0.2	3.2 ± 0.3
	800	1.10 ± 0.04	2.56 ± 0.02

The variations in energy fracture and therefore, toughness, can be related to changes in the crack path, specifically how the crack interacts with the local microstructure of the composite.

Fig. 7.9. SEM micrograph of bridging induced by the copper phase that results in energy dissipation through crack deflection. W-30Cu sample tested at 675 °C

SEM examination of the fracture surfaces, Fig. 7.9 (see Chapter 6 for further analysis) showed evidence of bridging induced by the copper phase residing between the W skeleton. The fracture surfaces exhibited broken ligaments spread across the specimen thickness (Fig. 7.10 and scheme Fig. 7.11a), as well as complex crack growth patterns in the W skeleton. Notice that the crack propagates through two distinct zones with unique morphologies. The first one is the W skeleton characterised by a continuous straight path of transgranular fracture especially at low temperatures (Fig. 7.12a), whereas the second zone, the Cu phase, exhibits a discontinuous path with evidence of crack deflection, crack bifurcation, and many fractured ligaments that bridged the crack. Therefore, crack growth in the composites was frequently arrested by the ductile copper phase and required higher driving forces to continue extension, as higher is the content of copper, higher is the energy required to break the un-cracked region.

Fig. 7.10. SEM micrograph of bridging induced by the tearing of the Cu phase in a W-40Cu specimen tested at 425 °C. Extensive Cu deformation results in Cu ligaments and energy dissipation

Analogous to features observed with different copper contents, the SEM observation of the fracture surfaces revealed a transition from rough surface in the W skeleton of the samples tested at low temperatures to a smooth fracture plane in the samples tested at higher temperatures. When its DBTT is overcome, shifting from a transgranular fracture below the DBTT to an intergranular fracture over it, as depicted in the above schemes (Fig. 7.11). These two behaviours were distinctly evident; thus, it can be established that the crack growth resistance is a function of temperature and copper content.

Fig. 7.11. Schematic diagrams of crack propagation. a) At low temperatures ($T < 500$ °C), Cu phase causes local crack deflection and results in the formation of bridges in the crack wake, while generating an extensive plastic deformation that inhibits the crack growth. Transgranular fracture is predominant in W phase. b) At high temperatures ($T > 500$ °C), degradation of Cu phase lower the energy dissipation while predominant intergranular fracture of W phase is observed.

Two fracture surfaces of W-15Cu composite tested at low (25 °C) and high (675 °C) temperatures are presented in Fig. 7.12. At 25 °C the fracture surface shows clear cleavage; the energy is absorbed before crack propagation, not during crack propagation. At higher temperatures, the energy necessary to promote intergranular fracture decreases, so this mechanism is preferred for the crack advance. This change could be related to nature of the dislocation substructures observed in tungsten by Stephens in the late sixties (Stephens 1969), at temperatures greater than $0.1 T_m$, the dislocation structures in the refractory

metals are characterised predominantly by edge dislocations, while up to that temperature, screw dislocations characterise the structures.

Fig. 7.12. SEM micrographs of fracture surfaces of W-15Cu specimens tested at a) 25 °C and b) 675 °C under a vacuum atmosphere. The change in the fracture mode of the W skeleton can be observed: at low temperatures crack propagation is predominantly transgranular whereas intergranular fracture is observed at high temperatures

- Effect of the copper alloy composition

The fracture behaviour of the W based composite containing 30 wt% CuCrZr has also been analysed in all the temperature range. Fracture energy values are included in Table 7.1 and the resistance, obtained with the elastic equivalent approach, are represented in Fig. 7.13 on the same scale as W-30Cu material.

In all the temperature range, the load levels before crack propagation were higher for W-30CuCrZr composite than for W-30Cu, especially in the range 300 - 425 °C. However, as observed in the R-curves, the values of $dG_{ee}/d\Delta a_{ee}$ were quite similar in this interval, this could be related to the fact that, although higher loads are supported by W-30CuCrZr specimens, the maximum deflections are much lower, thus total energy fracture, both elastic and plastic, is similar and even lower for W-30CuCrZr.

At 550 °C, higher differences can be observed; the thermal degradation of Cu leads to lower values of fracture energy and fracture energy growth, approximately 48 kJ.m⁻²/mm and 79 kJ.m⁻²/mm, as noted in both graph types. Up to this temperature, the degradation of the Cu-based phase is mutual, although stronger for W-30Cu. This effect can also be noted from the shape of the curves, they are predominantly concave in W-30Cu, even at high temperatures, but this shape is less evident for W-30CuCr.

Fig. 7.13. Load vs. deflection diagrams and crack growth resistance curves of a) W-30Cu and b) W-30CuCrZr composites calculated with the equivalent elastic crack approach

7.6. Conclusions

An elastic equivalent crack has been defined through the LEFM and the fundamentals of the compliance method. The main objective was the investigation of the fracture mechanical properties of the W-Cu/CuCrZr composites presented in the previous Chapter.

Several issues, regarding sample sizes and results obtained, should be considered for linear elastic fracture mechanics to be applied. It is necessary that the plastic zone, i.e. the FPZ, near the crack tip has a small size as compared to the sample dimensions. These should be large enough to meet the requirements of the standards and to provide a size-independent fracture properties. However, lab-scale materials do not meet these demands, furthermore, the size of the final component in the reactor will be, in some cases, on the scale of the testing specimens.

In the view of the limitations, an elastic-plastic fracture theory approach instead of LEFM should be made. Besides, the ductile fracture should be defined with crack growth resistance curves. However, as exposed previously, the limitations of sample sizes, composition (very brittle material combined with a very ductile metal) and the testing environment make the proper measurement of the crack advance an impossible task. To solve this, a new method has been developed.

An equivalent elastic crack has been proposed with an approximation of the EEC model proposed by Elices (Elices & Planas 1993) and the compliance methods, but with the unique singularity that it can be used with small samples and with any span-to-depth ratio. The model was applied to calculate the R-curves of the W-Cu/CuCrZr composites defined in the previous Chapter, as well as for pure commercial tungsten as a reference. Energies related to the process were also evaluated with the Griffiths and RILEM equations. However, local fracture energy is not constant over the FPZ so this variation should be accounted with the fracture energy curves.

For the first time, R-curves of W based composites have been obtained. Results showed that W materials exhibit rising R-curve behaviour and that the crack growth resistance is a function of Cu-content and temperature. It is evident, however, that the energy of the high Cu-content samples is higher than that of the low Cu-content samples. This increase in energy fracture can be quantified by the slope of the resistance curve. W-40Cu composite had a significantly higher growth fracture energy than W-15Cu, while the behaviour of W-30Cu material was intermediate. In addition, the shape of the curves depends as well on the Cu content, shifting from a simple growing curve to a clearly exponential one when its content is the highest. It should be, however, remarked that at temperatures above 675 °C, the fracture energies exhibited by all the composites are quite low, as compared to pure tungsten. Up to this temperature, the Cu-phase is extremely degraded. Hence, its contribution to the fracture resistance is quite low, and the opposition to the crack growth lies exclusively on the W-phase, which is essentially a foam with 15 to 40 % of pores.

Furthermore, the variations in energy fracture and therefore, toughness, were correlated to microstructural changes in the crack path, specifically how the crack interacts with the Cu-phase at low temperature and with the preferred fracture mechanisms of pure tungsten at high temperatures. SEM examination of the fracture surfaces showed evidence of bridging induced by the copper phase residing between the W skeleton pores as well as complex crack growth patterns in W. This latter, exhibited transgranular fracture up to its DBTT, even in the pure state, over this temperature, intergranular fracture and Cu thermal degradation, leads to low values of fracture resistance curves.

Appendix 7.A. Correction of uncertainties in load-displacement curves

Before performing the analysis of the load-displacement curves, these should be corrected to avoid uncertainties in the measurement of either the slope (stiffness) of the elastic part of the curve or the total fracture work. Several sources of energy dissipation were identified and corrected by Elices (Elices et al. 1992) such as: i) the adjustment of the initial stiffness of the P-u curve, ii) the adequate design of supports and the system load, and iii) the estimation of the non-measured energy dissipation near the very end of the test, i.e. the curtailment of the tail part of the load-displacement curve in a three-point bend test.

Every measurement is made from a small preload to avoid the effect of the loading systems and test specimens, i.e. effects of backlash, specimen curvature, initial grip alignment... Which introduce significant errors in the displacement output when applying a small load to the test specimen. This procedure is like the one defined in the ASTM E111-97 (ASTM Standard E111-97 1997) to correct the uncertainty in Young's modulus and defined by Gabauer (Gabauer 2000). It includes two steps: determination of the upper limit (end of the proportional region) by linear regression. The upper bound is reached if the variance of the slope is a minimum. The starting point of the calculation by linear regression depends on the preload, which was adjusted to be 10 N. After step 1, the linear regression starts again at the upper limit but in the opposite direction to determine the lower limit of the proportional region. Once the lower limit is defined, displacement is corrected.

Fig. 7.14. Raw load versus displacement curve of W-40 wt% Cu tested at 800 °C in SELNB configuration

The energy of fracture is measured by the work performed by the testing machine on a SELNB specimen until crack propagates completely. This means that the area under the stable P-u curve equals the total amount of energy consumed during the test. It has been previously shown that the energy consumption outside the fracture zone is negligible. Thus, the area under the P-u curve represents the energy consumption in the fracture zone when the crack propagates through the beam. G_F is then obtained as the total energy consumption, W_{TOT} , divided by the cross-sectional area of the initial ligament over the notch, A_0 , i.e.:

$$G_F = \frac{W_{TOT}}{A_o} \quad (7.28)$$

To properly determine G_F , it must then be possible to determine not only the area under the P-u curve, W_0 , but also the areas representing W_1 , W_2 and W_3 in Fig. 7.15.

Fig. 7.15. Load deflection curve of a fracture test; Corrected and raw curves

Curves should be therefore corrected to account for these areas. The procedure is similar to the one exposed for the correction of the preload by linear regression. Once the crack propagates, load tends to zero. However, this value is not always reached so W_3 is considered until the load gets stable values, i.e. a plateau region.

Appendix 7.B. Machine compliance correction for the test machine

Any mechanical system subjected to a force will deform, however slightly. The load frame, load cell and grips of any testing system are not infinitely stiff and will deform slightly as force is applied to the specimen. This deformation is called system compliance, C_f , and can lead to significant errors in test results especially for stiff materials with small travel requirements. In many applications, such as tensile testing of plastics, the system compliance is often trivial when compared to the specimen deformation and the error can be ignored.

Most material test systems measure crosshead or actuator displacement and this can be used as a measure of specimen deformation. However, the displacement output recorded by the system is the sum of the system compliance and the specimen deformation, which creates the need to remove the system compliance from the sum. When extensometers cannot be used, testing compliance correction should be performed.

In the case of tensile testing, a virtual extensometer (see Chapter 3) was used, thus no compliance correction was needed. However, for elastic modulus and fracture toughness measurements, this information is required because all the experiments described in this chapter are performed without any crack opening gauge, such as a Linear Variable Differential Transformer (LVDT).

Fig. 7.16. Compression test performed on an alumina block at 800 °C

To evaluate machine compliance, compression tests were performed on an isotropic homogeneous high stiffness material (99 % purity alumina²⁵). Thus, the assumption of no deformation can be assessed. Tests were performed with multiple loads and unloads (Fig. 7.16) up to the maximum load withstood by our materials and under high vacuum and

²⁵ With the goal of simplifying, machine compliance has been considered linear and invariant with materials tested. For a deeper study, reader is referred to the work of Kalidindi (Kalidindi et al. 1997)

temperature (from RT to 1200 °C), i.e. the same set-up as the actual fracture tests. Thereby average results were obtained in all the temperature range.

Then, like it is done during nanoindentation system calibration, the machine and the specimen are modelled as two springs in series, in which case the machine compliance, C_f , and the specimen compliance, C_u , are related through the equation:

$$C_u = \frac{C_f C}{C_u - C_f} \quad (7.29)$$

where C is the compliance of an uncorrected test (original curve in Fig. 7.17). Applying the correction function to the actual load-displacement curve produces the subtle change plotted in Fig. 7.17). Though this change is quite moderate for materials with high deformation, such as W-40 wt% Cu, the difference is slightly bigger for the ones whose stiffness is high, and do not experience large deformations. In the first case, the “deformation” of the machine is small in comparison with the one of the system.

Fig. 7.17. Effect of machine and fixture compliance correction on the load-displacement curve of a W-40Cu sample tested at 800 °C in SELNB configuration

Chapter 8

Conclusions and Further Work

8.1. Conclusions

The objective pursued during the development of this thesis was to achieve a complete evaluation of the thermo-mechanical performance of novel divertor armour, heat sink, and thermal barrier materials. These materials included:

- Tungsten based alloys (W-2 wt% Ti and W-5 wt% Ta) and composites (W-1/5 wt% TiC and W-5 wt% Ta) for structural applications
- Tungsten based metal matrix composites (W-Cu and W-CuCrZr) for the heat sink
- Cermets of WC-Cu for thermal barriers applications

A comprehensive characterization has been made, with particular focus on the fracture performance of W-Cu composites, whose properties were developed in an additional chapter. In the latter, a novel and original methodology for obtaining the R-curve at high temperature has been proposed, providing, for the first time, the crack growth resistance curves of tungsten based composites.

In addition, it is worth highlighting the development and implementation of an original experimental setup for non-contact video-measuring of displacements and deformations during mechanical tests at very high temperature by means digital image correlation.

8.1.1. Tungsten materials for structural applications

The main requirements of tungsten materials for structural divertor applications comprise properties like high-temperature strength and stability, high recrystallization temperature, and enough ductility. However, the brittleness of tungsten commercial tungsten products is still the principal problem for their use in structural applications.

Three ductilisation strategies have been followed in Chapter 4: (1) alloying to produce a solid solution with Ti and Ta; (2) maintaining a UFG microstructure adding TiC dispersed particles; and (3) producing composite materials with Ta. These were manufactured by powder metallurgy and consolidated by hot isostatic pressing (HIP). The processing parameters, i.e. milling time were optimised to obtain UFG microstructures. Increasing the milling time lead to a decrease and homogenization of the grain size. However, this effect was narrowed by the O₂ contamination during the process.

The effect of the different alloying elements (Ti, TiC and Ta) and their percentage, as well as the processing parameters, were analysed through flexural and fracture tests in the temperature range between 25 °C and 1200 °C, both in air and under high vacuum atmospheres. Additionally, the micromechanisms of failure were identified by scanning electron microscopy. Consequently, the processing parameters to achieve the optimal densification and microstructure were identified.

However, despite this, the results revealed brittle mechanical behaviour in almost the entire temperature range for the alloys, with no improvement in the ductile to brittle transition temperature, as compared to pure tungsten. It has been reported that strength and recrystallization control can be improved with dispersed TiC particles which inhibit the grain growth. The intrinsic brittleness of tungsten, however, cannot be enhanced by particle dispersion or solid solution with Ti or Ta, nor even with W-15Ta composites. On the contrary, intergranular rupture is enhanced even more, and the DBTT is even higher than that of pure W.

- Ti addition

The addition of Ti can moderately enhance the strength and fracture toughness of W in all the temperature range tested. However, these results did not show an apparent decrease of the DBTT as compared to pure W. Even although the present processing conditions appear to develop a particle dispersion and fine grain structure, especially after 75 h milling time. This result could be associated with Ti segregation at the grain boundaries. Furthermore, a non-negligible O₂ concentration is also present in the alloys, which may also be segregated at the grain boundaries forming complex oxides and developing a high concentration of internal stresses which, in the end, lead to grain boundary decohesion and brittleness. Furthermore, the performance of these alloys under a possible loss of vacuum resembles the one exhibited by pure tungsten, so no improvement has been achieved regarding oxidation kinetics.

- TiC addition

Two materials with 1 and 5 wt% of strengthening TiC particles dispersed have been tested. The strengthening particles, mostly existing at grain boundaries, inhibit the growth of W grains during the sintering process, resulting in a nanometric grain size alloys. This microstructure is beneficial for the improvement of the mechanical strength and fracture toughness of W-based products, with maximum values of around 900 MPa and 8.5 MPa.m^{1/2}, respectively, for W-1TiC tested at 800 °C, though W-5TiC reached similar values. However, the refined microstructure is also responsible for the rise in the DBTT, above 1000 °C

obtained from the TPB tests. TiC hard particles strongly constrain the plastic behaviour of the W matrix by hindering dislocation movement and by generating the brittle precipitate W_2C in the grain boundaries. In contrast, the oxidation of the alloys was arrested up to 600 °C.

- *Ta addition*

Two W-Ta materials were manufactured with distinct microstructures: fine grains of a Ta(W) solid solution in the submicron range, surrounding Ta pools and non-milled W grains for W-5Ta alloy, and a biphasic microstructure composed of both W-rich and Ta-rich phases, in the case of the W-15Cu composite.

The thermal and mechanical properties of the W-5Ta material are dominated by the refined microstructure; it shows a sharp ductile-to-brittle transition in the range 1000 °C to 1100 °C but, by contrast, with very modest fracture toughness, due to decohesion of those small grains.

In the case of the W-15Ta system, it exhibits significantly higher fracture toughness and lower DBTT –around 400 °C– than the W-5Ta material. Therefore, the improvement in toughness of the W-15Ta system could be attributed to a change in the fracture initiation mechanisms, as the DBTT of this material is lower.

In short, it has been determined that the addition of Ta enhance the mechanical performance of pure W. However, as observed for previous materials, it has a detrimental effect on the DBTT, more noticeable with lower percentages of Ta.

8.1.2. Thermal barriers materials

In order to increase the operating temperature of the reactor, without compromising the joint between the PFM and the underlying component, it is necessary to develop materials that act as a thermal barrier. For this purpose, WC-Cu base cermets with different compositions (25, 50 and 75 vol% Cu) have been studied in Chapter 5. The mechanical and microstructural analysis was performed up to 800 °C under a high vacuum atmosphere, which is higher than the service temperature.

Fracture surfaces of WC-Cu composites revealed two fracture mechanisms: transgranular cleavage of WC particles and plastic deformation of the Cu phase. The dominant fracture mechanism depends strongly on the content of Cu and temperature; thus, macroscopic ductile behaviour and high rupture strains were observed for Cu-rich cermet (75 vol% Cu). On the contrary, the tensile behaviour of WC-25Cu was brittle up to fracture and up to 675 °C, where slight plastic yield appears. Besides, the high concentration of WC resulted in the highest values of tensile strength at 425 °C, 800 MPa. The behaviour of WC-50Cu cermet is in-between the observed for the above materials, with the DBTT at 425 °C.

The measured elastic properties and the estimated thermal expansion coefficient fit well the analytical models for composite materials, with values between the theoretic boundaries for all cases. However, the thermal diffusivity of the cermets is lower than expected by these rules. This is a consequence of its microstructure: two continuous three-dimensional structures (Cu and WC) that percolate the whole material. Therefore, slight percent of Cu

(25 vol% Cu) can significantly reduce the substantial difference in thermal expansion between W-based armour and the CuCrZr heat sink.

The thermal performance of these materials, together with their mechanical properties could indeed reduce the heat transfer from the PFM to the underlying element while supporting the high thermal stresses of the joint. However, high heat flux tests should be performed in advance to verify their performance under peak heat loads. This component could be either a heat sink with a low melting point, such as Cu or CuCrZr alloy, or any other element of the reactor where heat transfer is not required. Furthermore, the presence of these cermetes could allow the reactor to operate at higher temperatures, even above the DBTT of W, without compromising the underlying materials.

8.1.3. Heat sink materials

W-Cu composites were fabricated via liquid Cu infiltration of open porous W preforms with four different compositions: 15, 30 and 40 wt% Cu and 30 wt% CuCrZr. The resulting microstructures were optimal for heat sink and thermal management applications. The composites are highly dense and with a homogeneous distribution of W particles forming a continuous structure, while the Cu/CuCrZr phase is located around it forming an interpenetrated network structure.

An extensive microstructural analysis has been made using both SE microscopy and high-temperature X-Ray diffraction. Through this technique it was possible to assess that there is no interfacial reaction or mutual solubility at operation temperatures among W and Cu or CuCrZr, nor the presence of oxides or carbides impurities arising from the processing route. Simultaneously, the fracture surfaces revealed that the interfacial bonding of W and Cu/CuCrZr was strong even at high temperatures. These images also revealed two kinds of fracture mechanisms: transgranular cleavage of W particles and ductility of both the Cu and CuCrZr phases at low temperatures. At high temperatures, the intergranular fracture of the W skeleton along with the thermal degradation of the Cu-phase was observed.

Testing was performed up to 800 °C under a vacuum atmosphere -over this temperature, the performance of the materials is not relevant structurally-, and values of fracture toughness, tensile and bending strength were obtained for all the composites. A remarkable temperature dependence can be assessed from the measured mechanical properties. The yield strength and fracture toughness of W-30CuCrZr are superior, but the elastic modulus and rupture strain are lower than the W-30Cu composite.

When evaluating the influence of the wt% Cu on the performance of the composites, an explicit dependency on the Cu content has been assessed. The fracture mode transits from the dominance brittle fracture of W particles with constrained deformation of the Cu phase at low Cu content (W-15Cu) to the predominance of the ductile fracture of Cu when its ratio is higher (W-40Cu). With increasing temperature, the contribution of the Cu phase to the rupture strain of the materials increases, but steady degradation is observed at 800 °C. Meanwhile, there is no visible growth of W particles.

The limitations of the testing environment (large high vacuum chamber operating at temperatures above 800 °C) and the specimens themselves (millimetric-size samples

situated far away from the recording and measuring system), led to the development of a new experimental setup for the acquisition of the real stress-strain curves by means of digital image correlation.

To summarise, the metal matrix composites presented here would successfully drive away heat produced in the fusion chamber, avoiding the mismatch between materials by tailoring CTE and the thermal conductivity through the control of the porosity of the initial W skeleton. It is evident that the W skeleton determined the change in CTE, while the Cu network structure benefits increase in thermal conductivity. Furthermore, these materials exhibited improved mechanical properties at operation temperatures, i.e. below 350 °C, that can contribute to the structural support of the system.

However, since the mechanical strength of W-30CuCrZr is superior to that exhibited by W-30Cu, a detailed study on further compositions of CuCrZr-based composites is suggested for the future.

- *Fracture toughness of different testing configurations*

Through the new tensile setup, it was possible, not only to provide the real displacement of the tensile specimens but also to visually explain the difference in fracture toughness values when different testing configurations are used. This gap is even more pronounced at high temperature. Double-edge-notched tensile specimens of two composites with different yield strengths were tested and compared with the conventional single-edge-notched specimens in three-point bending.

When brittle behaviour is observed, their outcomes differ significantly because of the loss of symmetry of the fracture process. An important loss of symmetry in the stress condition is expected if cracks do not develop simultaneously. Consequently, a bending moment is produced and should be included in the fracture equation. Furthermore, once a crack propagates, it tends to surround the stress field ahead of the opposite crack, and it contributes even more to this asymmetrical condition. These results justified the selection of SELNB as the preferred testing configuration throughout this thesis.

On the contrary, when extensive plasticity is observed in the material, it tends to make the specimen fail by localised yielding, and thus, stress concentration due to the crack tip is subdued, which leads to necking formation at the crack tip that arrests the crack propagation. Therefore, the symmetry of the fracture process is maintained, and results are close to those obtained with SELNB specimens.

8.1.4. Fracture mechanics analysis

A further study of the fracture properties of these W-Cu/CuCrZr materials was included in Chapter 7, where the limitations of linear elastic fracture mechanics have been analysed and partially solved. An elastic equivalent crack was defined through the LEFM and the fundamentals of the compliance method, with the unique singularity that it can be used with small samples and with any span-to-depth ratio. Then, the fracture resistance, i.e. R-curves, of the W-Cu/CuCrZr composites and pure commercial tungsten was obtained for the first time.

Results showed that W materials exhibit rising R-curve behaviour and that the crack growth resistance is a function of Cu-content and temperature. It is evident, however, that the energy of the high Cu-content samples is greater than that of the low Cu-content samples. W-40Cu composite had a significantly higher growth fracture energy than W-15Cu, while the behaviour of W-30Cu material was intermediate. In addition, the shape of the curves depends as well on the Cu-content, shifting from a simple growing curve to a clearly exponential one when its content is the highest. It should be, however, remarked that at temperatures above 675 °C, the fracture energies exhibited by all the composites are quite low, as compared to pure tungsten. Up to this temperature, the Cu-phase is extremely degraded. Hence, its contribution to the fracture resistance is quite low, and the opposition to the crack growth lies exclusively on the W-phase, which is essentially a foam with 15 to 40 % of pores.

Furthermore, the variations in energy fracture and therefore, toughness, were correlated to microstructural changes in the crack path, specifically how the crack interacts with the Cu-phase at low temperature and with the preferred fracture mechanisms of pure tungsten at high temperatures. Evidence of bridging induced by the copper phase residing between the W skeleton pores as well as complex crack growth patterns in W was assessed. This latter, exhibited transgranular fracture up to its DBTT, even in the pure state, over this temperature, intergranular fracture and Cu thermal degradation, leads to low values of fracture resistance curves.

8.2. Perspectives and Future work

During the development of the work that led to this thesis, a comprehensive analysis of the thermo-mechanical performance of multiple materials for different divertor applications was performed. Such a broad range of objectives required to establish some boundaries to the specific themes to be treated, to avoid excessive dispersion and loss of depth of the study.

For this reason, it was decided to focus on the techniques²⁶ and materials exposed here, neglecting, in some case worth mentioning, promising materials for plasma facing applications. These include self-passivating alloys (WCr₁₀Y_{0.5} and WCr₁₀Ti₂) or tungsten coatings produced by magnetron sputtering, these latter, in particular, have been widely studied and numerous scientific contributions were generated²⁷.

From experience acquired during and from works in the literature, it appears that the strategies to lower the DBTT of tungsten for plasma facing applications involve the use W-W composites, either with foils or with W-fibres reinforcement. Self-passivating alloys have also gathered great attention in the last years, due to their unique performance in a loss-of-coolant incident. However, the DBTT of these materials is still quite high (over 900 °C), so further investigation is ongoing.

²⁶ Characterization techniques such as indentation (Vickers Hardness and Instrumented Indentation), High-Temperature X-Ray diffraction and X-Ray fluorescence of armour materials, high-temperature tribology tests (up to 800 °C), among others, were also made.

²⁷ The reader is referred to the Appendix A: Scientific Contributions for further information.

Concerning heat sink applications, an industrially viable route was assessed, so since the mechanical strength of W-30CuCrZr is superior to that exhibited by W-30Cu, a detailed study on further compositions of CuCrZr-based composites is suggested for the future.

The new approach developed for obtaining the crack growth resistance curves of W and W-based composites, provided overall values of the evolution of fracture properties with temperature. However, many aspects of this topic could be explored further. First, the parameters of the setting curve, which correlates fracture energy, temperature and crack growth, should be found. Secondly, the efficiency of the method will be tested with other W-based materials where stable crack growth is observed, such as the WC-Cu cermets included in Chapter 5.

Finally, a new investigation to provide new uses for the W-based alloys studied is ongoing. Their refined microstructure, combined with their superior strength and hardness could indeed provide new materials for drilling tools, and components where friction is a significant concern. Therefore, the tribological properties of these materials have been studied up to 800 °C under two atmospheres: air and argon, though no concluding results have been obtained yet.

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Appendix A

Scientific Contributions

A.1. Summary of Interests

My work is centred on the characterization of materials at the nano and micro scale. The materials studied are mainly for energy applications, especially refractory alloys for fusion devices, composites and coatings. Areas of current research include:

- Fundamentals of fracture of materials
- High temperature mechanical properties (i.e. flexural, tensile and fracture properties) under special atmospheres (high/low temperature, high vacuum...) and up to temperature above 1200 °C
- Micro-mechanics of metals and ceramics by means of instrumented indentation
- Surface behaviour of materials at high temperature by means of tribology studies
- Microstructural analysis (Scanning electron microscopy, EDX, EBSD, High Temperature XRD...)

A.2. Education

2012 - Present	PhD in Materials Engineering, Thesis: Performance of Structural Materials for the DEMO divertor- Supervisors: D. José Ygnacio Pastor Caño and D. Pablo Pérez Zubiaur, Universidad Politécnica de Madrid, Spain
2011-2012	MSc, in Engineering of Structures, Foundations and Materials, Universidad Politécnica de Madrid, Spain
2010-2011	MSc Research in Engineering and Architecture, specializing in Industrial and Materials Engineering, Universidad de Extremadura, Spain

2007-2010	BA in Materials Engineering, Universidad de Extremadura, Spain
2003-2007	BA in Building Engineering, Universidad de Extremadura, Spain

A.3. Training

June 2013	Preparation, characterization and application of coatings and thin films, Institute of Ceramics and Glass (ICV), High Council for Scientific Research (CSIC), Spain.
April 2013	Durability and preservation of the built heritage geo-materials, Moncloa Campus of International Excellence, Spain
June 2012	Structural Models and Materials Impact on Impact: Practical Applications, Universidad Politécnica de Madrid, Spain
November 2011	Image Analysis Course, INFAIMON Company, Spain
July 2011	High Resolution Electron Microscopy Workshop, Universidad Complutense de Madrid, Spain
March 2008	Rehabilitation and Pathology of Structural Elements, Building Labour Foundation, Spain
June 2007	Calculations and Budgeting with PRESTO, Cáceres Chamber of Commerce, Spain
November 2006	Programme for training in Occupational Risks Prevention, BALBO Company, Spain
August 2003	Training course on Autocad 2000i, Atenea Training Academy, Spain

A.4. Research and professional experience

2015 - Present	Teaching Assistant at the Universidad Politécnica de Madrid, Spain
2014 (4 months)	Short Research Stay at the Dept. of Materials Science of the Oxford University in the UK under the supervision of Dr D.E.J. Armstrong.
2011-2015	Spanish National Research Centre for Metallurgy (CENIM) – Department of Materials Science, Civil Engineering School, Universidad Politécnica de Madrid <i>Graduate Research Assistant – PhD Student</i>
2010-2011	Laboratory Assistant for the performance of Tribological and Nanoindentation Tests at the Universidad Politécnica de Madrid, Spain
June 2006	Undergraduate Assistant at the Building Labour Foundation, Spain

A.4.1. Funding and Awards

April 2015	First Prize in the Materials Week 2015 Scientific Photo Contest
June 2014	High Council for Scientific Research (CSIC) short research stay award
September 2013	Phantoms Foundation fellowship to attend the congress Trends in Nanotechnology, TNT 2013
April 2013	First Prize in the Materials Week 2013 Scientific Photo Contest
September 2012	Phantoms Foundation fellowship to attend the congress Trends in Nanotechnology, TNT 2012
September 2011	High Council for Scientific Research (CSIC) Fellowship (2yr Funding Grant) - rejected
June 2011	High Council for Scientific Research (CSIC) PhD Studentship Award (4yr Funding Grant)

A.4.2. Scientific associations, affiliations, and services

2015 - present	Member, The Materials Research Society
2012 - present	Member, The American Ceramic Society
2011- present	Member, Spanish Materials Society (SOCIEMAT)
2010- present	Member, Spanish Structural Integrity Society

A.4.3. Articles in Referred Journals

1. **Tejado, E.**, A. v. Müller, J.-H. You, and J. Y. Pastor. 2017. "The thermo-mechanical behavior of W-Cu metal matrix composites for fusion heat sink applications: The influence of the Cu content." *Journal of Nuclear Materials*. **SUBMITTED**
2. **Tejado, E.**, A. v. Müller, J.-H. You, and J.Y. Pastor. 2017. "Evolution of Mechanical Performance with Temperature of W/Cu and W/CuCrZr Composites for Fusion Heat Sink Applications." *Journal of Nuclear Materials*. **SUBMITTED**
3. **Tejado, E.**, M. Dias, Correia J. B., T. Palacios, P.A. Carvalho, E. Alves, J. Y. Pastor. 2017. "New WC-Cu Thermal Barriers for Fusion Applications: High Temperature Mechanical Behaviour." *Journal of Nuclear Materials*. **SUBMITTED**
4. Müller, A.v., D. Ewert, A. Galatanu, M. Milwich, R. Neu, J.Y. Pastor, U. Siefken, **E. Tejado**, and J.H. You. 2017. "Melt Infiltrated Tungsten-copper Composites as Advanced Heat Sink Materials for Plasma Facing Components of Future Nuclear Fusion Devices." *Fusion Engineering and Design*, 1–5. doi:10.1016/j.fusengdes.2017.01.042.
5. Calvo, A., N. Ordás, I. Iturriza, J.Y. Pastor, **E. Tejado**, T. Palacios, and C. García-Rosales. 2016. "Manufacturing of Self-Passivating Tungsten Based Alloys by Different Powder Metallurgical Routes." In *Physica Scripta*. Vol. 2016. doi:10.1088/0031-8949/T167/1/01404.
6. **Tejado, E.**, P.A. Carvalho, A. Muñoz, M. Dias, J.B. Correia, U.V. Mardolcar, and J.Y. Pastor. 2015. "The Effects of Tantalum Addition on the Microtexture and Mechanical Behavior of Tungsten for ITER Applications." *Journal of Nuclear Materials* 467. doi:10.1016/j.jnucmat.2015.10.034.
7. Orellana, T., **E. Tejado**, C. Funke, W. Fütterer; S. Riepe; H. J. Möller; J.Y. Pastor. *How do Impurity Inclusions Influence the Mechanical Properties of Multicrystalline Silicon?* *International Journal of Metallurgical & Materials Engineering*. 1 - 101, pp. 1 - 11. GRAPHT, 05/02/2015.
8. González, C., M. Panizo-Laiz, N. Gordillo, C.L. Guerrero, **E. Tejado**, F. Munnik, P. Piaggi, et al. 2015. "H Trapping and Mobility in Nanostructured Tungsten Grain Boundaries: A Combined Experimental and Theoretical Approach." *Nuclear Fusion* 55 (11). doi:10.1088/0029-5515/55/11/113009.
9. Muñoz, A., B. Savoini, **E. Tejado**, M.A. Monge, J.Y. Pastor, and R. Pareja. 2014. "Microstructural and Mechanical Characteristics of W-2Ti and W-1TiC Processed by Hot Isostatic Pressing." *Journal of Nuclear Materials* 455 (1–3). doi:10.1016/j.jnucmat.2014.06.064.
10. Gonzalez-Arrabal, R., M. Panizo-Laiz, N. Gordillo, **E. Tejado**, F. Munnik, A. Rivera, and

- J.M. Perlado. 2014. "Hydrogen Accumulation in Nanostructured as Compared to the Coarse-Grained Tungsten." *Journal of Nuclear Materials* 453 (1–3). doi:10.1016/j.jnucmat.2014.06.057.
11. Gordillo, N., M. Panizo-Laiz, **E. Tejado**, I. Fernandez-Martinez, A. Rivera, J.Y. Pastor, C.G. De Castro, J. Del Rio, J.M. Perlado, and R. Gonzalez-Arrabal. 2014. "Morphological and Microstructural Characterization of Nanostructured Pure α -Phase W Coatings on a Wide Thickness Range." *Applied Surface Science* 316 (1). doi:10.1016/j.apsusc.2014.07.061.
12. Orellana, T., **E. Tejado**, C. Funke, S. Riepe, J.Y. Pastor, and H.J. Möller. 2014. "Influence of High Aluminium Content on the Mechanical Properties of Directionally Solidified Multicrystalline Silicon." *Journal of Materials Science* 49 (14). doi:10.1007/s10853-014-8192-5.

Educational Publications

1. **E. M. Tejado**, Á. Ridruejo, K. Konstantopoulou, T. Palacios, and J.Y. Pastor. *Laboratory experiments. Case study of a virtual approach*. 2011 Research in Engineering Education Symposium. 2011 Pages: 728-735. ISBN 978-84-695-2615-6
2. T. Palacios, K. Konstantopoulou, Á. Ridruejo, **E. M. Tejado**, and J.Y. Pastor. *Classroom experiments in the new degree of Materials Engineering at UPM*. 2011 Research in Engineering Education Symposium. 2011, Pages: 571-578. ISBN 978-84-695-2615-6
3. J.Y. Pastor, T. Palacios, y **E. Tejado**. *Open Course Ware en Ciencia e Ingeniería de Materiales: punto de apoyo para los docentes preuniversitarios de Ciencias*. Actas del II Congreso de Docentes de Ciencias. ISBN 978-84-680-1580-4

A.4.4. Presentations at International Conferences

September 2016	<i>Self-passivating tungsten alloys of the system W-Cr-Y: characterization and testing</i> ; A. Calvo; N. Ordás; I. Iturriza; F. Koch; R. Neu; H. Greuner; G. Pintsuk; A. Litnovsky; T. Wegener; M. Rasinski; J.Y. Pastor; E. Tejado; C. García-Rosales, 29th edition of the Symposium on Fusion Technology (SOFT 2016), Prague, Czech Republic
September 2016	<i>Melt infiltrated W-Cu composites as advanced heat sink materials for plasma facing components of future nuclear fusion devices</i> ; A.V. Müller; E. Tejado; A. Galatanu; D. Ewert; H. Greuner; R. Neu; J.Y. Pastor; U. Siefken; J.-H. You. 29th edition of the Symposium on Fusion Technology (SOFT 2016), Prague, Czech Republic
August 2016	<i>Thermal and mechanical properties of W/Cu composite materials for ITER heat sink applications</i> . E. Tejado; A.V. Müller; J. -H. You; J.Y. Pastor. XXV International Materials Research Congress, Cancun, Mexico

April 2016	<i>Nuevos materiales para la energía de fusión</i> ; E. Tejado, J.Y. Pastor, MULTIMAT-CHALLENGE: Materiales Multifuncionales para los Retos de la Sociedad (S2013/MIT-2862), Madrid, Spain
March 2016	<i>Study of the grain thermal stability in the nanostructured tungsten coatings</i> ; N. Gordillo; C. Gómez de Castro; J. del Río; E. Tejado; G. Balabanian; J.M. Perlado; R. González-Arrabal; NanoSpain 2016, Logroño, Spain
December 2015	<i>Thermo-Mechanical Properties of novel W-Cu composites</i> ; E. Tejado; A.V. Müller; J. -H. You; J.Y. Pastor. MRS Fall Meeting & Exhibition, Boston, USA
September 2015	<i>Capabilities of nanostructured tungsten for plasma facing material</i> ; R. González-Arrabal; N. Gordillo; A. Rivera; M. Panizo; G. Vallés; C. González; C. Guerrero; G. Balabanian; I. Marín-Bragado; E.M. Bringa; R. Iglesias; E. Tejado; J.Y. Pastor; J. Molina; M.J. Inestrosa-Izurietia; J. Moreno; L. Soto; C. Pavez; F. Munnik; J.M. Perlado; Inertial Fusion Sciences and Applications (IFSA 2015), Seattle, USA
September 2015	<i>Mechanical and tribological characteristics of tungsten alloys</i> ; E. Tejado and J.Y. Pastor. UROMAT 2015, European Congress and Exhibition on Advanced Materials and Processes, Warsaw, Poland
May 2015	<i>Manufacturing of self-passivating tungsten based alloys by different powder metallurgical routes</i> ; A. Calvo; N. Ordás; J.Y. Pastor; E. Tejado; T. Palacios; C. García-Rosales. 15th International Conference on PLASMA-FACING MATERIALS and COMPONENTS for FUSION APPLICATIONS, Cadarache, France
April 2015	<i>Micromechanical behaviour of materials for energy purposes</i> , E. Tejado and J.Y. Pastor, Nanomeasure2015, Barcelona, Spain
June 2014	<i>On the use of W-TiC alloys for ITER divertor components</i> ; E. Tejado, J.Y. Pastor, A. Muñoz; National Congress on Materials, Barcelona, Spain
October 2014	<i>Microstructure, mechanical properties and wear performance of nanostructured tungsten coatings for fusion applications</i> . E. Tejado; N. Gordillo; M. Panizo-Laiz; R. González-Arrabal; J.M. Perlado; J.Y. Pastor. The Nuclear Materials Conference, Clearwater, USA
October 2014	<i>The effects of tantalum addition on the micro texture and mechanical behaviour of tungsten for ITER applications</i> . E. Tejado; P.A. Carvalho; A. Muñoz; J.Y. Pastor. The Nuclear Materials Conference, Clearwater, USA
June 2014	<i>On the use of W-TiC alloys for ITER divertor components</i> . E. Tejado, J.Y. Pastor and A. Muñoz. National Congress on Materials, Barcelona, Spain
May 2014	Adhesion and mechanical properties of implanted nanostructured tungsten, N. Gordillo; E. Tejado; M. Panizo-Laiz; J.Y. Pastor; J.M.

- Perlado; R. Gonzalez-Arrabal. E-MRS 2014 SPRING MEETING, Lille, France
- May 2014 *The role of grain boundaries on light species behaviour in nanostructured W.* M. Panizo-Laiz; N. Gordillo; E. Tejado; J.Y. Pastor; F. Munnik; J.M. Perlado; R. Gonzalez-Arrabal. E-MRS 2014 SPRING MEETING, Lille, France
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- Mach 2014 *Hydrogen accumulation in nanostructured tungsten as compared to coarse grained tungsten.* M. Panizo-Laiz; N. Gordillo; F. Munnik; E. Tejado; J.Y. Pastor; R. González-Arrabal; J.M. Perlado. Nanospain 2014, Madrid, Spain
- March 2014 *Morphology, microstructure and stress-state characterization of nanostructured tungsten.* N. Gordillo; M. Panizo-Laiz; E. Tejado; J.Y. Pastor; J. Del Rio; C. Gómez; J.M. Perlado; R. González-Arrabal. Nanospain2014, Madrid, Spain
- February 2014 *Mechanical characterization of W-5Ta and W-5TiC composites produced by Hot Isostatic Pressing;* E. Tejado, J.Y. Pastor. Monitoring Meeting on High Heat Flux Materials (MAT-HHFM), EFDA, Garching, Germany
- October 2013 *Microstructural and mechanical characteristics of W-2Ti and W-1TiC processed by Hot Isostatic Pressing;* A. Muñoz, ; B. Savoini; M.A. Monge; J.Y. Pastor; E. Tejado; R. Pareja. ICFRM 16, 16th International Conference on Fusion Reactor Materials, Beijing, China
- September 2013 *Mechanical characterization of nanostructured tungsten films for nuclear applications.* E. Tejado; N. Gordillo; M. Panizo-Laiz; R. González-Arrabal; I. I. Fernández-Martínez; J.Y. Pastor. TNT2013, Trends in Nanotechnology International Conference, Seville, Spain
- September 2013 *Structure and mechanical properties of nanostructured tungsten films for nuclear applications.* E. Tejado; N. Gordillo; M. Panizo-Laiz; R. González-Arrabal; I. I. Fernández-Martínez; J.Y. Pastor. EUROMAT 2013, European Congress and Exhibition on Advanced Materials and Processes, Seville, Spain
- September 2013 *Microstructure and mechanical properties at high temperature of SiC-matrix by electrophoretic deposition and polymer infiltration and pyrolysis process.* T. Juan-Mangas; J.Y. Pastor; E. Tejado; A. Iveković; S. Novak. EUROMAT 2013, European Congress and Exhibition on Advanced Materials and Processes, Seville, Spain

- September 2013 *Microstructure and mechanical properties of tungsten alloys with TiC and Ti additions.* E. Tejado; A. Muñoz; J.Y. Pastor. EUROMAT 2013, European Congress and Exhibition on Advanced Materials and Processes, Seville, Spain
- July 2013 *High temperature characterization of W-5Ta composites produced by Hot Isostatic Pressing;* E. Tejado; J.Y. Pastor. Monitoring Meeting on High Heat Flux Materials (MAT-HHFM), European Fusion Development Agreement (EFDA). Bucharest, Romania
- May 2013 *Hydrogen accumulation in nanostructured as compared to massive W.* R. González-Arrabal; N. Gordillo; M. Panizo-Laiz; F. Munnik; K Saravanan; E. Tejado; J. Y. Pastor; J.M. Perlado. 14th International Conference on Plasma-Facing Materials and Components for Fusion Applications, Jülich, Köln, Germany
- May 2013 *Mechanical Characterization of Tungsten-Titanium-Lanthana alloy: Influence of Temperature and Atmosphere.* T. Palacios; E. Tejado; J. Y. Pastor; Á. Muñoz. 14th International Conference on Plasma-Facing Materials and Components for Fusion Applications, Jülich, Köln, Germany
- April 2013 *Capabilities of Nanostructured W as Plasma Facing Material in future fusion reactors.* R. González-Arrabal; N. Gordillo; A. Rivera; I. Fernández.-Martínez; M. Panizo-Laiz; J. Y. Pastor; E. Tejado; K. Saravanan; F. Munnik; J.M. Perlado. 2013 MRS Spring Meeting & Exhibit, Moscone West, San Francisco, USA
- February 2013 *High temperature characterization of W-Ti and W-TiC based composites produced by HIP.* E. Tejado; J.Y. Pastor. Monitoring Meeting on High Heat Flux Materials (MAT-HHFM), European Fusion Development Agreement (EFDA), Garching, Germany
- September 2012 *The Impurities Role In The Mechanical Behaviour Of Multicrystalline Silicon Substrates.* E. Tejado, J.Y. Pastor, T. Orellana Pérez, C. Funke, W. Futterer. Thirteenth European Inter-Regional Conference on Ceramics - CIEC 13, Barcelona, Spain
- September 2012 *Nanostructured tungsten as a first wall material for the future nuclear fusion reactors.* N. Gordillo; R. González-Arrabal; A. Rivera; I. Fernández.-Martínez; Briones F.; J Del Río; C. Gómez; J.Y. Pastor; E. Tejado; M. Panizo-Laiz; J.M. Perlado. Trends in Nanotechnology (TNT 2012), Madrid, Spain
- July 2012 *Mechanical characterization of multicrystalline silicon wafers.* E. Tejado, J.Y. Pastor, T. Orellana Pérez, C. Funke, W. Futterer. 4th International Congress on Ceramics (ICC4), The American Ceramic Society, Chicago, USA.

June 2012	<i>Mechanical characterization of small laboratory specimens of W, W-2Ti, W-2Ti-1Y2O3 and W-2Ti-1La2O3 produced by hot isostatic pressing; Monitoring Meeting on High Heat Flux Materials (MAT-HHFM), European Fusion Development Agreement (EFDA). Ljubijana, Slovenia.</i>
March 2012	<i>Caracterización mecánica de sustratos de silicio multicristalino para aplicación en células solares; E. Tejado, J.Y. Pastor, T. Orellana Pérez, C. Funke, W. Futterer. XXIX Spanish Structural Integrity Society Congress, Gijón, Spain</i>
March 2012	<i>Efecto de las impurezas en el comportamiento a fractura de sustratos de silicio multicristalino. E. Tejado; T. Orellana, J.Y. Pastor, C. Funke, W. Futterer. XII National Congress on Materials - IBEROMAT XII, Alicante, Spain</i>
February 2012	<i>Mechanical characterization of W-V and W-Ti tungsten ODS alloys at high temperature in vacuum atmosphere. E. Tejado, J.Y. Pastor. Monitoring Meeting on High Heat Flux Materials (MAT-HHFM), European Fusion Development Agreement (EFDA), Garching, Germany</i>
September 2011	<i>Impact of impurities on the mechanical strength of multicrystalline silicon; T. Orellana, C. Funke, W. Futterer, E. Tejado, J.Y. Pastor. 26th European Photovoltaic Solar Energy Conference and Exhibition, Hamburg, Germany</i>
June 2011	<i>Impact of impurities on the mechanical properties of block cast multicrystalline silicon. T. Orellana, S. Riepe, E. Tejado, J.Y. Pastor, C. Funke, H.J. Möller. Freiburger Silicon Days-Semiconductor materials, process technology and Diagnostics, Institute for Experimental Physics, TU Bergakademie Freiberg, Chemnitz, Germany</i>
April 2011	<i>Mechanical properties of epitaxial wafer equivalents. E. Tejado, J.Y. Pastor, T. Orellana Pérez, C. Funke, W. Futterer. XXVIII Spanish Structural Integrity Society Congress, Gijón, Spain</i>

A.4.5. Participation in Research Projects

1. SEGURIDAD Y DURABILIDAD DE ESTRUCTURAS DE CONSTRUCCIÓN (SEDUREC) CONSOLIDER-INGENIO 2010. Ministerio de Educación y Ciencia. Proyecto: CSD00C-06-14102. September 2006 to September 2011. UPC, Instituto Eduardo Torroja de Ciencias de la Construcción (CSIC) y UPM. Principal Investigator: Vicente Sánchez Gálvez. Number of researchers involved: 12.
2. Fabricación asistida por láser y caracterización mecánica de óxidos eutécticos de Al2O3 para la optimización de sistemas de generación y conversión de la energía.

- Comisión Interministerial de Ciencia y Tecnología. Proyecto: MAT2009-13979-C03-02. January 2010 to December 2012. Universidad de Zaragoza, UPM, Universidad de Sevilla. Principal Investigator: José Ygnacio Pastor Caño. Number of researchers involved: 5. Project manager: Manuel Jiménez Melendo (Universidad de Sevilla).
3. Convocatoria de ayudas para la realización de programas de actividades de ID entre grupos de investigación de la Comunidad de Madrid Proyecto: S-S2009/MAT-1585 MATERIALES ESTRUCTURALES AVANZADOS, ESTRUMAT. January 2010 to December de 2013. UPM, Universidad Carlos III, Universidad Rey Juan Carlos, IMDEA-Materiales y Universidad Complutense de Madrid. Principal Investigator: José Ygnacio Pastor Caño
 4. Convocatoria de ayudas para la realización de programas de actividades de I+D entre grupos de investigación de la Comunidad de Madrid Proyecto: S2009/ENE-1679 DESARROLLO DEL PROGRAMA DE ACTIVIDADES I+D MULTIDISCIPLINARES DE LA INSTALACIÓN CIENTÍFICO-TÉCNICA SINGULAR DEL CENTRO DE TECNOLOGÍAS PARA LA FUSIÓN TECHNOFUSION. January 2010 to December 2013. UPM, Universidad Carlos III, Universidad Autónoma de Madrid, CSIC, UNED y CIEMAT. Principal Investigator: José Ygnacio Pastor Caño. Number of researchers involved: 3.
 5. Development and basic characterization of tungsten base materials for structural applications. EFDA-ITER project: MAT-WALLOYS 2011, Tungsten and Tungsten Alloys Development. January to December 2011. UPM- EUTATOM (CIEMAT). Principal Investigator: José Ygnacio Pastor Caño. Number of researchers involved: 3.
 6. Development and basic characterization of tungsten base materials for structural applications. EFDA-ITER project: MAT-WALLOYS 2012, Tungsten and Tungsten Alloys Development. January to December 2012. UPM- EUTATOM (CIEMAT). Principal Investigator: José Ygnacio Pastor Caño. Number of researchers involved: 3.
 7. Development and basic characterization of tungsten base materials for structural applications. EFDA-ITER project: MAT-WALLOYS 2013, Tungsten and Tungsten Alloys Development. January to December 2013. UPM- EUTATOM (CIEMAT). Principal Investigator: José Ygnacio Pastor Caño. Number of researchers involved: 3.
 8. Desarrollo y caracterización mecánica de materiales nanoestructurados para operación bajo condiciones extremas para sistemas de generación de energía: comportamiento mecánico. Comisión Interministerial de Ciencia y Tecnología. Proyecto: MAT2012-38541-C02-02. January 2013 to December 2015. Universidad Politécnica de Madrid. Principal Investigator: José Ygnacio Pastor Caño. Number of researchers involved: 4. Project manager: Raquel Gonzalez Arrabal (Universidad Politécnica de Madrid).

9. Development and basic characterization of tungsten base materials for structural applications. EFDA-ITER project: MAT-WALLOYS 2014-18, Tungsten and Tungsten Alloys Development. January 2014 to December 2018. EUROFUSION. Principal Investigator: José Ygnacio Pastor Caño. Number of researchers involved: 3.
10. Convocatoria de ayudas para la realización de programas de actividades de I+D entre grupos de investigación de la Comunidad de Madrid Proyecto: S2013/MIT-2862 Materiales Multifuncionales para los Retos de la Sociedad MULTIMAT. October 2014 to 2018. UPM, Universidad Carlos III, Universidad Rey Juan Carlos, Hospital de La Paz, y Universidad Complutense de Madrid. Principal Investigator: José Ygnacio Pastor Caño.
11. Compuestos cerámica-metal y aleaciones refractarias de W para su aplicación bajo condiciones de servicio severas: diseño microestructural y nuevas rutas de procesamiento. Comisión Interministerial de Ciencia y Tecnología. Proyecto: MAT2015-70780-C4-4-P. January 2016 to December 2019. Universidad Politécnica de Madrid. Principal Investigator: José Ygnacio Pastor Caño. Number of researchers involved: 3. Project manager: Begoña Ferrari (Instituto de Cerámica y Vidrio, CSIC).

A.4.6. Participation in projects with companies

1. Ensayos de adhesión de placas de vidrio en función de la temperatura. PRODINTEC. July 2012 – July 2014. Principal Investigator: José Ygnacio Pastor Caño. Number of researchers involved: 3.
2. Estudio del fallo estructural de una excavadora. Juzgado de Gavá. July 2013 – July 2014. Principal Investigator: José Ygnacio Pastor Caño. Number of researchers involved: 4.
3. Contrato entre AXA Corporte Solutions Assurance y la Universidad Politécnica de Madrid para la realización de informe de pericia relativo al incendio acontecido en instalaciones de Intier el 26 de junio de 2013. AXA seguros. October 2014-October 2015. Principal Investigator: José Ygnacio Pastor Caño. Number of researchers involved: 4.

Appendix B

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