

UNIVERSIDAD POLITÉCNICA DE MADRID

Escuela Técnica Superior de Ingenieros de
Camino, Canales y Puertos



**Synthesis and characterization at high
temperature of colloidal processing
cemented carbide and cermet**

TESIS DOCTORAL

Presentada para optar al título de Doctor por:

Sandra Tarancón Román

Ingeniera de Materiales

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Bajo la dirección de:

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Abstract

The demanding working conditions of cutting tools, characterized by exposure to heat and abrasion, require materials with exceptional hardness, toughness, and wear resistance, which must be sustained at elevated temperatures. Cemented carbides, commonly known as hard metals, meet these requirements, making them the predominant choice for cutting tools and rock drilling applications. However, the rising demand for critical materials such as tungsten and cobalt has raised concerns about their supply and cost, prompting the exploration of alternative binders and processing methods.

Although recycling of these cutting tools is vital to ensure sustainability and resource conservation, existing methods still remain inefficient and uneconomical in fully recovering materials. Consequently, the development of novel material systems is imperative to ensure industry continuity and sustainability.

This research focuses on the formulation and evaluation of colloidal suspensions of cemented carbides (WC-FeNi) and cermets (Ti(C,N)-FeNi) with a Fe/Ni metallic binder composition of 85/15 wt%. These compositions aim to reduce the dependence on critical materials while enhancing the high-temperature performance of cutting tools.

The materials were synthesized using water-based colloidal suspensions and their stability was confirmed via rheological analysis, enabling uniformly distributed spherical particles to be atomized. The sintering process was subsequently evaluated under various atmospheres (N_2H_2 , high vacuum, and argon), to achieve a dense and hard material under a viable commercial route. These properties were satisfied by the argon atmosphere.

Mechanical and thermal properties of the developed systems -including hardness, flexural strength, fracture toughness, wear resistance, and thermal diffusivity - were assessed up to 800 °C temperature and compared to commercial cemented carbides.

The WC-FeNi system exhibited mechanical properties comparable to those of the reference materials, with a strength improvement of up to 15 % at intermediate

temperatures. Its high hardness, low wear rate, and temperature-dependent thermal conductivity make it a promising candidate for industrial applications.

On the other hand, the Ti(C,N)-FeNi system, prepared with HPMC, exhibited inferior mechanical properties compared to PVA-based systems, with higher porosity leading to reduced hardness, flexural strength, and fracture toughness. Nonetheless, its thermal properties, including thermal conductivity and wear resistance at elevated temperatures, were notable, suggesting the need for further optimization to broaden its application scope.

In summary, the results demonstrate that the WC-FeNi system, processed by a colloidal route, could be an excellent alternative to the Co-based. Its competitive mechanical and thermal properties, coupled with the environmental benefits of its composition and manufacturing process, position it as an attractive option for high-performance industrial applications.

Resumen

Las herramientas de corte están sometidas a condiciones de trabajo extremadamente exigentes, donde el calor y la abrasión son factores clave durante su operación. Estas circunstancias requieren materiales que combinen alta dureza, tenacidad de fractura y resistencia al desgaste, propiedades que deben mantenerse incluso a altas temperaturas, dado que son esenciales para garantizar la eficiencia, durabilidad y precisión en los procesos de corte. Los carburos cementados, también conocidos como metales duros, cumplen con estos requisitos, lo que los convierte en los materiales más utilizados para la fabricación de herramientas de corte y aplicaciones de perforación de rocas. Sin embargo, la creciente demanda de materiales críticos, como el wolframio y el cobalto, ha generado preocupación por su disponibilidad y el consiguiente aumento de precios, despertando el interés de la comunidad científica en desarrollar materiales y métodos de procesamiento alternativos.

Aunque el reciclaje de las herramientas de corte es crucial para promover la sostenibilidad y conservar los recursos, los procesos actuales no logran aún recuperar todos los materiales de forma eficiente o económica. Por ello, es fundamental desarrollar nuevas composiciones que garanticen la continuidad y sostenibilidad de la industria.

Esta investigación se centra en la fabricación y evaluación de suspensiones coloidales de carburos cementados (WC-FeNi) y cermets (Ti(C,N)-FeNi), en los cuales la composición del ligante metálico Fe/Ni fue fijada en un 85/15 % en peso, respectivamente. Estas composiciones fueron seleccionadas con el objetivo de desarrollar materiales alternativos que, no solo reduzcan el contenido de elementos críticos, sino que también mejoren el rendimiento de las herramientas de corte a alta temperatura.

En la fabricación de los materiales se emplearon suspensiones coloidales de base agua, siendo su estabilidad evaluada a través de su comportamiento reológico, obteniendo una atomización adecuada de partículas esféricas y uniformemente distribuidas. Posteriormente, se estudió la sinterización de las muestras verdes en diferentes atmósferas (N_2H_2 , vacío y argón), siendo esta última la más adecuada

para obtener un material denso y de alta dureza, además de ser comercialmente viable.

El análisis detallado de las propiedades mecánicas y térmicas de los materiales sinterizados incluyó la evaluación de la dureza, resistencia a la flexión, tenacidad de fractura, resistencia al desgaste y difusividad térmica en un rango de temperaturas desde ambiente hasta 800 °C, comparándolos con sistemas comerciales de carburo cementado utilizados como referencia.

El material WC-FeNi mostró propiedades mecánicas comparables a las del material de referencia, con mejoras de hasta un 15 % en la resistencia mecánica a temperaturas intermedias. Su elevada dureza, baja tasa de desgaste y conductividad térmica, decreciente con la temperatura, lo posicionan como un candidato prometedor para aplicaciones industriales.

Por otro lado, el sistema Ti(C,N)-FeNi, fabricado con HPMC como dispersante, presentó propiedades mecánicas y térmicas inferiores a las obtenidas con PVA, además de mayor porosidad, lo que resultó en una menor dureza, resistencia a la flexión y tenacidad a la fractura en comparación con los carburos cementados. No obstante, este sistema destacó por mantener su conductividad térmica y una mejor resistencia al desgaste a altas temperaturas, por lo que la optimización de sus propiedades mecánicas podría ampliar su campo de aplicación potencial.

En conclusión, los resultados obtenidos indican que el sistema WC-FeNi, procesado por vía coloidal, representa una alternativa viable a los carburos cementados basados en cobalto. Sus propiedades mecánicas y térmicas, junto con los beneficios medioambientales derivados de su composición química y ruta de fabricación, lo posicionan como una opción competitiva para aplicaciones industriales de alto rendimiento.

Motivation and Objectives

The materials used in the manufacture of cutting tools are advanced structural materials with exceptional properties, including high hardness, fracture toughness, and wear resistance, which enable their use at elevated operating temperatures. Cemented carbides, composed of a ceramic tungsten carbide (WC) phase embedded in a metallic cobalt (Co) matrix, exhibit an ideal combination of these characteristics. However, the European Union classified both WC and Co as strategic raw materials due to their intensive use and limited availability.

The search for alternatives to fully or partially replace WC and Co in cutting tools presents a significant challenge, primarily due to their exceptional mechanical properties. WC is renowned for its extraordinary hardness and wear resistance, while Co enhances the fracture toughness of the composite. These attributes have long established WC-Co systems as the preferred choice for cutting tools, particularly in applications that require extreme durability under harsh conditions.

One of the key difficulties in exploring alternative materials is to achieve comparable or superior performance while maintaining compatibility with existing manufacturing processes and machined materials. Traditional cutting tools, which are produced by powder metallurgy, have been optimized over the past decades. However, the adoption of new materials often requires modifications to the production infrastructure, incurring high initial costs and a steep learning curve. To address this challenge, colloidal suspensions have been proposed as a means to produce fine powders with controlled stability and homogeneity. The use of water as a low impact solvent in these suspensions permits the addition of stabilizing agents to adjust properties such as pH and viscosity, further improving particle uniformity.

This research explores two potential alternatives to tungsten and cobalt in cutting tools. First, titanium carbonitride (Ti(C,N)) is investigated as a substitute for the ceramic phase, and second, iron (Fe) and nickel (Ni)-based systems are examined as alternatives to Co for the metallic binder phase. Colloidal processing has been chosen as an environmentally friendly manufacturing route because of its advantages in controlling grain size and distribution, precise adjustment of suspension viscosity, and reduction of organic binders. These factors minimize pore

formation and enable the creation of homogeneous microstructures, even in materials with a high concentration of ceramic phases. Accordingly, the WC-FeNi and Ti(C,N)-FeNi systems were evaluated and compared with commercial WC-Co composites.

The study includes an evaluation of the rheological behaviour of the colloidal suspensions and optimization of sintering conditions to achieve high-density materials. Subsequently, the mechanical behaviour, microstructure, and fractography of the materials are analyzed, along with the thermal and tribological characterization of the sintered compounds. The overarching goal is to balance mechanical performance, material availability, compatibility with current manufacturing processes, and validation for industrial applications.

The objectives of this thesis, conducted within the framework of several R&D projects funded by the Spanish Government (MAT2015-70780-C4-4-P: "Ceramic-metal composites and refractory W alloys for severe service conditions: microstructural design and new processing routes," PID2019-106631GB-C44: "MICROMattersUPM: Mechanical, tribological, thermal, and microstructural characterization of advanced ceramic/metal composites under extreme service conditions," and PID2022-137274NB-C33: "Thermo-mechanical characterization of ceramic materials fabricated through additive post-processing techniques"), are summarized as follows:

- **Objective 1:** Evaluate the thermo-physical and thermo-mechanical properties of the WC-FeNi and Ti(C,N)-FeNi systems.
- **Objective 2:** Assess the viability of WC-FeNi and Ti(C,N)-FeNi systems' mechanical properties compared to commercial cemented carbides.
- **Objective 3:** Optimize sintering conditions to obtain dense materials suitable for industrial applications.
- **Objective 4:** Study the rheological behaviour of colloidal suspensions for WC-FeNi and Ti(C,N)-FeNi systems.

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List of Acronyms

ASTM	American Society for Testing and Materials
BET	Brunauer, Emmet y Teller
CAGR	Compound annual growth rate
CRM	Critical raw materials
DRX	X-ray diffraction
EDM	Electrical discharge machining
EDX	Energy dispersive spectroscopy
FESEM	High resolution scanning electron microscope
XRX	X-ray fluorescence
HPMC	Hydroxypropyl methylcellulose
HIP	Hot isostatic pressing
HSS	High alloy steel
HTMA	Tetramethylammonium hydroxide
HV	Vickers hardness
LD ₅₀	Lethal dose 50 %
MMC	Metal matrix composite
XRF	X-ray fluorescence
μDRX	X-ray microdiffraction
N ₂ H ₂	Hydrogenated nitrogen or diazene
NZE	Net Zero Emissions
PEI	Polyethylenimine
PVA	Polyvinyl alcohol
SE	Secondary electrons
SRM	Strategic raw materials
SSA	Specific surface area
TPNB	Glycol ether

List of Symbols

a	Crack length
A_s	Average cross-sectional area of the track
B	Specimen width
C_p	Specific heat
D	Translational diffusion coefficient
d	Distance between crystal lattice planes
d	Length diagonals hardness footprint
d_{BET}	Average particle size
D_e	Effective ball track diameter
$d(H)$	Hydrodynamic radius
D_v	Particle size distribution in suspension
$F()$	Geometrical factor
F_{agl}	Agglomeration factor
k	Bolztmann constant
K_I	Mode I stress intensity factor
K_{IC}	Fracture toughness, Mode I stress intensity factor under plane strain
L_s	Support spacing
m	Weight
m_a	Weight in air
m_e	Weight in ethanol
m	Cross's exponent
n	Whole number
P_c	Critical load for fracture bending tests
Q	Radiant energy
R	Ball radius
r_t	Wear track radius

S_0	Area occupied by 1 cm ³ adsorbent
t	Time
$t_{0.5}$	Time to half minimum
T	Temperature
T_M	Maximum temperature
V_B	Ball wear volume
V_m	Nitrogen monolayer volume
V_M	Material wear volume
W	Specimen thickness
x	Sliding Distance
α	Thermal diffusivity
$\dot{\gamma}$	Shear rate
δ	Deflection of the bending beam for bending testing
ε	Strain
η	Viscosity
η_∞	High shear viscosity
η_0	Viscosity at rest
θ	Angle between incident and diffracted beams
Φ	Volume fraction
λ	Thermal conductivity
λ	Wavelength
ρ	Density
ρ_e	Ethanol density
ρ_{Exp}	Experimental density
ρ_r	Relative density
ρ_{th}	Theoretical density
σ	Stress
σ_f	Flexural strength

1. Introduction

The manufacturing sector is considered the cornerstone of product manufacturing, regardless of size, shape, or functionality. Over the past decades, technological advancements have facilitated the shift from mass production to mass customization, driving the development of innovative products and more efficient processes. These advancements have focused on minimizing energy consumption, waste, production time, and costs.

Modern manufacturing can be categorized into four primary methods: subtractive, formative, additive, and continuous processes, as illustrated in Figure 1.1.

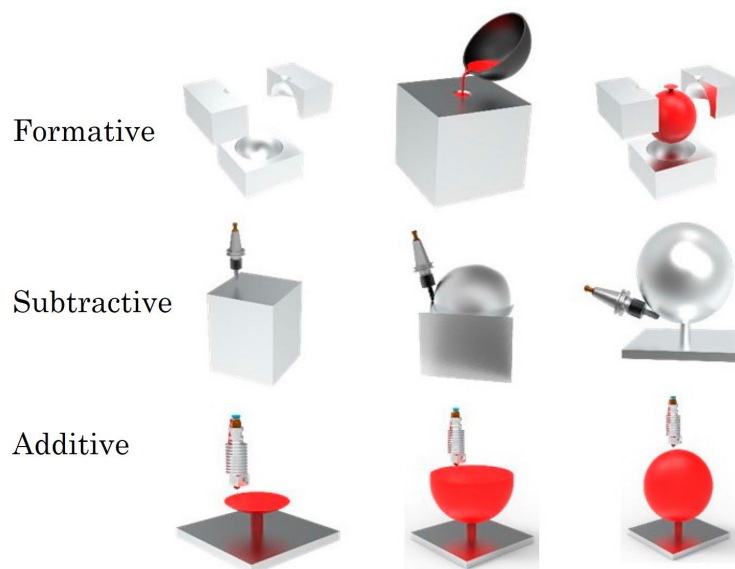


Figure 1.1. Manufacturing processes (from top to bottom): formative, subtractive, and additive. Image retrieved from [1], [2].

Subtractive processes involve the removal of material through machining techniques such as turning, milling, and grinding. Formative or near-net shape processes result in outputs at or close to their final shape; examples include stamping, forging, and injection moulding. Continuous processes have traditionally included composites' pultrusion and plastics and metals' extrusion. However, these processes are now often classified as additive manufacturing (AM) techniques, such as welding, rapid prototyping, and 3D printing, as defined by the

standard terminology *for Additive Manufacturing Technologies* [2]. According to this standard, AM is the process of joining materials to create objects from 3D model data, typically layer by layer, in contrast to subtractive manufacturing methods.

Despite substantial advances in the AM of metals and ceramics, the use of additively manufactured metal components in applications requiring tight tolerances and high precision remains limited. This is due to the challenges of achieving sufficient accuracy, uniform material properties, and high-quality surface finishes [3]. Consequently, subtractive techniques remain prevalent for scenarios that require superior precision and surface finish. These methods have been extensively automated through computer numerical control (CNC) systems, enabling the production of complex geometries and also enhancing productivity.

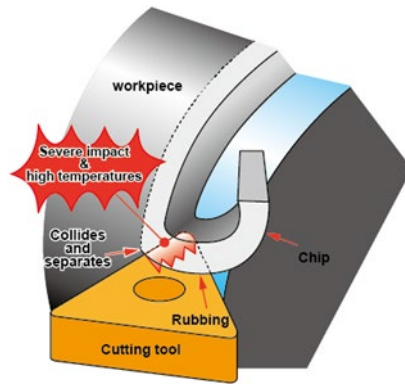


Figure 1.2. Diagram illustrating the turning process during machining from [3]

During the machining process, material (chip) is removed from a blank (workpiece) by the action of the cutting tool, as illustrated in Figure 1.2 for the turning process, to give it the desired shape and dimensions, thus obtaining complex parts with tight tolerances. Cutting tools are critical in machining, as they are designed to resist wear and deformation at high temperatures and pressures, ensuring precision and quality. Proper design and the correct choice of cutting tools are essential to maximize the efficiency of the machining process, thus minimizing costs and reducing tool wear. In this context, the selection of the material should maximize the following properties [4]:

- **Hardness:** They must withstand plastic deformation and wear while maintaining sharpness despite cutting forces and continuous contact with

the workpiece. The selection of a hard material reduces wear and extends tool life.

- **Wear Resistance:** Wear is expected as these elements are subjected to constant friction and abrasion. In general, wear behaviour is directly related to hardness, which is a function of the volume fraction and grain size. Therefore, a material with high abrasion resistance minimizes edge deterioration, reducing the need for frequent replacement after use.
- **Fracture Toughness:** Even though hardness is essential, if the tool is too brittle, it may break under impact loads. High fracture toughness ensures that the tool can absorb energy without breaking and withstand severe cutting forces.
- **Heat resistance:** In high-speed machining, the temperature at the cutting edge can exceed 1.000 °C [5], leading to phenomena such as diffusion and oxidation of the cutting tool, abrasion, and adhesion (the chip can adhere to the flank face). A material with high heat resistance will maintain mechanical properties, hardness, and sharpness at elevated temperatures, allowing faster and more efficient cutting operations.
- **Chemical Stability:** Certain cutting tools may chemically react with the workpiece or corrode when exposed to air and high temperatures. Under such conditions, chemical wear may occur, as chemical species diffuse between the tool surface and the chip. This diffusion alters the contact conditions and accelerates the tool failure.
- **Thermal Conductivity:** The ability to dissipate heat from the wear surface and avoid localized temperature-induced softening depends on the thermal conductivity. A material with high thermal conductivity efficiently conducts and disperses the heat generated during cutting, preventing softening at the tool's edge. This enhances tool life and improves the quality of the surface finish.

The performance of cutting tools is influenced by several factors, including the material of the workpiece, the cutting speed and depth, the geometry of the tool and the cooling conditions. Among these, cutting speed and feed rate are critical parameters in conventional machining processes, as they significantly affect surface finish, productivity, and tool endurance.

Depending on the machining process, whether it is turning, milling, or drilling, the workpiece or the tool rotates at varying speeds, dictated by its relative motion. Tangential speed, which is the speed at which the tool's edges cut through the material, is crucial as it determines both the production volume and the tool's lifespan. This parameter is measured in meters per minute (m/min). If the cutting speed is too low, it leads to inefficiencies and wasted time. On the contrary, excessive speed can result in premature tool wear due to overheating at the interface between the tool and the workpiece, compromising both tool life and machining quality. Furthermore, chip formation during cutting is also influenced by the cutting speed. An incorrect speed can lead to chip accumulation in the tool, reducing precision and safety.

On the other hand, the feed rate refers to the speed at which the tool moves along the workpiece per unit of time. It is measured in millimeters per revolution (mm/rev) or millimetres per minute (mm/min). While increasing the feed rate can improve productivity, it also amplifies the forces generated during the process. Excessive feed rates can reduce machining accuracy, accelerate tool wear, and shorten tool life. Additionally, higher feed rates increase friction, potentially damaging the tool and the workpiece.

Cooling conditions are critical to ensure cutting tools' efficiency, durability, and finish quality during machining. Friction between the tool and the workpiece generates significant heat, which the coolants dissipate. In some cases, coolants also function as lubricants, reducing overheating and improving operational stability and accuracy. However, the use of industrial cutting fluids raises environmental concerns, and advances in dry machining techniques have been explored over the last decade as a sustainable alternative.

Lastly, the machining parameters also depend heavily on the material of the tool. For example, cemented carbide tools can operate at cutting speeds than high-speed steel tools because of their superior ability to withstand elevated temperatures. Similarly, titanium and high-alloy steels generate more heat during machining. This is attributed to their low thermal conductivity and work hardening caused by high friction [7], [8]. In such cases, more efficient cooling systems are required to protect the tool and the workpiece [6], [7].

1.1. History of Cutting Tool Materials

Cutting tools are typically manufactured from bulk materials such as cubic boron nitride (cBN), diamond, and metal matrix composites (including cemented carbides and cermets). In addition, wear-resistant coatings are often applied to high-speed steel (HSS) tools or cemented carbide (WC-Co). These materials offer distinct properties that make them well-suited to specific applications. Figure 1.3a shows the classification of these materials according to their hardness and fracture toughness, highlighting those that will be most relevant for this research. On the other hand, Figure 1.3b shows the percentage of use of each material in the industry.

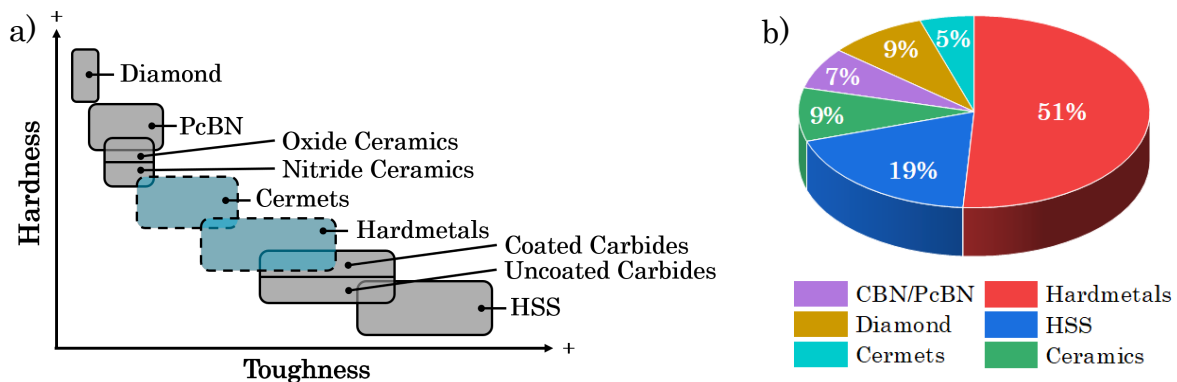


Figure 1.3. a) Classification of materials according to their hardness and fracture toughness; b) Use of each material in the turning industry [8], [9].

The manufacture of cutting tools presents a significant challenge: identifying materials that effectively combine high hardness and wear resistance with high toughness. Although these properties are essential, they are often in conflict. As previously discussed, hardness and wear resistance enable tools to maintain their sharpness and functionality for extended periods, whereas toughness ensures that they can withstand impacts without breaking during use.

Achieving an optimal balance between these attributes is particularly challenging. For instance, ceramic materials provide excellent wear resistance but are typically brittle, compromising their fracture toughness. Conversely, certain steels offer more outstanding toughness but lack the hardness to endure prolonged wear under demanding conditions. As a result, the development of materials that strike the right balance between hardness and toughness is critical for producing effective cutting tools.

Over time, material science advancements have significantly improved the properties of cutting tools. This progress has resulted in modern tools that are more durable, efficient, and capable of operating at higher operational speeds, although it has entailed considerable challenges.

Throughout history, notable eras have been named after the dominant materials of their time, such as the Stone Age and the Iron Age. These names underscore the vital role that materials have played in the evolution of society. Naming historical periods after materials used in toolmaking highlights their importance in driving progress, enabling civilizations to develop and refine more efficient cutting methods. While the complexity and applications of tools have evolved over centuries, their significance remains fundamental to the ongoing advancement of the modern world.

The development of the first commercial tooling steel alloy is attributed to Robert Forester Mushet. In 1868, he made a groundbreaking discovery: adding tungsten (W) to steel significantly improved its hardness, even when air-cooled. This finding marked a pivotal moment in the history of metallurgy, spurring the development of new alloys and facilitating the widespread adoption of tool steels. [10], [11].

At the beginning of the twentieth century, metalworking was still a highly specialized skill reserved for trained craft workers who used tool steel as the primary material to manufacture cutting instruments. However, with the rise of mass production, driven by growing industrial demand, especially in emerging sectors such as the automotive industry, the limitations of tool steel began to become apparent. One of the main shortcomings of steel in this context was its limited heat resistance, which caused it to soften at high temperatures (above 700 °C), especially at the interface between the material and the tool, thus hindering high-speed cutting processes.

The industrial need to improve efficiency in the manufacturing of complex components prompted the search for alternative materials to address the drawbacks of traditional steel. This led to the development of high-speed steel (HSS), a high-alloy steel that incorporates significant quantities of tungsten (W), cobalt (Co), vanadium (V), and chromium (Cr), in addition to iron (Fe) and carbon (C). The extensive solid solution alloying of these elements with the ferrite matrix significantly strengthened the steel and increased its hot hardness, enabling it to

operate effectively at higher speeds [12]. In the following years, new grades¹ of HSS were developed, highlighting the addition of cobalt. Addition of Co increases the solidus temperature of steel and the red harness² by slowing down the rate of softening of martensite, allowing it to operate at significantly higher cutting speeds [10], [13].

This advancement significantly improved the efficiency of cutting processes and had a direct impact on industrial productivity. High-speed steel reduced production times and associated costs by enabling faster and more precise cuts, establishing itself as a cornerstone of modern manufacturing.

The success of high-speed steel, coupled with the industry's demand for higher temperatures and faster cutting speeds, led to the development of cemented carbide. This material represented a significant milestone in the evolution of cutting tools. Between 1907 and 1928, Franz Skaupy directed the "Study Group of Electric Lighting," a subsidiary of OSRAM tasked with developing fluorescent tubes and producing tungsten lamp filaments. Following the First World War, this group sought a replacement for diamond as the wired drawing matrix for tungsten lamp filaments. Leveraging existing tungsten sintering technology, they attempted to produce solid tungsten carbide (WC) by sintering tungsten powder with carbon to achieve a ductile material. However, the resulting products, WC and W₂C, were exceptionally hard, but also highly brittle and prone to cracking during cooling.

In 1923, Karl Schröter, a colleague of Skaupy, patented an innovative material under the title *Gesinterte harte Metallegierung und Verfahren zu ihrer Herstellung* ("Sintered hard metal alloy and process for its production") (DE420689). This patent outlined a process using tungsten carbide as the base material, produced either by carburizing tungsten powder in a suitable gas phase or mixing it with elemental carbon in the form of soot, charcoal, or graphite. Adding a small amount of metal powder —such as cobalt (Co), nickel (Ni), or iron (Fe)—produced a hard and tough composite material. This material, manufactured through pressing and sintering, established the foundation for modern cemented

¹ AISI M2 (0.85 C, 0.30 Mn, 0.30 Si, 4.0 Cr, 2.0 V, 6.0 W, 5.0 Mo; red hard) is the most widely used industrial HSS.

² Red hardness, also called heat resistance, is defined as the maximum temperature at which steel retains a given hardness achieved through heat treatment. For example, high-speed steel retains Rockwell C hardness of up to 60 at 620 °-650 °C.

carbide production. The optimal carbon content in tungsten monocarbide was determined to be 3–7 % (w/w).

Although WC-Co was initially designed for wired drawing dies in the electric lighting industry, its exceptional properties soon made it indispensable for cutting tool manufacturing. Recognising its potential, the Krupp company acquired the patent and introduced the material to the international public under the brand name "WIDIA" at the Leipzig Spring Fair in 1927. Derived from the German words *wie* and *Diamant* ("like diamond"), the WIDIA brand focused on cemented carbide tools with inserts specifically designed for turning and milling cast iron and hardened steels [10], [14]. Up to 1932, WIDIA cemented carbides were exclusively based on WC - Co, but in 1932, TiC-containing hard metals were introduced at Krupp with the designation 'WIDIA X'. This material was better suited for turning steels than the original WIDIA, although the difficulties associated with its brazing limited its use. With throw-away tool tips, alloys with higher proportions of TiC could be used, and consideration was given to tools based on TiC instead of WC because of its resistance to diffusion wear in steel cutting [15].

Just as the introduction of high-speed steel revolutionised the manufacturing industry, the development of cemented carbides, also known as hardmetals³, elevated machining to an entirely new level. These materials offered significantly more excellent durability and heat resistance while enabling cutting speeds up to four times higher than those achievable with high-speed steel.

Although subsequent advancements in the manufacturing industry have led to the development of hard and superhard materials, such as cubic boron nitride (cBN) and synthetic diamond, cemented carbides remain the material of choice for applications where efficiency and precision are paramount. Their exceptional ability to retain hardness under extreme temperatures and high-pressure conditions continues to make them indispensable in critical machining processes.

1.2. Cutting tools materials

As indicated in the previous section, cutting tools are usually manufactured using bulk materials, such as high-speed steels or metal matrix composites (cemented

³ Both terms are completely equivalent. However, "Hardmetals" is rather used in Europe, while "Cemented carbides" is rather used in USA, but also in European English literature [10].

carbides and cermets) but also hard and superhard materials (oxides, cBN, or diamond), as well as wear protection coatings on tools made of HSS or cemented carbide (WC-Co) are current alternatives; each of which excels in certain properties, making them suitable for specific applications. Some of these properties are included in the Figure 1.4 by García *et al.* [16] from AB Sandvik Coromant R&D, where common cutting tool materials are included.

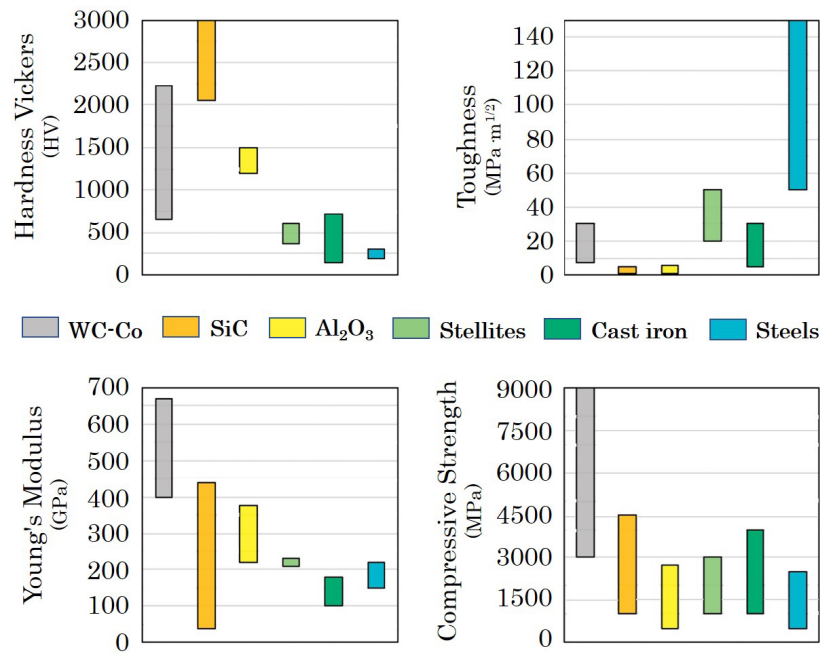


Figure 1.4. Mechanical properties (Vickers microhardness, fracture toughness, Modulus of elasticity and compressive strength) of different materials: hard metal (WC-Co), silicon carbide (SiC), aluminium oxide (Alumina, Al₂O₃), Stellites⁴ (i.e., cobalt-based alloy with additions of Cr, C, W and/or Mo), cast iron and steel. Image retrieved from [16].

For machining applications, high hardness and high fracture toughness with low coefficient of friction are crucial, but also high oxidation and chemical resistance against the machined material [16]. For instance, despite its high hardness of 70–100 GPa, diamond cannot be used for machining ferrous alloys at elevated temperatures due to the dominance of chemical wear under such conditions. This limitation restricts its industrial applications to machining non-ferrous and non-metallic materials, such as aluminium alloys, ceramics, and stone. Additionally, diamond exhibits poor thermal stability at temperatures above 700 °C.

Cubic boron nitride (cBN) is notable for its excellent hot hardness and greater resistance to thermo-chemical degradation. When exposed to oxygen at high

⁴ Stellite alloys are generally resistant to cavitation, corrosion, erosion, abrasion and galling.

temperatures, cBN forms a passivation layer of boron oxide, enhancing its stability. Unlike diamond, cBN offers superior thermal stability and chemical resistance, making it suitable for machining ferrous metals. However, the hardness of cBN, at approximately 40–55 GPa, is only half that of diamond. Furthermore, its production costs, significantly higher than those of synthetic diamonds, limit its widespread industrial use [17] its commercial feasibility to only specific applications, such as the machining of nickel and cobalt-based superalloys. Furthermore, cBN has limitations in terms of low flexural strength and toughness, which may affect its performance in high-speed machining [16].

Hard ceramics used for abrasive applications are mainly aluminium oxide (Al_2O_3), zirconium oxide (ZrO_2), and silicon nitride-based materials with or without aluminium and oxygen additions (i.e. SIALON). In addition to high hardness (up to 30 GPa and 8 GPa, for Al_2O_3 and ZrO_2 , respectively, and 16 GPa for Si_3N_4), these materials also offer high corrosion resistance and the ability to withstand high temperatures without chemical degradation. As with cBN, the biggest drawback of these oxide ceramics is their relatively low fracture toughness compared to cemented carbides⁵, which are usually less than 5 $\text{MPa}\cdot\text{m}^{1/2}$ for Al_2O_3 . This limits its use in applications such as machining tools for machining [18].

On the other hand, cutting metals, such as high-speed steels or Co-based alloys (“Stellites”), excel in fracture toughness, with values close to 50 $\text{MPa}\cdot\text{m}^{1/2}$ [19], [20], although Stellite alloys, i.e. cobalt-based alloys with additions of Cr, C, W and/or Mo, stand out in hardness and resistant to cavitation, corrosion, erosion, abrasion, and galling. Some of these alloys retain their properties at temperatures of up to 600 °C; however, their hardness remains only one-fourth that of hardmetals and even lower than silicon carbide (SiC)-based ceramics. Furthermore, the criticality of their primary component —discussed later in this chapter— along with their genotoxic and carcinogenic properties significantly restricts their range of applications.

As a result, WC- and TiC-TiN-based ceramics dominate the cutting tool market, offering an excellent balance between hardness and toughness. Since the distinctions between these materials are often misunderstood, the next section will clarify their definitions.

⁵ Commercially available cemented tungsten carbide (WC–Co) grades used as cutting tools have toughness values of up to 25 $\text{MPa}\cdot\text{m}^{1/2}$.

1.2.1. Cemented carbides and Cermets

The manufacturing process of cemented carbides, or hardmetals, involves sintering fine carbide particles with a metal binder to produce a compound with exceptional hardness and strength, characterised by an isotropic and homogeneous microstructure. Although this description can also apply to cermets, key differences in their composition justify their distinction. Both materials are classified as metal matrix composites (MMCs). However, they are regarded as separate categories because of their unique properties and the advanced degree of development they have achieved compared to those of other MMCs.

The primary distinction between cemented carbides and cermets lies in their composition. Cemented carbides are renowned for their extreme hardness and wear resistance. They are composed of carbides, nitrides, or borides of metals such as vanadium, chromium, molybdenum, or tungsten, which are embedded within a metal matrix, typically cobalt or nickel. The most common cemented carbide is the WC-Co system, where the volume fraction of WC particles generally ranges from 0.70 to 0.90. The particle size typically varies between 0.2 and 15 μm [21].

In contrast, the term *cermet*, a blend of "ceramic" and "metal" words, refers to a composite material that began development after World War II. The objective in creating cermets was to combine the high hardness and high-temperature resistance of ceramics with the toughness and impact resistance of metals, while avoiding the use of tungsten as the primary ceramic phase. Despite some variability in definitions, the term *cermet* has historically been associated with titanium carbide (TiC)-based metal matrix composites. These typically consist of TiC or Ti(C,N) hard phases embedded within a metallic matrix, usually nickel or cobalt, as in the case of cemented carbides.

Cermets were developed to address certain limitations of cemented carbides, such as their susceptibility to oxidation and degradation at elevated temperatures. Early cermets, composed of TiC and Ni, provided high hardness but lacked the toughness and abrasion resistance of cemented carbides. These properties were further enhanced by substituting Ni with a Ni-Mo alloy and introducing small amounts of aluminium (Al). These modifications improved the wetting of ceramic particles and strengthened the metallic matrix.

A significant breakthrough occurred by incorporating nitrogen into the Ti(C,N) ceramic phase, resulting in improved wear resistance, resistance to plastic deformation, and fracture toughness. This advancement led to modern cermets

exhibiting excellent resistance to wear and corrosion at high temperatures. These properties make them ideal for high-speed cutting applications and extreme environments demanding superior performance [22].

Both MMCs offer tremendous advantages in tailoring the hardness and fracture toughness values by changing the proportions of the hard particles and the metallic binder phase, as shown in Figure 1.5 for the WC-Co system. At the same time, both properties are also affected by the interspacing between ceramic particles and the metallic binder (i.e. mean free path), limiting the maximum amount of metallic binder in the composites, which should be ideally the lowest possible to ensure complete wetting of the ceramic particles, while maintaining high hardness.

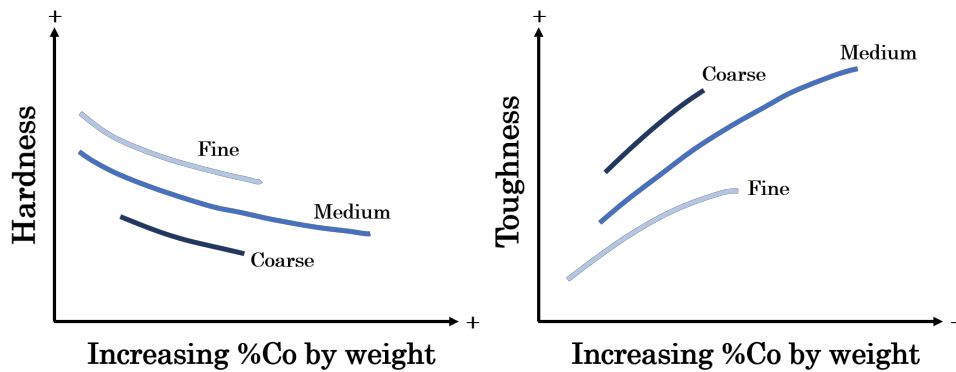


Figure 1.5. Variation in hardness (left) and fracture toughness (right) of different grades of WC-Co, that is fine (1–2 μm), medium (3–4 μm) and coarse (>5 μm) grain size, with increasing cobalt (Co) content. Image retrieved from [18].

However, the grain size of the main component also plays an essential role, since the hardness of the bulk material can also be tailored by changing the particle size of the ceramic phase [18], in agreement with the Hall–Petch relationship [23], illustrated in the Figure 1.5 for fine (1 to 2 μm), medium (3 to 4 μm), and coarse (>5 μm) grain size particles. Significant advances in the refinement of the ceramic phase have been made in the cemented carbide industry in the last decades, achieving materials with high hardness (up to HV10: 2800) and strength (compressive strength up to 8000 MPa) with still moderate toughness for applications where an extreme wear resistance of the tool is mandatory, for example, water jet nozzles with high water pressures (up to 4000 bar) [24]. This was achieved by adding small amounts of grain growth inhibitors, such as vanadium and chromium.

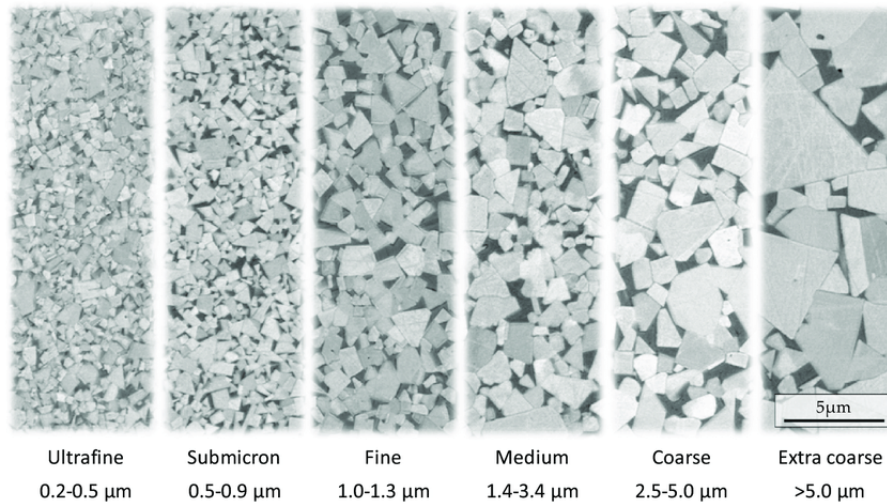


Figure 1.6. WC-Co microstructures for different grain sizes. Images courtesy of [16].

Chromium also improves the durability and performance of the tool by increasing corrosion and wear resistance [25], [26], [27]. The same benefits are targeted when other elements are added together with carbon, to favour the formation of secondary high-hardness carbides. The list of elements includes molybdenum, vanadium, tantalum, niobium, titanium and tungsten, the latter added in small amounts to hardmetals and cermets, respectively. All of these elements have melting points above 2500 °C, resulting in extremely hard carbides stable at high temperatures [28], [29], [30]. The presence of TiC, NbC and TaC has been shown to increase the wear resistance of hardmetals at high contact temperatures (above 800 °C) and the erosion-corrosion resistance [31] of cermets devised for the petroleum production and refinery, chemical engineering, coal and hydroelectric industries. In addition, several studies have shown that the addition of Ta or TaC to TiC and Ti(C,N) cermets can improve the wettability between the hard phase and the metal binder phase and also inhibit the grain growth of the cermets [32], [33].

1.2.2. Manufacturing methods

The properties of cemented carbides depend mainly in the composition and the interactions between phases, i.e. the homogeneous distribution of the metallic and ceramic phases, so the processing method is a key factor.

The most common processing route for cermets is the conventional powder metallurgy (PM) route, which imply the milling of powders through attrition ball

milling (up to 36 h) or, for up to 2-7 days in a ball mill, using organic liquid media (normally ethanol or isopropanol) and a binder or lubricant such as polyethylene glycol (PEG) or paraffin wax; after milling the powders are dried, and could be granulated for a better pressing behavior.

Powders are shaped by uniaxial pressing or cold isostatic pressing followed by sintering at high temperatures, usually in vacuum or under a hydrogen atmosphere. The desired geometry of the part is then achieved through various shaping technologies:

- **Direct forming or die pressing:** This method is commonly employed for large production volumes and relatively simple geometries, such as cutting inserts or milling tools.
- **Extrusion:** Used for components with a high length-to-diameter ratio. In these cases, plasticisers (e.g. waxes) are added to the powder mix to ensure smooth flow through the extrusion die.
- **Powder injection moulding (PIM):** Suitable for small parts with intricate geometries. The plasticised material is injected into a mould, which is subsequently opened to release the shaped part. This is considered an indirect forming method.

Once the part is shaped by pressing, extrusion, or injection moulding, it undergoes a high-temperature sintering process. For WC-Co materials, sintering is typically carried out at 1400 °C, resulting in a fully dense liquid phase sintered body [34], [35]. Pressure-aided sintering, i.e. hot isostatic pressing (HIP), has become a standard technology for producing defect-free materials of outstanding strength for simple shapes.

1.3. Critical raw materials in the machining market

1.3.1. International Market Context

In 2023, the global cutting tool market was valued at approximately \$92 billion and is projected to exceed \$176 billion by 2034, reflecting a compound annual growth rate (CAGR) of 8.8 % (Figure 1.7a). Although these figures may seem impressive, it is essential to note that they span numerous industries associated with this application, as illustrated in Figure 1.7b.

The widespread application of cutting tools across various industries has led to a growing global demand, driving the need for more efficient and precise manufacturing processes. This increasing demand has also heightened expectations regarding the materials used to produce these tools. Market competitiveness compels manufacturers to continually pursue innovations that enhance tool performance, making material selection a critical factor in maintaining a competitive edge.

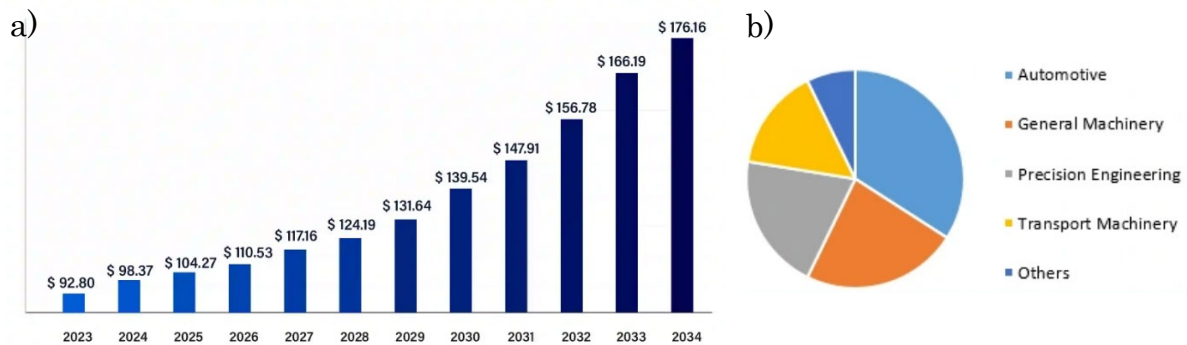


Figure 1.7. Cutting tools market: a) Expected machine tools market size 2023 to 2034 (USD Billion); b) Metal cutting market percentage by application in 2023 [36], [37].

The widespread application of cutting tools across various industries has led to a growing global demand, driving the need for more efficient and precise manufacturing processes. This increasing demand has also raised expectations regarding the materials used to produce these tools. Market competitiveness forces manufacturers to continually pursue innovations that improve tool performance, making material selection a critical factor in maintaining a competitive edge.

Metals such as tungsten and cobalt are crucial for the production of cemented carbides; however, the supply of these resources could be limited sooner than expected. Both elements are considered critical raw materials (CRM)⁶ for the European Union industry and the US and China markets, as observed in Figure 1.8. Furthermore, of the 34 critical raw materials identified for the EU, both Co and W have been included in the list of strategic raw materials (SRM), which includes 17 materials expected to grow exponentially in terms of supply, which have complex production requirements and therefore face a higher risk of supply issues. Cobalt supply has concentration problems and a high risk of disruption, as

⁶ According to the European Commission, critical raw materials are raw materials of high economic importance for the EU, with a high risk of supply disruption due to their concentration of sources and lack of good, affordable substitutes.

it is extracted mostly as a by-product of copper and nickel and the most mines and refineries are concentrated in the Democratic Republic of Congo and China, respectively. Furthermore, political stability in production countries is considered to be medium to very weak [38].

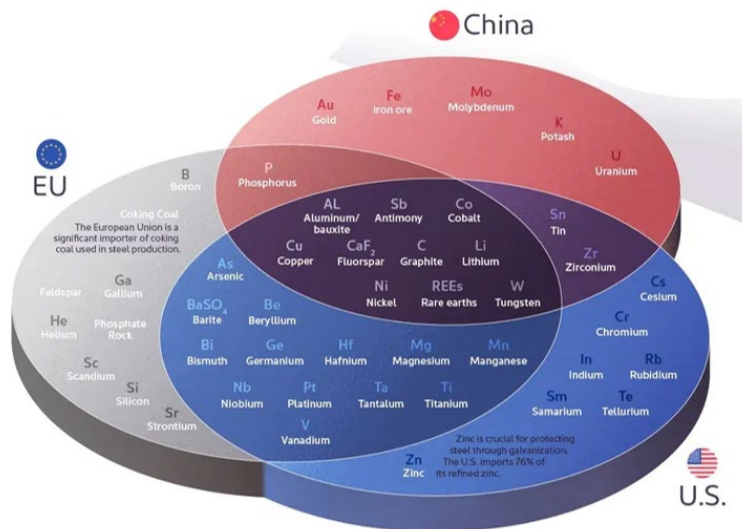


Figure 1.8. The critical minerals to China, the EU and the U.S.

1.3.2. The case of cobalt

The demand for cobalt (Co) has grown significantly due to the rapid development of clean energies and the expansion of the electric vehicle market, globally and in the EU, as it is an essential component in lithium-ion batteries whose primary function is to extend their service life.

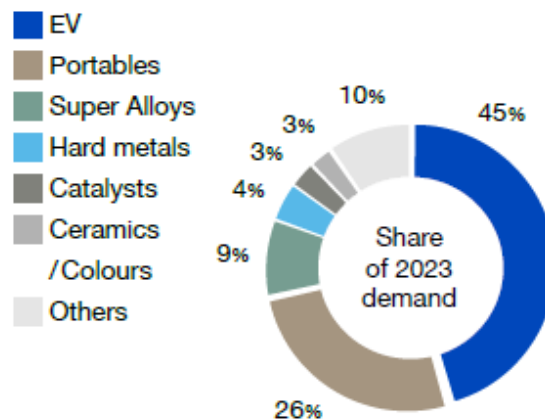


Figure 1.9. Cobalt demand percentage by end-use and share of demand growth. Data from Benchmark mineral intelligence.

As shown in Figure 1.9, 45 % of Co is destined for electric vehicles, and a further 26 % for portables, i.e. more than 70 % of this material is used by two industries with a strong presence in modern society. Although only 8 % is destined for hardmetals, the high demand for Co in these industries will cause its price to soar. In recent decades, Co production has increased in line with demand and although there have been some fluctuations, the price has risen significantly, as shown in Figure 1.10 [38].

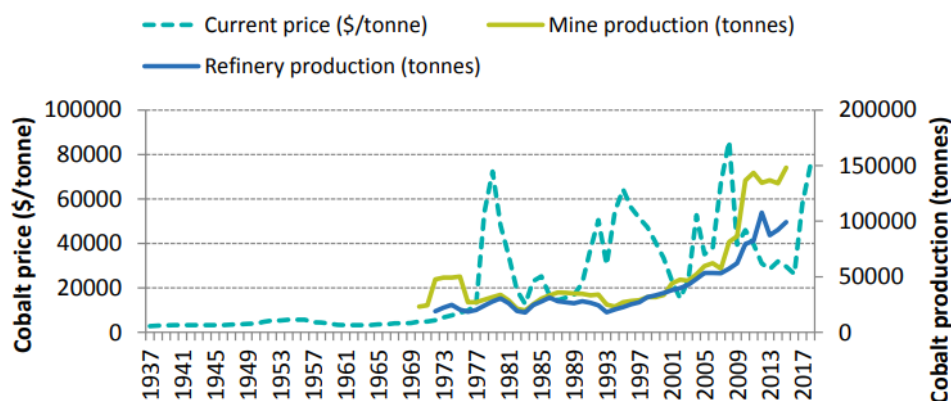


Figure 1.10. Historical mine production and prices of cobalt from 1937 to 2017.

However, to limit global warming to 1.5 °C, as defined in the Net Zero Emissions (NZE) scenario, it is expected that the demand for critical minerals will intensify rapidly over the next 15 years [39], [40]. This could have significant repercussions on market balance. Figure 1.11 presents the consumption projections and the quantities of material supplied [38].

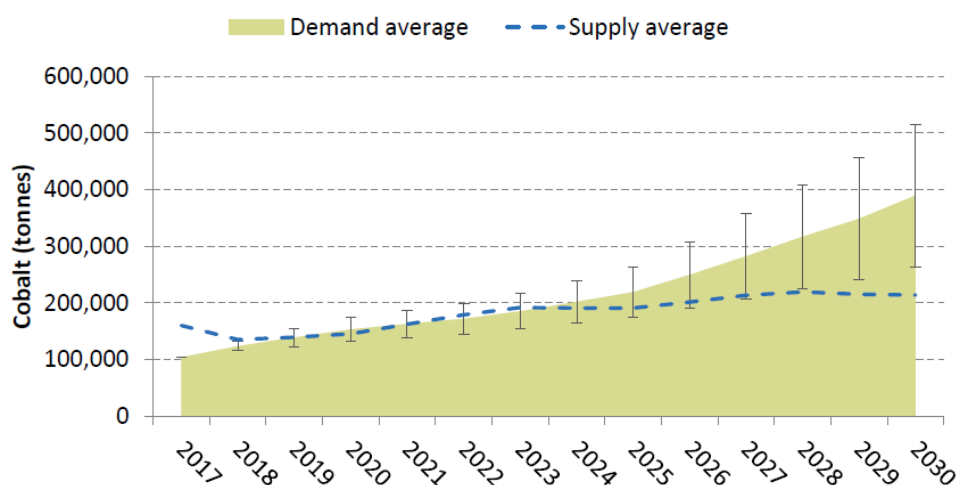


Figure 1.11. Year-on-year cobalt surplus/deficit in average mine supply and demand scenarios.

With future projections, it becomes clear that Co will play a crucial role in the coming years, especially in the transition to clean energy and the development of sustainable technologies. However, we face a significant challenge: the growing demand for that mineral is on track to exceed the global supply capacity by a great deal. This imbalance between supply and demand could cause availability problems, a considerable increase in prices, and tensions in supply chains. Therefore, it is urgent to take action or alternative solutions to reduce dependence on this critical material.

Future projections highlight Co's pivotal role in the coming years, particularly in the transition to clean energy and the advancement of sustainable technologies. However, a significant challenge looms: the rising demand for cobalt is set to exceed global supply capacity. This imbalance between supply and demand could lead to serious availability issues, substantial price increases, and disruptions in supply chains.

Consequently, it is imperative to take proactive measures and explore alternative solutions to reduce dependence on this critical material.

1.3.3. The case of tungsten

In contrast, though tungsten belongs to the group of metals with a recycling input rate above 25 %, its high number of applications and low replacement capacity make it an SRM. Tungsten is relatively rare in the Earth's crust and is extracted mainly from wolframite (WO_4) and scheelite (CaWO_4). Globally, more than 30 countries contribute to the global supply of tungsten. However, the top three countries accounted for 92 % of total production in 2016, with China being the first producer, followed by Vietnam and Russia. Tungsten is produced in smaller amounts throughout Europe, with Austria, Portugal, and Spain among the top W producers during the last years, even if the amounts extracted were not very large [41].

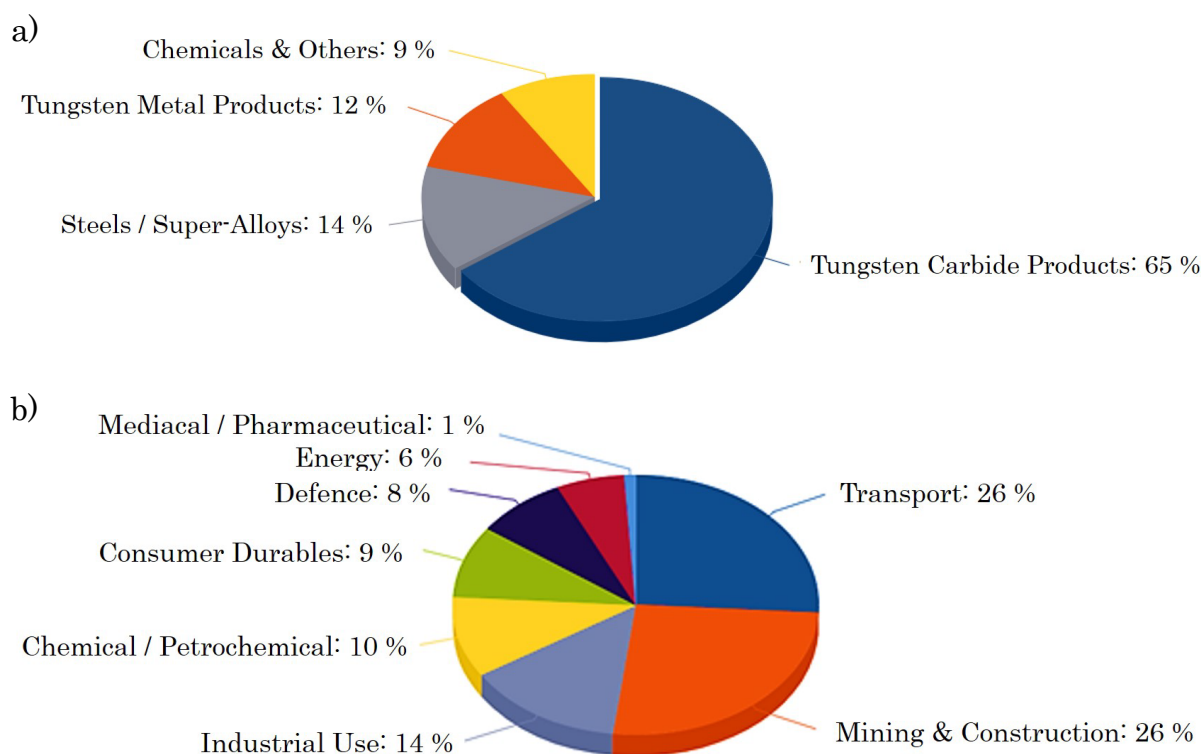


Figure 1.12. a) Global breakdown of the first-use segments for tungsten in 2021, b) End-Use by industry for tungsten in 2021. Graph retrieved from the International Tungsten Industry Association.

As shown in Figure 1.12, the tungsten consumed in the EU is used to produce tungsten carbides. The next most prominent application is tungsten alloys, which are used in a broad range of industries. These include lighting technology, electrical and electronic technology, high-temperature applications (e.g., furnaces and power stations), welding, spark erosion, space travel, aircraft devices, armaments, and laser technology. Such applications typically require high hardness and temperature resistance, which limits the feasibility of substitution to low-performance alternatives.

Potential substitutes for tungsten carbides include cemented carbides based on alternative metals such as molybdenum (Mo), niobium (Nb), or titanium (Ti), as is the case with cermets. In particular, titanium carbides and nitrides show promise as substitutes, but further research —such as the work presented in this investigation— is required to reduce costs and enhance performance. On the contrary, substitutions for tungsten in other applications appear to be more viable. For example, refractory metals like molybdenum or, to a lesser extent, niobium (classified as a critical raw material in the EU in 2020) could replace tungsten in

steel products. Also, gas turbine engine superalloys might be substituted with silicon carbide or silicon nitride ceramic composites. Carbon nanotube filaments and carbon-reinforced composites are being studied as alternative materials for power electronics packaging in the lighting and electronics sectors.

This underscores the importance of reducing cobalt dependence in tooling materials and exploring alternative compositions that minimise reliance on critical resources. While manufacturers and suppliers can adopt sustainable practices such as repairing and refurbishing used tools to extend their lifespan, recycling materials and developing competitive alternatives that partially or fully replace strategic elements must also be prioritised.

1.3.4. Recycling of cemented carbide materials

As previously mentioned, the cemented carbide sector is strategically important because of the limited availability and price volatility of its primary raw materials, tungsten (W) and cobalt (Co). Despite the growing industrial demand for these elements, their availability has remained unchanged, highlighting the critical need to recycle cemented carbide scrap for environmental and economic benefits.

In 2023, the cemented carbide recycling market was valued at \$3.7 billion and is projected to grow to \$7.3 billion by 2030, representing a compound annual growth rate (CAGR) of 10.5 % between 2024 and 2030 (see Figure 1.13).

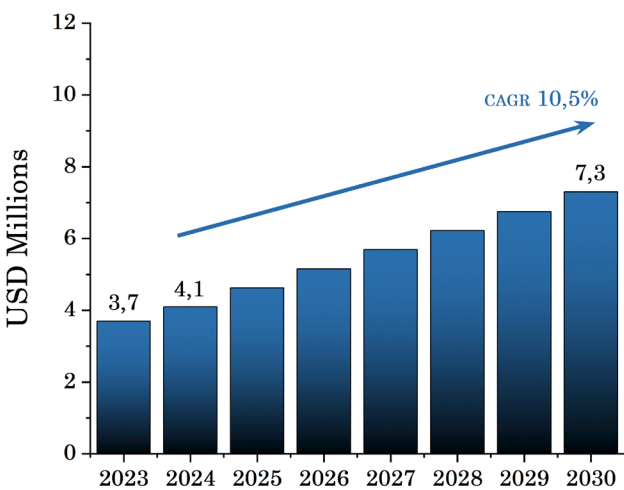


Figure 1.13. Global cemented carbide recycling market.

The growth of the cemented carbide recycling market is due to the increasing demand for applications such as cutting tools, mining, and other industrial areas around the world. These tools, mostly made of cemented carbide, have a significant wear and tear, making recycling essential to recover valuable materials and reduce costs.

Recovery of these materials is already an established practice in the cemented carbide industry, with remarkable recovery rates that reach approximately 42 % tungsten (W) and 22 % cobalt (Co) from by-products and manufacturing scrap. Recycling cutting tools are becoming more relevant as industries seek to reduce costs and environmental impact. The increasing adoption of these processes is expected to increase the recovery of valuable materials from worn tools and machinery, favouring a circular economy and promoting more sustainable practices [42], [43], [44].

Technological advancements in cemented carbide recycling, especially for WC-Co waste, have been a critical driver of market growth in recent decades. This waste includes used cutting tools and production waste, known as hard waste, and by-products of the manufacturing process, such as wires, shavings, and dust, known as soft waste. WC and Co are recycled mainly by direct and chemical processes. The direct process, for example, includes physical and/or chemical treatments designed to decompose scraps and recover materials, which are then reintroduced into the same production sector after cleaning, classification, separation, and treatment at high temperatures, as outlined in Figure 1.14 [45].

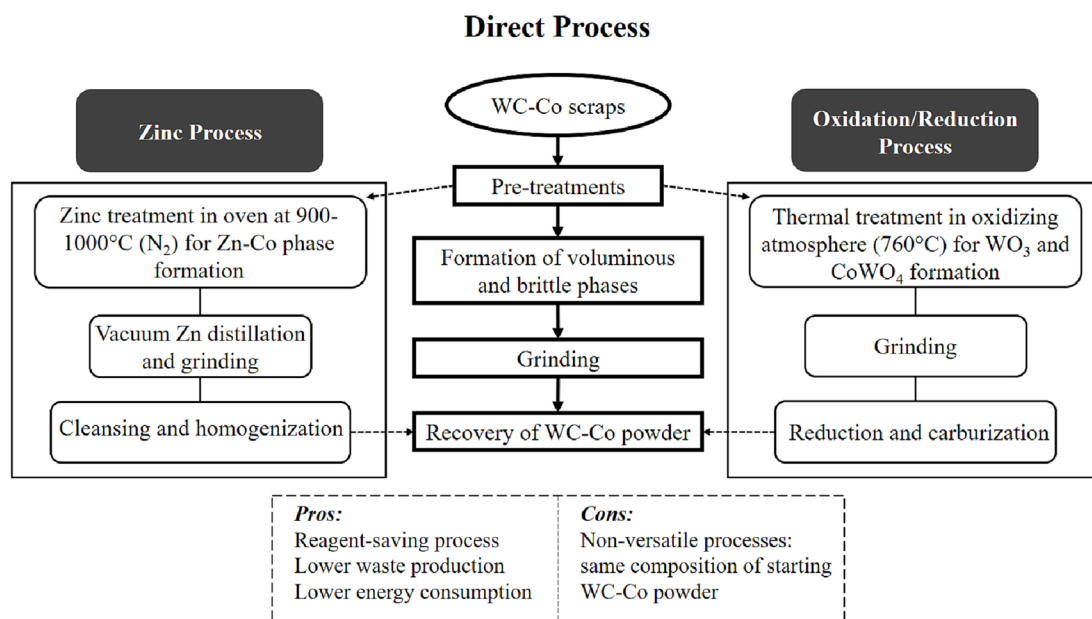


Figure 1.14. The direct recycling process from materials of WC-Co base cutting tools [42].

Despite its operational simplicity, this method has several drawbacks, including inadequate waste sorting and cleaning, which directly affect the quality of the resulting powder. Furthermore, the process lacks flexibility to adjust the material's composition, as it maintains the fixed proportions of tungsten and the binder.

Nevertheless, despite these limitations, the reduced energy and chemical consumption compared to chemical recycling makes the direct method a viable and valuable alternative, mainly when recycled products are manufactured from cemented carbides.

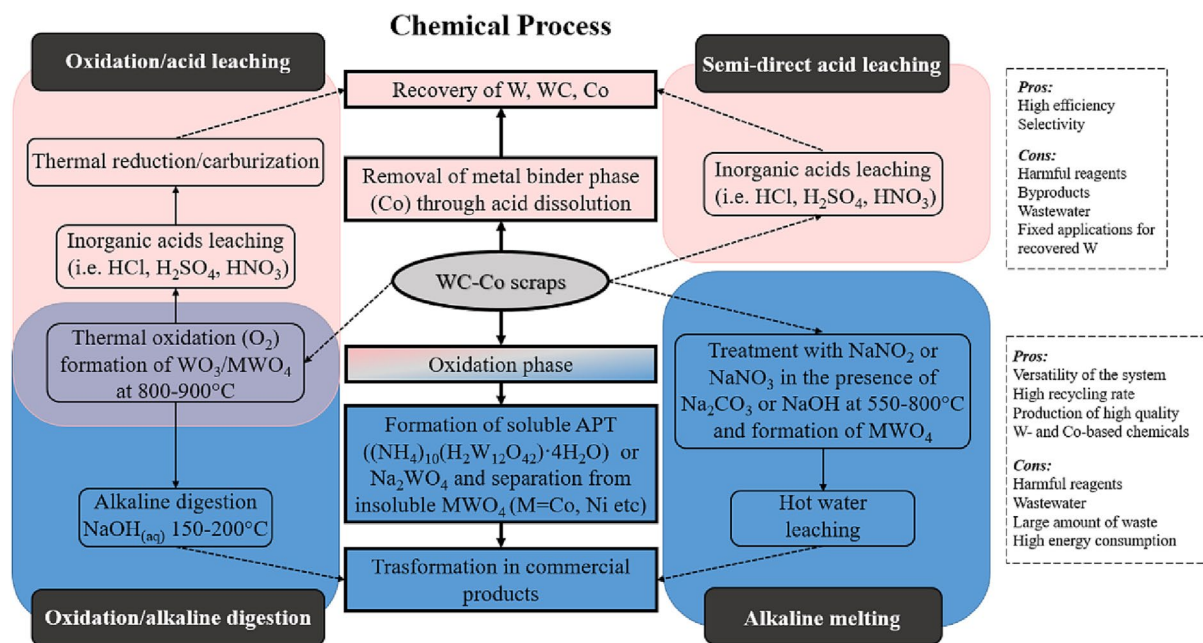


Figure 1.15. Process WC-Co Chemical Cutting Tools Materials Recycling Machine [42]

Chemical recycling, on the other hand, consists of a multiphase chemical transformation of waste that combines heat and chemical treatments to obtain intermediate products that are then processed to extract pure metals. The most common methods include reduction-oxidation or digestion reactions and acid leaching, as illustrated in Figure 1.15. Currently, chemical processes are the most versatile and selective, and they apply to any tungsten (W)-based material, allowing the obtaining of high-purity raw materials that can be used in various sectors. However, its main disadvantages are high energy and economic costs, hazardous reagents, and significant wastewater generation [46].

1.4. Search for alternatives

While enhancing circularity by recycling materials from WC-Co cutting tools is essential to promote sustainability and conserving resources, this field remains in development. As noted previously, current recycling processes, although practical, often fail to recover all materials optimally or cost-effectively and face technical challenges that impede their large-scale implementation.

Therefore, alongside advances in recycling technologies, it is equally important to invest in the research and development of alternatives to conventional materials to ensure the continuity and sustainability of the industry.

1.4.1. Materials Alternatives

The search for alternatives is focused on developing new materials that can replace Co and improve the properties of cutting tools to reduce the use of material and extend their service life. Currently, numerous investigations are being conducted to find options that match or exceed the performance of traditional materials but with less environmental impact and greater availability.

Many studies focus on the modification of alloy components to improve the mechanical properties of cemented carbides [47]. To this end, the effects of the addition of uncommon elements, such as Mo_2C , ruthenium and rhenium [48], or alloys, such as $\text{TiNb}_{24}\text{Zr}_6$ [49], are analysed to increase the strength and hardness of the material. Furthermore, WC-based materials have been sintered with pre-alloyed Co-VC- Cr_3C_2 binders, achieving optimal densities at lower sintering temperatures, inhibiting grain growth and improving toughness [50].

Other authors are exploring alternative binders to process cobalt-free cemented carbides because of their criticality and concerns about their impact on health and limited availability. Fudger *et al.* used hot isostatic pressing sintering to consolidate cemented WC carbides using $\text{Fe}_{88}\text{Ni}_8\text{Zr}_4$ and $\text{Fe}_{91}\text{Ni}_8\text{Zr}$ binders. This method obtained almost entirely dense materials, achieving higher fracture toughness and hardness than commercial cemented carbide WC-10Co [51]. Nicolas-Morrilas *et al.* investigated cobalt-free cemented carbides using pre-alloyed Fe-16Cr-3Al binders, where the formation of aluminium oxides generated porous and heterogeneous microstructures. However, when Fe-15Ni and Fe-15Ni-10Cr binders were used, they obtained a dense microstructure with excellent

corrosion resistance and a combination of high hardness and fracture toughness, comparable to that of the cobalt-cemented carbides used in industry [52].

Some studies use thermodynamic calculations to analyse the expected carbon range in cemented WC carbides that lack cobalt and instead incorporate binders containing 20 wt % Fe-Mn, Fe-Mn-Si, and Fe-Mn-Ni. In comparison to other binder systems, the primary challenge in replacing cobalt as the main binder component has been its wider carbon window (C-window). The C-window refers to the carbon range within which the formation of phases detrimental to mechanical properties is avoided.

A wider C-window is desirable, as it provides excellent stability in the microstructure and mechanical properties against potential compositional variations (in the order of 0.05 wt%C), inherent to the manufacturing process. These analyses demonstrate that the incorporation of silicon and nickel expands the carbon range in this context and, therefore, the industrial viability of such carbide grades. However, it has been shown that cemented carbides with 25 wt% nickel exhibit significantly lower hardness compared to those Ni-free Fe-Mn binders [53].

Fürst *et al.* [54] investigate binders such as Ni-Fe, Ni-Fe-Cr, Ni-Fe-Al and Ni-Al for cobalt-free cemented carbides for percussion drilling applications. The influence of maximum sintering temperature and atmosphere and the effect of annealing treatments were determined on these materials. Their studies observed that the addition of iron and chromium reduces the grain size of the ceramic phase, but only iron contributes to improved wear resistance.

1.4.2. Manufacturing alternatives

As highlighted, recent research focusses on replacing cobalt with alternative elements while enhancing material properties to match or surpass the performance of traditional materials. The processing method is a key factor that determines the microstructure and properties of the final product.

Powder metallurgy, which is based on the dry mixing of powders, is the most widely used method for producing metals. It is also widely applied in cutting tool materials, as the process incorporates additional steps such as compacting and sintering to achieve the final material. Powder metallurgy is regarded an efficient

technology for reducing metal production costs as it enables the manufacture of high-quality components with complex geometries and favourable mechanical properties while minimising the need for additional machining.

However, its application in the production of refractory materials, such as tungsten carbides, presents significant challenges and is not always fully effective. In such production, the powder preparation step is critical, as it should provide the appropriate size and dispersion of phases as well as incorporate pressing additives. However, nanosized particles are prone to agglomeration due to the high surface free energy, reducing with it their mixing capability. Furthermore, nanocrystalline WC powders tend to rapid grow resulting in the nano-grain lose their nanoscale characteristics during conventional sintering, decreasing with it the desired properties, such as hardness, strength, liquid phase distribution or wear-resistance.

On the other hand, in many sintering methods, a very high sintering temperature is required to obtain fully dense bodies, and this should indeed be higher for coarse starting particles. The exceptionally high melting point of tungsten (3400 °C) requires sintering at temperatures around 1400 °C which makes it even more challenging maintaining a refined microstructure. These elevated temperatures involve high energy costs and may also lead to material deformation, volatilisation of certain elements, and potential W contamination from moulds, tools, or the environment.

Based on the issues mentioned above, multiple physical (high-energy ball milling, magnetic stirring, ultrasonic) and chemical methods (solution reaction, chemical vapour reaction synthesis, etc.), with or without the use of additives (such as transition group carbides and rare earth elements) have been explored [55]. For example, Ha and Kim [56] used a combination of both methods to produce ultrafine WC/Co powders with water-soluble salts containing W and Co. These were later synthesised into the oxide precursor powders by spray drying and subjected to a carbothermal reduction process via high-energy milling, resulting in a dense material with 100-150 nm grain size. A similar process was later followed by Park and Kang [57] to obtain ultrafine cermets with improved fracture toughness, although this effect was limited to TiC contents of 70 wt%. Other reaction techniques, such as solution combustion synthesis, have been explored for the production of a variety of ceramics and ceramic-metal composites, including Fe-TiC cermets [58] but, despite the benefits arising from low cost and energy savings, it is difficult to control due to the high reaction rates. Moreover, most of these

methods are in the laboratory research stage, limited by the process, raw material sources, cost, safety, and other issues.

1.4.2.1. Colloidal sintering technique

Although powder metallurgy is a widely used and effective technique, especially for metals, some drawbacks can be solved using colloidal techniques commonly applied in ceramic processing. Figure 1.16 shows a schematic of the colloidal process from the initial mixing of the raw powders to obtaining the final powders ready for the sintering process.

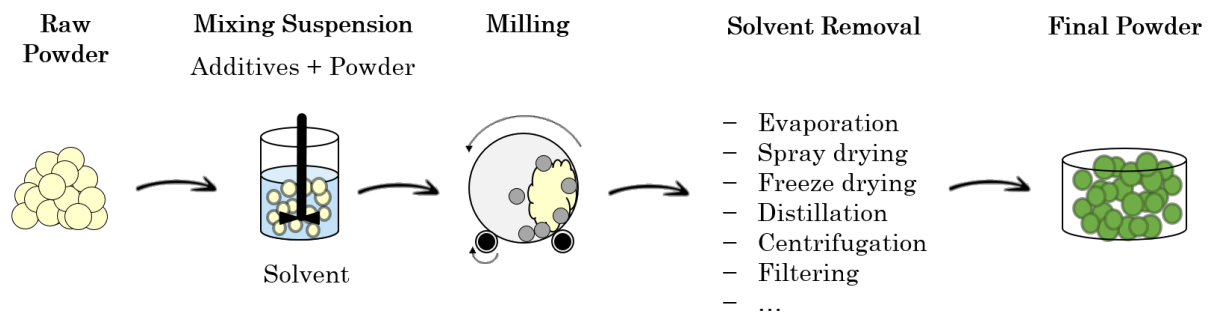


Figure 1.16. Colloidal processing route.

Colloidal processing is a liquid-assisted powder preparation method that can help prevent or minimise the challenges associated with traditional powder metallurgy. The use of a solvent reduces the surface reactivity of the powder particles by limiting their exposure to oxygen molecules. A colloid consists of two distinct phases, and suspensions, where solid particles are dispersed within a liquid medium, are a type of colloid. Suspensions are widely used in ceramic processing and have recently been applied to metals and cermets. To enhance the stability of particles in suspension, it is crucial to develop repulsive forces between them. This can be achieved by adding polymers or surfactants, which act as dispersing agents.

Therefore, colloidal processing offers several important advantages. Chiefly, it provides superior control over particle size, enabling a much more uniform distribution compared to the broader range of sizes typical in powder metallurgy. The purity and homogeneity achieved through the even dispersion of powders in a liquid medium allow for the homogeneous mixing of different components. Additionally, powders produced using this technique, due to their smaller size and more precise distribution, can be sintered at temperatures lower than those

required in traditional powder metallurgy. This reduces energy consumption and lowers the risk of defects in the final sintered material [59].

The use of water as a solvent in colloidal suspensions, thanks to its ability to dissolve a wide range of substances, allows the incorporation of different additives that improve the stability of the suspension or modify properties such as pH or viscosity. Water also does not pose significant toxicity risks to workers or environmental contamination, as it can be easily treated, recycled, or disposed of safely with minimal environmental impact. This helps to reduce the costs associated with waste management and minimises the ecological footprint of the process. Water is also an abundant and economical resource, making it an accessible and cost-effective option, especially in large-scale industrial applications.

Colloidal processing effectively achieves stable dispersions dominated by repulsive forces between small ceramic particles. This is achieved by using dispersants such as polyvinyl alcohol (PVA); it is commonly used as a dispersant, stabiliser, and binder for industrial applications. PVA is a water-soluble polymer produced by partial hydrolysis of polyvinyl acetate. Although PVA is virtually harmless, it may exhibit some toxicity if accidentally ingested with an LD₅₀⁷ ranging from 15 to 20 g/kg [60], it is subjected to special regulations for its waste management and disposal to protect human health and the environment. Since PVA is an expensive polymer with a slow rate of biodegradation, the use of other dispersants that offer the same or superior performance without negligible toxicity has attracted much attention. In this sense, HPMC (hydroxypropyl methylcellulose) is a promising alternative due to its minimal toxicity and solubility in various polar and aqueous organic solvents [61], [62], gaining a lot of attention in the biomedical field. HPMC could replace PVA in its function of stabilising, binding, and dispersing colloidal suspensions and improving some of its properties in ceramics production field [63]. Furthermore, PVA may form agglomerates in suspension, while HPMC is less likely to do so, favouring a more uniform particle dispersion. In addition, HPMC offers excellent thermal stability and resistance to decomposition compared to PVA, making it more suitable for processes involving high temperatures [62], [64]. Another benefit of HPMC is its flexibility to adjust rheological properties depending on the degree of substitution and concentration [65], [66], which provides an advantage in applications requiring precise flow control and offers

⁷ In toxicology, the median lethal dose, abbreviation for lethal dose 50 %

exceptional adaptability for processes that require varying rheological conditions due to compositional changes.

2. Experimental methodology

This work has focused on the two primary stages in the development of materials, manufacturing and mechanical characterisation. These stages provide, in this case, a broad understanding of the characteristics of cermets. First, the manufacturing process of the materials via colloidal processing is described, highlighting the starting components and their properties. Once the materials have been sintered, their mechanical properties are characterised. The workflow of this investigation is shown in Figure 2.1.

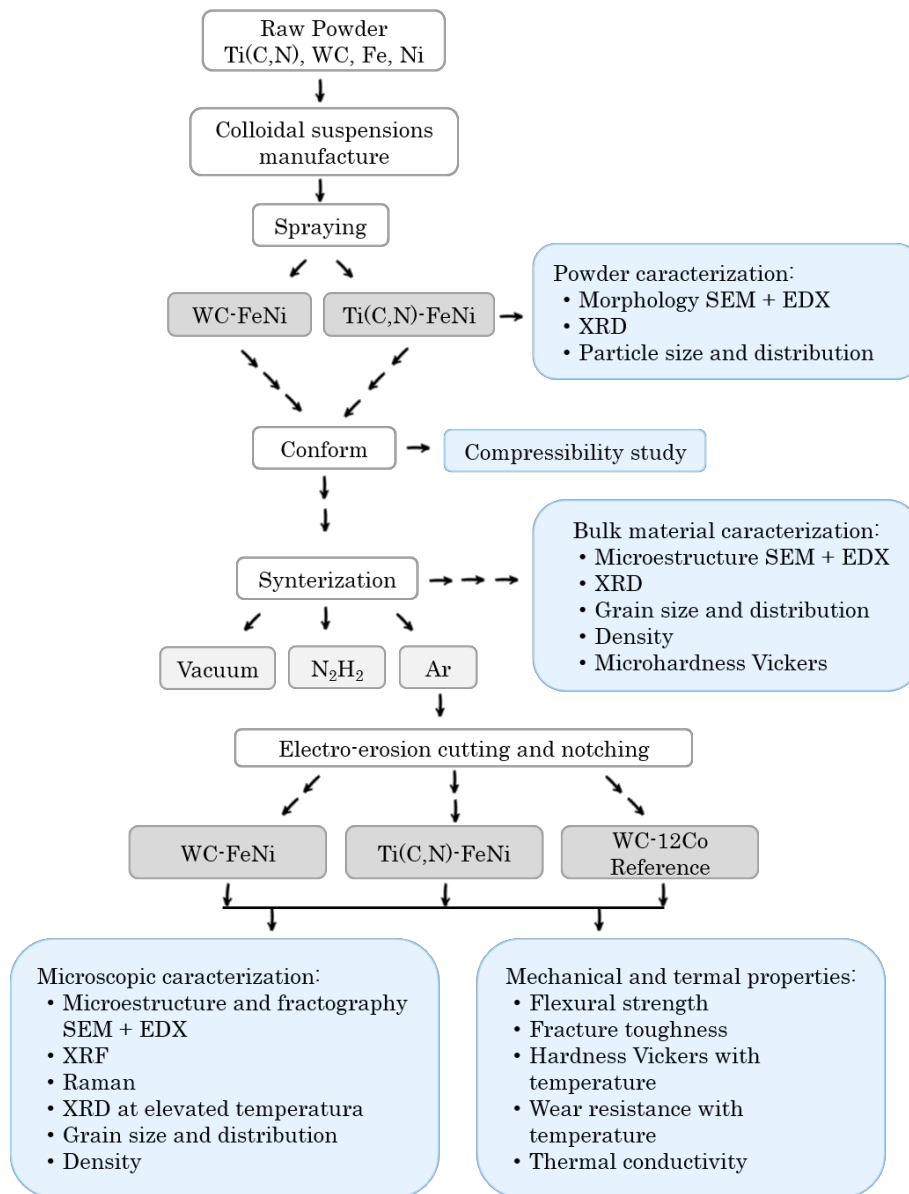


Figure 2.1. Scheme of the experimental procedure followed for the manufacture and characterization of materials.

2.1. Raw materials

Commercial powders from the following suppliers were used as starting materials: titanium carbonitride (Ti(C,N) grade C) from H. C. Starck (Germany); tungsten carbide (WC-040) from Hyperion Materials & Technologies (Spain); iron metal (Fe SM) from H. C. Starck (Germany); nickel metal (Ni 210H) from INCO (Canada); and black carbon from ISTAM (Germany). The morphologies of the various powders are shown in Figure 2.2.

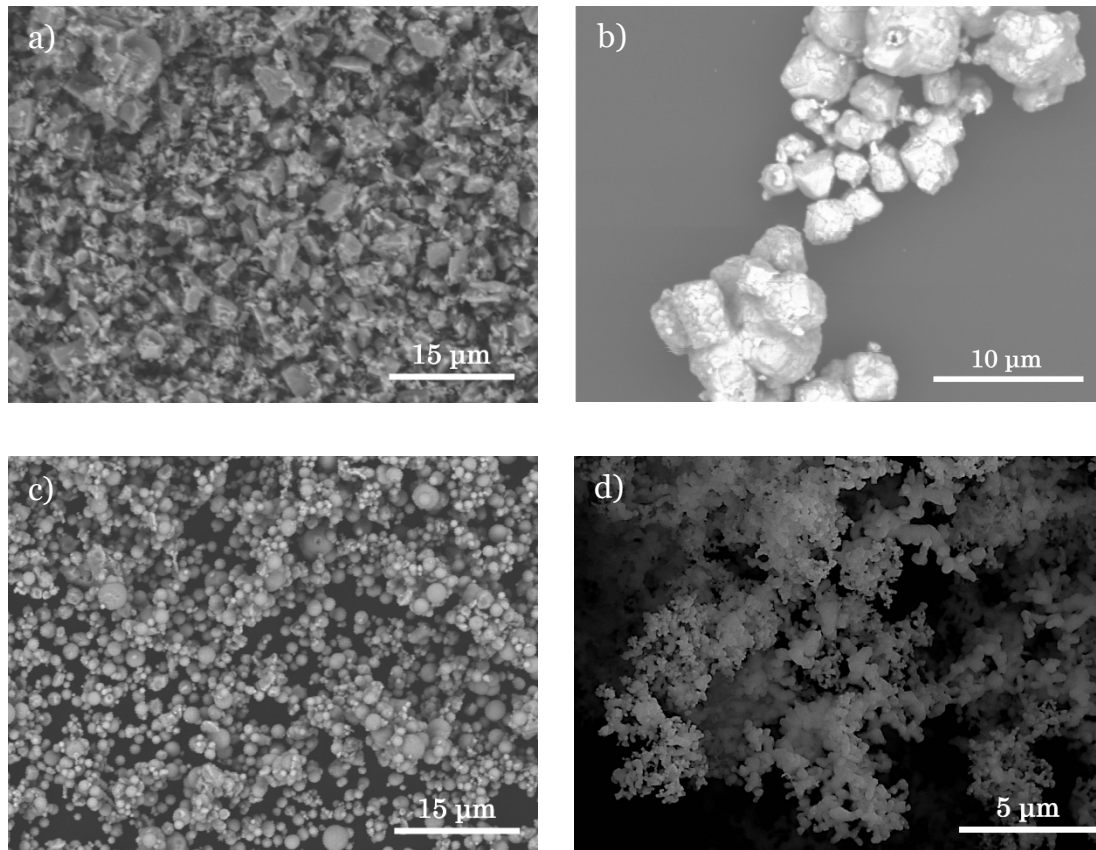


Figure 2.2. Morphology of the raw powders: a) Ti(C,N), b) WC, c) Fe and d) Ni.

It is possible to see how the Ti(C,N) powder is composed of irregular and angular particles (Figure 2.2 a), while a smoother morphology with rounded shapes is observed in the other elements. The main characteristics of these commercial powders are summarised in Table 2.1. As shown in Figure 2.2, the particle size distribution is unimodal for Ti(C,N) and WC and bimodal for Fe and Ni.

Table 2.1. Characteristics of starting powders. D_v (distribution particle size in suspension), SSA (specific surface area), d_{BET} (Brunauer-Emmett-Teller diameter) and F_{ag} (agglomeration factor) [67].

Powder	D_{V50}/D_{V60} (μm)	SSA (m^2/g)	Density (g/cm^3)	d_{BET} (μm)	F_{ag} (D_{V50}/d_{BET})
Ti (C,N)	2.1	3.0 ± 0.1	5.10 ± 0.01	0.4	5.25
WC	7.9	0.14	15.63 ± 0.01	2.75	2.87
Fe	3.5	0.6 ± 0.1	7.78 ± 0.01	1.2	2.92
Ni	1.75	3.9 ± 0.1	8.9 ± 0.1	0.19	9.21

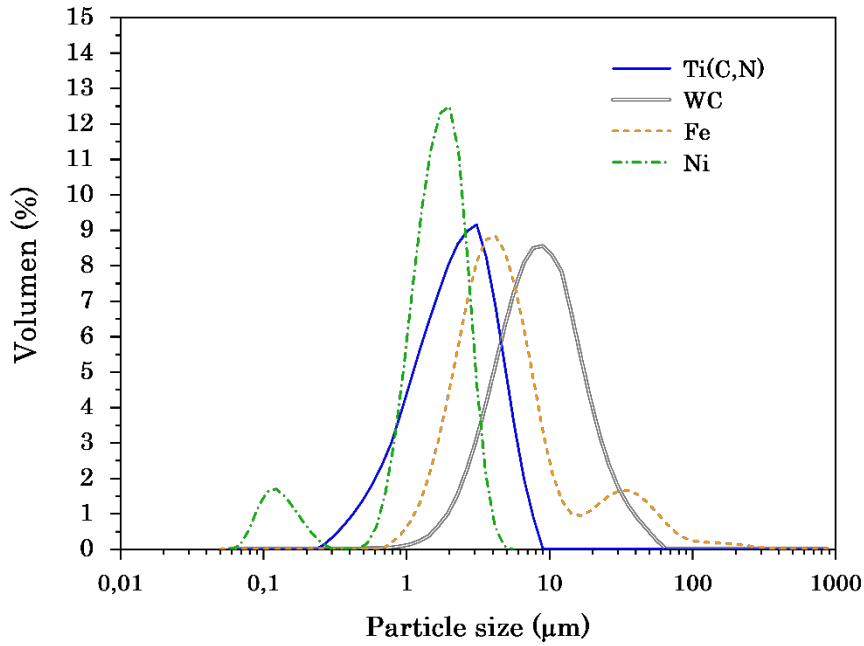


Figure 2.3. Raw powder size distribution.

The suspensions were prepared in deionised water with various additives to ensure stability and dispersion. In addition to the primary components, the following additives were used: tetramethylammonium hydroxide (HTMA) supplied by Merck KGaA (Germany); hydroxypropyl methylcellulose (HPMC) and TPnB glycol ether

(TPNB), both supplied by Zschimmer & Schwarz (Spain); and polyethyleneimine (PEI) used as a dispersant, provided by Sigma-Aldrich (United States).

Previous studies have optimised the proportions of additives and secondary components used in Ti(C,N) and WC-based materials manufactured by this colloidal route. In his research, M. de Dios [68] identified that a Ti(C,N) suspension with a high solid content (80 vol% Ti(C,N) and 20 vol% FeNi) exhibited the most stable composition and achieved the best combination of mechanical properties. Similarly, M. García-Ayala [69].optimised the additive concentrations required to stabilise the surfaces of W and WC in suspensions based on these elements; their findings have been therefore addressed in this thesis.

In this work, the characterisation of the initial powders or their interaction with the aqueous medium of the suspension has not been conducted, as this analysis was addressed in previous theses that served as a foundation for this research. However, in the characterisation of the powders of the final materials, many of the same techniques have been used and will be described in the following sections [68][69].

2.2. Production of the materials

2.2.1.Preparation of suspensions

High-solids-content colloidal suspensions were formulated using elemental powders and additives, with water as the dispersing medium. A critical consideration when developing a material composed of multiple elements is ensuring the uniform dispersion of the phases to produce a high-quality final material. In this work, colloidal processing was employed. Colloids are systems in which particles are dispersed in a liquid medium without forming molecular bonds, appearing physically homogeneous despite their particulate nature. Here, water served as the liquid medium, while WC and Ti(C,N) acted as the ceramic elements, and Fe and Ni as the binder metallic elements.

The primary challenge lies in creating stable homogeneously dispersed suspensions while avoiding oxidation reactions. This study aimed to manufacture two materials using common elements WC and Ti(C,N) in suspensions (35 % vol solids). Deionised water was used as the dispersion medium for both WC and

Ti(C,N) suspensions, prepared separately from the Fe and Ni suspensions. In all cases, the particles were added to deionised water containing the appropriate amount of dispersant, with the pH adjusted to 10 using HTMA.

Once the pH was stabilised, TPNB and HPMC were introduced to prevent particle adhesion to the atomiser walls. The amount of branched PEI added was determined based on previous optimisation studies. The suspensions were mechanically stirred for fifteen minutes and ground for two hours using grinding balls. Silicon nitride balls were employed for the WC and Ti(C,N) suspensions, while nylon balls were used for the Fe-Ni suspensions because of their lower hardness.

After the grinding process, the WC and Fe-Ni suspensions, as well as the Ti(C,N) and Fe-Ni suspensions, were combined for further processing [68], [69]. Table 2.2 displays the different percentages of each item assigned to the final compositions.

Table 2.2. Manufactured materials and compositions.

Denomination	Composition Volume (%)			Composition Metallic phase by weight (%)		
	Ceramics		Metal			
	Ti(C,N)	WC	Fe-Ni	Fe	Ni	C *
WC-FeNi-0.5C		80	20	85	15	0.5
Ti(C,N)-FeNi-0.5C	80		20	85	15	0.5

* C (wt. %) added regarding the weight of the Fe-Ni metallic phase

2.2.2. Atomization

Atomisation is when a water-based or organic-based suspension is introduced into a hot air system, where it is pulverised and transformed into a dry powder with uniformly distributed elements. The atomisation process can produce various powder morphologies, including uniform solid spheres, elongated shapes, doughnut-like structures, and hollow granules. However, for subsequent pressing or compaction of the powder, achieving solid and uniform spheres is considered the optimal condition [70].

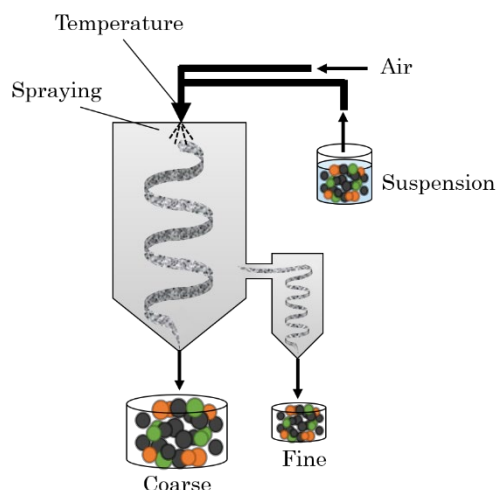


Figure 2.4. Schematic of the atomisation process of a suspension.

The suspensions were atomized at a temperature of 200 °C, with a nozzle of 1 mm diameter and an airflow of 32 bar, using the Spray Dryer SD-05 from LabPlant-Keison (United Kingdom). By the atomization system, the particles resulting from the process were classified into two groups: coarse and fine granules, as shown in the process diagram in Figure 2.4. However, once the atomization was completed, the morphology of the two sizes was analysed, determining that both were suitable, so they were unified, becoming part of the same material. Following this method, two different compositions were formulated: 80 %WC-20 %FeNi-0.5 %C, and 80 %Ti(C,N)-20 %FeNi-0.5 %C, referring to volume content, as specified in Table 2.2. However, to simplify the nomenclature for the rest of the document, the materials will be referred to as WC-FeNi and Ti(C,N)-FeNi

2.2.3. Pressing

After atomizing the powders, it is necessary to compact them to obtain the desired geometry. The shaped part (in green) must have enough strength and consistency to remain intact until it is sintered. There are several forming techniques, but uniaxial cold pressing was chosen in this work.

A compressibility study was conducted to ensure that adequate pressure was applied to the powder material. In this way, it is possible to evaluate the sample density as a function of the pressure supplied to achieve a compromise between the relative density in green and the applied pressure. To conduct this study and

eliminate the effect of sample size, circular dies of two different diameters were used, 5 mm and 10 mm. Compaction was performed by applying incremental pressure ranging from 100 MPa to 1200 MPa using the INSTRON 1275 universal testing machine (USA) equipped with a 1000 kN load cell. The pressure for compacting the final parts was selected on the analysis of the powders' behaviour under these conditions.

A rectangular die measuring 40×45 mm for producing the final shape was custom-designed and manufactured specifically for this study. The vertices were rounded to minimise the stress concentration at the corners, which could otherwise lead to cracking and subsequent brittle fracture of the material.

2.2.4.Sintering

Sintering is a forming process that aims to produce parts by compacting metallic, ceramic, or, in this case, cermets. In the process, the powder is agglomerated into shape and then heated to a temperature that always remains below the melting temperature of the main constituent element. In general, the high temperature causes the powder particles to weld together. In this case, the mechanism during sintering is first dissolution and then precipitation, as explained later.

Sintering is a manufacturing technique that produces parts with definitive or near-definitive shapes. However, during the process, the parts undergo dimensional changes as a result of the coefficient of thermal expansion. Compacted materials must exhibit a high green density to achieve optimal properties, as previously mentioned. Additionally, the coefficient of thermal expansion must remain low to minimise significant size variations in the parts, which could result in fractures if the stresses exceed the material's tolerance.

The green powders were sintered using an Interbil furnace (Spain) with a dense alumina tube (99.5 % purity). This furnace features aluminium heads at both ends, which seal the working atmosphere. This study used three sintering atmospheres: argon flux, N_2H_2 and high vacuum (6×10^{-5} mbar). The sintering temperature was set at 1450 °C in all cases, achieved using the silicon carbide resistors of the furnace. The heating rate was maintained at 10 °C/min until the target temperature was reached, with a dwell time of 2 hours to complete the sintering process.

2.3. Characterization of the materials during production

2.3.1. Powder size distribution

The specific surface area of the powders was determined by volumetric gas adsorption. This technique evaluates the quantity of gas adsorbed on the surface of the material as a function of the applied partial pressure and, using an appropriate theoretical model in accordance with the type of sample to be analysed, it calculates the sample's specific surface area.

The equipment used for this analysis was the Monosorb Surface Area Analyser from Quantachrome Corporation (United States), using nitrogen gas as an adsorbent at -195 °C over two hours. The specific surface area was determined according to the Brunauer–Emmett–Teller (BET) model, in accordance with the following equation:

$$SS_A = \frac{v_m \cdot S_0}{m} \quad (2.1)$$

where v_m is the monolayer volume of nitrogen adsorbed in cm³, S_0 is the surface area occupied by 1 cm³ of adsorbent in m², and m is the mass of the sample in grams.

The particle size was determined using a laser diffraction analyser called Mastersizer S from Malvern Instruments (United Kingdom). This laser diffraction measurement system measures the variation in the intensity of scattered light when a laser passes through a stream of scattered particles. Large particles scatter light at small angles to the laser, whereas small particles scatter light at large angles. This equipment uses the Fraunhofer model, representing the distribution of particle sizes as a function of the total volume of the sample. The average size of these can be calculated using the Stokes-Einstein equation, shown below:

$$d(H) = \frac{k \cdot T}{3 \cdot \pi \cdot \eta \cdot D} \quad (2.2)$$

where $d(H)$ is the hydrodynamic radius of the particles, k is the Boltzmann constant, T is the temperature in kelvin, η is the viscosity of the medium, and D is the translational diffusion coefficient.

Assuming that the particles are spherical and homogeneous, it is also possible to apply an indirect method to estimate the equivalent diameter of the particles. It is

necessary to use the BET approach again to establish a relationship between the particle size and the specific surface:

$$d_{BET} = \frac{6}{SSA \cdot \rho} \quad (2.3)$$

where SSA is the specific surface area, and ρ is the density.

The average particle size ratio to d_{BET} is called the agglomeration factor (F_{agl}). If the agglomeration factor of the powdered material is close to 1, it means that the particles can be considered correctly dispersed; however, if the value of the agglomeration factor is high, it is synonymous with the particles analysed being poorly dispersed. This means that agglomerates have formed at some point in the manufacturing process, which can lead to problems during the later sintering stage.

2.3.2. Rheology of the suspensions

Viscosity measures a fluid's resistance to deformation when external forces are applied. It reflects energy losses due to friction or collisions between the fluid's constituent molecules. The fluid is placed between two parallel plates separated by a defined distance to determine viscosity. When one of the plates —typically the upper one— is moved at a constant speed while a shear stress is applied, the resulting velocity profile can be measured.

Viscosity is then calculated as the applied shear stress ratio to the fluid's velocity gradient [71], [72]. If we represent the shear stress versus the velocity for behaviours that deviate from Newton's law, we obtain the flow curves, commonly used to express the rheological behaviour of fluids, as reflected in Figure 2.5.

In Newtonian fluids, the steady-state viscosity is linear; conversely, in pseudoplastic fluids, the apparent viscosity decreases as the shear rate increases. Rheological measurements, therefore, enable the analysis of changes in suspension behaviour when subjected to a specific force. The response of each suspension is directly linked to interactions between particles and between particles and the medium, so changes in the nature or concentration of dispersant, pH, particle size distribution, or particle shape can significantly affect the results.

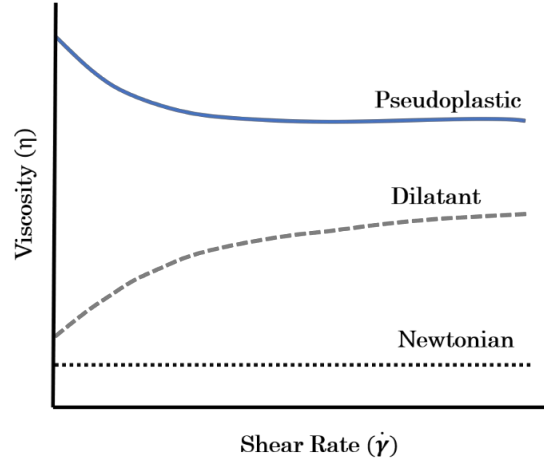


Figure 2.5. Steady shear viscosity versus shear rate for Newtonian or ideally viscous fluids, pseudoplastic or shear-thinning fluids and dilatant ones.

The Cross model is one of the most widely used approaches for studying variations in suspension behaviour under low and high shear conditions. It is widely integrated in rheometer software, making it a standard tool in rheological analysis [71], [73] . This model includes extrapolated values of viscosity at rest and high shear according to the equation:

$$\eta(\dot{\gamma}) = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (C \cdot \dot{\gamma})^m} \quad (2.4)$$

where η is the viscosity in mPa · s; η_{∞} is the viscosity at high shear; η_0 is the resting viscosity; C is Cross's constant in s; $\dot{\gamma}$ is the shear velocity at s⁻¹, and m is Cross's exponent.

Based on the above considerations, rheological measurements of the Fe-Ni WC and Ti(C,N) suspensions were performed using a Haake Mars 60 rheometer from Thermo Scientific (Germany). The device had a 60 mm diameter double-cone fixed plate and a working angle of 2° (DC60-2°). Two control modes were used: controlled rate (CR) and controlled stress (CS).

For the CR tests, the shear rate increased linearly from 0 to 1000 s⁻¹ over 3 minutes, held at 1000 s⁻¹ for 1 minute, and then decreased to 0 s⁻¹ over 3 minutes. For the CS tests, the shear stress was increased from 0 to 35 Pa for the Ti(C,N) suspension and from 0 to 10 Pa for the WC suspension, with the stress applied linearly for 3 minutes and then reduced back to 0 Pa over the same duration without any dwell tension. The samples temperature was maintained at 20 °C during each measurement.

2.3.3. Dilatometry studies

A dilatometry study was conducted on pressed samples to ensure that the dimensional changes that occurred during sintering remained within acceptable limits, thus not jeopardising the manufacturing process. This technique records the linear dimensional changes (expansion or contraction) experienced by the samples as the temperature varies in the dilatometer furnace. Measurements are obtained through contact between a push rod and samples, with data collected by a high-precision displacement detection system, enabling the dimensional changes to be monitored as a function of temperature.

For this analysis, a DTA-TG system from Perkin Elmer (United States) was used to obtain the dilatometric curves of the samples. The testing conditions included a maximum temperature of 1450 °C under an inert argon atmosphere, with the heating and cooling ramps set at 5 °C/min.

2.3.4. Density measurements

Two experimental methods were employed to determine the porosity and, consequently, the density of the sintered materials: image analysis and liquid immersion in pure ethanol of known density (Archimedes method). Both measurements were performed at room temperature.

The analysis of SEM images was conducted using ImageJ software developed by the National Institutes of Health (United States). Before processing, the images were filtered to remove noise and other imperfections that could interfere with the analysis. The filtered images were then converted to binary format, separating the properly sintered material from the pores using pixel-based segmentation. The superficial porosity in the material was quantified by counting the pixels of each colour. This process was applied to an average of fifteen images taken at different magnifications for each material.

For the experimental determination of density using the Archimedes principle, a high precision analytical balance ($\pm 10^{-4}$ g), the AG245 model from Mettler Toledo (United States), was used. Theoretical densities were calculated by applying the rule of mixtures, which enabled the calculation of relative densities and, consequently, the porosity of each material. The relevant expressions for these calculations are as follows:

$$\rho = \frac{m_a}{(m_a - m_e)} \cdot \rho_e \quad (2.5)$$

$$\text{Porosity} = 100 - \frac{\rho}{\rho_{th}} \cdot 100 \quad (2.6)$$

where ρ is the density material; m_a the weight in the air; m_e the weight in pure ethanol, ρ_e the ethanol density; and ρ_{th} the theoretical density.

2.4. Microstructural characterization

To ensure proper metallographic preparation of the samples, the study material was embedded in a specialised epoxy resin designed for materials with high hardness. The embedding process was carried out using the OPAL 460 hot-drawing hydraulic press from ATM (Germany), operating at 180 °C and 250 bar pressure, which are the polymerisation conditions of the selected resin.

After embedding, the samples were roughened under continuous water cooling using a SiC sanding routine ranging from FEPA 80 to 1200. The surfaces were then polished with diamond suspensions of 6 µm, 3 µm, and 1 µm grain size, combined with a water-based lubricant. Both roughening and polishing were performed on the LaboPol-30 automatic polisher from Struers (Denmark).

When microstructural analysis under a scanning electron microscope (SEM), the samples were metallized by depositing a thin carbon layer, 9 nm thick, on the surface. This was achieved using the EM ACE600 metalliser from Leica (Germany).

2.4.1. Optical and Scanning Electron Microscopy

Primary, the microstructure and hardness indents were examined using an Axiovert 100 optical microscope from Zeiss (Germany). For higher magnification, the morphology of the atomised powders, the microstructure and fractography of the sintered materials, and the wear test traces were characterised using a high-resolution field emission scanning electron microscope (FESEM).

The FESEM uses an optical-electronic system that scans the sample with a moving beam of electrons, generating various types of radiation from electron-material interactions. The system focusses the outgoing beam from the electron gun onto the sample. At each point of interaction, a signal is produced, collected, and

processed to create an image. For this study, an Auriga microscope from Zeiss (Germany) was used, equipped with detectors for secondary electrons (SE) and energy dispersive spectroscopy (EDX). The latter includes an additional X-ray detector and the QUANTAX-Spirit analysis software, both supplied by Bruker (USA).

These detectors were employed to observe the microstructures and fractography resulting from the mechanical tests and the wear surfaces generated after the tribological tests. Additionally, they were used to estimate the porosity present in the material, allowing comparisons with the results obtained using the Archimedes method, described in Section 2.3.4.

2.4.2.X-ray Diffraction

X-ray diffraction (XRD) is based on the optical interference that occurs when monochromatic radiation passes through a specific thickness comparable to the wavelength of the radiation. When irradiated on the sample to be analysed, X-rays with Angstrom wavelengths, of the same order as the interatomic distances of the components of crystal lattices, are diffracted with angles that depend on these interatomic distances and are collected in the detector. When the tube or sample and detector are moved to change the 2θ diffraction angle, the intensity is measured, and the diffraction data are recorded, being able to match the angle of the diffracted beam with the crystal phase. The Debye-Scherrer method applies Bragg's law and consists of irradiating with X-rays on a sample formed by a multitude of crystals placed randomly in all directions, applying the equation:

$$n \cdot \lambda = 2d \cdot \sin\theta \quad (2.7)$$

where n is an integer; λ is the wavelength in nm; d is the distance between the planes of the crystal lattice in nm; and θ is the angle between the incident and diffracted beams.

By using this technique, several analyses were carried out: to study the atomized particles and thus rule out any contamination; to identify the phases present in the sintered materials in each of the atmospheres, ruling out reactions or unwanted elements; and to determine the changes produced in any of the materials as the temperature increased. In this last test, the sample was heated and monitored according to temperature. The relative intensity of the detected peaks and their position were considered to analyse the data collected by X-ray

diffraction. The equipment used was the D8 Advance Diffractometer from Siemens-Bruker (Germany) using Cu K α radiation ($\lambda = 1,540,598 \text{ \AA}$). The diffraction patterns were measured in 2θ with 0.03° jumps from 30° to 70° .

Furthermore, after detecting anomalies on the surface of some of the materials, a more precise analysis was performed using X-ray microdiffraction (μ DRX). The theoretical rationale is the same as in the case of XRD, but a narrower beam is used instead to make highly localized measurements of a concentrated area. The equipment used was the X'Pert PRO from PANalytical (Netherlands), and the parameters used on this occasion were the same, except for the 2θ range extended to 85° . The measurements made at high temperatures were carried out using the latter equipment, to which a high-temperature chamber was attached. The HTK2000 of Anton Paar (Austria), with platinum heating filament, operated in an oxidizing atmosphere in the air.

2.4.3.X-Ray Fluorescence

X-ray fluorescence (XRF) has the primary purpose of semiquantitative elemental chemical analysis of the elements between fluorine (F) and uranium (U). XRF is a spectroscopic technique that uses the secondary or fluorescent emission of X-radiation generated by exciting a sample with a radiation source. The energy absorbed by the atoms in the sample generates the production of secondary X-rays, or fluorescence, emitted by the sample. These X-rays have an intensity proportional to the concentration of each element in the sample.

However, this technique has some limitations, since the data obtained in a semi-quantitative analysis are only reliable for elements whose atomic number is greater than 13 (aluminium). For this reason, lighter elements may be undetected, or their proportions may not be accurate. The equipment used to define the percentage of each element present in the composition of the materials was the Axios wavelength dispersion spectrometer (4 kW) from PANalytical (Netherlands).

2.4.4.Raman Spectroscopy

Raman spectroscopy is a high-resolution photonic technique that provides chemical and structural information on almost any organic and/or inorganic

material or compound, thus allowing its identification. The analysis by Raman spectroscopy is based on the phenomenon of light scattering, which allows for the study of molecular rotations and vibrations.

When photons from the incident light beam hit the material's surface, most light passes through the sample, but a small fraction is scattered. If after the photon-molecule interaction, the photon is scattered at a frequency different from the incident one, the shock will be inelastic because there is an energy transfer between the two. Each material undergoes a different frequency change, characteristic of its polyatomic structure, and the nature of the chemical bonds that form it.

This technique was mainly used to identify the different oxides originating in the samples after different tests, such as three-point bending, hardness at high temperatures, or tribological tests. The equipment used for this was the Xplora from Horiba Scientific (France), using a green laser of lateral excitation with 532 nm wavelength, apertures of 1200 T and 1800 T, a target of x100 magnification, and a measuring range of 40-2000 cm^{-1} .

2.4.5. Optical Profilometer

The roughness of the test surfaces should be assessed prior testing to ensure the validity of the tribological tests within the standard. Similarly, it is necessary to know the depth of the marks originating during the testing campaign.

Optical profilometers use white light interference to measure and analyse the surface profile of micro and nanostructures. The incoming light is divided into an interferometer chamber; one beam of emitting light goes directly to the interior reference surface and the other to the sample to be analysed. After reflection, the emissions are recombined within an interferometer, suffering constructive and destructive interference, producing a pattern of dark and bright lines called "*fringes*". The profilometer used was the Zygo NewView 7200 (United States) in conjunction with the MetroPro programme. With this equipment, both the roughness of the materials and the wear footprint maps were determined, allowing the depth of the profile generated during the tribology test to be calculated and, consequently, the total volume of material removed. Surface roughness measurements were made at a resolution of 0.71 μm , obtaining maps of

0.35x0.25 mm dimension. On the contrary, the footprint depth generated during the tribology tests was analysed was 1x1.5 mm maps and 2.19 µm resolution.

2.5. Mechanical characterization

Mechanical properties characterization should have specific specimen geometries and dimensions, which depend mainly on the test and material type, however, most dimensions included in this document are out of standard due to the limited material available. Nevertheless, the aspect ratios set out in the various ASTM standards have been maintained. The machining conducted on the specimens to obtain the desired geometry was carried out by electrical discharge machining (EDM), achieving a high level of precision.

2.5.1. Hardness measurement

Hardness tests employ static methods that involve applying a force to a material and measuring the size of the resulting indentation made by a harder object. The hardness of a material is influenced by factors such as the applied force and temperature. To investigate the behaviour of different materials under varying conditions, we measured Vickers microhardness using an Akashi MVK-EIII hardness tester (Japan) equipped with a Vickers diamond indenter.

The test conditions were selected according to the ASTM E384 [74] standard. Loads of 5 N and 10 N were applied for 15 seconds and each condition was repeated ten times at room temperature. The diagonals of the resulting indentations were measured using the aforementioned optical microscope. The hardness values were then calculated using the following equation:

$$H_V = 0.0018544 (F/d^2) \quad (2.8)$$

where F is the applied load in N and d is the average length of the diagonals of the footprint in mm.

The CETR-Bruker Universal Testing Machine (UMT), equipped with an integrated oven, was used to evaluate the influence of temperature on the hardness of various materials. The machine was reconfigured for hardness testing using a Vickers adapter comprising a Ni-based alloy support and a diamond indenter. The

test procedure was conducted following the ASTM C1327 standard [75], involving the application of a sustained load of 100 N for 15 seconds. Rows of ten indentations were created, ensuring that the spacing between indentations exceeded three times the diagonal length, as prescribed by the standard. Tests were performed at 25 °C, 200 °C, and 400 °C, and the heating process was controlled with a ramp rate of 5 °C/min and 10 min dwell time to ensure consistency in all tests.

2.5.2. Bending Tests

The bending stress is calculated based on the simple beam theory, so for a prismatic beam such as the one shown in Figure 2.6, if two planes A and B are drawn parallel to each other, when applying a point force P it is observed how the upper part of the planes (concerning the neutral axis) is approaching, and, while at the bottom it is moving away.

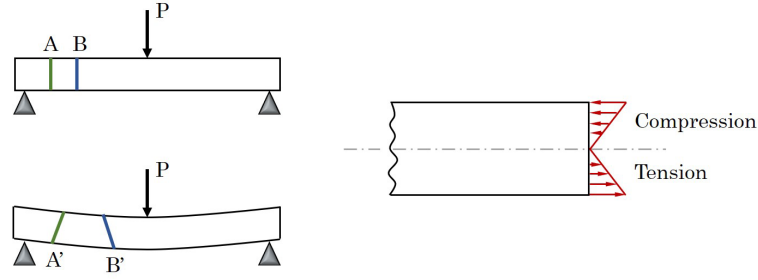


Figure 2.6. Distribution of loads generated in a beam with a three-point bending configuration. Planes A and B correspond to the moment before the test, while A' and B' represent the positions of those shots during the test.

In this way, it can be said that there are compressive forces in the upper part, the tension in the lower part, and zero in the neutral axis [76]. The forces produced in turn, create bending stresses, which can be calculated for the specific geometries of this work, as is the case with linear elastic deformation. Both properties are included in the respective equations:

$$\sigma_f = \frac{3 \cdot P \cdot L_s}{2 \cdot B \cdot W^2} \quad (2.9)$$

$$\varepsilon = \frac{6 \cdot \delta \cdot W}{L_s^2} \quad (2.10)$$

where for the bending stress equation, P is the maximum load in N, L_s is the distance between the supports in mm, B is the width of the specimen in mm and W is the thickness of the specimen in mm. For the deformation equation, ε is the deformation, and δ is the beam deflection.

However, this method is restricted to the elastic regime; when it is exceeded and plastic deformation occurs, the bending stress is replaced by the yield flexural strength at 0.2 % deformation for comparison purposes, and this condition must always be indicated in the results.

The mechanical flexural strength was determined with the three-point bending test configuration described above, in which the specimen is placed on two parallel supports and the load is applied to it right in the centre, between the supports, as shown in Figure 2.7. To minimise the influence of friction during testing, but specially at high temperature testing, cylindrical and freely rotating supports were used. These supports were designed to allow for unrestricted rotation along their longitudinal axis, thus reducing any frictional interference and ensuring more accurate results.

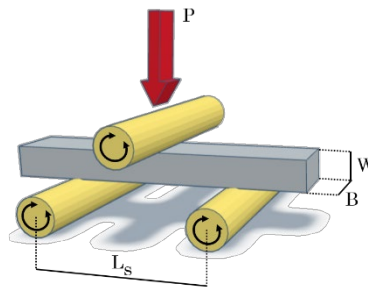


Figure 2.7. Diagram of the assembly of the three-point bending test, where P is the applied load; L_s is the distance between supports, and W and B are the thickness and width of the specimen, respectively.

All materials properties were evaluated from RT to 800 °C at 200 °C intervals, with heating ramps of 10 °C/min and a dwell time of 10 min before testing. To replicate the operating conditions of these materials, no inert atmosphere was used, so maximum temperature was limited to 800 °C due to the oxidation of the metallic phase. To achieve the desired temperature, a silicon carbide furnace with Eurotherm MTS 653 controller (United States) was used, mounted within the loading area of the Instron 3369 universal testing machine (United Kingdom), equipped with alumina loading bars, and a cooling system that protects the load cell. The test conditions were established under the ASTM C1161 and ASTM

C1211 standards.[77], [78], where the test speed was 0.2 mm/min, and the distance between supports 20 mm. An average of two rectangular specimens per temperature were evaluated, measuring 2.3 x 1.8 x 40 mm.

2.5.3. Fracture Toughness Tests

Fracture toughness is a fundamental material property that characterises the resistance of a material to brittle fracture in the presence of a discontinuity, such as a crack. Defects are particularly detrimental to fracture strength, as the cohesive forces between its atoms govern the material's fracture resistance. When a tensile stress is applied, and the theoretical cohesive strength of the material is exceeded at the tip of a crack, fracture occurs due to the stress concentration at that location.

The fracture toughness test configuration used is identical to that used in the bending test. To calculate this property, it is necessary to apply a load to a specimen with a pre-introduced crack, as illustrated in the accompanying diagram of Figure 2.8.

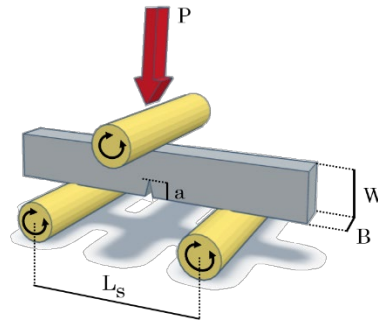


Figure 2.8. Schematic of the fracture toughness test with a three-point bending configuration, where P is the applied load; L_s the distance between supports, W and B the thickness and width of the sample respectively, and a the notch introduced.

The initial cracks were introduced in the smallest surface via femtosecond laser, since fatigue precracking, the common procedure for metallic materials, was not possible due to the brittleness of these composites. Figure 2.9 shows the surface image of one of these precracks where, as previously observed in [21], no heat-affected zones can be detected and the the diameter of the crack tip was lower than 10 μm .

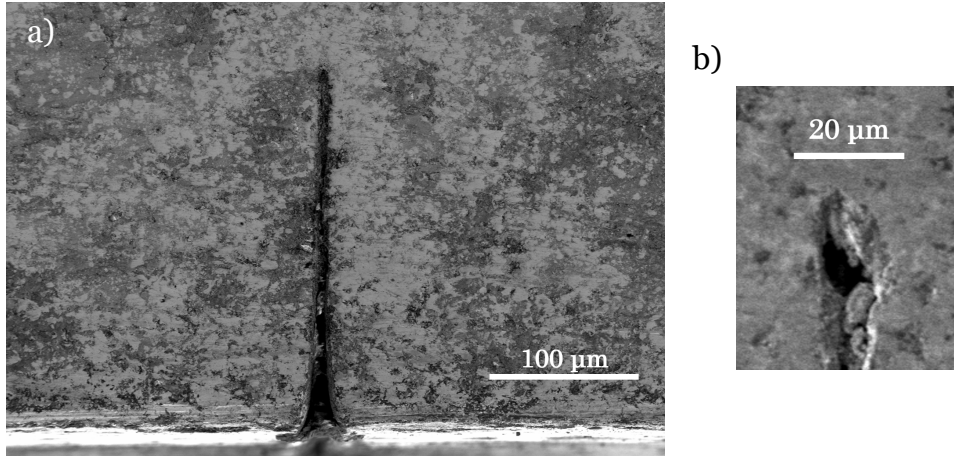


Figure 2.9. a) Laser-introduced notch for fracture toughness measurement, b) Higher magnification image of the notch end.

The total crack lengths were measured with the FESEM, achieving mean values of 135 μm. To establish both the dimensions of the specimens (1.5 x 2.1 x 40mm), and the test conditions, the ASTM C1421 and E1820 standards were followed [79], [80]. The reason for applying two different standards is found in the materials. As they are made up of one part ceramic and one part metal, the behaviour is not entirely associated with either of the two types. As in the bending test, the materials were evaluated in an oxidizing atmosphere up to 800 °C, using a test speed of 0.2 mm/min and distances between supports of 20 mm.

The critical stress intensity factor was calculated under the assumption of a plane strain condition. This assumption was validated by the specimen dimensions, which were significantly greater than the notch dimensions. The substantial size difference ensured the suitability of the plane strain approximation for the analysis [81]. For specimens evaluated by bending at three points, the equations collected by Tada *et al.* are generally applied [82]:

$$K_I = \sigma \sqrt{\pi a} \cdot F\left(\frac{a}{W}\right) \quad (2.11)$$

$$\sigma = \frac{6 \cdot P \cdot L_s}{4 \cdot W^2} \quad (2.12)$$

where P is the maximum or critical character applied in N; L_s is the distance between supports; a is the length of the notch in mm; and W is the thickness of the specimen; and $F\left(\frac{a}{W}\right)$ is the geometrical factor expressed as:

$$F\left(\frac{a}{W}\right) = \frac{1}{\sqrt{\pi}} \cdot \frac{1.99 - \frac{a}{W} \cdot \left(1 - \frac{a}{W}\right) \cdot \left(2.15 - 3.93\left(\frac{a}{W}\right) + 2.7\left(\frac{a}{W}\right)^2\right)}{\left(1 - \frac{a}{W}\right)^{\frac{3}{2}} \cdot \left(1 + \frac{2 \cdot a}{W}\right)} \quad (2.13)$$

However, these equations are only valid for the relationships $L_s/W = 4$, and the stress intensity factor for short cracks may be overestimated. Considering the limited quantity of material, the geometrical factor proposed by Guinea *et al.* was used instead. This expression was developed in 1998 to determine the stress intensity factor for any L_s/W ratio greater than 2.5, with an accuracy equal or better than existing formulas [83]. The stress intensity factor can be calculated from the critical load and beam cross-section using the proposed equations:

$$K_{Ic} = \frac{3 \cdot P \cdot L_s \cdot \sqrt{a}}{2 \cdot W^2} \cdot \frac{A - \frac{a}{W} \cdot B + \left(\frac{a}{W}\right)^2 \cdot C - \left(\frac{a}{W}\right)^3 \cdot D + \left(\frac{a}{W}\right)^4 \cdot E}{\left(1 - \frac{a}{W}\right)^{\frac{3}{2}} \cdot \left(1 + \frac{2 \cdot a}{W}\right)} \quad (2.14)$$

where P is the maximum or critical character applied in N; L_s is the distance between supports; a is the length of the notch in mm; W is the thickness of the specimen in mm; and variables A - E correspond to:

$$A = 1.989 - 0.356 \cdot \frac{W}{L_s} \quad (2.15)$$

$$B = 1.217 - 0.315 \cdot \frac{W}{L_s} \quad (2.16)$$

$$C = 3.212 - 0.705 \cdot \frac{W}{L_s} \quad (2.17)$$

$$D = 3.222 - 0.020 \cdot \frac{W}{L_s} \quad (2.18)$$

$$E = 1.226 - 0.015 \cdot \frac{W}{L_s} \quad (2.19)$$

As in determining the flexural strength, the equations used in this analysis are only valid within the elastic regime. However, plastic deformations were observed due to the ceramic-metallic nature of the materials and the presence of iron among their constituents. In such cases, the relevant standards recommend discarding these results. Nevertheless, for this study, these have been retained, with their unique conditions explicitly acknowledged and fracture toughness was calculated using the secant method at 5 %, as described in the ASTM E1820 standard. [80]. To achieve this, a secant line was constructed with a slope equal to 95 % of the elastic load slope of the force-displacement curve. This approach was used to determine the critical load (P_C).

2.5.4. Tribological properties

Assessing the ability of a material to withstand wear during use or handling is of significant importance, as it provides a reliable estimate of its operational lifespan. Wear is characterised by material loss due to the relative motion between two contacting surfaces under load. This loss of material can occur through various mechanisms, such as the detachment of the material from the surface of the weaker component or mechanical processes such as abrasion. Abrasion is caused by irregularities on the harder surface that cut and groove the softer surface, leading to material degradation.

One of the most widely employed systems for friction tests conducted without lubrication is the "ball-on-disc" configuration. In this setup, the sample is flat and securely mounted on a sample holder that rotates at a constant speed, while the counter body is a stationary ball applying a specified load to the sample. During the test, the ball abrades the surface of the material being tested, producing a circular wear track on the sample, as illustrated in the accompanying diagram in Figure 2.10. The tangential friction force is measured with a sensor and recorded over time and multiple turns, showing the evolution of the coefficient of friction during the test.

The equipment used for the tests was a CSM Instrument High Temperature Tribometer (Switzerland), which includes an integrated furnace capable of reaching temperatures up to 700 °C. This equipment was used thanks to the Advanced Materials Group of Czech Technical University in Prague, who kindly allowed me to carry out the tribological tests described in this paper. Although such tests are characterised by high variability, the ASTM G99 and ASTM G133 standards [84], [85] were consulted to define and standardise the test parameters.

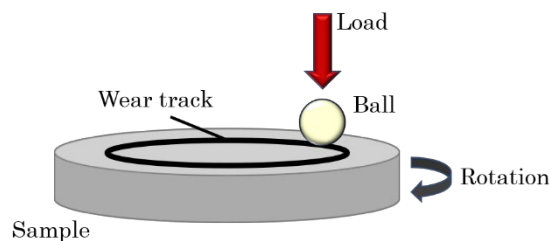


Figure 2.10. Outline of the ball-on-disk tribology test.

The load applied during the tests was 15 N for experiments carried out at room temperature. This load was reduced to 10 N for tests performed at higher

temperatures to avoid exceeding the maximum nominal force of the system, as the high coefficient of friction of the samples at elevated temperatures posed a risk to the integrity of the equipment. The selected rotational speed was 10 cm/s, applied for 32000 cycles, resulting in a circular path with a radius of 2 mm. This corresponds to an approximate total sliding distance of 400 m. All tests were carried out without lubrication in an oxidising atmosphere (air) in a temperature range from room temperature to 700 °C.

A 6 mm diameter Al_2O_3 ball was chosen as the counterbody due to its high hardness and low chemical reactivity, making it well suited for these conditions. The friction coefficient data for each material was collected and analysed using the InstrumX software.

To quantify the material loss during the test, the total sliding distance was taken into account, and the volume of material removed was measured. This was accomplished by determining the width and depth of the circular wear track formed on the sample. Measurements were conducted using the optical profilometer described in Section 2.4.5. In this way, it was possible to obtain the cross-sectional area of the footprint originated during the test, allowing the total volume to be calculated with the equation:

$$V_M = 2 \cdot \pi \cdot r_t \cdot A_s \quad (2.20)$$

where V_M is the volume torn from the material in mm^3 ; r_t the test radius, and A_s the cross-sectional area of the footprint.

As they are materials with high resistance and hardness, both the Al_2O_3 ball and the materials under test suffered a certain amount of wear during the test. To estimate the amount of Al_2O_3 removed from the ball, it was necessary to measure the dimensions of the flat footprint left on it using an optical microscope and apply them to the following equation included in the ASTM G99 standard, which contemplates this type of situation:

$$V_B = \frac{\pi}{6} \cdot \left(R - \sqrt{R^2 - \left(\frac{D_e}{2}\right)^2} \right) \cdot \left(3 \cdot \left(\frac{D_e}{2}\right)^2 + \left[R - \sqrt{R^2 - \left(\frac{D_e}{2}\right)^2} \right]^2 \right) \quad (2.21)$$

where V_B is the volume torn from the ball in mm^3 ; R is the original radius of the ball in mm; D_e is the effective diameter of the footprint on the ball. Once the volumes removed during the test were known, it was possible to calculate the wear rate of each of them:

$$\text{Wear rate} = \frac{V}{P \cdot x} \quad (2.22)$$

Considering that V is the volume removed either from the material (V_M) or from the ball (V_B) in mm^3 ; P is the force applied in N and x the total distance travelled in m.

2.6. Thermal properties

The ability to dissipate heat from the wear surface, thereby preventing any localised temperature-induced softening, is determined by the thermal conductivity of the composite. In ceramic-metal composites, thermal conductivity arises from the contributions of phonons (quanta of lattice vibrations) and electrons. In ceramics, however, thermal conductivity is solely governed by phonon (lattice) contributions, as electrons do not play a significant role [21].

Thermal diffusivity is a property of materials related to thermal conductivity. It represents the rate at which the temperature of a body changes as heat is transmitted through it, i.e. thermal diffusivity is the rate at which heat diffuses through a material. On the other hand, thermal conductivity refers to the intrinsic ability of a material to transfer or conduct heat because of a temperature gradient. According to the second law of thermodynamics, heat always flows toward the lowest temperature, since molecules move faster at high temperatures, transferring heat through the material at a higher speed.

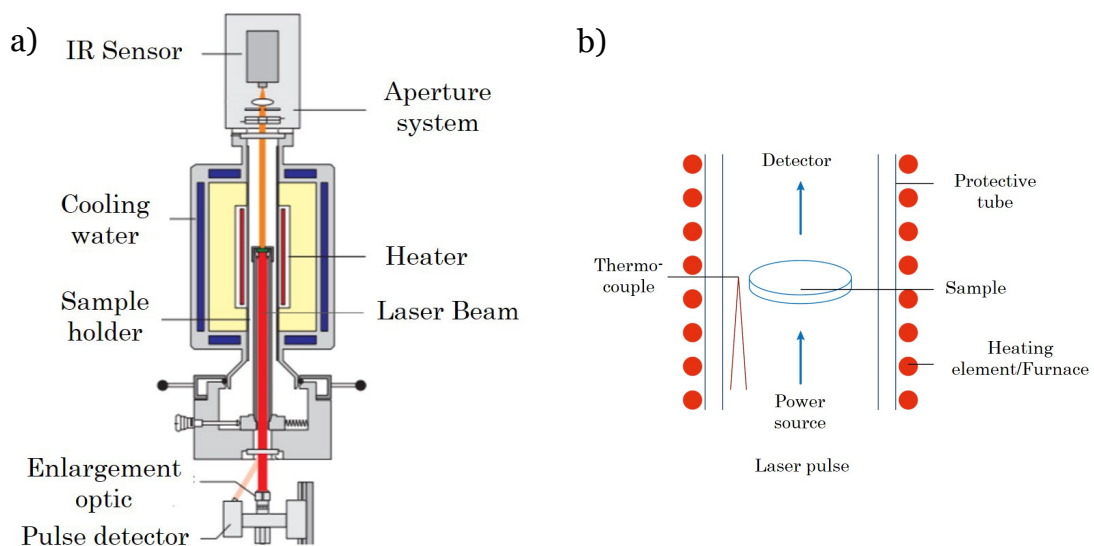


Figure 2.11. a) Diagram of the thermal conductivity measurement system. b) Enlargement of the sample area inside the oven.

The laser flash method, initially proposed by Parker *et al.* in 1961, is often used to measure the thermal diffusivity of solid materials [86] and, from it, the thermal conductivity. During the test, a sample is subjected to a laser pulse; this pulse of light causes the incidence surface (bottom) to be heated, recording the resulting temperature increase on the opposite (upper) side employing an infrared detector, as shown in the diagram of Figure 2.11. The resulting temperature vs. time curve describes how quickly a material reacts to a change in temperature, i.e., thermal diffusivity. Therefore, the higher the thermal diffusivity, the faster the temperature increase will reach the upper face [87], [88]. Applying the laser flash method requires the samples to absorb the laser pulse and have high emissivity [89]. A black powdered coating composed of high-emissivity carbon is usually applied to increase absorption and emissivity by accurately measuring the laser pulse. The sample holder is located inside a tube furnace, allowing diffusivity to be obtained at different temperatures.

As indicated by the applied ASTM E1461 standard [90], the recorded temperature signal is processed using different mathematical models that solve the differential equation for heat conduction in the transient regime:

$$\frac{\partial T(x,t)}{\partial t} = \alpha \frac{\partial^2 T(x,t)}{\partial x^2} \quad (2.23)$$

where T is the temperature in °C, x is the position in cm, at the time in seconds, and α is the thermal diffusivity in cm²/s. Carslaw and Jaeger [91] solved this equation for the particular case of a thermally insulated solid of thickness e , obtaining the equation of the temperature distribution at any point in the solid, where $T(x,0)$ corresponds to the initial temperature and position:

$$T(x,t) = \frac{1}{e} \int_0^e T(x,0) dx + \frac{2}{e} \sum_{n=1}^{\infty} \exp\left(\frac{-n^2 \cdot \pi^2 \cdot \alpha \cdot t}{e^2}\right) \cdot \cos\frac{n \cdot \pi \cdot x}{e} \int_0^e T(x,0) \cdot \cos\frac{n \cdot \pi \cdot x}{e} dx \quad (2.24)$$

Conversely, if a pulse of radiant energy is instantaneously and uniformly absorbed within a thin surface layer of known thickness, the initial temperature distribution can be described by the following expression:

$$T(x,0) = \frac{Q}{\rho \cdot C_p \cdot g} \quad \text{for } 0 < x < g \quad (2.25)$$

$$T(x,0) = 0 \quad \text{for } g < x < e \quad (2.26)$$

where Q is the radiant energy, ρ the density of the material, and C_p is the specific heat. Assuming that g is small, the distribution of temperatures on the back face ($x = e$) for any instant would be represented according to the following:

$$T(e, t) = \frac{Q}{\rho \cdot C_p \cdot e} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \cdot \exp\left(\frac{-n^2 \cdot \pi^2 \cdot \alpha \cdot t}{e^2}\right) \right] \quad (2.27)$$

Defining two dimensionless parameters V and ω :

$$V(e, t) = \frac{T(e, t)}{T_M} \quad (2.28)$$

$$\omega = \frac{\pi^2 \cdot \alpha \cdot t}{e^2} \quad (2.29)$$

Since T_M is the maximum temperature reached by the posterior surface, combining the above equations, the formula is obtained:

$$V = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \cdot \exp(-n^2 \cdot \omega) \quad (2.30)$$

In this way, it is possible to obtain the constant value $\omega = 0.13879$ when the temperature reaches half its maximum value, for $V = 0.5$, calling the time it takes to reach that temperature $t_{0.5}$. This time is easy to obtain, and thermal diffusivity can be defined as:

$$\alpha = 0.13879 \cdot \frac{e^2}{t_{0.5}} \quad (2.31)$$

where α is the thermal diffusivity in cm^2/s ; e the thickness of the sample in m; and $t_{0.5}$ is the time to half minimum in seconds.

The laser pulse method also makes it possible to indirectly estimate the specific heat, C_p , of the samples, comparing the temperature increase in the tested sample with that of a standard sample, in this case graphite, assuming that both absorb the same amount of energy. Both samples must be evaluated under the same conditions, have the same diameter and thickness, and have similar diffusivities and specific heats. Having determined the specific heat as the amount of heat that a substance absorbs before increasing its temperature by one unit and knowing the value of the thermal diffusivity, it is possible to calculate the thermal conductivity by the equation:

$$\lambda = C_p \cdot \alpha \cdot \rho \quad (2.32)$$

where C_p is the specific heat in $\text{J/Kg} \cdot ^\circ\text{C}$; α is the thermal diffusivity in cm^2/s ; and ρ the density in kg/m^3 .

All these equations are only valid if sample is homogeneous, adiabatically isolated, the heat conduction is one-dimensional, and the width of the laser pulse is minimal compared to the measurement time $t_{0.5}$. However, multiple factors vary these conditions; for example, the pulse width is much higher when testing thin samples of high thermal diffusivity [92], [93], [94], [95], [96], and radial heat losses increase

at high temperatures when testing thick samples [97]. Nonuniform heating of the sample occurs during any thermal diffusivity experiment [98], so it is complicated to predict and avoid. As a result, to date, no general correction has been developed that encompasses and solves all possible problems. Instead, individual or paired corrections have been introduced that consider some deviations separately. Considering all this, the thermal properties were calculated using the LFA Analysis programme that analyses the experimental data applying different corrections such as Aski [99], Degiovanni [100], or Clark-Taylor, Cowan and Degiovanni.

Thermal diffusivity measurements were performed using a Netzsch LFA 427 Laser Flash apparatus (Germany), equipped with support designed for Al_2O_3 samples. The equipment was operated under high vacuum conditions (10^{-5} mbar) to minimise atmospheric interference.

The sample geometry consisted of parallel flat discs with a diameter of 12.5 mm and a thickness of 3 mm. Laser pulses of 0.1 ms duration and 650 W power were applied during the tests, with 3,000 data points recorded per measurement.

The effect of temperature on each material was investigated over a range of 25 °C to 800 °C in increments of 100 °C. A heating ramp of 10 °C/min was employed, with measurements registered only when the temperature deviation was less than ± 2 °C to ensure accuracy and consistency.

3. Manufacture of materials

Powder metallurgy is a manufacturing process for metallic materials that begins with the compaction of powders to achieve a desired shape and size. However, when the raw material is ceramic, alternative techniques better suited to the properties of ceramics must be employed, such as those involving colloidal suspensions.

Colloidal processing involves dispersing ceramic or metal-ceramic powders in a liquid medium to create a stable and homogeneous suspension. Depending on the selected method, the liquid medium is subsequently removed during either the compaction stage or the atomisation stage. This process produces powders which are later shaped and sintered to form the final material.

This section details the stages to synthesise the material and presents the results obtained at each step.

3.1. Preparation of suspensions

Colloidal suspensions have two distinct phases: a liquid medium and solid particles dispersed within it. Achieving stable and homogeneous suspensions requires a thorough understanding and precise control of the interaction forces between the various species, including solid-liquid and solid-solid interactions.

A critical factor in attaining optimal stability is understanding the surface behaviour of solid particles within the liquid medium. The choice of solvent is equally important, as the properties significantly influence the behaviour of suspended particles.

Traditionally, volatile organic compounds derived from non-renewable petrochemical sources have been widely used as solvents in industrial processes. However, these solvents are associated with high toxicity and pose significant risks to both human health and the environment. In response to increasing concerns over climate change and the introduction of more stringent environmental regulations, alternative, environmentally friendly solvents are being adopted.

[101]. Water as a solvent solves these problems by being environmentally friendly. However, it generates other types of problems related to reactivity. Many elements, especially metals, tend to react with water, causing oxidation/corrosion.

For a suspension to be deemed stable, the particles must exhibit repulsive forces to prevent agglomeration and be protected against oxidation. As used in this research, ensuring proper dispersion and preventing oxidation of the particles are critical considerations, particularly when colloidal systems with powders such as WC, Ti(C,N), Fe, and Ni are prepared. Consequently, it is essential to both disperse and protect the particles effectively.

Numerous studies have demonstrated that this dual effect can be achieved by introducing polymers into the suspension, such as the dispersant polyethyleneimine (PEI) and/or the stabiliser polyvinyl alcohol (PVA). These studies have also explored the influence of pH and varying concentrations of these additives, highlighting their effectiveness in preventing the oxidation of transition metal particles, such as nickel [102], iron, or titanium [103], [104], cermets [105] and even carbides [106], while at the same time, they have managed to form dispersed suspensions.

PVA is one of the most general non-ionic hydrophilic polymers, although many others achieve the same results [107]. HPMC (Hydroxypropyl methylcellulose) is a non-ionic hydrophilic cellulosic derivative. Like PVA, it is widely used in many fields due to its ease of use and excellent film-forming ability to maintain suspension stability [108], [109]. In addition, it has previously been used to disperse solid solutions that have subsequently been atomized [110], [111], [112].

In the studies mentioned above, PVA was used, making it pertinent to investigate the possible effects of different additives on the behaviour of materials. For this reason, in this research, HPMC as a hydrophilic polymer, together with PEI, has been decided to ensure the adequate stability and dispersion of the suspensions. The two colloidal suspensions with a high weight content were formulated from the elemental powders and additives mentioned, using water as a dispersing medium, as shown in the diagram of the Figure 3.1.

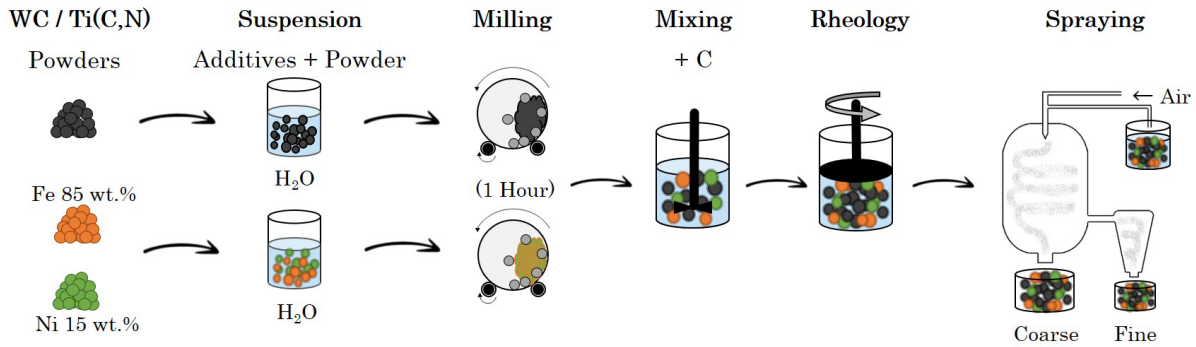


Figure 3.1. Preparation scheme for colloidal suspensions.

3.2. Rheological analysis

All suspensions were subjected to rheological analysis to assess their stability and ensure adequate particle dispersion. Rheological measurements provided insight into changes in suspension behaviour under an applied force, as particle-particle interactions directly influence the response of each suspension.

When a colloidal suspension undergoes rheological tests, the shear profile generated within the fluid creates a velocity gradient around the particles. However, because the particles are rigid and move through the fluid at a single speed, this velocity gradient induces particle rotation. The energy expended in rotating the particles reduces the energy available for the flow or creep. As a result, the presence of particles increases the viscosity of the suspension, requiring a greater applied force to achieve the same level of flow that would otherwise occur in a particle-free liquid [113]. This behaviour is defined as non-Newtonian and, more specifically, pseudoplastic behaviour. It is the most common in colloidal suspensions since it is shown in the presence of solid particles in a fluid.

When subjected to shear stress, the material's structure breaks down as the speed increases, and the particles are arranged in parallel layers, able to flow more efficiently, which causes a decrease in viscosity. When this process is complete, the fluid changes behaviour, showing it is closer to Newtonian. However, if the dispersed phase concentration is too high, the particles could interact, forming large aggregates. In this way, by increasing the shear stress, the progressive breakdown of the aggregates would be caused, showing a rheological curve with a plastic behaviour, which would allow the presence of the same in the suspension to be identified.

A study was conducted based on the model proposed by Cross to evaluate the behaviour of suspensions based on Newton's law, as it is one of the most widely used to study the differences existing at low and high shear speeds. The flow curves obtained in the study of the two materials analysed are presented in the following figure.

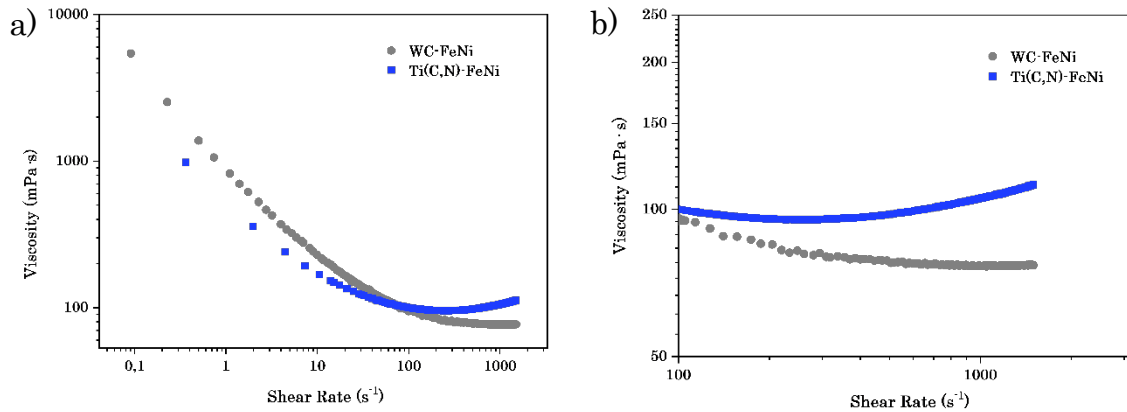


Figure 3.2. a) Shear viscosity versus shear rate; b) Magnified curve at high shear speeds. Both graphs on logarithmic scales of the materials WC-FeNi and Ti(C,N)-FeNi.

Figure 3.2 shows the pseudoplastic behaviour expected in colloidal suspensions, where the viscosity decreases as the shear rate increases. The high viscosities shown at low shear rates result from the particles in the different suspensions. The viscosity recorded at zero shear (η_0) refers to the stability of the suspension against phenomena of phase segregation and sedimentation of heavy particles [114]. A higher viscosity value indicates lower particle mobility and a more stable suspension at rest. When the shear rate is increased, the viscous forces result in an increasingly anisotropic suspension structure with particle orientation in the flow direction, resulting in behaviour that increasingly resembles Newtonian flow. In other words, the viscosity decreases progressively until it stabilises.

The viscosity parameter at high shear (η_∞) is an important indicator of the effectiveness of the suspension homogenisation and dispersion processes. Lower viscosity values at high shear rates reflect better homogenisation of the suspension and reduced presence of agglomerates within it [115].

Both materials showed similar behaviour regarding the pseudoplasticity index, with values of 0.54 for WC-FeNi and 0.42 for Ti(C,N)-FeNi. An explanation for the subtle but higher index shown by the WC may lie in the higher density of the particles of this suspension compared to the particles of Ti(C,N). A higher density

of the ceramic particles could slightly hinder movement at low shear rates, ruling out the rest of the elements, as they are found in the same proportion in all suspensions.

However, at shear rates above 100 s^{-1} , it was possible to observe a slight change in Ti(C,N)-FeNi behaviour with respect to WC-FeNi; while the latter remained stable, the Ti(C,N)-based material exhibited a gradual decrease in viscosity until a change in slope was observed, where the viscosity slightly increased. While density was the main differentiating factor between the suspensions at low shear rates, it is plausible that the average particle size distribution contributed to the observed variation in behaviour at higher shear rates. Figure 3.3 presents the particle size distribution, as determined in previous studies [69], [116].

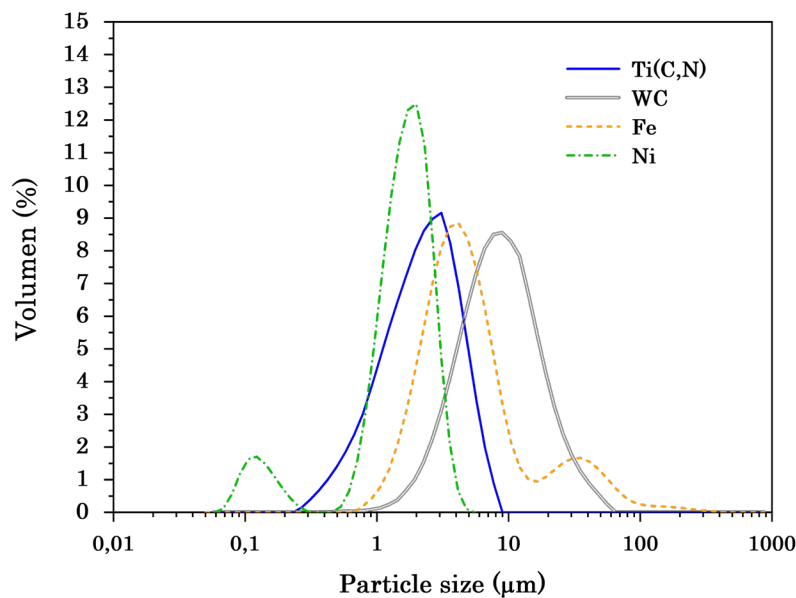


Figure 3.3. Initial particle size distribution [69], [116].

As with many other factors, the viscosity of a suspension is strongly influenced by the volumetric fraction (Φ), which describes the proportion of the total volume occupied by specific particles. An increase in the volumetric fraction brings the particles together, resulting in a more significant interaction and friction between them, increasing the viscosity. However, despite the similarity in the area beneath the Ti(C,N) and WC curves, attention was directed toward the position of the individual peaks. The peak corresponding to Ti(C,N) shifted to the left, indicating smaller particle sizes that facilitate improved coupling.

An analysis of the agglomeration factor for each element, as presented in Table 3.1, revealed a clear relationship between the agglomeration factor and particle size. The element with the highest agglomeration factor was Ni, which also exhibited the smallest particle size, followed by the Ti(C,N) particles.

Table 3.1. Characteristics of starting powders [69], [116].

Powder	DV ₅₀ /DV ₆₀ (μm)	SSA (m^2/g)	Density (g/cm^3)	d _{BET} (μm)	F _{agl} (D ₅₀ /d _{BET})
Ti (C,N)	2.1	3.0 ± 0.1	5.10 ± 0.01	0.4	5.25
WC	7.9	0.14 ± 0.1	15.63 ± 0.01	2.75	2.87
Fe	3.5	0.6 ± 0.1	7.78 ± 0.01	1.2	2.92
Ni	1.75	3.9 ± 0.1	8.9 ± 0.1	0.19	9.21

As discussed previously, a lower viscosity at high shear rates enhances the homogenisation of suspensions and reduces the presence of agglomerates. However, particles as small as Ti(C,N) tend to occupy the spaces between larger particles, forming agglomerates. It is not until the shear rate exceeds 100 s^{-1} that these smaller particles begin to separate. As the agglomerates disperse, the effective surface area of the particles increases, leading to a slight increase in viscosity due to greater friction. Consequently, the smaller particle size of Ti(C,N) resulted in suspensions exhibiting a minor increase in viscosity at high shear rates as the agglomerates disintegrated.

Despite these slight variations in viscosity, the overall rheological behaviour of the suspensions demonstrated sufficient stability, homogeneity, and dispersion to proceed with subsequent processing stages. Therefore, it was concluded that the substitution of PVA with HPMC yielded suspensions with comparable performance.

3.3. Atomization

Atomisation is a technique in which a water-based or organic-based suspension is introduced into a hot air system that pulverises it, converting the suspension into dry powder. This process is widely employed to produce particulate material intended for use in subsequent compaction processes.

The powder generated by atomisation is characterised by the formation of fine particles with diverse shapes, ranging from solid and uniform spheres to elongated doughnut-shaped granules, and even hollow structures [117].

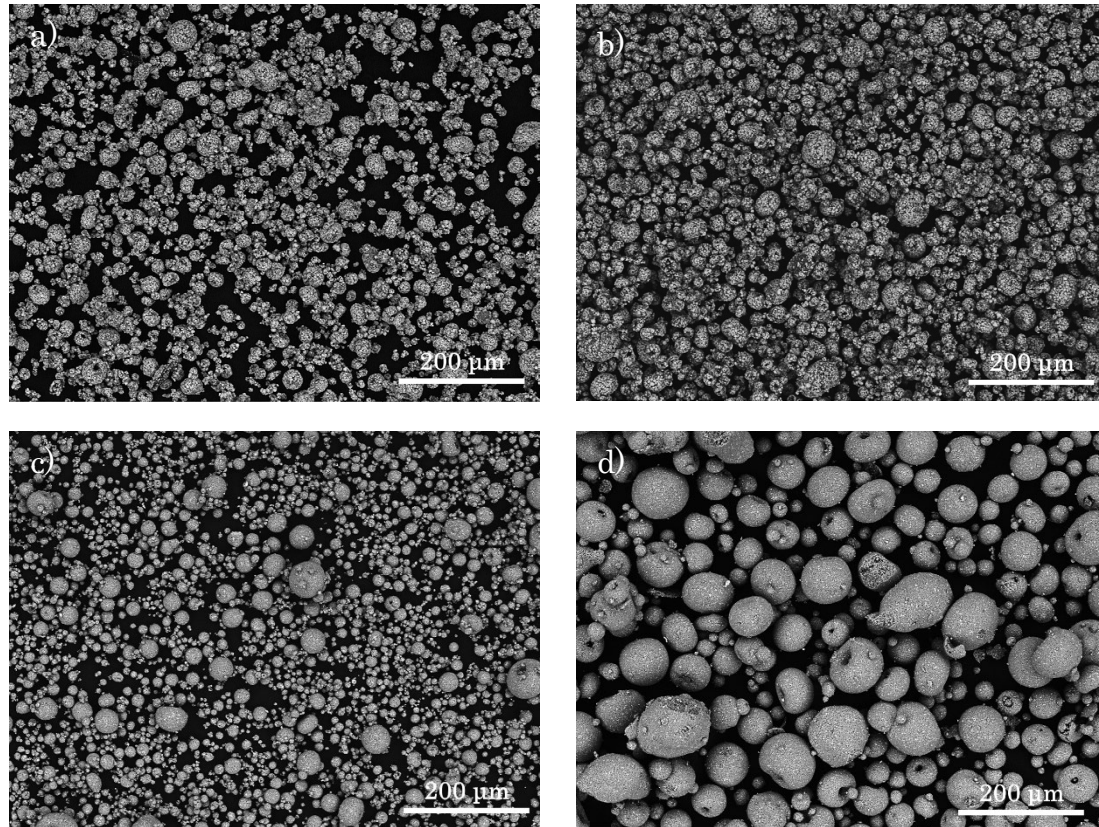


Figure 3.4. TM1000 images of atomized materials; placing the fine powder on the left, and on the right the coarse powder of the materials: a) and b) WC-FeNi; c) and d) Ti(C,N)-FeNi.

The two suspensions WC-FeNi and Ti(C,N)-FeNi were atomized through a 1 mm nozzle, thanks to an airflow at a temperature of 200 °C. During the process, three main stages can be described: first, the generation of droplets or atomizing, then the conversion of those droplets into particles through the evaporation of the solvent, and finally, the collection of the particles separated by size [118].

In powder characterization, it is imperative to study the size and morphology of the particles after atomization, as these data offer information on how the process has been developed and whether it has developed correctly. Figure 3.4 displays the images taken of the collected particles, differentiating between fine and coarse powders. Analysis of these images allowed three key observations. First, all three suspensions facilitated the atomisation of particles that were predominantly

perfectly spherical. Second, the particle size was smaller for the fine dust than for the coarse dust. Third, no large agglomerates were observed in the samples.

A closer examination of the granules obtained after atomization, as depicted in Figure 3.4, revealed that most particles in both suspensions were perfectly spherical. However, some granules were slightly oval, while others displayed a small crater or dimple in their centre. This phenomenon is typical of ceramic materials during atomisation, mainly when the suspension is basic. The cratered particles are hollow, with their outer structure collapsing [117], as shown in greater detail in Figure 3.5.

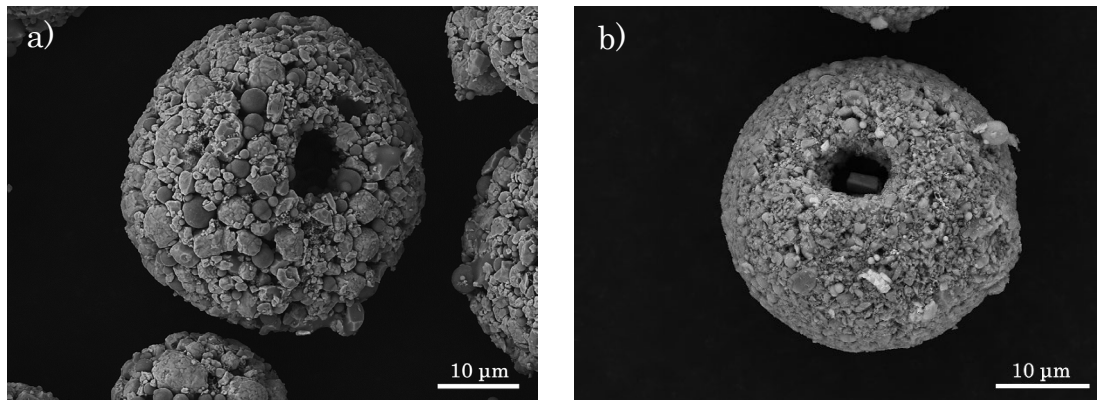


Figure 3.5. Detail of the particles with a central dimple of each of the materials: (a) WC-FeNi; b) Ti(C,N)-FeNi.

Both solid and hollow spherical particles are originated from the composition and behaviour of the pulverised droplets. Understanding this phenomenon requires a detailed explanation of the droplet formation process: at the initial stage, as the droplet of suspension enters the hot air stream, the water on the surface of the droplet evaporates first. The water vapour within the droplet is then expelled outward. If a liquid interface persists, the evaporation continues uniformly, causing the droplet to dry and contract evenly, ultimately forming a perfectly spherical and solid granule.

However, in some cases, particles within the droplet gain sufficient mobility to pack densely on its surface, forming a rigid solid layer. This external layer prevents the granule from contracting uniformly, forming hollow particles with a collapsed outer structure [117], [119]. In this way, the flow of moisture generated causes the particles and the solvent to be attracted to that outer layer, increasing the thickness of the layer and generating a gap inside [120]. Finally, due to the

pressure difference between the interior and exterior of the particle —caused by either the rupture of the outer layer or the expansion of internal gas— a collapse occurs, resulting in the formation of a crater or dimple in the granule. Although the presence of these hollow particles is a well-documented phenomenon in the atomisation of ceramic materials, it is not expected to pose significant issues during the sintering process, as their volume relative to the solid particles is negligible.

3.3.1.Characterization of atomized powder

A critical factor in the sintering process is the particle size distribution, as multimodal or overly broad distributions can adversely impact the quality and density of the final product. Additionally, understanding the chemical composition of the powder is essential, as the presence of impurities can hinder the success of the sintering process. Consequently, a study evaluated all materials based on these characteristics.

Maximum particle size must be minimised to ensure a homogeneous distribution and adequate density in the sintered material [121]. Various studies on sintering principles have established that the maximum particle size difference should not exceed a ratio of 1:10 [122], [123], [124], [125].

The average particle size was estimated using ImageJ free software to determine whether the difference between the fine and coarse granules suited this relationship. Figure 3.6a and b illustrate how the software generates a binary image from the micrograph acquired using the microscope. This process involves defining, counting, and estimating the size of each particle. However, the software cannot differentiate between particles that overlap or are in direct contact.

To minimise errors and ensure a representative sample, an average of ten images per material was analysed

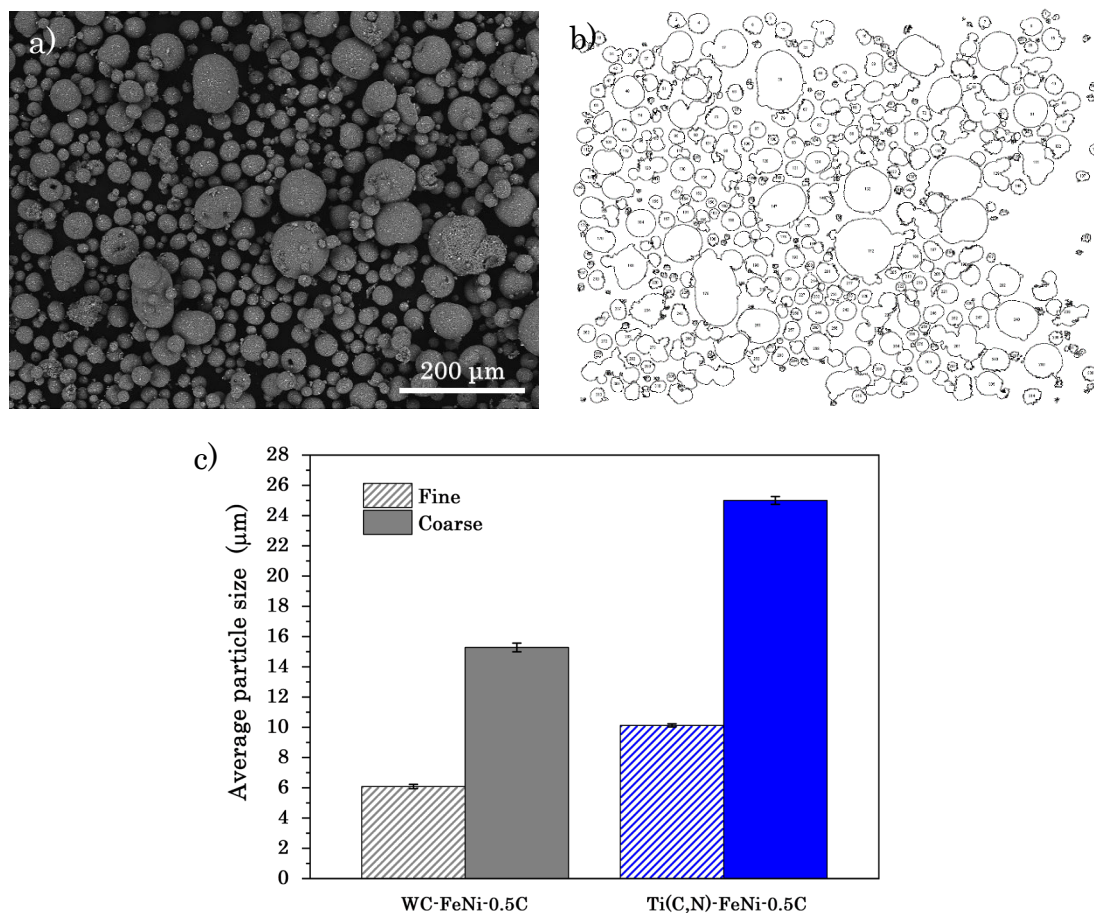


Figure 3.6. Particle size assessment. a) SEM image of atomized Ti(C,N)-FeNi powders; b) ImageJ analysis of the area occupied by each particle; and c) Graphic representation of the average size found in the materials depending on the thickness of the powders.

Figure 3.6c shows the different study materials, distinguishing between fine and coarse powders. On the Y-axis, the normalized diameter of the particles found in each material was presented, allowing the differences between them to be observed. The Ti(C,N)-FeNi grains exhibited fine and coarse particle sizes around 10 μm and 25 μm , respectively. On the contrary, the WC-FeNi showed smaller particles, with 7 μm for fine particles and 15 μm for coarse particles. The size ratio between the fine and coarse granules did not exceed 1:3.

Taking into account the results obtained on the sphericity and homogeneity of all particles and the minor differences in size between coarse and fine powder, which were well below the limit mentioned above of 1:10, powders were mixed and morphological characterization was carried out. The average particle diameter, specific surface area and agglomeration factor of each composition are detailed in Table 3.2 and Figure 3.7.

Table 3.2. Characterization of the particles that make up each material.

Name	ρ_{th} (g/cm ³)	SSA (m ² /g)	dBET (μ m)	Particle size (μ m)	Fagl (D50/d _{BET})
Ti(C,N)-FeNi	5.65	1.63	0.65	7.31	11.2
				18.9	29.1
WC-FeNi	14.05	0.14	3.05	16.0	5.3

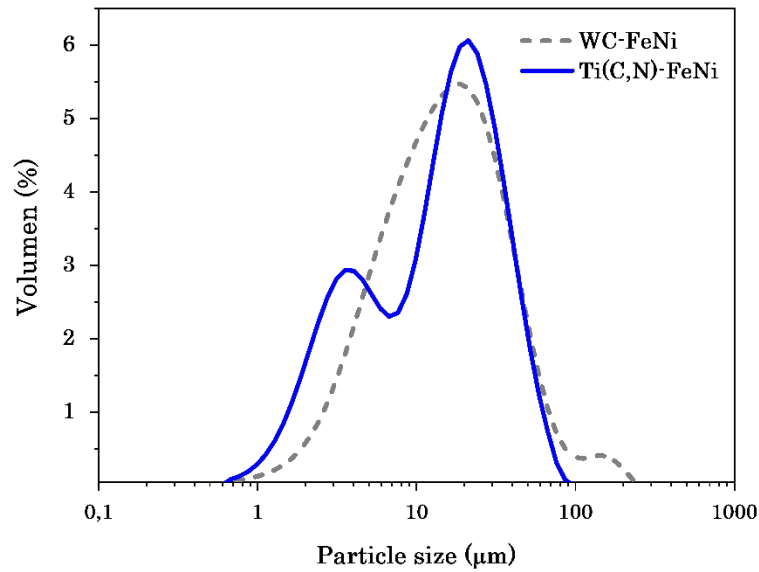


Figure 3.7. Atomized particle size distribution.

In Figure 3.7 the particle distribution was measured using a laser diffraction technique, where the powders were suspended in water. It is observed that WC-FeNi exhibited a monomodal particle size distribution centred at 16 μ m, with an agglomeration factor of 5. On the other hand, Ti(C,N)-FeNi showed a bimodal particle size distribution with two peaks centred at 7 μ m and 19 μ m, respectively, with agglomeration factors of 10 and 30. These data coincide with those presented in Table 3.1 and are consistent with the images in Figure 3.3. The discrepancy between the results obtained with ImageJ and the laser diffraction technique was attributed to the limitations of the software to discern between particles in direct contact.

Considering all the available information, it could be stated that the conditions applied were appropriate when evaluating the atomization process. The granules obtained were spherical, homogeneous, and primarily solid. The only difference

between fine and coarse powders was their size, making them easily combined into a single material. In addition, the narrow distributions of all materials, with moderate particle sizes, allowed the powders to produce high-density, high-quality sintered materials.

Understanding the shape and size is essential for successful sintering. However, the information obtained from particle analysis alone was insufficient. Ensuring the correct chemical composition was equally critical for the sintering process. The presence of impurities, whether resulting from contamination or unwanted reactions, such as oxide formation, can adversely affect the sintering process and compromise the final properties of the material. To rule out the presence of unwanted elements, each of the powders for the three materials was subjected to X-ray diffraction (XRD) analysis, as illustrated in Figure 3.8.

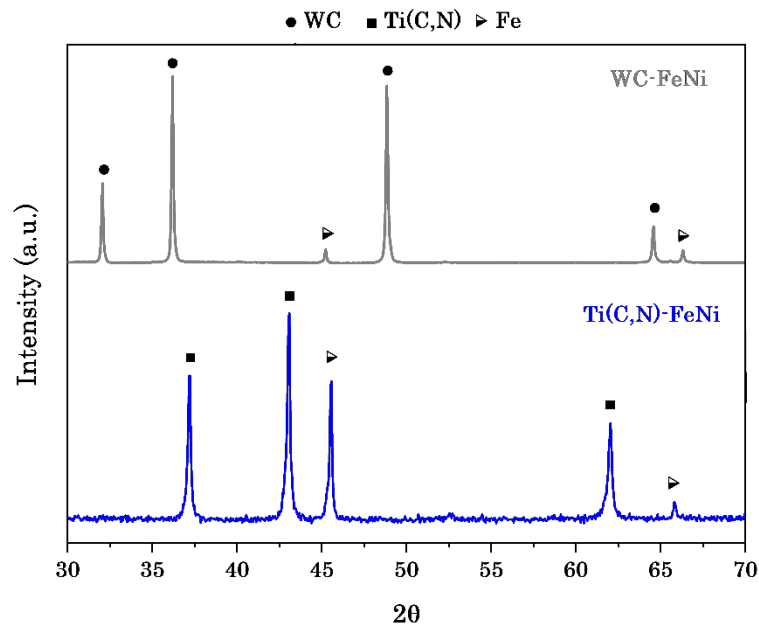


Figure 3.8. X-ray diffraction patterns recorded in atomized powders. WC-FeNi at the top, and Ti(C,N)-FeNi at the bottom.

The upper diffractogram corresponding to the WC-FeNi material identified prominent peaks associated with WC and Fe patterns. On the contrary, peaks corresponding to Ti(C,N) and Fe were recorded in the lower diffractogram. X-ray diffraction analysis confirmed the absence of elements outside the intended composition and demonstrated that no foreign oxides or compounds were formed during manufacturing.

However, due to the materials' low weight content of Ni and C, the corresponding peaks for these elements were undetectable. This does not imply their absence, but indicates that the peak intensities were so low that they were indistinguishable from background noise.

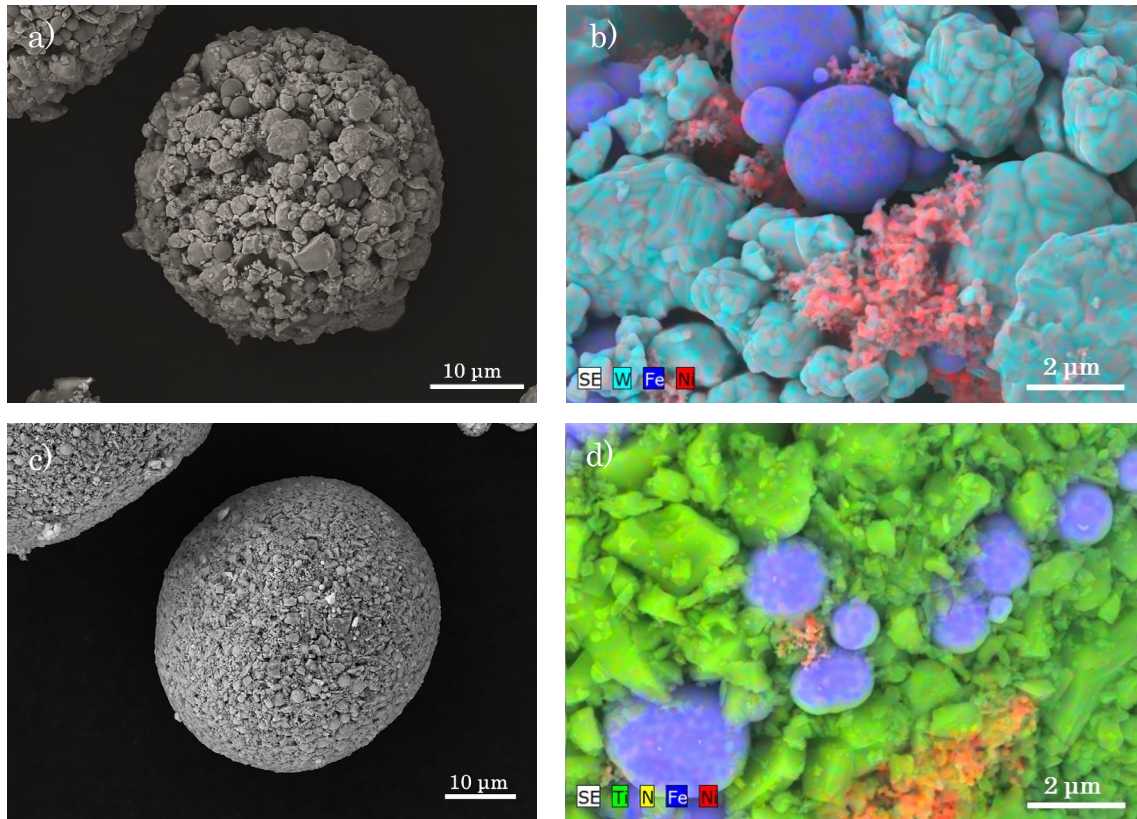


Figure 3.9. SEM images and EDX detail of the powders a-b) WC-FeNi, and c-d) Ti(C,N)-FeNi. The sky-blue particles belong to the WC, the green particles to Ti(C,N), while the colours expected to dark blue and red images correspond to Fe and Ni, respectively.

The different elements introduced into the suspensions must be uniformly distributed across all atomised powder particles for effective sintering. Uniform distribution ensures that each particle possesses the same chemical composition, which is crucial for consistent reactions during the sintering process. This results in uniform densification that improves the structural integrity of the final material [126]. Figure 3.9 collects images of two atomized particles, as well as the details of the elements of which they were composed. The micrographs showed two spherical atomized granules; in Figure 3.9a and b, the WC acted as a base material with a somewhat angular and rough appearance, housing the characteristic coral-shaped particles of Ni and the perfect spheres of Fe. In the case of Figure 3.9c and d, the

metal particles were also evenly distributed, but the angular ceramic particles of Ti(C,N) were used as support.

Therefore, it was concluded that, in both materials, the ceramic and metallic phases initially introduced into the suspension were uniformly distributed throughout the particles, creating favourable conditions for the subsequent sintering stage.

4. Selection of sintering atmosphere

Sintering from powders is a critical step in the manufacture of cemented cermets and carbides. Precise control of the sintering atmosphere is essential for the production of materials with superior mechanical properties, making them suitable for demanding applications, such as cutting tools. However, effective control of the sintering atmosphere is futile if the chosen atmosphere is incompatible with the material, to assess this compatibility, sintering was performed under various atmospheres to identify optimal and industrially viable conditions.

4.1. Compressibility of powders

Compressibility refers to the ease with which powders can be compacted in their green state, that is, before sintering. This property is critical for achieving efficient and uniform densification during the subsequent sintering process. Although porosity is inherent in the green stage, it must be eliminated during sintering by filling of voids, which occurs in the presence of a liquid phase [127]. The higher the relative density in green, the smaller the space between the particles, and the higher the density of the final part. For this reason, it is vital to conduct a preliminary compressibility study and thus determine the ideal load for each of the study materials. To this end, two cylindrical dies of 5 and 10 mm diameter are available, with the powder compacted at different pressures, as shown in Figure 4.1. This figure shows the measured compressibility curves (green density as a function of compaction pressure) for both materials.

The relative density values in the green, shown in Figure 4.1, exhibited an increase in density as the forming pressure increased, reaching 64 % density at 500 MPa pressure, this value is similar that recorded in the manufacture of cemented carbides [128], and thus guaranteeing the compaction process of the three materials. However, after drawing an area of apparent stabilisation, the relative density continued to increase with increasing pressure. The plastic behaviour of the metal matrix explains this behaviour. Up to 500 MPa, the ceramic phase reaches its maximum compaction, but the metal phase deforms and eliminates

porosity [129], [130], [131]. One would think that the higher the relative density of the material, the better properties will be achieved, so compacting at 1200 MPa would be the best option. However, at pressures above 500 MPa, the ceramic particles could collapse, compromising the homogeneous distribution of each element achieved during the atomisation process.

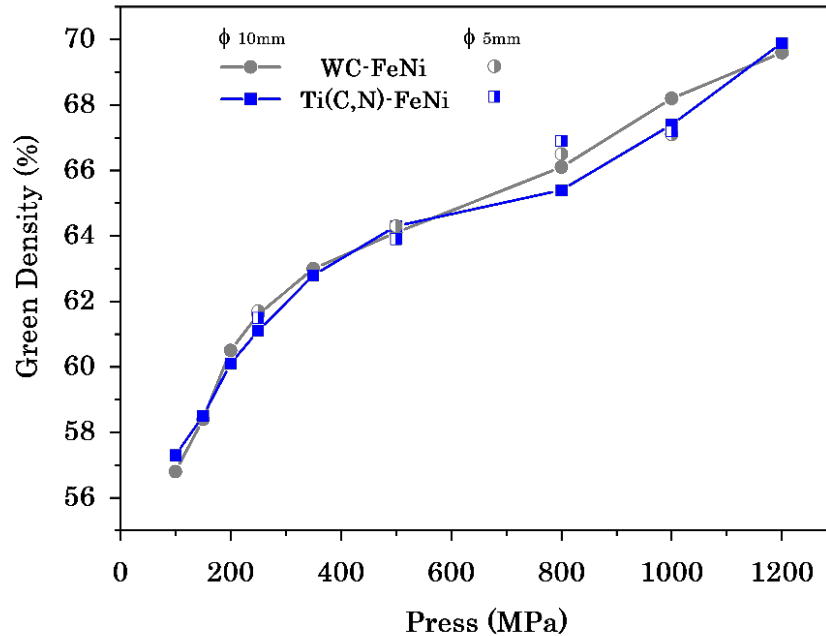


Figure 4.1. Study of the compressibility of green powders with 5 and 10 mm diameter dies for WC-FeNi and Ti(C,N)-FeNi materials.

Since the ultimate objective of this research is the characterisation of the manufactured materials, it was crucial to obtain a sufficiently large sample to proceed with sintering. To achieve this, it was necessary to evaluate whether the size of the press die would influence the compaction results. For this study, a die with a diameter of 5 mm was selected, representing half the size of the original die. Figure 4.1 shows the data obtained, showing that the size of the die was indifferent to the behaviour of the powders up to 1000 MPa of pressure, where it seemed that the relative density curve stabilised.

Medium-sized rectangular components are typically compacted using hydraulic presses with steel dies designed to counteract the substantial internal forces exerted on the powder, transmitting these forces radially to the die. The challenges associated with compaction increase with a higher proportion of the ceramic phase, and these issues may only become evident after sintering.

Furthermore, producing more significant components with greater diameters and heights exacerbates the compaction difficulties associated with iron-, nickel-, or cobalt-based cermets. Common issues encountered during the cold compaction of cermets and cemented carbides include air occlusion, insufficient bonding between phases, laminations, random porosity, and heterogeneous density within the compact [132]. Some of these issues arise during the compaction process, necessitating slight modifications to the die and lubrication of the die wall, despite the potential risk of oxidation reactions in the material.

On the basis of the results of the compressibility study and the implementation of these modifications, it was determined that increasing the die size did not compromise the green density of the materials. However, to ensure repeatable results, pressures below 800 MPa were applied, as this threshold represented the first point at which green density variations could be observed due to die size.

Given that the matrix predominantly consists of ceramic materials and a larger die was used, the required load per unit of surface area was exceptionally high. Consequently, a pressure of 500 MPa was applied. The experimental results achieved exceeded this applied pressure while adhering to the recommended practices for working with cemented carbides and cermets [128].

4.2. Evaluation of sintering atmospheres

The sintering atmosphere must fulfil several functions, such as protecting the material from oxidation during the process, establishing the right conditions to promote contact between adjacent particles, preventing undesirable reactions, and, if necessary, removing residues left over from previous processes [127]. Due to the highly reactive nature of the elements that make up the materials, it was decided to use only inert atmospheres such as N_2H_2 (Hydrogenated Nitrogen), Vacuum ($\times 10^{-4}$ mbar) and Ar (argon). The samples were sintered in a tube furnace by subjecting them to 1450 °C for two hours, based on a previous study [116].

4.2.1. Microstructure

After being sintered, the materials were subjected to roughing and polishing to finally be chemically attacked, revealing the microstructures shown in Figure 4.2 and Figure 4.3 for each of the sintering atmospheres selected.

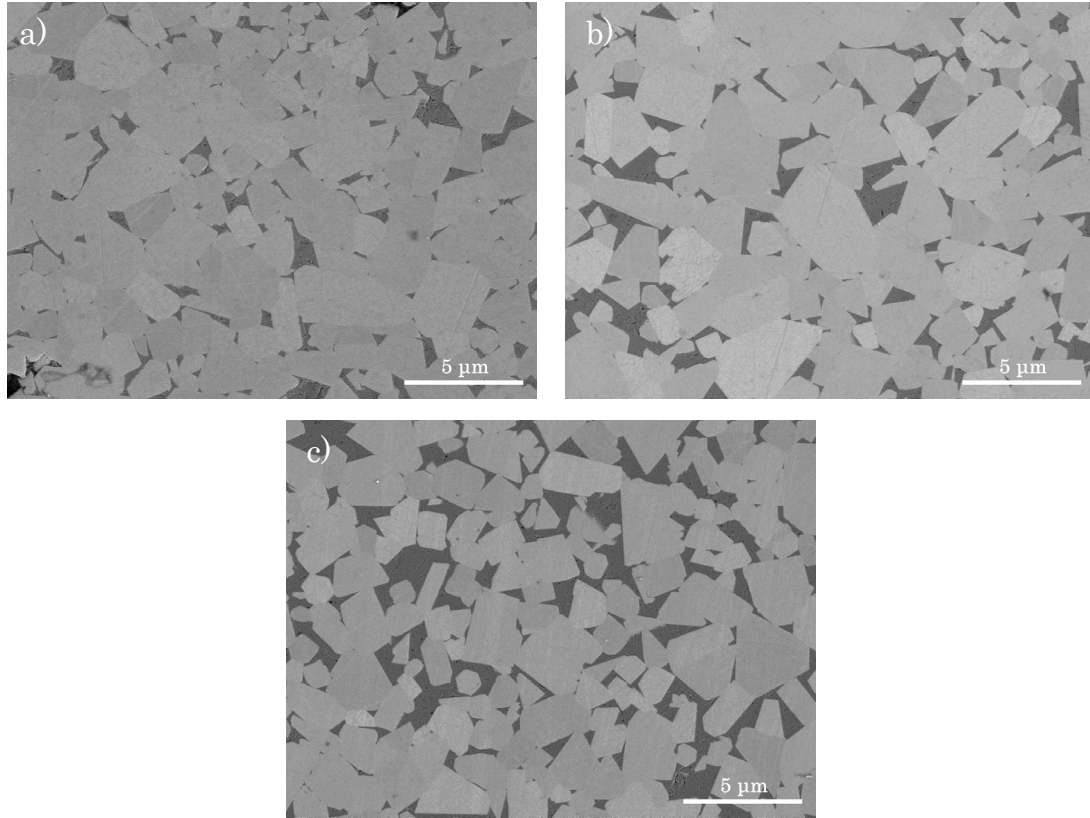


Figure 4.2. SEM micrographs of the surface of the WC-FeNi material in each of the sintering atmospheres a) N₂H₂, b) vacuum (x10⁻⁴ bar) and c) argon. The light grey grains correspond to the WC, while the dark greys show the FeNi metallic phase. The areas shown in black belong to the pores.

In the set of micrographs, two distinct phases were identified. In the WC-FeNi material, the phase with bright contrast corresponded to the ceramic phase, while the darker phase was associated with the metallic FeNi phase. Conversely, the darker phase represented the ceramic phase in the Ti(C,N) material, whereas the lighter phase was attributed to the metallic FeNi phase. The characteristic geometric shapes of the structures formed through liquid phase sintering were clearly observed in both materials.

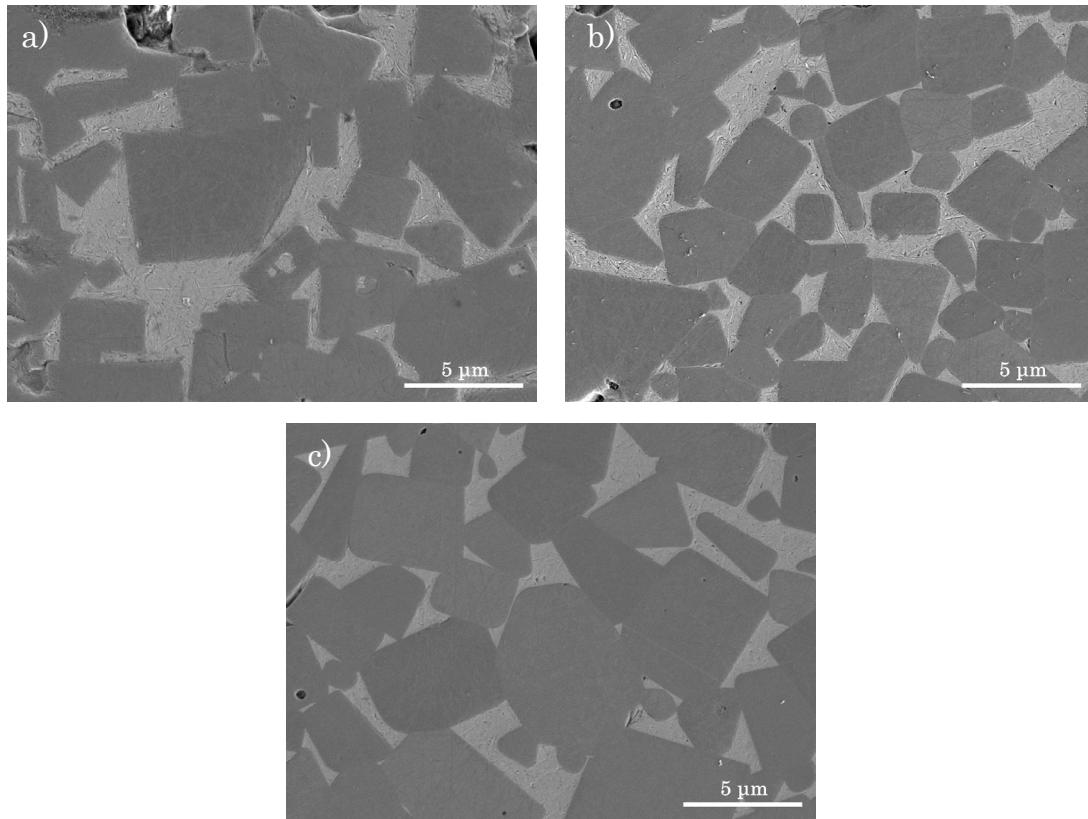


Figure 4.3. SEM micrographs of the surface of the Ti(C,N)-FeNi material in each of the sintering atmospheres: a) N_2H_2 , b) vacuum ($\times 10^{-4}$ bar) and c) argon. The dark-toned grains correspond to Ti(C,N), while the lighter-toned grains show the FeNi metallic phase. The areas shown in black belong to the pores.

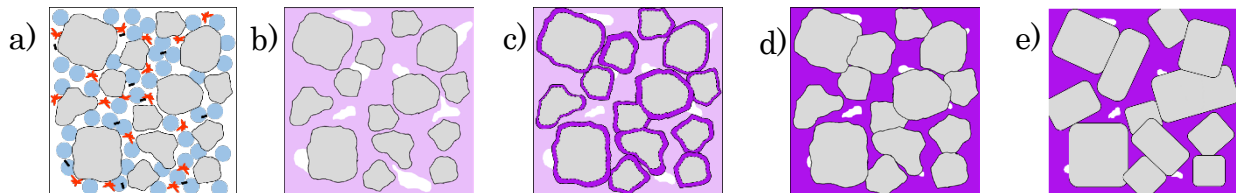


Figure 4.4. The different stages of sintering take place in the liquid phase. a) Initial state, b) Liquid phase fusion, c) Diffusion, d) Ostwald reprecipitation and maturation and e) Cooling.

Liquid phase sintering follows the scheme shown in Figure 4.4; it is necessary to have phases with two different melting points, one that melts at high temperatures, as is the case of WC and Ti(C,N) ceramics respectively; and another phase with lower melting points, such as the metallic one formed by Fe and Ni. When the sintering temperature is reached, a stage of diffusion and rearrangement of particles occurs, where the metallic elements with a lower melting point melt to

form a FeNi liquid phase. The prominent role of Fe in this process is noteworthy, as Ni is used to improve the wettability of Fe in the ceramic phase. In this way, when the liquid phase FeNi surrounds the solid particles of WC and Ti(C,N), it acts as a solvent for Ti, W, C, N atoms, improving their mobility and promoting the diffusion and rearrangement of ceramic particles. A small but sufficient fraction of the atoms partially dissolve in the liquid phase, with subsequent precipitation taking place in the areas where there is a lower concentration of dissolved material, i.e. in the contact areas between the particles. The percentage of C added in the initial composition plays a fundamental role in the precipitation of the FeNi phase as it decreases the liquid temperature, allowing sintering to occur at lower temperatures.

As the sintering progresses, larger grains tend to grow at the expense of smaller ones due to preferential reprecipitation while existing pores close. This phenomenon is called Ostwald maturation [133]. The tiny grains that dissolve have a more spherical-like geometry, while the large grains that grow have flat faces [134], [135]. After controlled cooling in which the liquid phase solidifies, it is possible to appreciate a dense material with the characteristic geometric shape mentioned above, which can be observed in the micrographs of Figure 4.2 and Figure 4.3. The shape of the grains changes from the initial rounded structure to a faceted one, requiring only a very slight modification of the anisotropic solid-liquid surface energy [135], as shown in Figure 4.5.

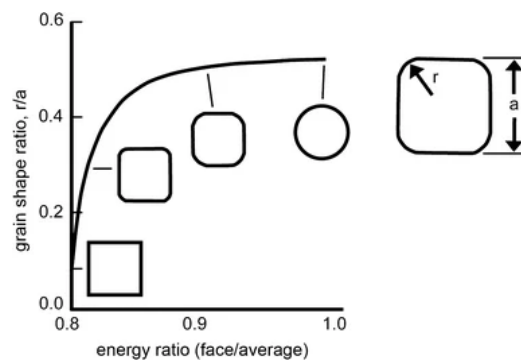


Figure 4.5. Grain shape variation with surface energy anisotropy [135].

However, after the sintering process, porosity is commonly trapped within the material. This residual porosity can result from several factors, including insufficient mobility of the metallic phase to infiltrate and fill pores, poor phase

distribution during green compaction, or a preferential affinity of the material components for the sintering atmosphere.

Regardless of the underlying cause, the result is the same: an inability of the metallic phase to penetrate all areas of the material during sintering, leading to residual porosity.

4.2.2.XRD Analysis

All materials showed signs of correct sintering. An XRD analysis was performed, which is found in Figure 4.6, to verify that the appropriate reactions had occurred after sintering and that no unwanted oxides had appeared.

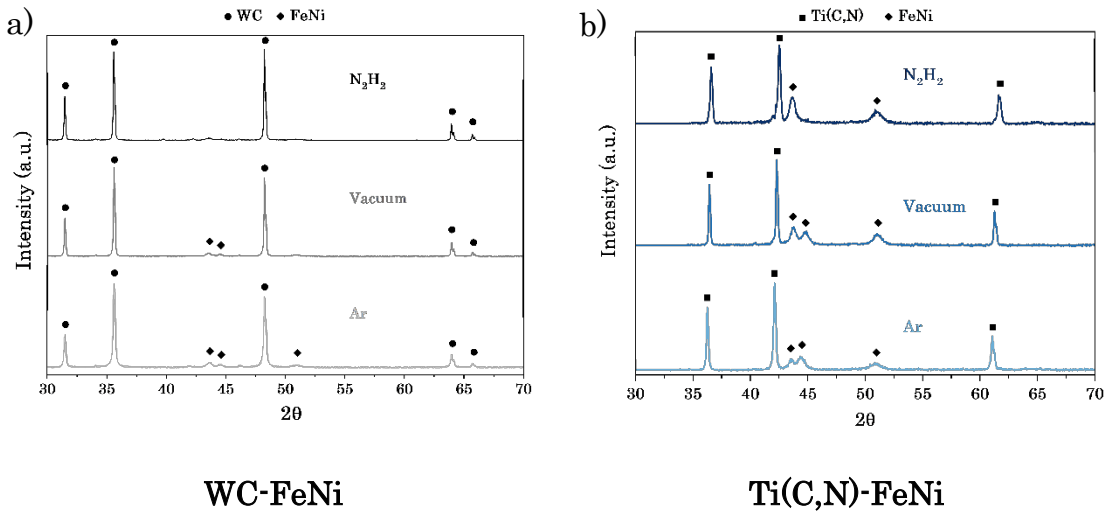


Figure 4.6. X-ray diffractograms obtained from each material and sintering atmosphere. a) WC-FeNi, and b) Ti(C,N)-FeNi.

In all atmospheres, the same peaks could be detected. In the WC-FeNi, the prominent peaks corresponding to the WC appeared remarkably. On the contrary, two other peaks in values of 2θ of 43.5° and 44.7° associated with FeNi were also identified. Those of the FeNi alloy replaced the Fe peaks indexed in the analysis of the initial powders because of the reaction produced in the sintering. These peaks were most noticeable in Ar's atmosphere, decreasing in vacuum and practically disappearing in N₂H₂. The Ti(C,N)-FeNi material presented similar results: the prominent peaks corresponding to Ti(C,N) showed a higher intensity than the rest. In the Ar and vacuum atmospheres, the indexed FeNi appeared at the same values of 2θ as in the previous case, but the relative intensity made them more easily

appreciated in this material than in the WC-FeNi. However, for the N_2H_2 atmosphere, the peak around the 44.7° position, that should be reflected as in the WC diffractogram, was not detected. In fact, these samples displayed an outer layer which was not present in the materials sintered under the Ar or vacuum atmospheres. A microdiffraction analysis was conducted comparing the exterior and interior of the materials to determine their composition and relate it to the disappearance and/or decrease of any of the FeNi peaks.

- WC-FeNi in N_2H_2

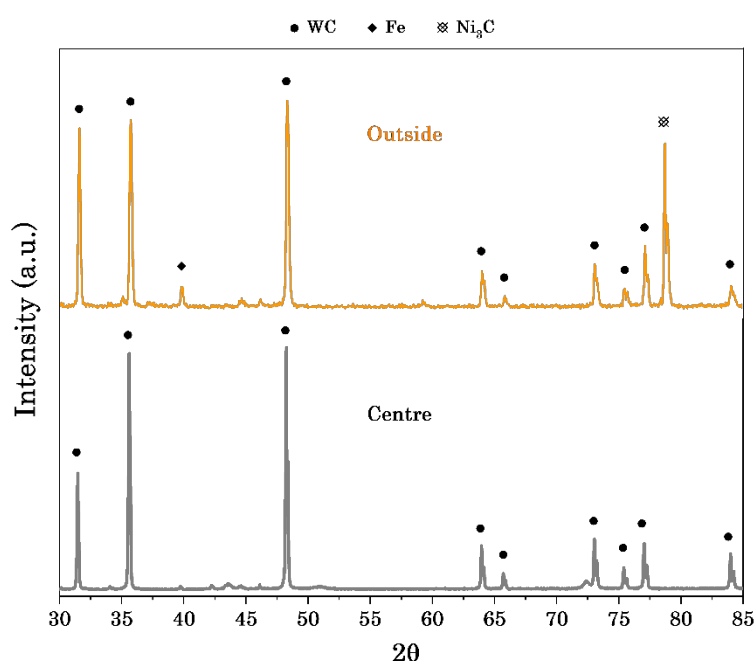


Figure 4.7. Peaks of the Ray micro diffractograms of the N-sintered WC-FeNi material N_2H_2 . a) Outer layer, and b) Centre of the sample.

After comparing the two zones, as shown in Figure 4.7, it was observed how the intensity of the WC peaks was reduced on the outside of the sample, being much lower than the intensity present in the inner zone, evidencing a decrease of this compound/element in the generated layer. At the same time, it was possible to distinguish the appearance of two new peaks at 39.9° and 78.8° , corresponding to Fe and Ni_3C , respectively. The appearance of Fe on the surface was also evident with an EDX analysis performed on the external area of the cross-section of the same sample. A decrease in WC in favour of the Fe was observed, as seen in Figure 4.8.

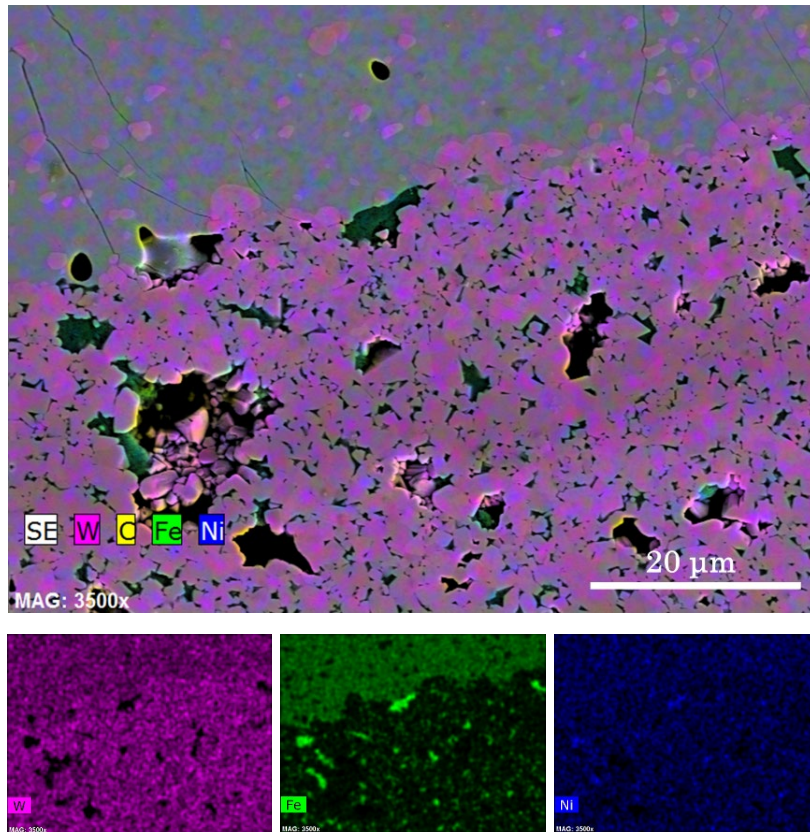


Figure 4.8. SEM-EDX micrographs of the outer surface of the WC-FeNi material sintered in N_2H_2 atmosphere.

The EDX analysis, together with the results obtained with μ DRX, led us to think that during the sintering process in the N_2H_2 atmosphere, part of the C of the WC could have been dissolved, a fraction of it in the N_2 of the atmosphere, and other combined with Ni, forming Ni_3C . This would mean a decrease in the presence of FeNi in the material, leaving free Fe on the surface. In this way, the absence of the 44.7° peak, would be related to the decrease of FeNi after sintering in this type of atmosphere. This peak would have been replaced by those detected at 39.9° and 78.8° , corresponding to Fe and Ni_3C , respectively, producing a gradual modification of the composition of the material, especially on the surface.

- Ti(C,N)-FeNi en N₂H₂

The outer layer generated during the sintering under N₂H₂ it was also found in the Ti(C,N)-FeNi material, so microdiffraction analysis was also performed and results are shown in Figure 4.9.

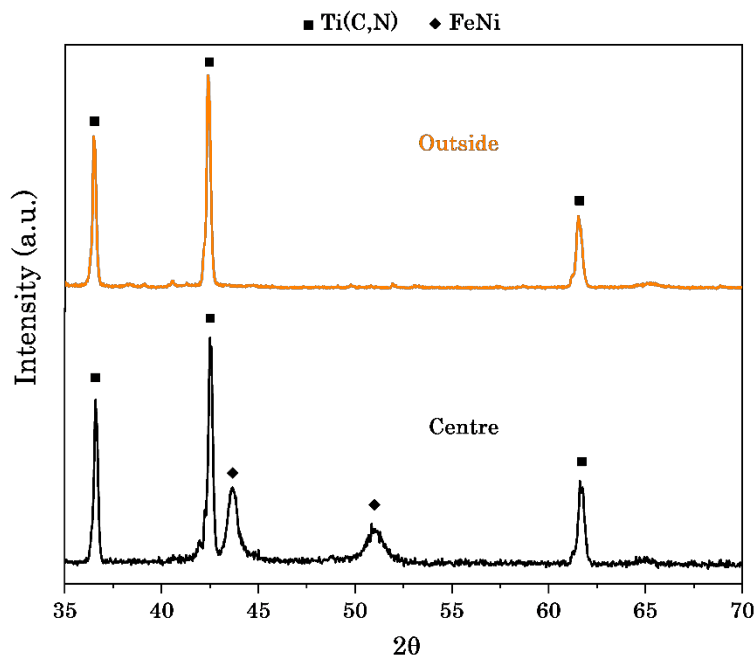


Figure 4.9. Peaks of the microdiffractograms of Rays of the material Ti(C,N)-FeNi sintered in N₂H₂. a) Outer layer, and b) Centre of the sample.

The intensity of the Ti(C,N) peaks was not affected when the two zones were compared, indicating that this compound had not been affected during the sintering process. No new peaks were detected, as in the previous case. However, at 44.7° and 51.2° the peaks detected in the inner zone corresponding to FeNi, disappeared entirely in the outer layer, indicating that the presence of this compound had been eliminated during the formation of the layer.

The absence of Fe and the reduction of Ni on the surface were also confirmed by the EDX analysis, which revealed the complete disappearance of Fe and a significant decrease in Ni content, Figure 4.10. An increase in the activity of N₂H₂ in the sintering atmosphere could promote its dissolution in the Ti(C,N) structure, leading to carbon depletion, as reported in previous studies [136]. However, the μ DRX and EDX analyses showed no reductions in Ti(C,N) content.

The most plausible explanation for these observations is the migration of FeNi into the material's interior. This migration may have filled some of the porosity of the material, resulting in a surface layer deficient in Fe and Ni after sintering.

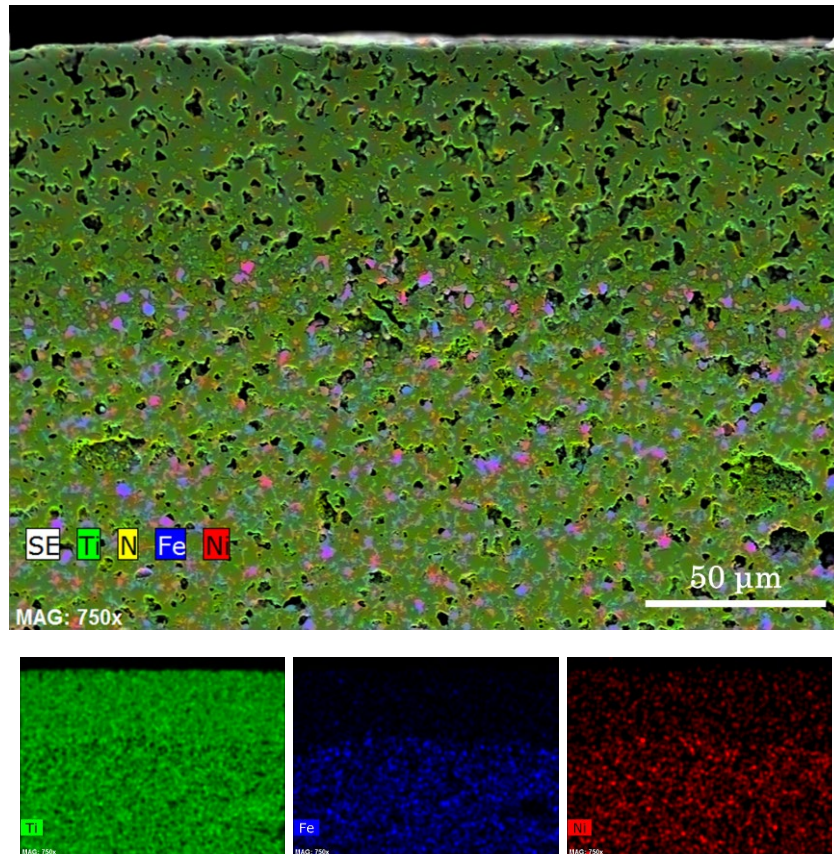


Figure 4.10. SEM-EDX micrographs of the outer area of the N_2H_2 sintered $Ti(C,N)-FeNi$ material.

4.2.3. Density

The properties can vary significantly depending on the sintering atmosphere used. The density was measured with the Archimedes method to determine the existing differences, and the porosity was calculated, as reflected in Table 4.1.

Table 4.1. Characterisation of samples sintered at 1450 °C for two hours.

Material	ρ_{th} (g/cm ³)	Atmosphere	ρ_{Exp} (g/cm ³)	Porosity (%)
WC-FeNi	14.05	N ₂ H ₂	13.67 ± 0.01	2.74 ± 0.08
		Vacuum	13.99 ± 0.02	0.5 ± 0.2
		Ar	13.82 ± 0.03	1.7 ± 0.2
Ti(C,N)-FeNi	5.6	N ₂ H ₂	4.66 ± 0.01	21 ± 3
		Vacuum	5.03 ± 0.02	12.9 ± 0.5
		Ar	5.339 ± 0.005	5.31 ± 0.05

An analysis of the porosities of the materials across different atmospheres revealed a notable distinction between WC-FeNi and Ti(C,N). The WC-FeNi material achieved high densification levels, exceeding 97 % in all atmospheres. In contrast, the Ti(C,N) material exhibited significant variability, with porosities ranging from 5 % to 21 %.

Sintering temperatures for WC and Ti(C,N) are typically between 1400–1600 °C and 1350–1500 °C, respectively. Therefore, the sintering temperature of 1450 °C used in this study was appropriate for both materials. However, WC has a relatively higher solubility in the liquid-phase FeNi compared to Ti(C,N), which may account for the differences in densification and porosity observed between the two materials [137], [138], so it is possible that by achieving a higher degree of dissolution and reprecipitation, better densification has been achieved, and with it a lower percentage of porosity.

The pores originate in the pre-existing gaps between the particles, but during sintering, these are occupied by the liquid phase. Due to the capillary phenomenon, tiny pores are the first to be eliminated, followed by larger ones [139]. However, if pores are still present in the microstructure after sintering, it may be due to one of the mentioned causes. If there is a heterogeneous distribution of the phases within the green material, many metallic particles could be surrounded by ceramic particles, causing areas with a lack of metallic phase and others with an excess of it [135]. On the other hand, if some material elements have a preferential affinity for the sintering atmosphere, reactions would occur during this process that would unbalance the system.

In both cases, the metallic phase either fails to flow uniformly through the ceramic matrix or does not react adequately with the other elements. This results in regions within the material that are insufficiently or inadequately wetted, which hinders proper sintering.

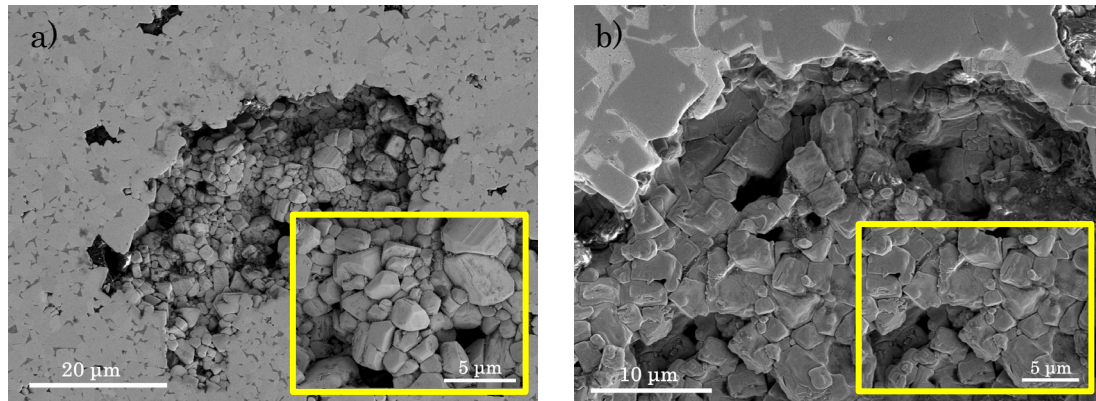


Figure 4.11. Large two-pore SEM micrography, with an image at higher magnifications of the interior. Materials sintered in N_2H_2 atmospheres a) WC-FeNi b) Ti(C,N)-FeNi.

A combination of these factors is likely what occurred in the sintered materials in N_2H_2 . In Figure 4.11a and b, the surfaces of the particles of WC and Ti(C,N) were subjected to a process of dissolution since they lost their rough texture, becoming smooth. However, when the C of the ceramic phases and the Ni of the metallic phase reacted with the N_2 of the atmosphere, the wettability of Fe in the ceramic phase decreased as it was not combined in the form of FeNi. This resulted in heterogeneous sintering with areas devoid of the metal phase needed to achieve proper densification, increasing porosity in the two materials.

4.2.4. Hardness and Grain Size

The Vickers hardness of each sintered material was measured using applied loads of 5 N and 10 N for materials sintered under the three atmospheres. The recorded hardness values under these two loads were comparable, with a maximum variation of only 9 %, thus only those at 10 N loads are presented.

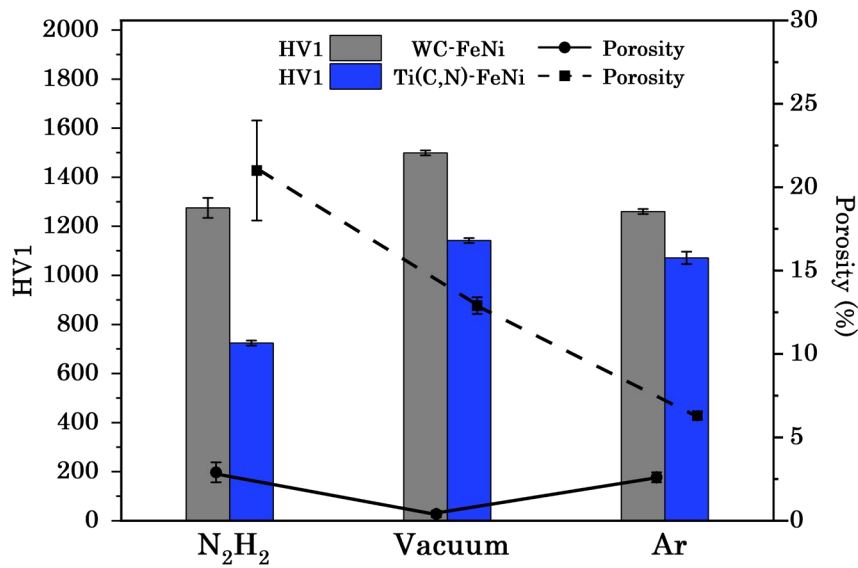


Figure 4.12. Vickers HV1 hardness and porosity of each of the materials and sintering atmosphere.

Figure 4.12 illustrates the hardness values obtained for the WC-FeNi and Ti(C,N)-FeNi systems under different atmospheres. The hardness measured under vacuum and argon conditions was high, although slightly lower than the values reported in previous studies [140], [141], [142]. However, due to the reactions that occurred during sintering and that caused the outer layers, the hardness values obtained in the atmosphere of N₂H₂ were lower than those revealed in the rest of the atmospheres.

Considering the calculated porosity and representing it on the hardness data, it can be seen how the porosity is inversely proportional to the hardness results, i.e., the lower the porosity, the higher the hardness recorded [143], [144]. This discrepancy arises because hardness measurements on porous materials account for the pores and the well-consolidated regions, lowering the overall result. Furthermore, if the area immediately below the indentation collapses due to porosity, the measured hardness will be significantly lower than the actual value. This effect is evident in the Ti(C,N) material sintered under an N₂H₂ atmosphere, where the hardness was reduced to nearly half its theoretical value due to a high porosity of 20 %.

Once again, the results obtained in vacuum and argon atmospheres were remarkably similar. The Ti(C,N)-FeNi material sintered in argon exhibited a hardness of approximately 12 GPa and a lower percentage of porosity.

For WC-FeNi, the hardness results were consistent across all studied atmospheres, with values close to 14 GPa. These results were not significantly affected by porosity, as the material achieved high density in all atmospheres, with porosity levels below 4 %.

The average grain size in cermets and cemented carbides is also closely correlated with hardness, this was determined with ImageJ software, allowing for the definition and measurement of the area of each grain for all materials.

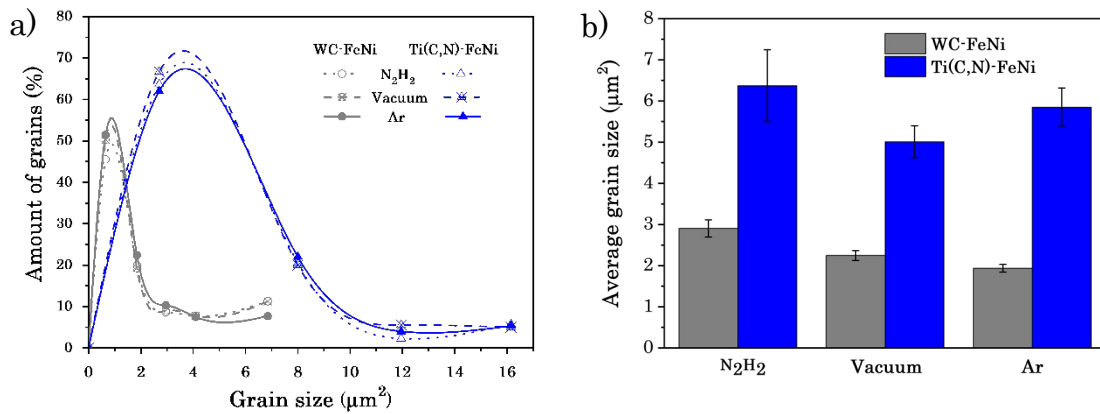


Figure 4.13. The area of each grain is a function of the sintering atmosphere for each material. a) Distribution of the percentage of each area size, and b) Average sizes of the areas.

Figure 4.13 shows the percentage of grains of different sizes present in the microstructure of the materials in each of the atmospheres. Although the size of the grains was the same within each material, the WC presented a much narrower distribution, with more than 50 % of the particles around 0.5 μm^2 . In contrast, in Ti(C,N), approximately 65 % of the particles had a grain size close to 3 μm^2 . The average size of the grains in each microstructure was determined to obtain a more complete view of these materials, as shown in Figure 4.11b. This allowed us to appreciate the difference in sizes between the two materials, with Ti(C,N) doubling the average measured value of the WC. When the effect of the atmospheres, it was observed that all of them presented remarkably similar values for the same material, with differences equivalent to the measurement's margin of error. However, it is remarkable that in both materials, the atmosphere of N_2H_2 presented the highest average grain sizes and the most significant uncertainty.

When these results with hardness, it was observed that the WC-FeNi material, which exhibited higher hardness across all atmospheres, also had the smallest

grain size. The slight variations in grain size under different sintering conditions for this material corresponded to the observed variations in hardness. Similarly, the Ti(C,N) material displayed the same behaviour: atmospheres that resulted in lower hardness were associated with larger grain sizes.

A finer grain size facilitates a more homogeneous distribution of the metallic phase within the ceramic phase, enhancing the material's properties in comparison to those with larger grain sizes. This analysis confirmed that porosity was not the only factor influencing hardness; grain size also played a critical role.

After analysing the compositional results obtained through XRD, μ DRX, and EDX, where unwanted reactions were identified in both sintered materials in N_2H_2 , and considering the hardness data with respect to density and grain size, argon was selected as the optimal sintering atmosphere. This decision was based on the balance of hardness, densification, and grain size. Argon provided the best results for Ti(C,N) without significantly compromising the performance of WC.

Additionally, argon atmospheres are widely used in industrial processes, making sintering more commercially viable without sacrificing the desirable properties.

4.3. Sintering in Ar

A dilatometric study was performed at 1450 °C in the same atmosphere intended for the sintering process, thus simulating identical conditions, to ensure that dimensional changes during sintering did not compromise the integrity of the materials. These tests are particularly valuable, as they enable the measurement of a material's expansion or contraction in response to temperature changes. This information is critical to understanding and optimising sintering processes by identifying the critical temperatures and contraction rates.

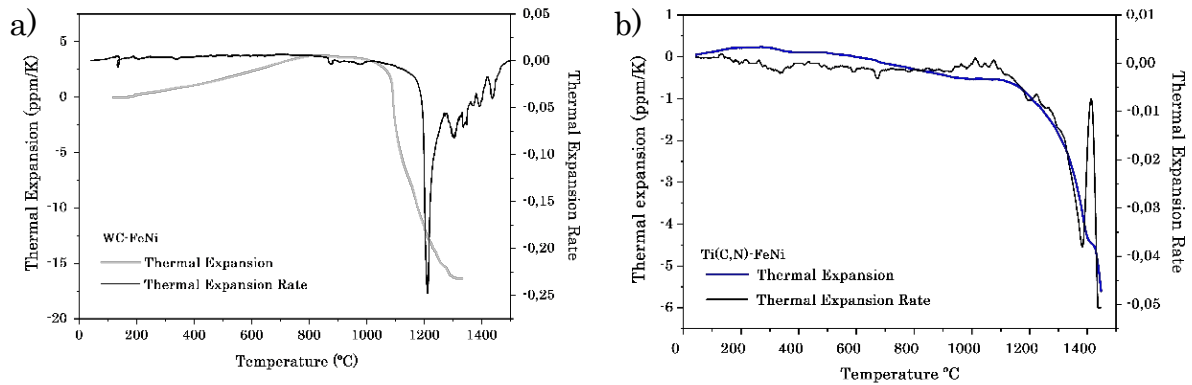


Figure 4.14. Thermal expansion ($\Delta l/l$) and thermal expansion rate ($\Delta l/\Delta t$) as a function of temperature for samples sintered in Ar. a) WC-FeNi and b) Ti(C,N)-FeNi.

Figure 4.14 shows the dilatometry results of the two materials in Ar. Initially, the contraction suffered was different in each case. In the case of Ti(C,N), the contraction of the material occurred steadily but smoothly up to 1200 °C, while in WC, an increase in thermal expansion was observed up to approximately 800°C. From this temperature, the sample began to contract very slowly, imperceptibly. When 1200 °C was reached, both materials abruptly began the contraction process that continued progressively until the maximum sintering temperature.

A comparative study of the materials confirmed that those with a bimodal particle size distribution, as observed in Section 3.3.1 for Ti(C,N), experienced faster contractions than those with a unimodal distribution. Smaller particles facilitated the onset of contraction at lower temperatures than materials composed predominantly of larger particles, which later dominate the contraction process [145]. In this study, the temperature at which the influence of larger particles became predominant was determined to be 800 °C.

Furthermore, the observation that both materials began to contract significantly at approximately 1200 °C suggests that this phenomenon is associated with the formation of the FeNi alloy and, consequently, the onset of liquid-phase diffusion.

The dimensional changes observed in both materials during sintering were minimal, indicating no risk of structural failure. As a result, the materials were successfully compacted and sintered using the largest die. Post-sintering contraction evaluations revealed reductions of up to 34 % in WC and 32 % in Ti(C,N). These results were aligned with the measurements obtained from the dilatometric tests, reaffirming that materials with larger grain sizes underwent less shrinkage during the sintering process.

5. Mechanical Characterisation

The mechanical characterisation of manufactured materials is a key focus of this research, as it provides an understanding of their behaviour under various load and temperature conditions. As previously described, the materials were successfully manufactured with appropriate microstructure and high relative density, but evaluating their mechanical properties in comparison with those of commercial materials is essential to assess their industrial validity. To this end, the H12 material, a hardmetal supplied by Hyperion Materials & Technologies was selected as a reference.

5.1. Presentation of study materials

5.1.1. Composition

According to the manufacturer's specifications, the H12 material consists of a ceramic matrix of tungsten carbide (WC) and a metallic phase containing 12 wt% cobalt. From this point onward, it will be referred to as WC-12Co. However, the provided composition does not specify the presence of additional elements, making it necessary to conduct an X-ray fluorescence (XRF) analysis to determine its exact composition. The detailed elemental composition of the WC-12Co material used as a reference is presented in Table 5.1.

Table 5.1. X-Ray Fluorescence results of WC-12Co Material.

Element	wt % normalised
W	75.8
Co	11.8
Zr	7.3
Fe	3.9
And	0.8
Cr	0.4

Compositional analysis of the material identified a total of sixteen elements. However, only the six elements with a representation greater than 0.3 % are included, with the remaining compositional elements considered negligible. Due to the limitations of the XRF technique, quantitative data are only reliable for elements with atomic numbers greater than thirteen. As a result, lighter elements are either undetected or their presence cannot be confirmed with certainty, so carbon content is omitted from Table 5.1. Additionally, the data have been normalised, assuming that all detected tungsten (W) is present in the ceramic phase as WC.

The analysis revealed that the most abundant elements were tungsten (W) and cobalt (Co), with the Co content closely aligned with the percentage provided by the manufacturer. Small amounts of zirconium (Zr) and yttrium (Y) suggest their deliberate addition in the form of oxides. These oxides are commonly introduced to enhance oxidation resistance, as they form stable compounds at high temperatures. Furthermore, Zr and Y oxides mitigate excessive grain growth and contribute to the production of harder cemented carbides [146]. The presence of iron (Fe) may improve the material's toughness, while the presence of chromium (Cr) likely enhances its oxidation resistance.

After the main elements of the WC-12Co reference material were identified, the same XRF analysis was conducted on the materials sintered in argon. The objective was to confirm that the initial elements were retained in the correct proportions and to verify the absence of impurities introduced during the sintering process. The results of this analysis are presented in Table 5.2.

Table 5.2. X-ray Fluorescence Compositional Analysis Results of WC-FeNi and Ti(C,N)-FeNi Materials.

WC-FeNi-0.5C			Ti(C,N)-FeNi-0.5C		
Element	wt % th	wt % norm	Element	wt % th	wt % norm
WC	88.7	90.2	Ti	71.9	76.2
Fe	9.9	8.6	Fe	24.4	20.7
Ni	1.4	1.2	Ni	3.6	3.1

As expected, the compositional results did not reveal any unwanted elements and showed a high agreement between the theoretical values introduced and the experimental values. Since C and N are light elements, they were not detected; however, it is assumed that they are combined within the materials in the form of WC and Ti(C,N), respectively. Not considering the content of C and N could be the reason for the slight deviation between the results, although it did not exceed a 15 % error.

5.1.2. Density

In Section 0, the density of the two manufactured materials has already been measured as a function of the sintering atmosphere; however, the increase in the size of the sintered part is a determining factor in measuring this property again. The feasibility of increasing the size of the pressing die without affecting the sintering process is crucial. A simple way to confirm this increase while comparing the manufactured materials with the commercial ones is to determine the density using the Archimedes method. In Table 5.3, the obtained data and the calculated porosity are collected.

Table 5.3. Characterisation of the different materials.

Material	ρ_{th} (g/cm ³)	ρ_{Exp} (g/cm ³)	Porosity (%)
WC-12Co	14.3	14.187 ± 0.001	1.0 ± 0.1
WC-FeNi	14.05	13.874 ± 0.004	1.3 ± 0.3
Ti(C,N)-FeNi	5.6	5.42 ± 0.02	4.3 ± 0.3
Ref Ti(C,N)-FeNi [147]	5.6	-	$0.44 \pm 0.01^*$

* Standard deviation in %. The standard error is not available in the reference.

An analysis of the porosities of the materials revealed that both WC-FeNi and Ti(C,N)-FeNi achieved densification levels comparable to those obtained using the smaller die. This result represents a significant advancement, as the sintering of ceramic components is inherently challenging due to their fragile nature.

Consequently, the ability to produce larger pieces with low porosity is a noteworthy accomplishment.

The Ti(C,N)-FeNi material did not exceed the density of the reference cermet, as the latter already exhibited exceptionally low porosity, measured at 0.44 %. On the contrary, the WC-FeNi material achieved densification similar to that of the WC-12Co reference material. Successful sintering a material with a density comparable to that of a commercial counterpart is a significant milestone that underlines the effectiveness of the manufacturing process.

Nonetheless, it is important to note that in estimating the density of WC-12Co, the negligible contribution of minority elements identified in the XRF analysis was assumed. By disregarding these elements, the density of the commercial material may have been overestimated, potentially indicating a porosity within the material than the initially estimated.

5.1.3. Microstructure

To find differences between the microstructures of the three materials, a sample of each one was polished, obtaining the images presented in Figure 5.1 a, b, and c.

On all micrographs, two distinct phases were observed. The ceramic phase appeared brighter in WC-based materials, while the darker phase corresponded to the Co-rich and FeNi-rich metallic phases, respectively. Conversely, the ceramic phase was darker in the Ti(C,N) material, while the FeNi metallic phase exhibited a lighter tone.

Evidence of liquid-phase sintering was apparent in all cases, as indicated by the characteristic geometric shapes associated with this process, as described in Section 4.2.1. The results showed minimal differences between the microstructural characteristics of the fabricated materials and those of the reference material. This similarity indicates that the manufacturing methods employed successfully replicated the microstructural characteristics of the reference material with a high degree of precision.

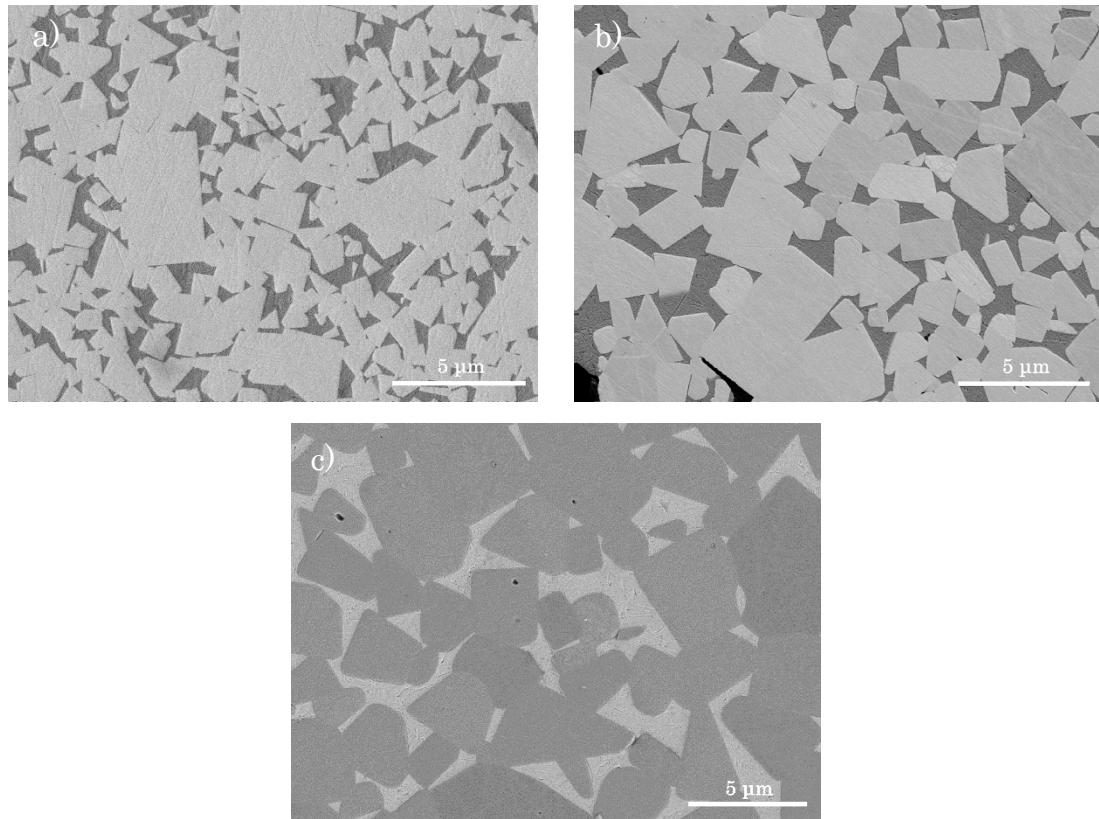


Figure 5.1. SEM micrographs of the surface. a) WC-12Co, b) WC-FeNi. The light grey grains correspond to the WC, whereas the dark greys show the metallic phase. c) Ti(C,N)-FeNi. The dark-toned grains correspond to Ti(C,N), while the lighter-toned grains show the FeNi metallic phase. In all cases, the areas shown in black are pores.

5.2. Mechanical properties and effect of temperature

The analysis of mechanical properties is essential to evaluate the performance of the materials developed. Tests have been conducted to measure the flexural strength, hardness, fracture toughness, and wear resistance of the manufactured materials, and how temperature affects these properties. The results obtained are intended to provide an overview of the structural integrity and durability of the materials compared to the reference materials. The data obtained from these mechanical tests are presented and analysed in the following sections, highlighting the most relevant characteristics.

5.2.1. Flexural Strength

The flexural strength was evaluated using a three-point bending configuration at a test speed of 200 $\mu\text{m}/\text{min}$ test speed. The tests were carried out from room

temperature to 800 °C in an oxidising atmosphere, with three tests performed for each material and condition. The stress-strain curves for the materials are presented in Figure 5.2.

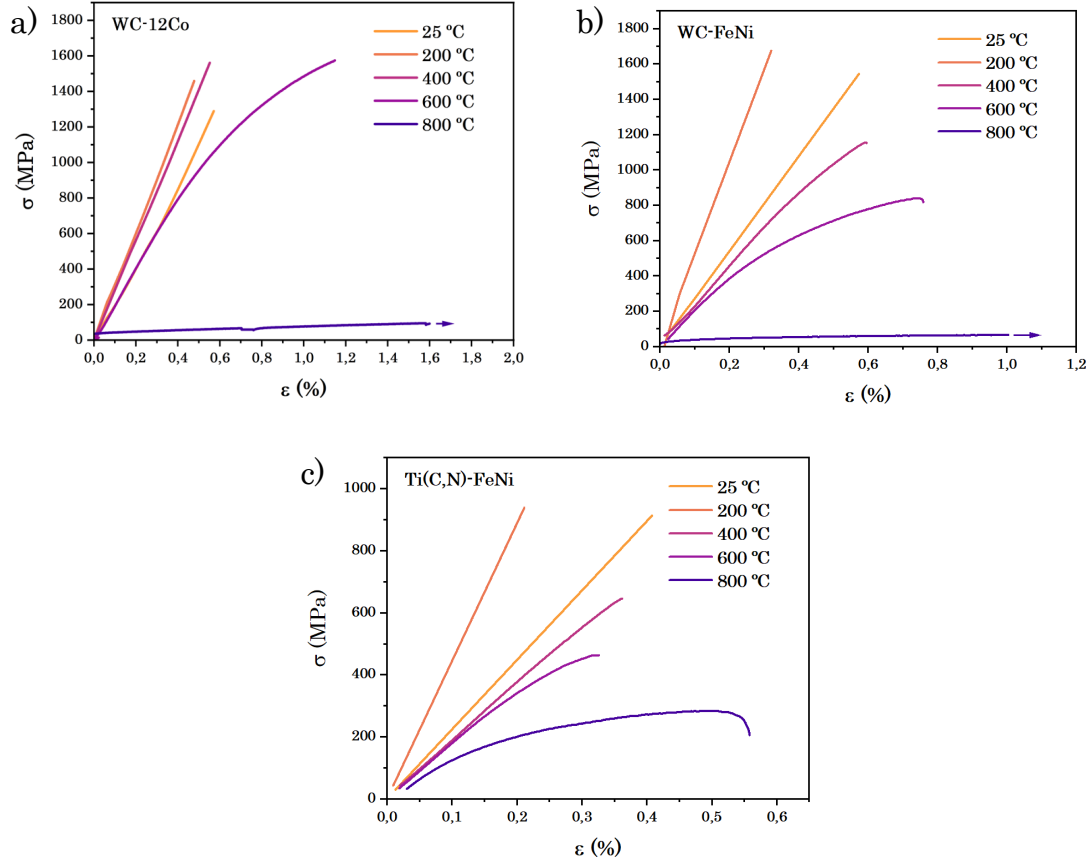


Figure 5.2. Stress vs. strain curves after three-point bending tests. a) WC-12Co, b) WC-FeNi and c) Ti(C,N)-FeNi.

The longitudinal and cross-sections were evaluated to identify potential anisotropy resulting from the manufacturing process. However, the results confirmed that the materials were isotropic, thus only the longitudinal cross-section results are shown.

The stress-strain curves demonstrated elastic behaviour up to fracture in all materials at room temperature and 200 °C, coinciding with their maximum flexural strength values. At 400 °C, a shift was observed in materials with a FeNi matrix, characterised by signs of plastic deformation and reduced observed strength. In contrast, the WC-Co material retained its brittle behaviour and superior properties up to 600 °C, when the first signs of ductility were observed.

At 600 °C, all materials exhibited a sharp decrease in flexural strength and increased plastic deformation. At 800 °C, materials containing WC displayed a

pronounced loss of mechanical properties, attributed to the degradation of tungsten in oxidising atmospheres, as reflected in their stress-strain curves. On the contrary, Ti(C,N)-FeNi, while following a trend similar to the other materials, maintained greater structural integrity, as evidenced by the shape of its curve at maximum temperature.

For ease of comparison, Figure 5.3 illustrates the average flexural strength as a temperature function, including error bars for clarity. It is important to note that the squared data points do not correspond to the ultimate strength but represent the elastic limit at 0.2 % plastic deformation in cases where macroscopic plastic behaviour was observed.

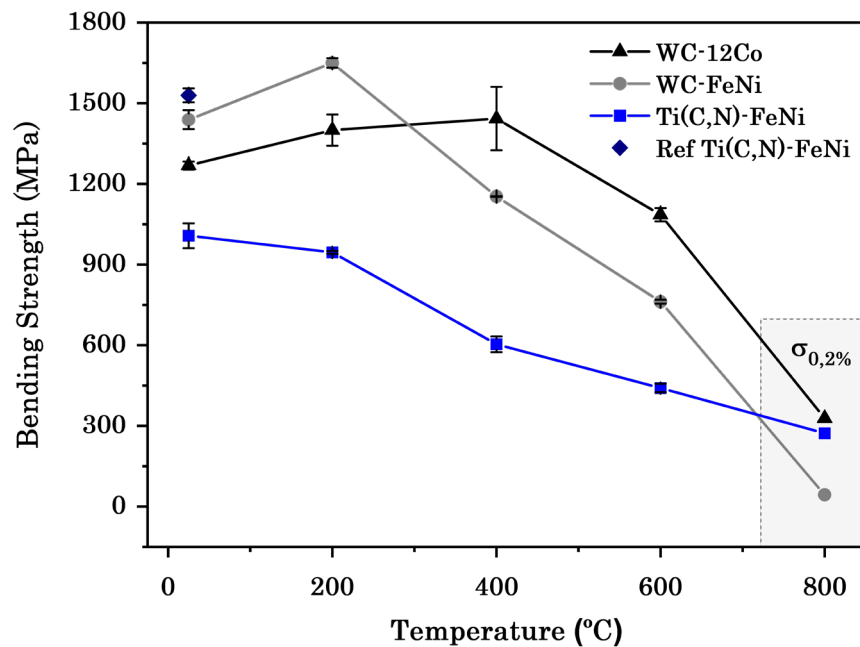


Figure 5.3. Medium flexural strength as a function of temperature for WC-12Co, WC-FeNi and Ti(C,N)-FeNi materials. Bending strength of Ti(C,N)-FeNi retrieved from [148] is also shown. The error bars correspond to the standard deviation of the experimental data. Due to plastic behaviour, the reframed region corresponds to the yield strength data of 0.2 %.

All materials displayed a similar behaviour at low and intermediate temperatures. The maximum flexural strength of the manufactured Ti(C,N)-FeNi material was 66 % lower than that of the Ti(C,N)-FeNi material reported in [148], however, its performance across the whole temperature range remains unknown, since its was only tested at room temperature.

Among the materials evaluated, those containing WC exhibited higher flexural strength, which gradually decreased with increasing temperature and was nearly absent at 800 °C. Among the WC-containing materials, the FeNi matrix provided a better resistance than the Co matrix, resulting in improved properties in the manufactured material relative to the commercial reference.

As the temperature increased, the the flexural strength initially showed a tendency to increase. However, this trend reversed at 400 °C, where oxidation of the FeNi phase reduced the strength of both WC-FeNi and Ti(C,N)-FeNi materials. Beyond this point, all materials exhibited an inversely proportional relationship between temperature and flexural strength: the higher the temperature, the lower the strength.

These observations suggest that the FeNi matrix improved the material's mechanical properties of the material compared to Co at temperatures below 200 °C. However, this advantage reversed at higher temperatures, where Co outperformed FeNi, because of its superior stability in oxidising environments.

5.2.2. Fracture Toughness

The fracture toughness as a temperature function was evaluated using the same assembly as in the three-point bending tests. However, the specimens included a pre-fabricated notch, introduced via laser, to facilitate this specific measurement.

The results are presented in Figure 5.4, which differentiates the materials that exhibited plastic deformation. Fracture toughness was calculated using a secant line with a slope equal to 95 % of the elastic zone, ensuring consistency and precision in the evaluation.

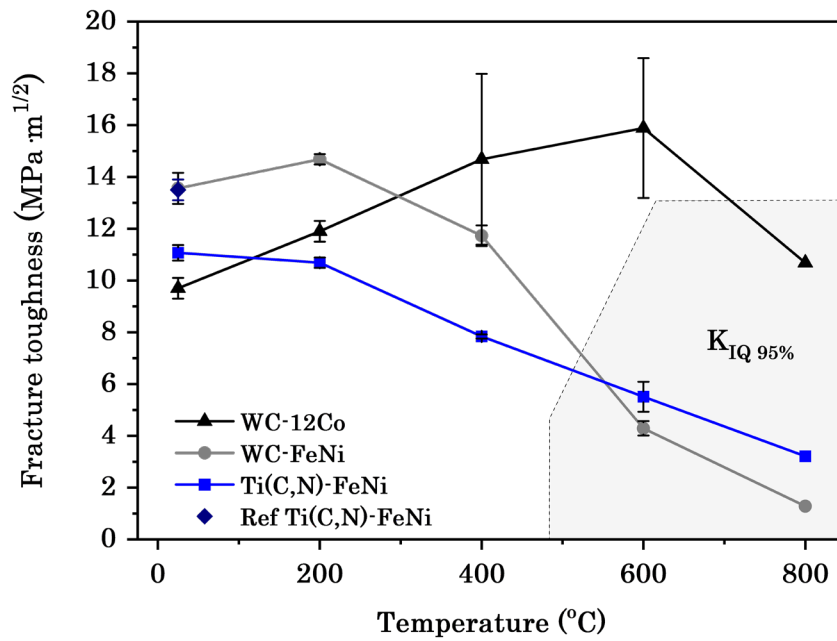


Figure 5.4. Temperature-dependent fracture toughness for WC-12Co, WC-FeNi and Ti(C,N)-FeNi materials. The error bars correspond to the absolute error of the experimental data. The boxed region corresponds to the data at 95 % of the elastic zone due to plastic behaviour.

Fracture toughness tests indicated brittle behaviour at low temperatures. Materials with a FeNi metallic phase exhibited better fracture toughness at room temperature than those with a Co phase. This is consistent with the findings of other studies, which report higher fracture toughness in materials with FeNi metallic phases compared to Co-based ones [149].

At room temperature, the fracture toughness of Ti(C,N)-FeNi was 11 MPa m^{1/2}, compared to 13.5 MPa m^{1/2} for the same material studied by M. de Dios and used as a reference. Although the toughness value at 25 °C was lower, at 200 °C, Ti (C, N) ·FeNi showed the first signs of FeNi phase deterioration, whereas the WC-12Co reference material maintained superior toughness.

Up to 400 °C, WC-FeNi and Ti(C,N)-FeNi materials displayed stable fracture toughness. Beyond this point, both materials experienced a sharp decline in toughness, consistent with the trends observed in flexural strength. On the contrary, WC-12Co improved its toughness up to 800 °C, where plastic deformation began to dominate.

Compared to all-ceramic materials, the metallic phase of cemented carbides and cermets plays a crucial role in enhancing fracture toughness. The metallic phase

undergoes plastic deformation before fracturing, absorbing energy during this process [147]. Combined with the ceramic phase, this deformation redistributes stresses within the microstructure, effectively preventing crack propagation and enhancing fracture strength.

At temperatures of 400 °C and above, the behaviour of FeNi-based materials became remarkably similar. The improved toughness of WC-12Co at elevated temperatures is attributed to the Co phase in its metallic matrix, which contributes to toughness at higher temperatures [150].

The reduction in mechanical properties observed at temperatures above 400 °C in the fabricated materials and 600 °C in the reference material suggests the formation of oxides in both the metallic and the ceramic phases. This conclusion is supported by the behaviour of WC-FeNi, which, despite sharing the same metallic phase as Ti(C,N)-FeNi, exhibited superior properties at all temperatures up to 600 °C.

At 800 °C, the properties of WC-FeNi decreased sharply, indicating a microstructural change in the WC phase. A similar trend was observed in WC-12Co, further supporting the hypothesis that oxidation of the metallic and ceramic phases significantly impacted mechanical performance.

However, fracture toughness values obtained at the highest test temperatures cannot be considered completely reliable; the substantial formation of oxides at the bottom of the notches, leading to rounding of the crack tip, made it difficult the precise measurement of notch size.

5.2.3. Fractographic Analysis

A fractographic study of each material was conducted to analyse, find and justify the mechanical behaviour at both micro and macroscopic levels. This made it possible to decide the failure mechanisms present at different temperatures and to detect the formation of oxides after tests at high temperatures in the presence of oxygen. Figure 5.5, 5.6, and 5.9 show images of the fracture surfaces obtained by SEM.

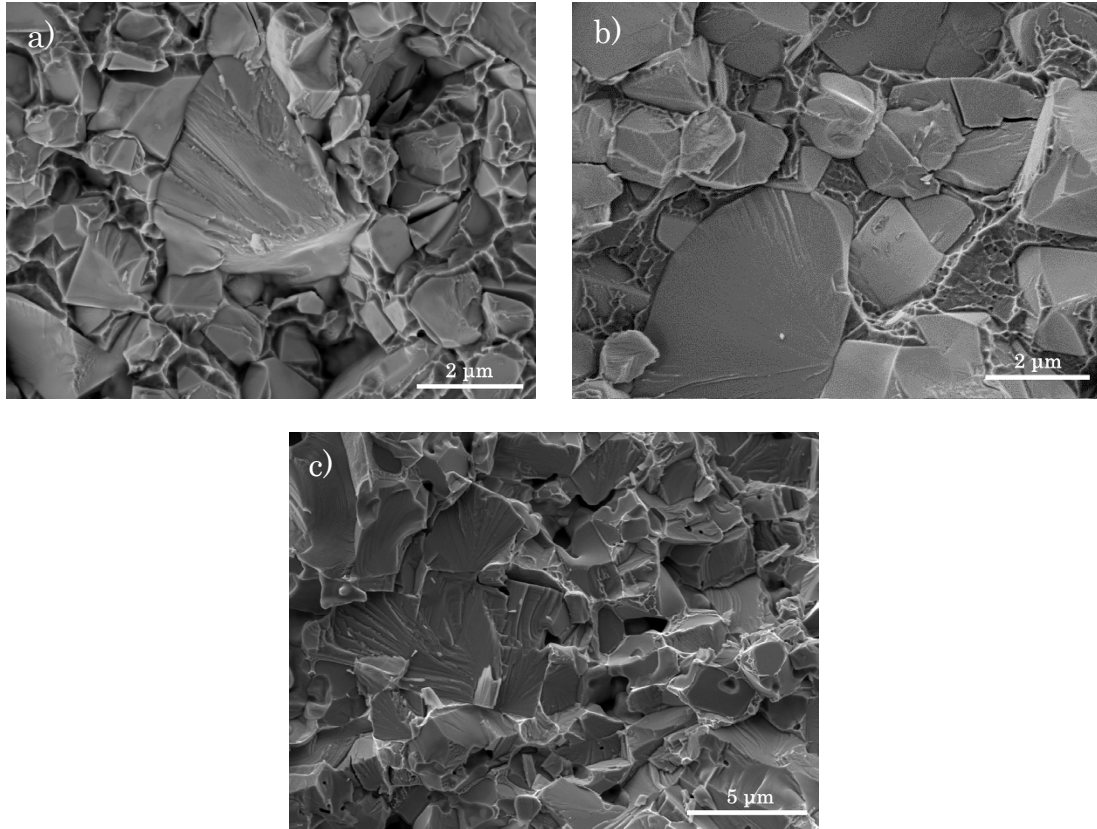


Figure 5.5. SEM obtained fracture surfaces at 25 °C. a) WC-12C, b) WC-FeNi, and c) Ti(C,N)-FeNi. The same behaviour was observed at 200 °C.

Figure 5.5 shows the fracture surfaces of the materials at 25 °C, with fractography identical to that observed at 200 °C. At the macroscopic level, the fractures exhibited brittle behaviour, consistent with the results of the bending and toughness tests. However, detailed microscopic analysis revealed four distinct types of fracture mechanisms: ductile fracture within the metallic phase, intergranular and transgranular brittle fractures in the ceramic phase, and delamination at the interface between the metallic and ceramic phases.

As a result of their ductile nature at room temperature, the FeNi and Co metallic phases underwent plastic deformation, which could be observed in the deformed areas surrounding the ceramic particles. In the ceramic phase, intergranular brittle fractures occurred where the grains joined, while larger grains of WC and Ti(C,N) exhibited characteristic cleavage patterns, indicating transgranular brittle fractures.

Additionally, some disjoint regions were observed where the metallic phase had detached from the ceramic phase were observed. Despite this, the overall adhesion

between the two phases was strong, contributing to the deviation of the crack propagation path. This energy dispersion through the metallic phase helped to achieve improved mechanical properties.

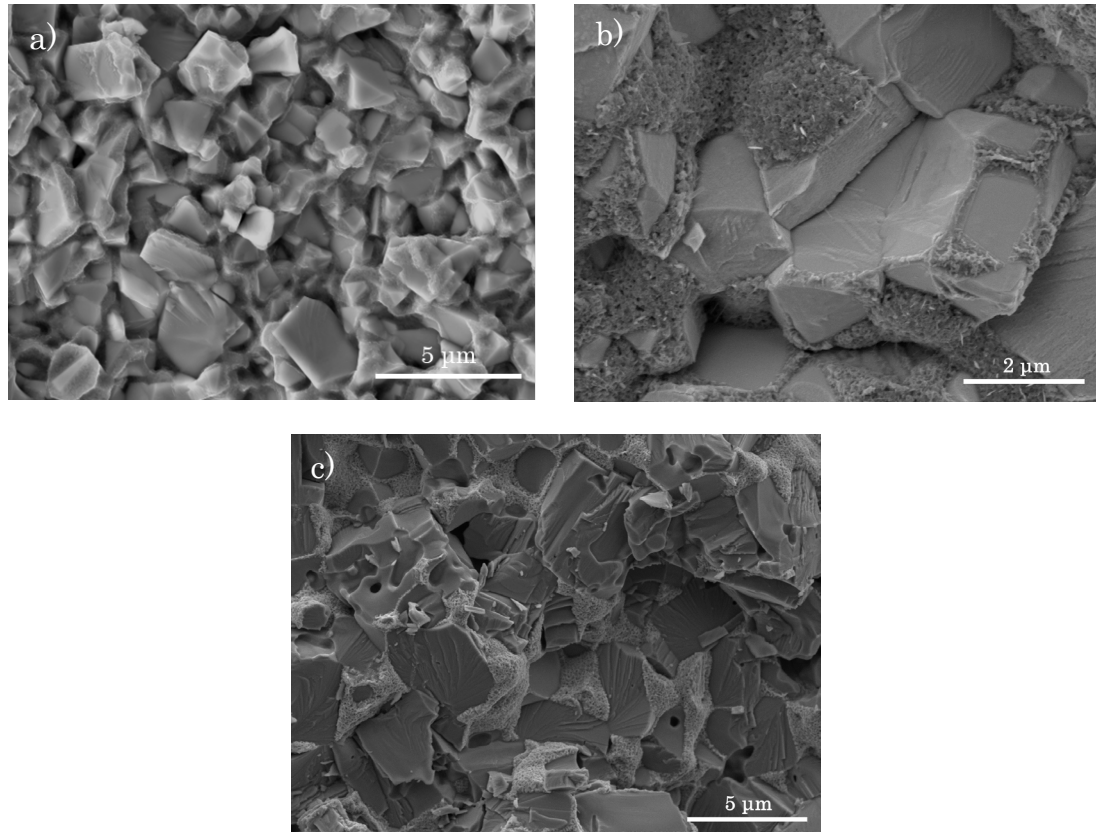


Figure 5.6. SEM obtained fracture surfaces at 400 °C. a) WC-12C, b) WC-FeNi, and c) Ti(C,N)-FeNi.

Figure 5.6, shows the fracture surfaces of the three materials at 400 °C. The analysis of these surfaces elucidates the differences in mechanical properties observed during testing. At this temperature, the resistance of the manufactured materials began to decline, coinciding with the formation of oxides in the metallic phase surrounding the ceramic particles in WC-FeNi and Ti(C,N)-FeNi.

In contrast, WC-12Co maintained ductile fracture behaviour in its metallic phase, exhibited intergranular and transgranular brittle fractures in its ceramic phase, and showed some decohesive zones. Despite this, it retained its mechanical properties and structural integrity without any signs of oxidation.

The fractography of WC-FeNi and Ti(C,N)-FeNi revealed the presence of oxides within their structures, contributing to the reduction in mechanical properties. The oxidation was primarily associated with the FeNi phase; however, nickel is

not expected to oxidise at temperatures below 700–1000 °C [151], [152], effectively ruling out the oxidation of Ni at 400 °C.

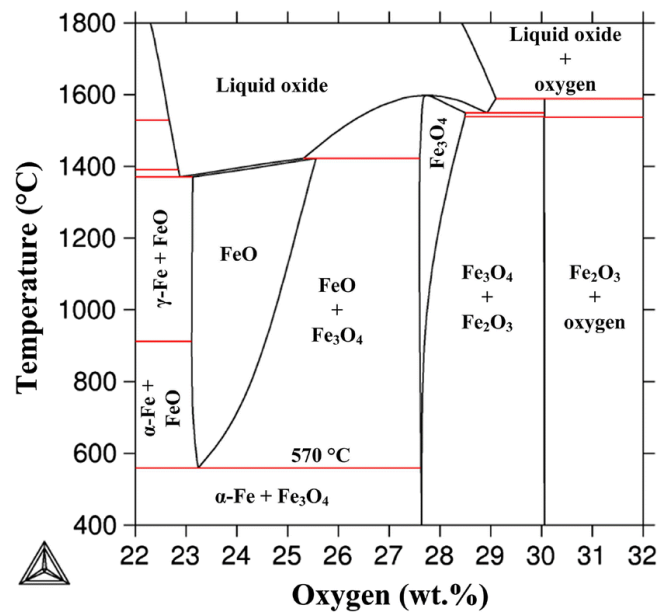


Figure 5.7. Binary phase diagram of the Fe-O system retrieved from [153].

As shown in the diagram of Figure 5.7 when iron is subjected to temperatures above 570 °C, it is possible to form three different oxides: wüstite FeO, magnetite Fe₃O₄ and hematite Fe₂O₃. However, at temperatures below 570 °C, only two phases of Fe are found, Fe₂O₃ and Fe₃O₄ [9], [10]. A Raman analysis was conducted to accurately identify the oxides at 400 °C, showing the results obtained in Figure 5.8.

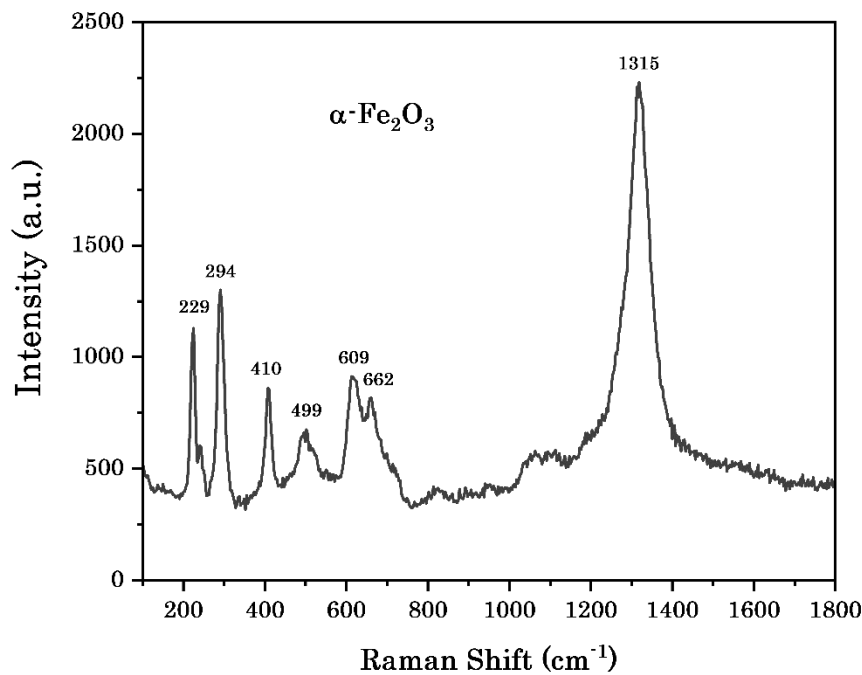


Figure 5.8. Oxide Raman Spectrum $\alpha\text{-Fe}_2\text{O}_3$ detected at 400 °C.

Raman analysis identified peaks corresponding to the oxide present at 400 °C in the FeNi metallic phase, which other authors have associated with $\alpha\text{-Fe}_2\text{O}_3$ [154]. Given the relatively low temperature, it is likely that the oxides detected were in an early stage of development.

Figure 5.9 illustrates the fracture surfaces of the three materials at 600 °C, where complete oxidation was observed. EDX maps are included for each fractography to provide further insight into the processes that occur on the surfaces.

Both WC-12Co and WC-FeNi exhibited signs of oxidation in both the metallic and ceramic phases. On the contrary, Ti(C,N)-FeNi underwent oxidation only in its metallic phase.

The WC grains began to expand in the ceramic phases of WC-12Co and WC-FeNi, eventually losing their structural integrity. Although WC is the primary component, the oxidation mechanism is entirely driven by tungsten (W). At temperatures below 400 °C, when tungsten is exposed to oxygen, the first oxidation stage begins, producing a fine oxide with a bluish-purple matrix, corresponding to $\text{WO}_{2.92}$ or $\text{WO}_{2.72}$. The presence of this oxide is a clear indicator of the onset of material degradation.

Oxidation remains superficial until the oxide layer completely covers the surface; diffusion processes emerge. In the subsequent stage, as the oxide layer completely envelops the W particles, these diffusion processes dominate, enabling the growth of $\text{WO}_{2.92}$ or $\text{WO}_{2.72}$ into WO_3 . At 600 °C, WO_3 —a porous and oxygen-permeable oxide with a yellowish matrix— can be appreciated. The growth rate of WO_3 depends on the diffusivity of oxygen ions within the oxide layer [155].

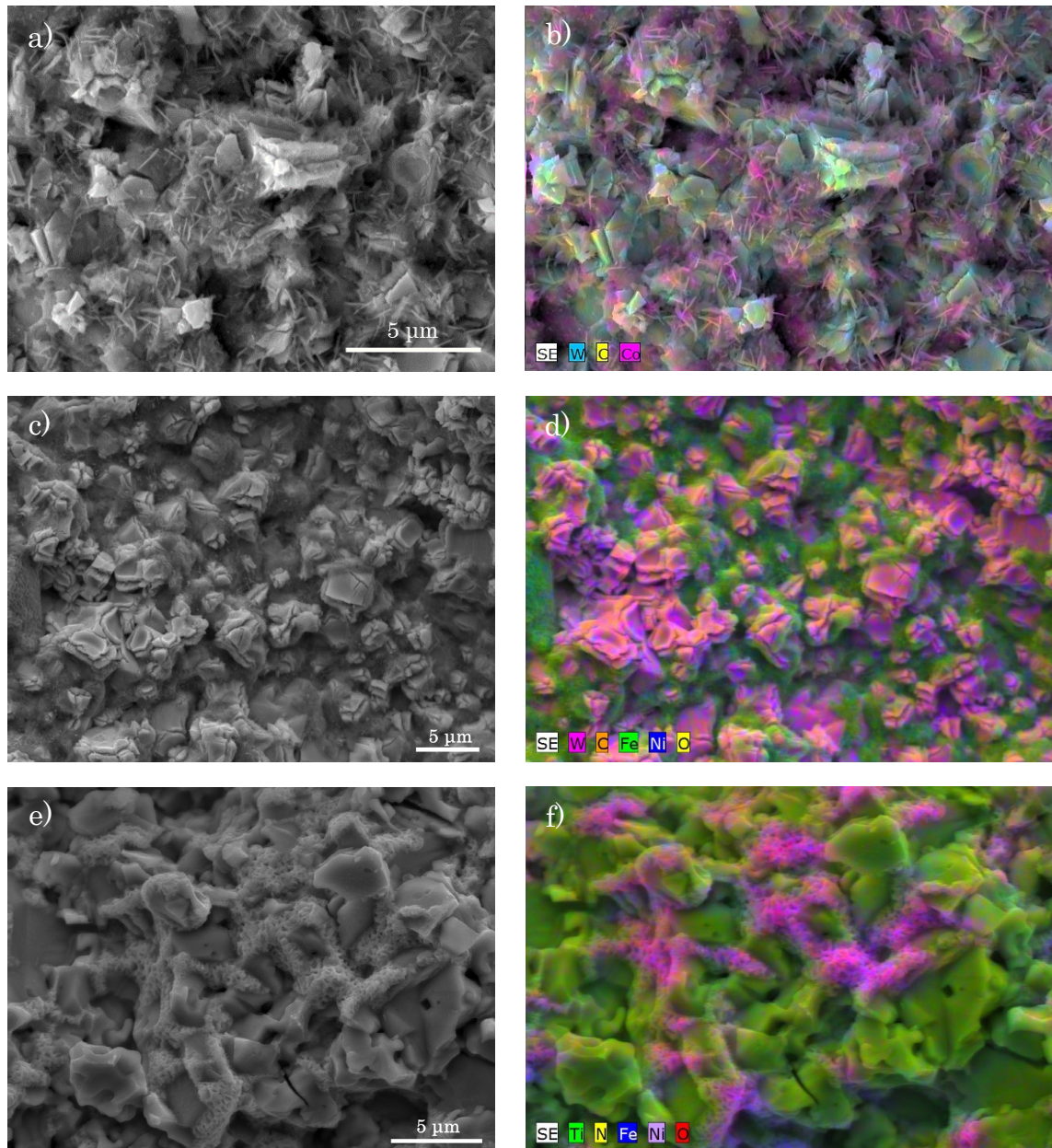


Figure 5.9. Fracture surfaces obtained by SEM-EDX at 600 °C. a-b) WC-12C, c-d) WC-FeNi, and e-f) Ti(C,N)-FeNi.

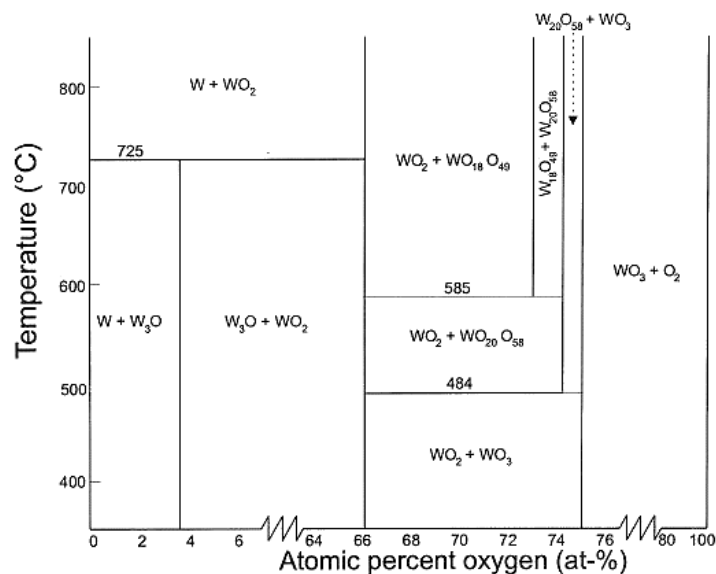


Figure 5.10. Binary diagram of the W-O system [156].

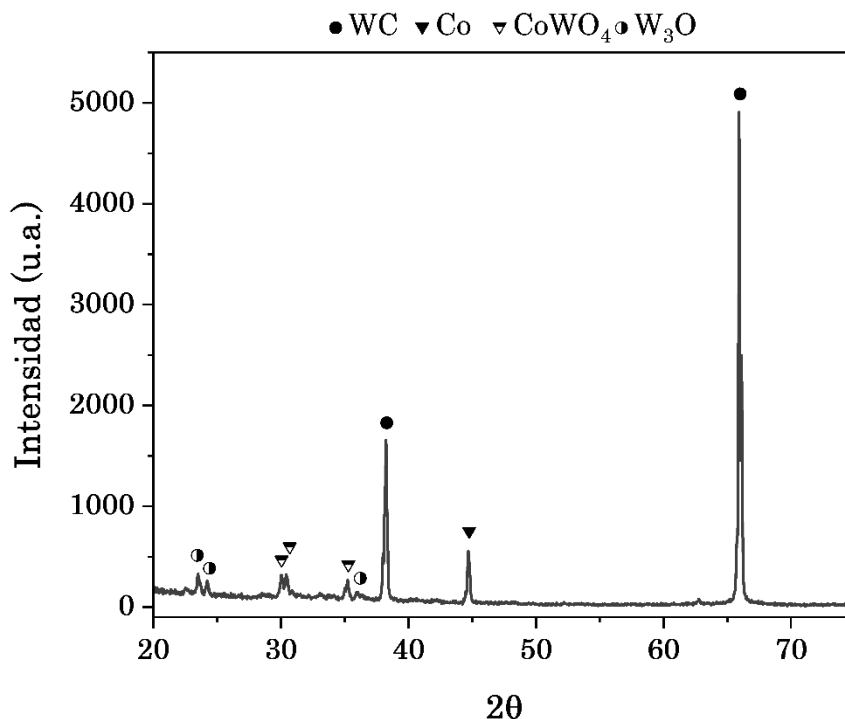


Figure 5.11. DRX peaks indexed at 600°C in the WC-12Co material.

To corroborate these results and verify whether, as suggested in previous research, oxides formed on the WC-Co substrates consist of WO₃ and CoWO₄ [156], a DRX analysis was performed on the WC-12Co sample. At the same time, it was heated to 600 °C. The indexed peaks are presented in Figure 5.11.

The analysis confirmed the presence of WC and Co at 600 °C, along with the two expected oxides: WO_3 and CoWO_4 . These findings support the degradation of the WC ceramic phase of the WC during the formation of WO_3 , which correlates with the observed decrease in flexural strength and toughness.

As noted previously, the metallic phases in all materials underwent significant oxidation at 600 °C. The $\alpha\text{-Fe}_2\text{O}_3$ oxide, initially formed in the FeNi phase at 400 °C, continued to increase in presence at higher temperatures, further diminishing mechanical properties.

On the contrary, the Co present in the metallic phase of WC-12Co combined to form CoWO_4 , as observed in the fractographic analysis. This oxide exhibited an acicular morphology, consistent with the findings of previous studies [157].

5.2.4. Hardness as a function of temperature

Together with flexural strength and high-temperature toughness tests, an analysis of the effect of temperature on hardness was also conducted. Vickers hardness tests were performed under a 100 N load (HV10) for 15 s, ranging from 25 °C to 400 °C.

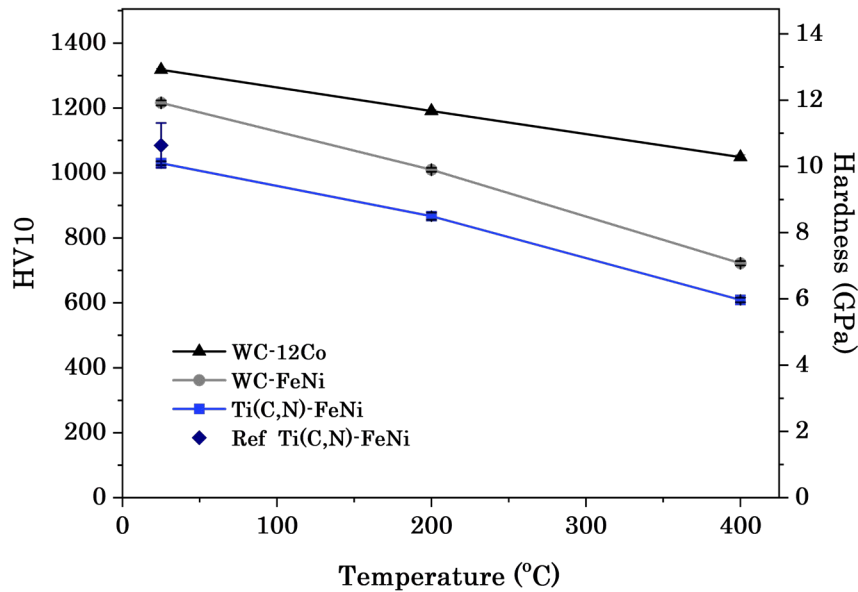


Figure 5.12. In-situ hardness of each of the materials as the temperature increases from 25 °C to 400 °C, along with the absolute error corresponding.

Although extending the tests to 800 °C would have been ideal, the oxidising atmosphere posed a risk to the integrity of the diamond indenter, limiting the evaluation to 400 °C. The results are presented in Figure 5.12.

The hardness trend observed in the manufactured materials mirrored that of the reference material: hardness decreased linearly with increasing temperature. However, WC-12Co consistently exhibited higher hardness values, averaging 11 % and 25 % higher than WC-FeNi at room temperature and 200 °C, respectively.

At 400 °C, this difference became more pronounced, with the hardness of the reference material being 31 % higher than WC-FeNi and 42 % higher than Ti(C,N)-FeNi. At room temperature, the hardness of the Ti(C,N)-FeNi material produced in [147] was comparable to the manufactured cermet, measuring 1085 ± 69 HV and 1030 ± 6 HV, respectively, marking the first property with values similar between the two materials.

Among the materials studied, WC-12Co demonstrated the highest hardness, with 1318 ± 4 HV, closely followed by WC-FeNi at 1216 ± 8 HV. Although both materials shared the same ceramic phase, the superior performance of WC-12Co was not attributed not to the ceramic phase alone but to the contribution of the metallic phase. Analysis of the elements comprising WC-12Co revealed small amounts of Zr and Y, probably added as oxides, specifically ZrO_2 stabilised with Y_2O_3 . These high-hardness and strong oxides, which remain stable at elevated temperatures, contribute to the enhanced hardness of the Co-based matrix in the analysed temperature range analysed [158].

Raman analysis of the surface was performed at 200 °C to explain the early decline in hardness observed in materials with a FeNi metallic phase. Figure 5.13 presents the peaks detected at 200 °C and 400 °C, corresponding to the rust phase, rust α - Fe_2O_3 , for comparison. At 200 °C, some peaks associated with α - rust α - Fe_2O_3 (e.g., 499 cm^{-1}) were identified, which had been more clearly defined at 400 °C. Additionally, faint indications of other peaks (e.g., 609 and 662 cm^{-1}) were observed, suggesting the early stages of oxide development that would become more prominent at higher temperatures.

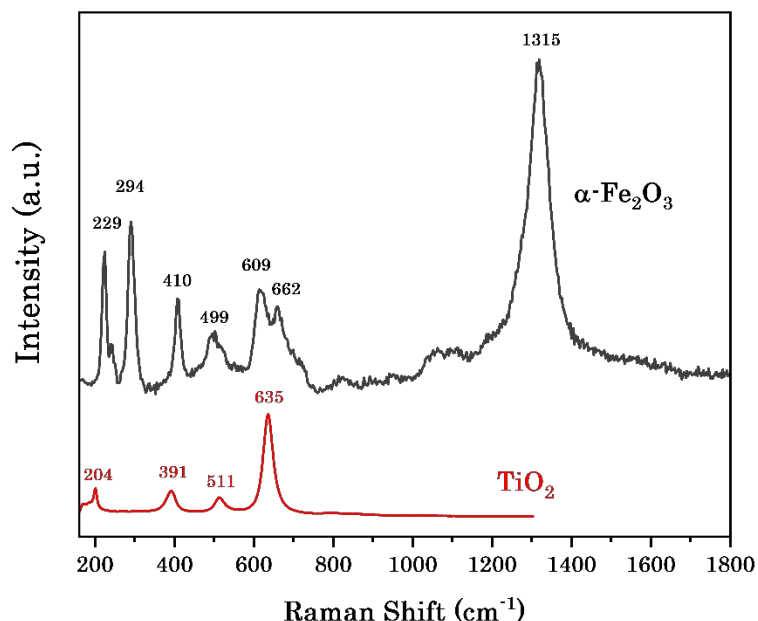


Figure 5.13. Comparative of and Oxide spectra Raman $\alpha\text{-Fe}_2\text{O}_3$ detected at 200 °C and 400 °C.

At 200 °C, the formation of $\alpha\text{-Fe}_2\text{O}_3$ appeared to have initiated. However, by the end of the hardness test, the results aligned with the satisfactory results observed in the bending and toughness tests conducted at the same temperature. The disappearance of the weak signals from some Raman peaks suggests early stages of oxide development. Thus, the oxidation detected at this temperature was concluded to be in its initial phase.

Because the oxide layer on the surface was thin, it did not significantly affect the overall mechanical behaviour of the material. However, during hardness measurements, the layers that progressively formed with increasing temperature were directly evaluated. At 200 °C, the oxidation of the FeNi phase began, causing a decrease in hardness, which continued linearly up to 400 °C. As the oxide layer grew, the hardness of the material gradually decreased.

On the contrary, WC-12Co did not show significant signs of oxidation, although its hardness also decreased linearly with temperature, as a consequence of increased ductility for the metallic phase. The reduction was less pronounced than that of FeNi-based materials, which can be attributed to the limited oxidation of the Co phase. Additionally, although minimal, trace elements such as Fe in the WC-12Co reference material contributed to susceptibility to oxidation.

Therefore, it was determined that the loss of hardness across all materials with increasing temperature resulted from surface oxidation. Materials with a predominantly Fe-based metallic phase exhibited more pronounced and rapid degradation than those with a Co-based phase. However, in both cases, the surface hardness declined as the temperature increased.

Further analysis of hardness as a function of atmosphere, discussed in Section 4.2.4, highlighted the significant influence of porosity and grain size on this property. The porosity of WC-12Co (1.0 %) was comparable to that of WC-FeNi (1.3 %), as noted in Section 5.1.2. A detailed study of the average grain surface area was conducted to assess the impact of grain size, following the methodology outlined in Section 4.2.4.

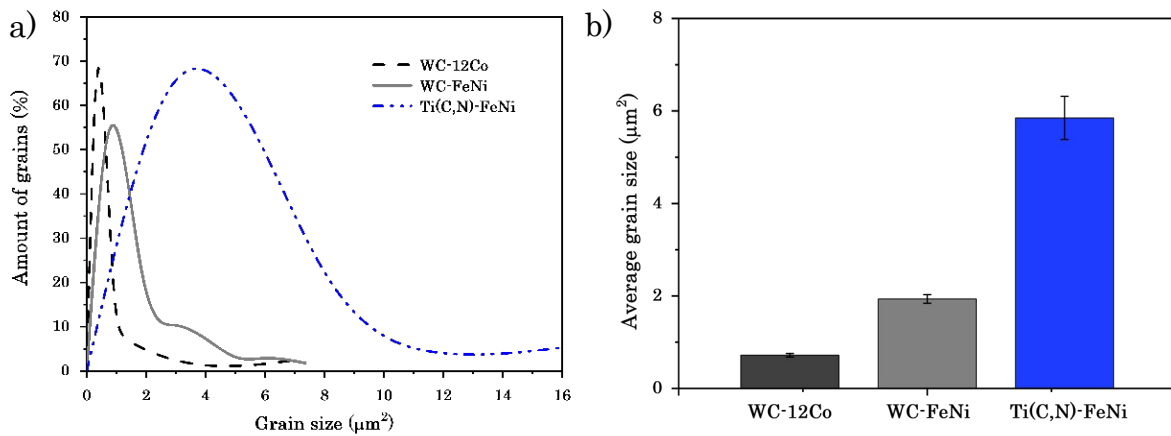


Figure 5.14. Area of each grain found in each material a) Distribution of the percentage of each area size, b) Average sizes of the areas, including the error bars referring to the standar error.

Figure 5.14a shows the percentage of grains of different sizes present in the microstructure of the three materials. The narrowest size distribution was found in WC-12Co, with 70 % of grains close to 0.5 μm^2 , followed by WC-FeNi, with 55 % of grains of 1 μm^2 . Ti(C,N)-FeNi had the widest distribution, with almost 70 % of particles of 3.5 μm^2 . The average area of the grains in each microstructure was estimated to provide a more general view of the materials, obtaining the results of Figure 5.14b. This analysis once again highlighted the correlation between the lower hardness and a broader grain size distribution, as observed in Ti(C,N)-FeNi. A similar conclusion was drawn for WC-FeNi, which exhibited a narrower size distribution and smaller grain size than that of Ti(C,N)-FeNi, resulting in intermediate hardness among the three evaluated materials.

On the contrary, WC-12Co demonstrated the highest hardness, coupled with the narrowest size distribution and the smallest grain size. These observations suggest that robust alloying elements in the metallic phase play a decisive role in controlling grain distribution and size, thereby contributing to the superior hardness.

In summary, the findings confirmed that, as previously observed, a smaller grain size is directly associated with higher hardness. Furthermore, the alloying elements in the WC-12Co reference material contribute significantly to its overall hardness. However, as the temperature increases, the progressive formation of surface oxides leads to a linear reduction in hardness across all materials. This reduction is more pronounced in materials with a metallic phase based on the Fe-Ni system.

5.2.5. Diffusivity and Thermal Conductivity

Following completion of mechanical strength tests and evaluation of hardness with increasing temperature, a study on the thermal diffusivity and conductivity of the materials was performed. Thermal conductivity is critical to determine efficiency in applications such as cutting and tool life. Effective heat dissipation is essential to mitigate issues such as excessive wear, thermal deformation, and material damage.

Thermal diffusivity measurements were performed to complement the tribological tests, assessing the thermal diffusivity of the manufactured materials alongside the reference material. The effect of temperature on thermal properties was evaluated through tests conducted over a range of 25 °C to 800 °C, in 100 °C intervals, with a controlled heating ramp of 10 °C/min.

The specific heat of each material is required to calculate thermal conductivity. However, as this data were unavailable, graphite was employed as a reference for calibration. The results of the tests are presented in Figure 5.15.

The results of this trial revealed two distinctly different behaviours. In composite materials with WC as the ceramic phase, thermal diffusivity decreased significantly with increasing temperature, dropping by nearly 50 %. On the contrary, the Ti(C,N)-FeNi material maintained stable thermal conductivity across the entire temperature range.

Remarkably, the manufactured WC-FeNi material exhibited a thermal behaviour comparable to that of the commercial reference material, demonstrating high thermal diffusivity values at room temperature.

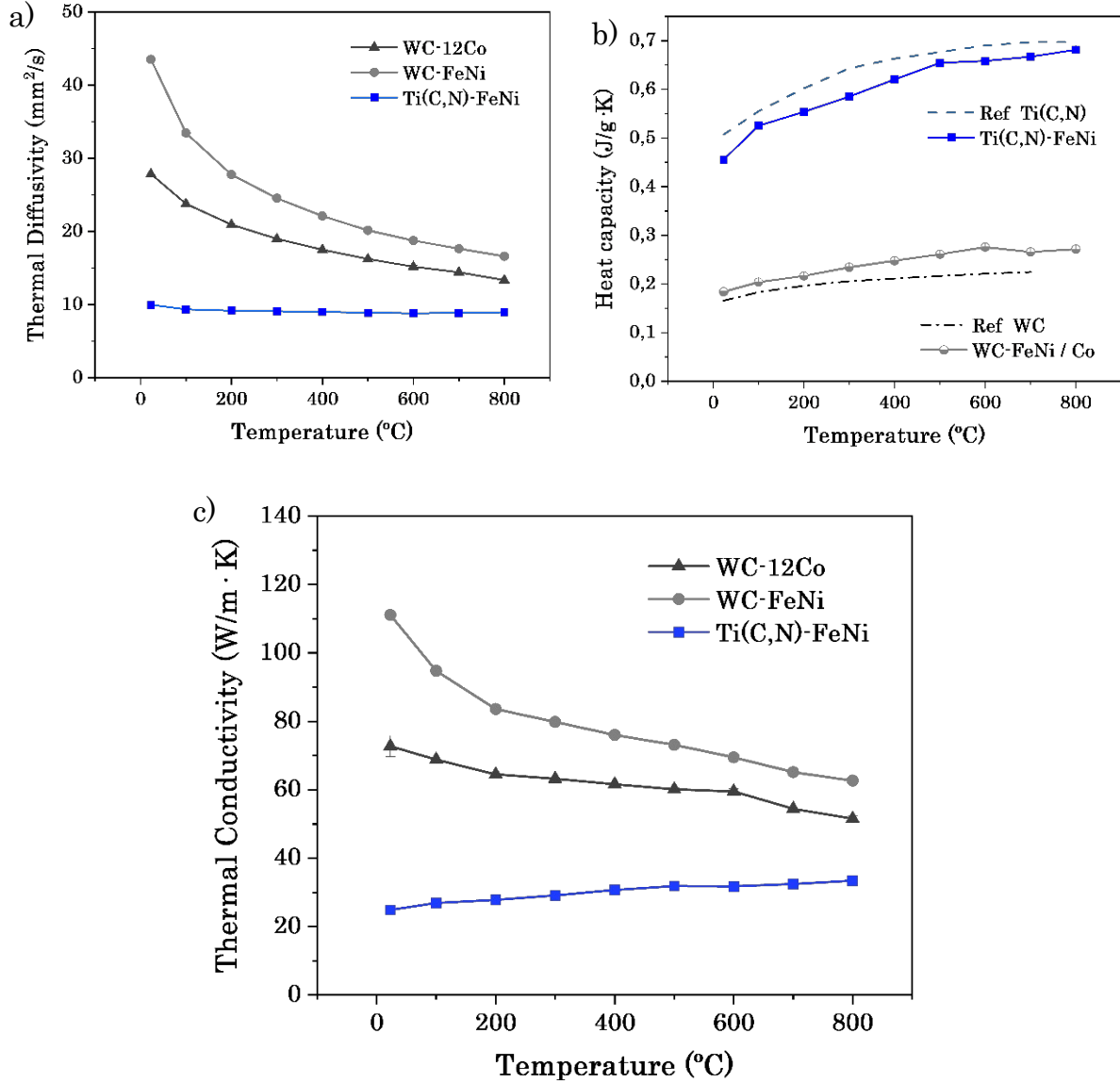


Figure 5.15. a) Thermal diffusivity, b) Specific heat and c) Thermal conductivity, in the temperature range of RT to 800 $^{\circ}\text{C}$ in vacuum ($\times 10^{-5}$ mbar). All measures are accompanied by the bar error corresponding to the absolute error of the experimental data.

The difference in the behaviour of materials based on WC and Ti(C,N) lies in their internal structure. The W-C has a complex mixture of metallic, covalent, and ionic bonds, allowing electrons to move freely and conduct heat more efficiently at room temperature [158].

This behaviour changes with increasing temperature; in metals, free electrons are the primary carriers of heat. As the temperature increases, atomic vibrations in the crystal lattice intensify, leading to more frequent collisions between electrons and atoms. These collisions reduce electron mobility, resulting in decreased thermal conductivity. In W-C bonds, the scattering of electrons increases with temperature, further limiting their heat transport capability. Conversely, Ti-C-N bonds, being predominantly covalent, remain stable regardless of temperature [159].

Thermal conductivity is also significantly influenced by the material's specific heat, which varies with temperature. The specific heat values observed in this study were consistent with those reported for WC and Ti(C,N) in similar materials [160], [161], [162], [163]. However, including Fe and Ni alloys caused a slight increase in the specific heat of Ti(C,N)-FeNi, mirroring the decrease observed in WC-FeNi.

Previous studies report that the thermal conductivity of Ti(C,N) at room temperature ranges from 15 to 35 W/m·K, WC ranges from 85 to 110 W/m.K, and metallic elements such as Fe, Ni, and Co exhibit values of approximately 75 W/m·K, 60 W/m.K, and 70 W/m.K, respectively [161], [163], [164], [165], [166], [167], [168]. The experimental results in this study corroborated these findings. The addition of Fe and Ni increased the thermal conductivity of the Ti(C,N) system but reduced it in the WC system. At low temperatures, the ceramic phase governed thermal conductivity. However, as the temperature increased, the contribution of the metallic phase became more significant.

At room temperature, the manufactured materials exhibited thermal conductivity values close to those of their dominant ceramic phases: 110 W/m·K for WC-FeNi and 25 W/m.K for Ti(C,N)-FeNi. At 800 °C, Ti(C,N)-FeNi maintained thermal stability, while the thermal conductivity of WC-12Co and WC-FeNi decreased significantly. WC-FeNi dropped to 62 W/m·K, and the reference material WC-12Co reduced to 51 W/m.K, showing an almost linear decline from 200 °C.

Heat generated by friction between the tool and the material must be dissipated efficiently during cutting processes to avoid excessive wear, thermal deformation, and material damage [160]. The results of this study complement the tribological analyses, as high thermal conductivity combined with a low coefficient of friction are strong indicators of good wear resistance.

This relationship was particularly evident in materials with a WC ceramic phase. The high thermal conductivity contributed to maintaining lower cutting temperatures, reducing the adhesion between the tool and the material. This ability to dissipate heat quickly helped to control the temperature, minimising the risk of thermal damage. On the contrary, materials with high thermal conductivity can support lower temperatures at the interface, reducing wear [169].

Materials such as WC-12Co and WC-FeNi, which showed higher thermal conductivity, exhibited lower wear rates during cutting, positioning them as superior options compared to Ti(C,N)-FeNi.

5.2.6. Tribological Analysis

The relationship between tribology and thermal conductivity plays a critical role in analysing the behaviour of materials in contact, as friction heat directly impacts the components' performance and durability. The study of friction and wear resistance is essential for characterising cemented carbides and cermets, mainly because their use in cutting tools depends heavily on these properties.

It is important to note that the friction and wear characteristics can vary significantly with increasing temperature due to mechanical and physicochemical changes. Tribological tests were carried out in the Advanced Materials Group laboratory belonging to the Czech Technical University in Prague, and these tests were conducted using the "ball-on-disk" technique to identify the wear mechanisms at play and investigate these properties.

In the tests, a load of 15 N was applied at room temperature, while a reduced load of 10 N was used at higher temperatures. The rotational speed was set to 10 cm/s, with a circular travel path of 2 mm radius for 32.000 cycles (approximately 400 m). The tests were performed without lubrication, covering temperatures from RT to 600 °C in an oxidising atmosphere. A 6 mm diameter Al₂O₃ ball was chosen as the counterbody due to its high hardness and low chemical reactivity.

Given the extraordinary hardness of the study materials and the Al₂O₃ counterbody, the harder material caused grooves on the softer surface during the test, leading to plastic deformation and the formation of a wear mark. Throughout the process, the friction coefficient values were recorded. The wear traces were

analysed following the removed tests to quantify the material and identify the underlying wear mechanisms.

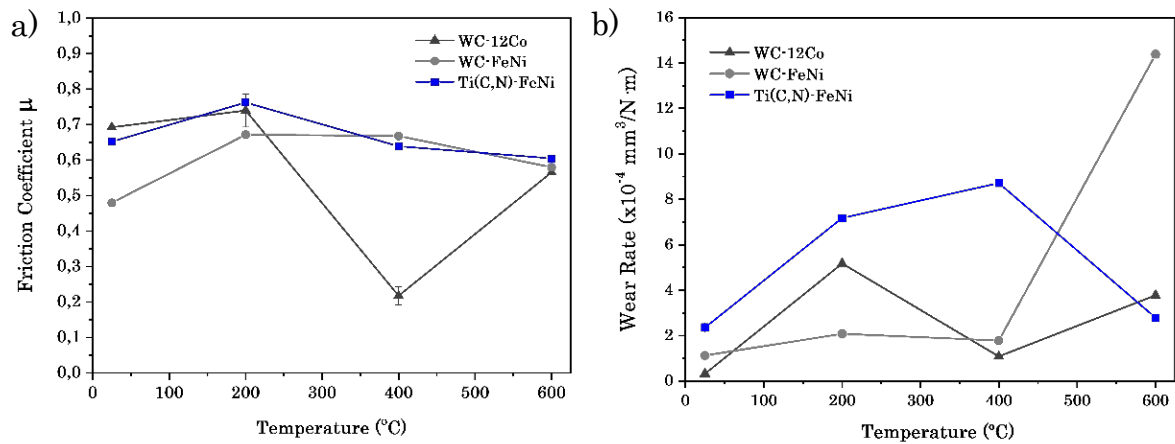


Figure 5.16. Tribology test results. a) Coefficient of friction of the materials as a function of temperature. b) Rate of wear and tear suffered by the materials. The error bars correspond to the absolute error of the experimental data.

Figure 5.16 presents the friction coefficient and wear rate results collected during the tribology tests for each material as a function of temperature. At 25 °C, WC-FeNi exhibited the best performance, with the lowest friction coefficient ($\mu = 0.480 \pm 0.008$), followed by Ti(C,N)-FeNi ($\mu = 0.652 \pm 0.001$) and the reference material WC-12Co ($\mu = 0.692 \pm 0.001$). These values were slightly higher than those reported by other authors for similar materials [170], [171].

The wear rates recorded for the materials at room temperature were remarkably similar. These results were better than anticipated, as the manufactured materials demonstrated lower friction coefficients than the reference material. A low friction coefficient is advantageous because it reduces friction between the tool and the material being cut. It offers multiple benefits, such as reduced heat generation during cutting, minimal tool wear, and an extended lifespan [169], [172].

As the temperature increased, all materials exhibited a similar trend: at 200 °C, the friction coefficient increased, leading to a rise in the wear rate. The increase in the coefficient of friction between two surfaces at elevated temperatures can be attributed to several factors related to changes in the surfaces of the material. These changes often arise from alterations in material properties or surface roughness variations, which are directly influenced by the formation of oxides.

At higher temperatures, as the materials reacted with the surrounding environment, oxide layers were formed. As discussed in earlier sections, these oxides, being less hard than the original material, contributed to increased wear rates. While it might be expected that the coefficient of friction would decrease as a result of the reduced resistance of oxides to wear, the opposite was observed. The coefficient of friction increased because the wear footprint increased, increasing the contact area between the material and the counter body. Furthermore, the formation of oxides on the surface increased the surface roughness, which subsequently intensified the friction at the contact points, further elevating the coefficient of friction.

However, these theories are only valid up to 200 °C. Beyond this temperature, oxidation processes became more active, resulting in a more significant reduction in the hardness of the material. This reduction further increased the wear rate while lowering the coefficient of friction, as the counter body could remove material with less resistance.

Given that their respective oxide layers largely dictated the behaviour of the materials above 200 °C, the following sections will describe the performance of each material individually in greater detail.

- WC-12Co

From 200 °C, the coefficient of friction of WC-12Co showed a relatively stable trend, with a slight downward slope to reach 600 °C (Figure 5.16). At 400 °C, a sudden and significant drop was observed in the friction coefficient and the wear rate, reaching a minimum value of $\mu = 0.22 \pm 0.03$. It is well established that friction between materials can decrease with increasing temperature if lubricating layers form on the surface. Previous sections of this work identified these lubricating layers as oxides generated on the surface of the material.

The metallic phases are most susceptible to oxidation at lower temperatures, so the anomaly recorded at 400 °C in WC-12Co was investigated to determine if it was related to surface oxidation. To explore this, a more in-depth analysis of the reactions that occur in WC-12Co between 200 °C and 600 °C was conducted.

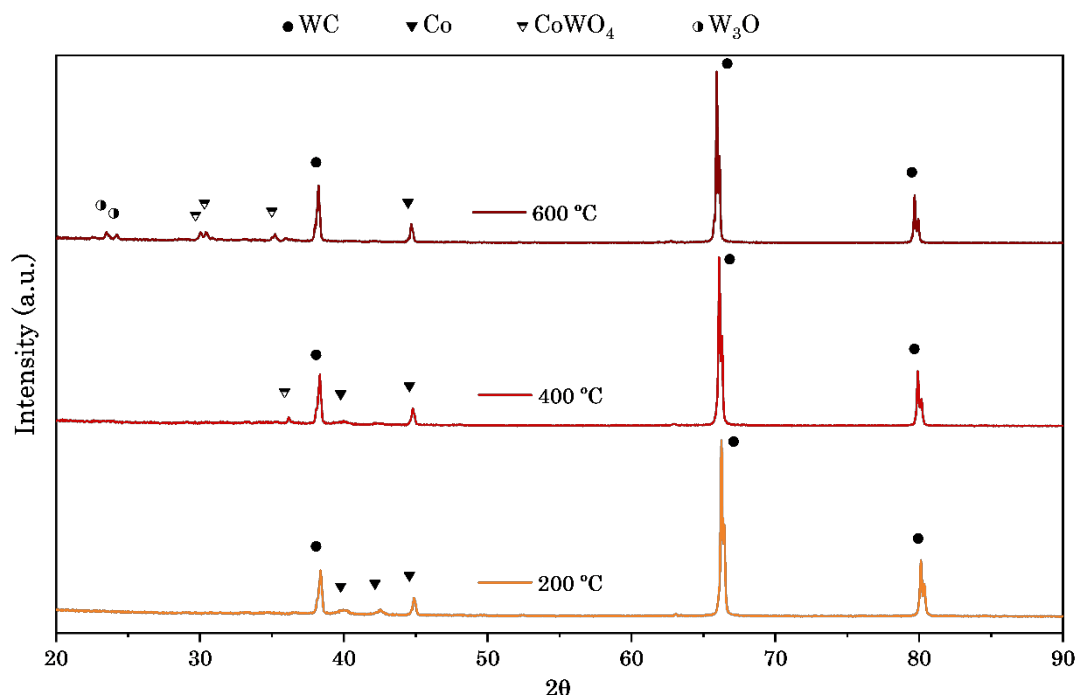


Figure 5.17. Comparison of indexed DRX peaks at 200°C, 400°C and 600°C in WC-12Co material.

Figure 5.17 confronts indexed peaks during the DRX analysis while the WC-12Co sample was heated at 200 °C, 400 °C and 600 °C. By comparing the elements present at each temperature and ignoring the peaks common to all of them, it was noticed how the peaks found at 40 ° and 42.5 ° corresponding to Co compounds, progressively disappearing as the temperature increased, coinciding with the appearance at 400 °C of a new peak associated with CoWO_4 . This Oxide's appearance could cause the anomalous tribological behaviour suffered by WC-12Co when it reached 400 °C. CoWO_4 would have functioned as an excellent lubricant, sharply decreasing the coefficient of friction and the wear rate with it. The appearance of this oxide probably explains the anomalous tribological behaviour observed in WC-12Co at 400 °C. CoWO_4 may have acted as an effective lubricant, significantly reducing both the coefficient of friction and the wear rate [173].

At 600 °C, the peaks associated with the Co compounds became imperceptible and the coefficient of friction returned to the trend observed at lower temperatures, aligning the material's properties with the rest. At the same temperature, the wear rate stabilised at a value close to, but slightly lower than, that recorded at 200 °C.

The loss of superlubricity observed at 400 °C is likely attributable to the formation of WO_3 on the surface [174]. The presence of WO_3 diminished the wear resistance, contributing to extensive oxidation of both the metallic matrix and the ceramic phase. Figure 5.18 illustrates the oxide formation pattern in WC-12Co.

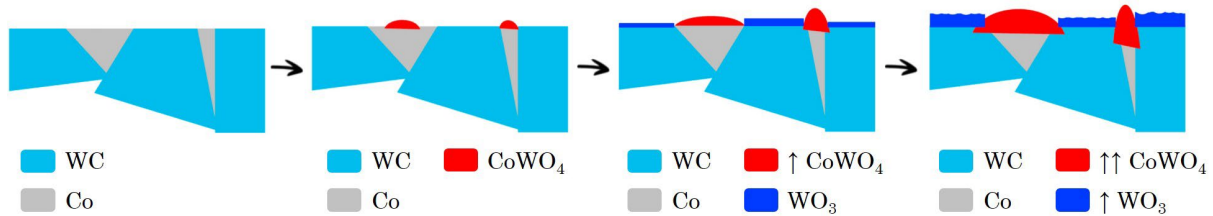


Figure 5.18. Diagram of the oxidation process in the metallic and ceramic phase of a cemented carbide WC-Co[173]

Initially, WC and Co remain in their original states; however, the early stages of CoWO_4 formation begin as the temperature increases. The presence of these oxides at 400 °C is minimal and does not significantly impact the mechanical properties, as evidenced by the flexural strength and toughness tests. (Sections 5.2.15.2.1 and 5.2.2). Although it was impossible to detect these oxides on the fractographic surfaces of Section 5.2.3, due to their small size, their presence acted as a lubricant on the material's surface. This led to a decrease in both the coefficient of friction and the wear rate. As the temperature continued to rise, CoWO_4 oxides developed progressively, and at 600 °C, W oxides formed. However, the proliferation of WO_3 , which tends to be much faster than CoWO_4 and is volatile, accelerated the degradation of the material [175].

At 600 °C, WC-12Co exhibited a reduction in the lubricity provided by CoWO_4 at 400 °C, attributed to the formation of WO_3 on the surface. The presence of WO_3 increased the material's susceptibility to wear, as extensive oxidation was observed in both the metallic and ceramic phases.

To further investigate the mechanisms of material loss [176], SEM images were captured to examine the details of the wear traces, allowing the identification of several distinct types of material removal [177], [178], [179], [180], as shown in the Figure 5.19.

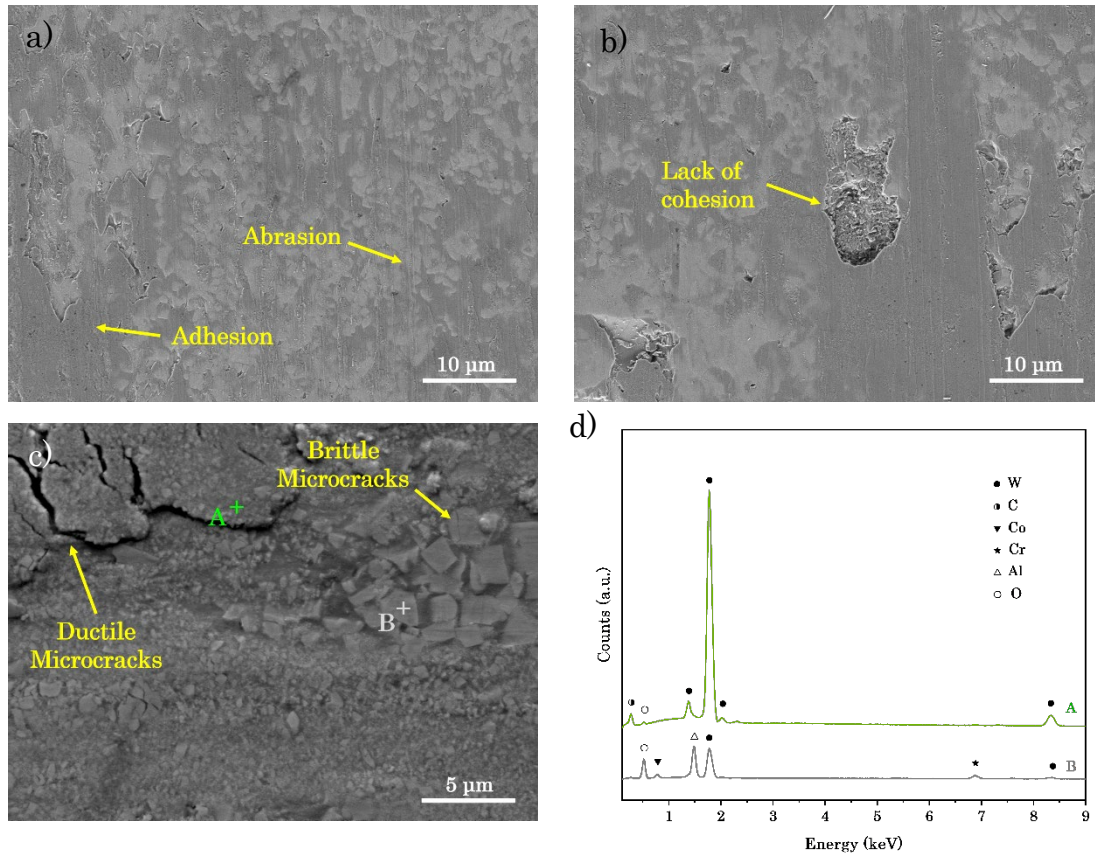


Figure 5.19. Material WC-12Co, a), b) y c) ISEM Details Images footprints and wear mechanisms; d) EDX peaks detected at points A and B.

At low temperatures, the high hardness of both WC-12Co and the Al_2O_3 promotes the formation of continuous and defined lines in the direction of the test, resembling a shallow plough (Figure 5.19a) [181]. The observations suggested that the surface was scratched, with abrasion mechanisms partially contributed to material wear. Additionally, microcracks were identified in both the metal and ceramic phases, likely caused by repeated loading and unloading cycles during the test (Figure 5.19c) [182]. After a critical number of cycles, these microcracks can lead to the detachment of large fragments due to lack of cohesion, resulting in the formation of craters on the surface (Figure 5.19b). At the contact points between the sliding surfaces, high pressures may cause localised welding between the asperities of the two materials. These welded joints are severed during relative movement, generating fragments that can transfer to the opposing surface [177]. Thus, as can be seen in Figure 5.19, smooth areas associated with adhesion friction were formed where the direction of the test was clearly distinguished.

An EDX analysis was conducted at different footprint points to identify the nature of the observed adhesions. The graph in Figure 5.19d shows the peaks detected at points A and B of Figure 5.19c. At all the temperatures evaluated, the primary elements of the study material were identified. For WC-12Co, W, C, Co, Cr, and O were detected, along with residues from the Al_2O_3 counter body. These residues were concentrated primarily in the smooth areas associated with adhesive wear.

This analysis indicated that throughout the temperature range, WC-12Co maintained a higher hardness than the Al_2O_3 counter body, leading to wear and transfer of material from the counter body to the wear footprint.

Particular attention was given to the wear traces at 400 °C to determine whether the super-lubricity observed at that temperature had altered the wear mechanism. However, the presence of Al_2O_3 residues prevented the detection of any significant changes in behaviour at this temperature.

- WC-FeNi

Figure 5.20. shows the profiles of the footprints left by the Al_2O_3 counter-body on the surface of the WC-FeNi after testing, as well as the markings on the counter-body. When the shape and depth of the footprints in both materials were studied, it became clear how, at room temperature, wear was normal. Due to the high hardness of the materials studied, the wear on the counter body was more significant than in other tribological studies, coinciding in size and shape with the mark generated on the undermined Al_2O_3 ball with the footprint in the material.

As mentioned above, increasing temperature and environmental reactions led to the formation of oxide layers that were softer than those of the original material. These softer oxide layers allowed the counter body to tear the material away more quickly, generating more debris during the test. The wear rate increased further when these residues were not expelled from the test area because of the reduced surface resistance.

However, the coefficient of friction also rose because the detached material accumulated along the edges of the counterbody's footprint. This buildup around the ball contact area altered the shape of the footprint, enlarging the contact area. This behaviour was particularly evident at 200 °C and 400 °C, where the reduction in surface hardness caused the counterbody's effective mark to concentrate in a smaller area, increasing the depth reached during testing.

Additionally, the debris accumulated at the edges of the contact zone continued to erode the material. As the Al_2O_3 ball penetrated deeper, more material detached and adhered to the ball, further widening the footprint and amplifying the wear rate. This progression was strongly influenced by the degree of surface degradation [183].

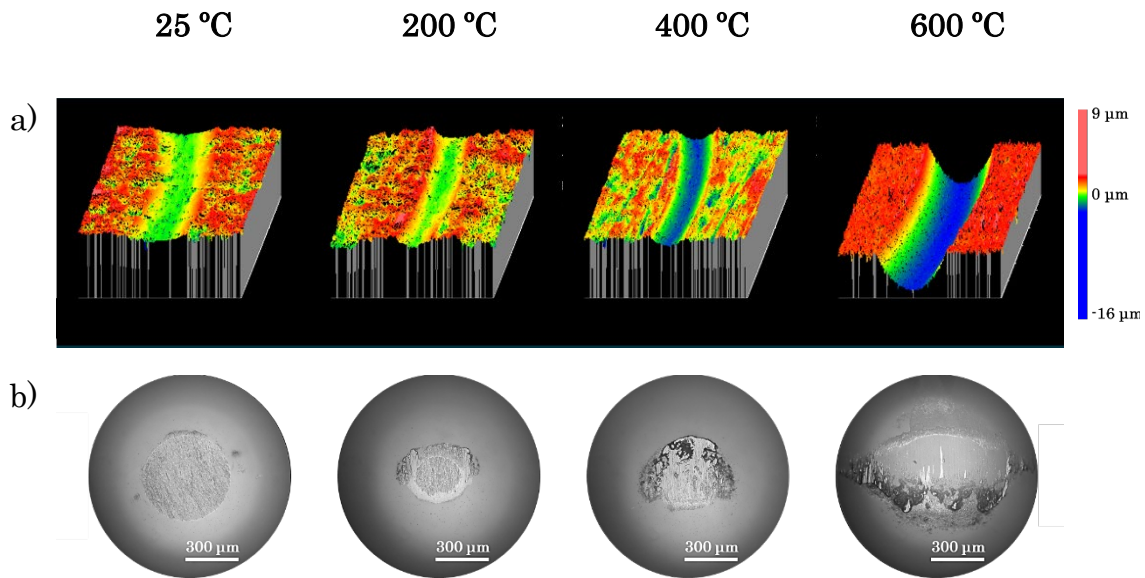


Figure 5.20. WC-FeNi material at each temperature, a) Profiles of the traces left after the tribology test, b) Marks on the Al_2O_3 counter body.

The measured footprints correlated with the attrition rate results. At 600 °C, WC-FeNi experienced a significant material loss, which was not observed at lower temperatures. This was evidenced by a more pronounced mark on the Al_2O_3 ball and the accumulation of more detached material from the generated debris.

In contrast, the friction coefficient of WC-FeNi remained stable at 200 °C across the test range, with only a slight tendency to decrease. The formation of $\alpha\text{-Fe}_2\text{O}_3$ in the metallic phase at 200 °C stabilised the friction coefficient by limiting its growth despite the increasing temperature. The wear rate displayed a similar trend but experienced a marked increase at 600 °C, with over 12 % of the material being detached during the tribological test.

As the growth of the $\alpha\text{-Fe}_2\text{O}_3$ layer had stabilised, it was concluded that another factor must be responsible for the increase in wear. In the fractographic analysis (Section 5.2.3), WO_3 was identified in the WC-12Co material as the oxide

responsible for increased wear. However, since WC-FeNi exhibited a different tribological behaviour compared to the reference material, a Raman analysis of the surface of WC-FeNi at 600 °C was conducted to investigate whether WO_3 was the cause of the sudden increase in wear.

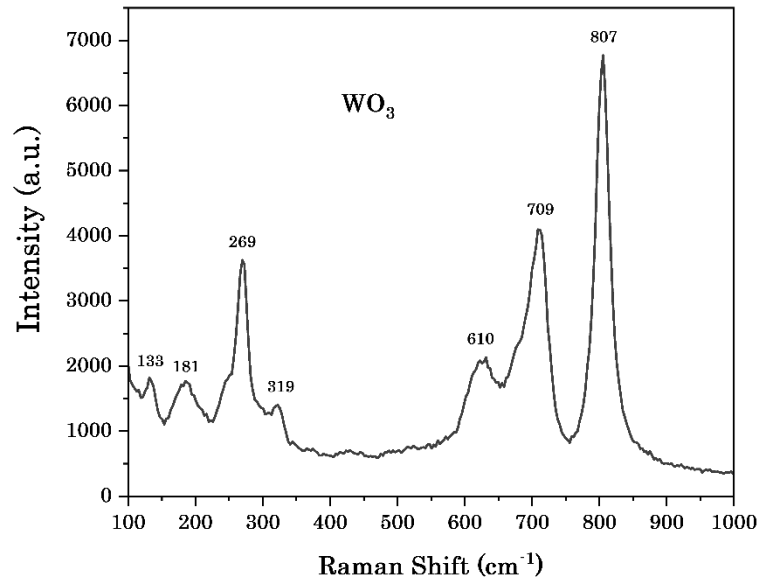


Figure 5.21. Oxide spectra Raman WO_3 detected at 600 °C in the WC-FeNi.

Comparing the peaks detected in the Raman spectrum of WC-FeNi, shown in Figure 5.21, with those reported by other authors [184], the presence of WO_3 was confirmed as Oxide in the ceramic phase at 600 °C. This detection linked the increase in the size of the footprint in the material to the widespread oxidation, which was the direct cause of the increase in the wear rate. In addition to WO_3 in the ceramic phase, the presence of $\alpha\text{-Fe}$ must also be considered in the metallic phase and the possible incipient formation of NiO [185].

Studies conducted in oxidising atmospheres suggest that the early stages of NiO formation could begin at 600 °C. However, in the tests carried out in this work, NiO was not detected, probably because of its low concentration or the dominance of peaks from other oxides. However, all oxides formed on the surface of WC-FeNi at 600 °C, particularly volatile oxides such as WO_3 — contributed to the reduction in hardness. This reduction in hardness increased the wear rate while simultaneously decreasing the coefficient of friction by lowering the resistance between the oxidised material and the counterbody.

SEM images were taken to detail the wear traces and examine the formation of oxides. Although the relative motion of the ball during each cycle removed the oxide layer formed on the material's surface during high-temperature tests, the newly exposed areas were immediately subjected to the oxidising atmosphere, facilitating further oxide formation. The SEM images in Figure 5.22 confirmed widespread oxidation of both the ceramic and metallic phases at 600 °C.

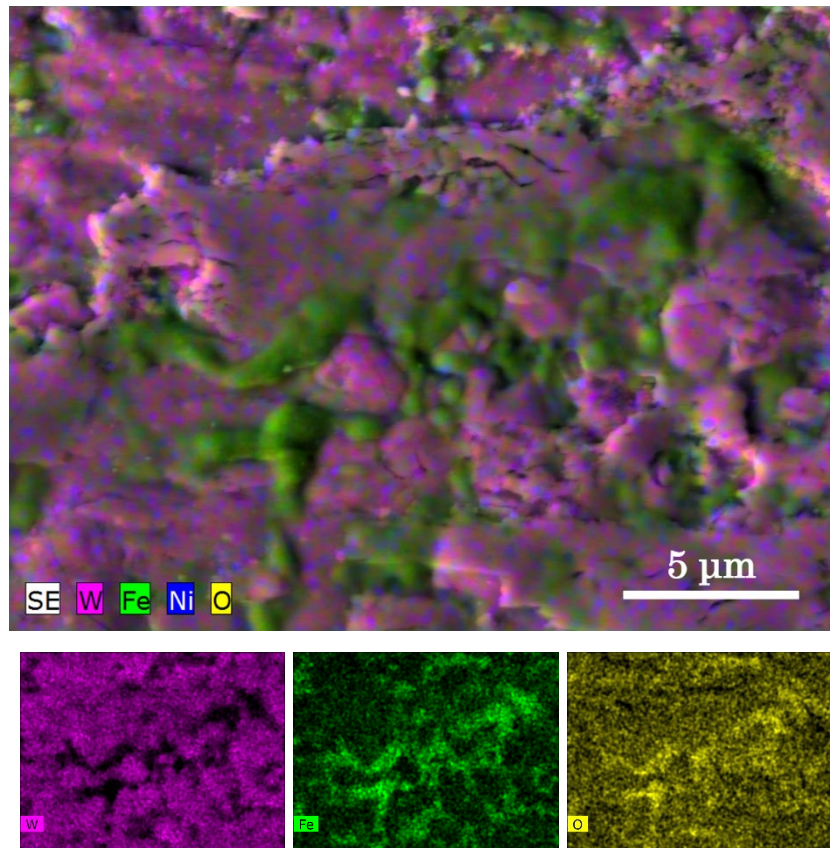


Figure 5.22. SEM-EDX micrographs of the tribological footprint at 600 °C of the WC-FeNi.

The SEM images of the details of the wear tracks, presented in Figure 5.22, allowed identification of the mechanisms of material loss. As observed in WC-12Co at lower temperatures, several predominant wear mechanisms were identified. Although shallow, continuous, well-defined lines aligned with the testing direction were indicative of abrasion mechanisms. The surface cracks, formed due to a lack of cohesion within the internal structure, resulted from the propagation of microcracks in both the brittle ceramic phase and the ductile metallic matrix.

These microcracks were caused by repeated loading and unloading cycles during the test.

Additionally, adhesion mechanisms were observed, where localised welding between the surfaces led to the transfer of material, creating areas with a rough and uneven appearance.

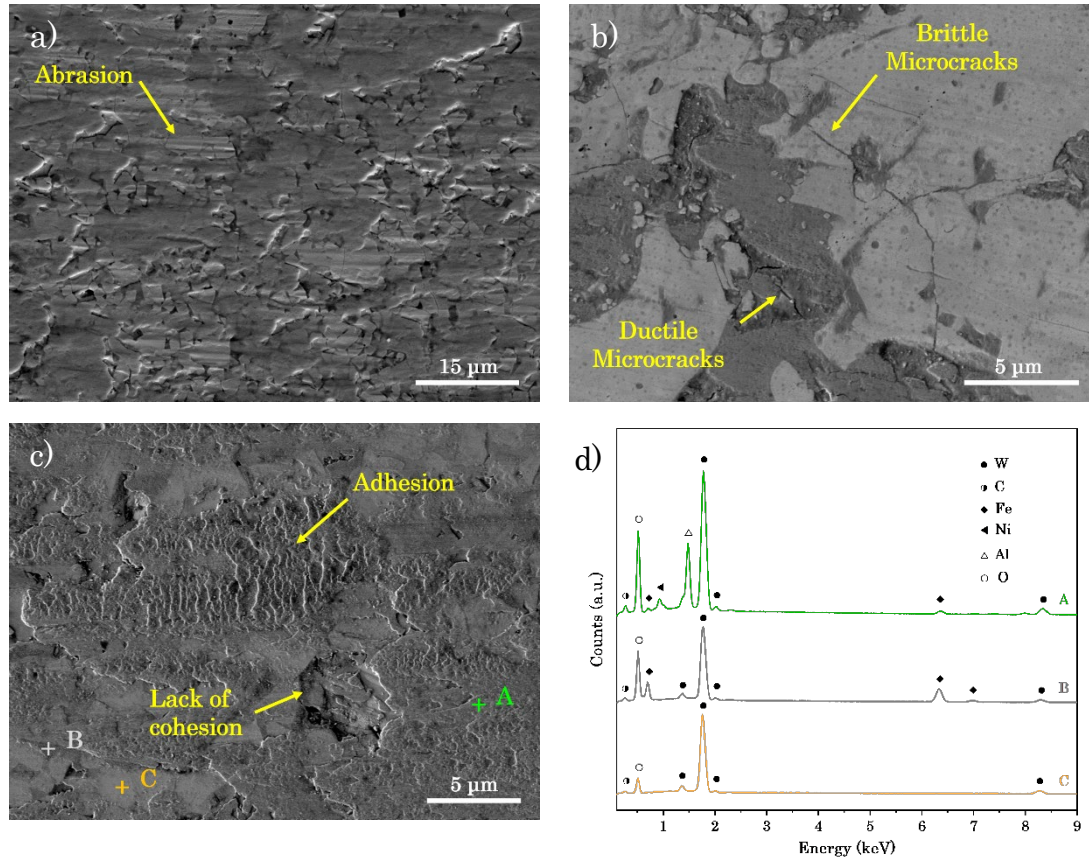


Figure 5.23. Material WC-FeNi, a), b) y c) SEM details image footprints and wear mechanisms; d) EDX peaks detected at points A, B and C.

Since the observed adhesions were not the same as those found in WC-12Co, EDX analysis was again performed at three points on the footprint surface to find the elements present. The peaks indexed in Figure 5.23 are represented in the graph of Figure 5.23d. In this material, as in the reference material, the main elements were detected: W, C, Fe, Ni and O at all the temperatures assessed. In the range of 25 °C to 400 °C, both included a material transfer from the Al₂O₃ counter body, which was also observed to the WC-FeNi, primarily concentrated in the rough areas generated by adhesive wear.

Taking into account the low wear rate exhibited by the material up to 400 °C, this resistance could be attributed to its hardness, which caused more significant wear on the counter body than on the tested material. However, at 600 °C, the formation of WO_3 led to significant material degradation. At this temperature, the Al_2O_3 ball became harder than the tested material, allowing it to penetrate the surface, tear off the material, and create a deeper wear footprint.

As a result, the wear footprint did not detect traces of material from the counter body. Instead, Fe and Ni residues from the tested material were found on the surface of the Al_2O_3 ball, as shown in Figure 5.24.

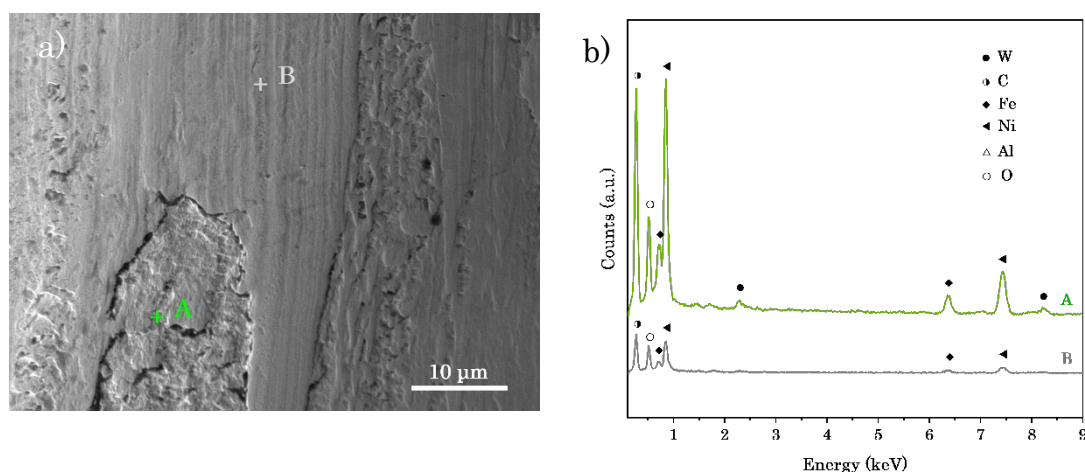


Figure 5.24. a) SEM image of the Al_2O_3 counter body used in the testing of WC-FeNi material; b) EDX peaks detected at points A and B.

The primary material transfer to the ball during the test predominantly originated from the metallic phase, as indicated by the detected peaks corresponding to Fe, Ni, and O.

The presence of W was almost negligible, demonstrating that the ceramic phase, due to its higher hardness, did not adhere to the Al_2O_3 counter body.

- $\text{Ti}(\text{C},\text{N})\text{-FeNi}$

Figure 5.25 shows the profiles of the footprints on the surface of $\text{Ti}(\text{C},\text{N})\text{-FeNi}$ after tribological tests, as well as the marks left by the sample on the Al_2O_3 ball.

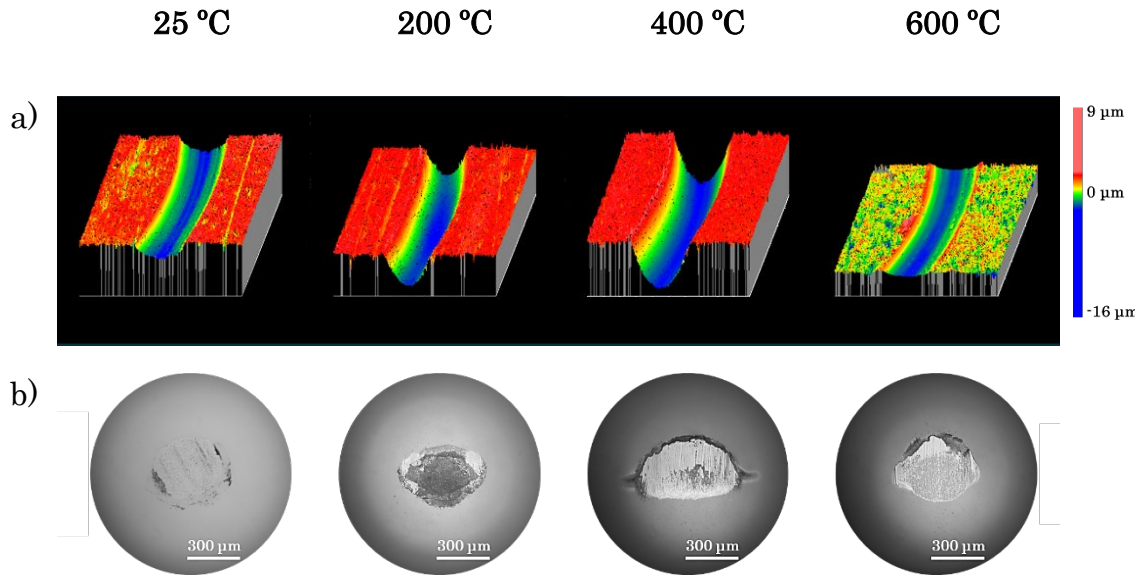


Figure 5.25. Ti(C,N)-FeNi material at each temperature, a) Profiles of the traces left after the tribology test, b) Marks on the Al₂O₃ counter body.

The friction coefficient and wear rate of Ti(C,N)-FeNi remained stable from 200 °C onward. This behaviour was consistent with expectations, as the coefficient of friction gradually decreased with increasing temperature while the amount of material detached from the surface increased.

The shape and depth of the wear footprints further supported these findings. As the temperature increased, the wear caused by the counterbody became more pronounced, reflecting the loss of surface properties at elevated temperatures.

The formation and growth of α -Fe₂O₃ oxide in the metal phase reduced the surface hardness of the material, making it easier for the counterbody to start. Like WC-FeNi, the accumulation of detached material around the contact zone between the ball and the Ti(C,N)-FeNi material altered the footprint's shape, increasing its area. As the Al₂O₃ counter body penetrated more deeply, the material was torn off and adhered to the ball, widening the footprint and increasing the wear rate, depending on the extent of surface degradation.

Despite the observed stability in Ti(C,N)-FeNi, an unexpected change occurred at 600 °C: instead of the attrition rate increasing, it decreased by nearly 6 %. The measured footprints confirmed this behaviour, showing a smaller footprint on the material, which reduced the amount of dislodged material and diminished the size of both the wear mark and the residue on the counter body.

Previous studies have highlighted the remarkable resistance of Ti(C,N) to oxidation, suggesting that at high temperatures, a protective layer of titanium oxide forms on the surface. This layer inhibits the formation of other oxides, more volatile oxides, thereby preserving the integrity at elevated temperatures [175]

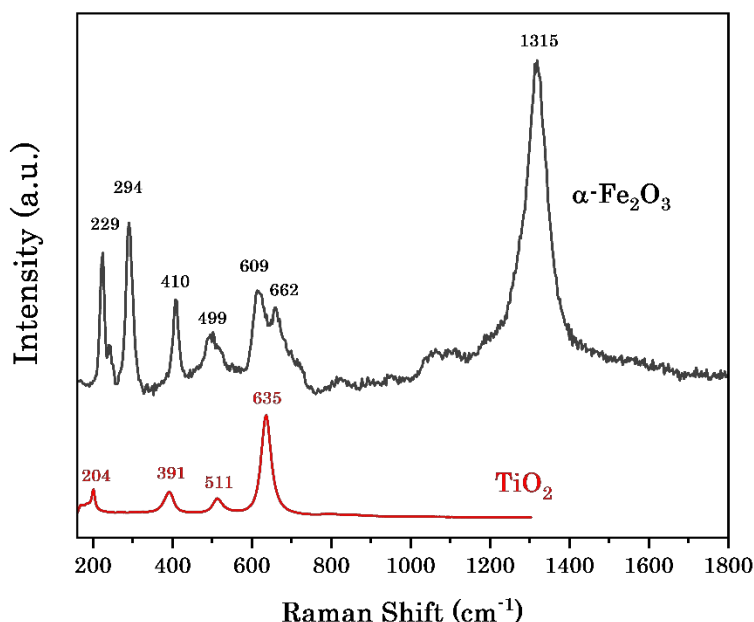


Figure 5.26. Overlapping peaks of the Oxide spectra Raman TiO_2 [186] and the $\alpha\text{-Fe}_2\text{O}_3$ detected at 600 °C in the Ti(C,N)-FeNi.

The Raman analysis performed on the surface of Ti(C,N)-FeNi at 600 °C, shown in Figure 5.26, revealed that the prominent peaks detected corresponded to the $\alpha\text{-Fe}_2\text{O}_3$. However, it was seen that many peaks could be superimposed or masked by larger or more intense ones, which complicated the identification of other oxides. Despite the limitations of this technique, the comparison of the detected peaks with those reported by other authors confirmed the presence of TiO_2 , as well as the possible existence of FeTiO_3 [186], [187], [188]. This led to the conclusion that the TiO_2 acted both as a lubricant and as a protective layer that prevented the formation of more aggressive oxides on the material's surface, thus reducing the coefficient of friction and the wear rate to 600 °C [175].

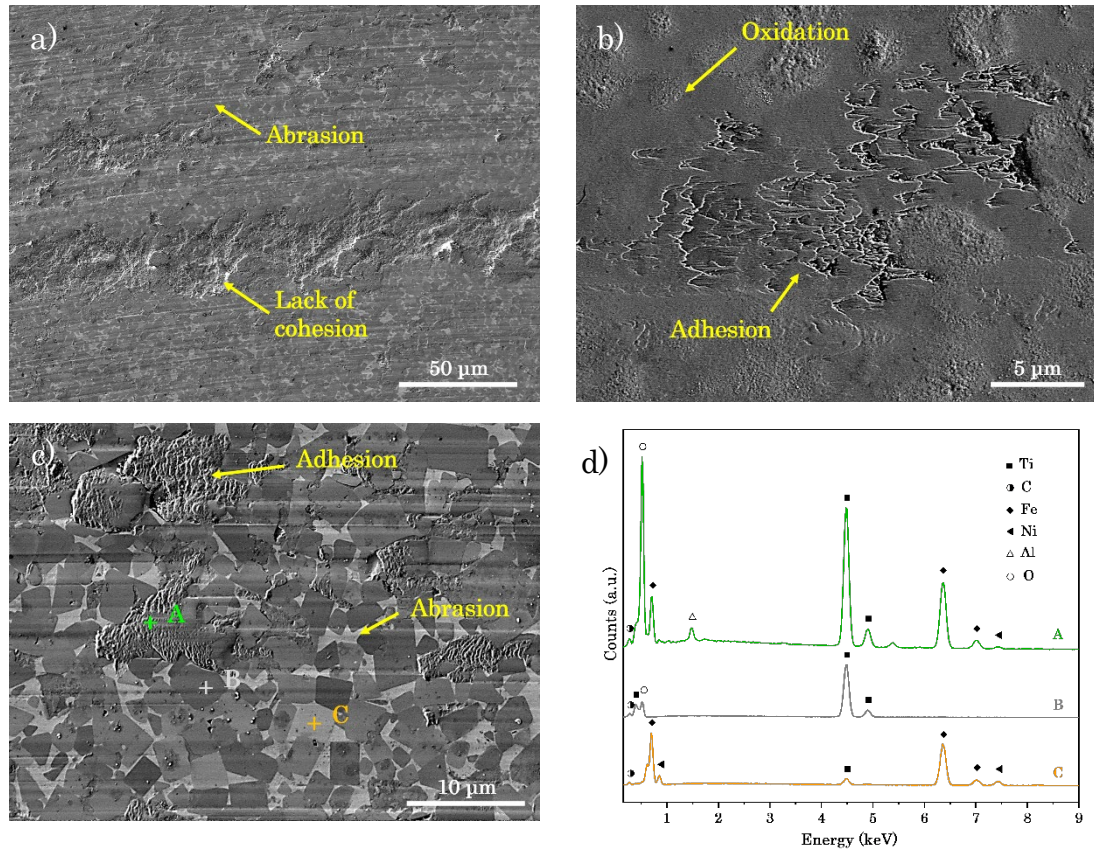


Figure 5.27. Material Ti(C,N)-FeNi, a), b) y c) ISEM Details Images footprints along with wear mechanisms; d) EDX peaks detected at points A, B and C.

In Figure 5.27, the wear traces originating on the Ti(C,N)-FeNi material were analysed to identify the removal mechanisms of the material. Several predominant wear mechanisms were observed similar to those of the previous two materials. Although shallow, continuous, and defined lines along the testing direction were indicative of abrasion mechanisms. Craters on the surface suggested a lack of cohesion within the material's internal structure. In addition, rough areas were identified as evidence of adhesion mechanisms resulting from welds formed during material transfer between the surfaces.

An EDX analysis was performed at three distinct points on the surface of the wear footprint at temperatures below 600 °C to determine the elements present. The peaks indexed in Figure 5.27 are represented in the graph of Figure 5.27d. In this material, the main elements were found to be Ti, C, Fe, Ni, and O. The remnants of Al_2O_3 from the counter body, concentrated in the rough areas generated by adhesive wear on other materials, was reduced. Although the hardness of Ti(C,N)-FeNi material was high, it was lower than that of the WC base materials, so the

wear suffered by this material, although moderate, was more significant. At 600 °C, however, signs of wear due to oxidation and adhesion were observed, where the microstructure visible in all traces at lower temperatures disappeared, giving way to a continuous main layer of Ti oxide, with specific amounts of Fe and Ni, as well as small Al adhesions₂₀₃. Although the EDX study did not allow the exact type of rust present on the surface of the footprints at 600 °C to be identified, this layer could be of TiO₂. This oxide, together with those formed by Fe and Ni, could have functioned as a lubricant and protective layer against further oxidation on the material's surface, reducing the coefficient of friction and the wear rate to 600 °C, as mentioned above. The Figure 5.28. displays wear footprint at this temperature, along with the peaks detected at specific points. The analysis revealed the coexistence and interaction of two distinct layers during the tribological tests: oxidised and nonoxidised layers. The latter was characterised by a tiny area that exhibited wear due to a lack of cohesion.

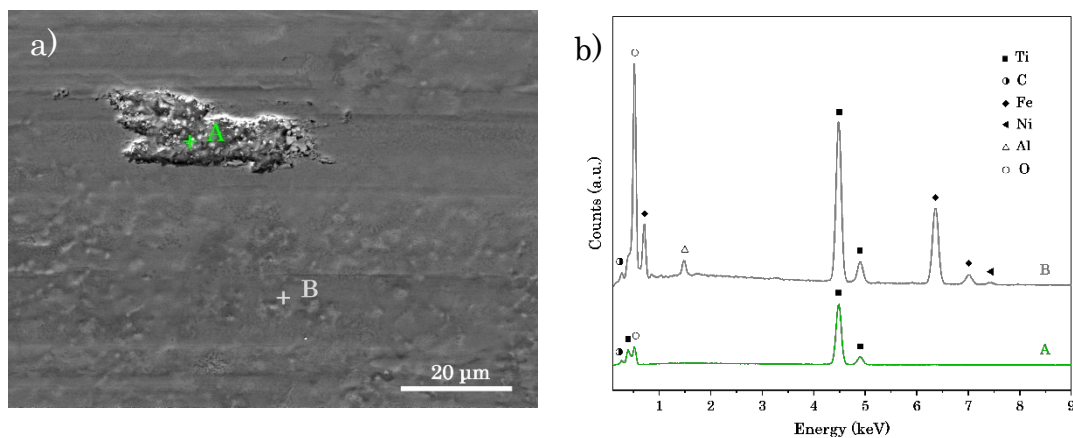


Figure 5.28. SEM image showing the details of the footprints at 600 °C of the material Ti(C,N)-FeNi; b) EDX peaks detected at points A and B.

Then again, given the low material removal rate observed at 600 °C, it was expected that the wear on the counter body would exceed that of the tested material and that residues from the test material would adhere to the counter body. The analysis confirmed the presence of residues from all elements of the test material, including both the metallic phase and the ceramic phase, around the contact area between the ball and the material, as shown in Figure 5.29.

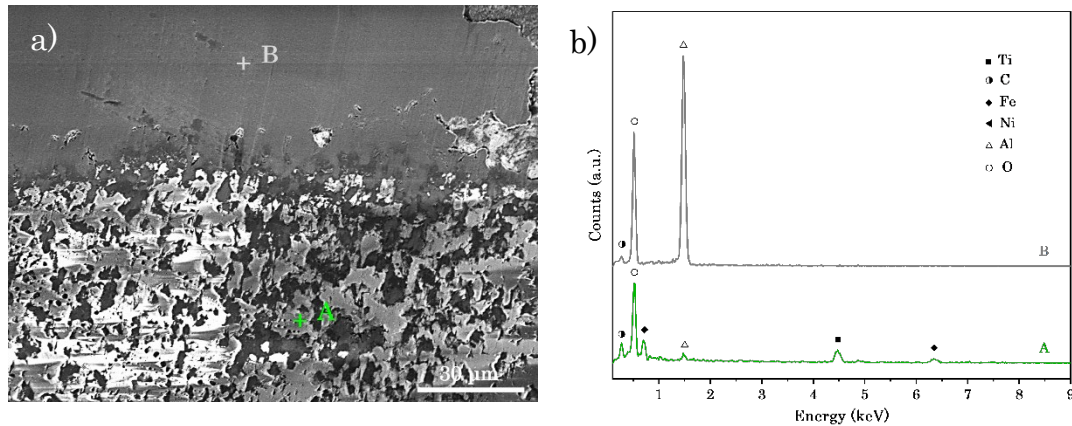


Figure 5.29. a) SEM image of the Al_2O_3 counter body used in the WC-FeNi material; b) EDX peaks detected at points A and B.

In summary, the materials studied exhibited similar behaviour at room temperature, with their high hardness values causing wear to the counter bodies during testing and resulting in material transfer between the specimen and the ball. As the temperature increased, the amount of material removed from the surface also increased, with debris accumulating around the ball and progressively widening the footprint with each cycle.

At 600 °C, WC-FeNi experienced significant degradation, making the counterbody material harder than the tested material. On the contrary, Ti(C,N)-FeNi developed a lubricating and protective layer that inhibited the formation of more degrading oxides, thereby reducing its wear rate.

Multiple wear mechanisms were observed to overlap as tests progressed, including abrasive, adhesive, and oxidative wear.

6. Conclusions and Future Work

6.1. Conclusions

The primary objective of this thesis was the development and characterisation of alternative materials for cutting tools, ensuring both sustainability and continuity for the industry. Given the scarcity of critical raw materials such as W and Co, this research focused on the manufacturing of new materials with a reduced environmental impact. The selected systems included WC-FeNi cemented carbides, and Ti(C,N)-FeNi cermets, with Ti(C,N) proposed as an alternative for the ceramic matrix and Fe and Ni as substitutes for the metallic matrix. The feasibility of replacing PVA with HPMC as a stabiliser and dispersant for colloidal suspensions was also evaluated.

A comprehensive characterisation was conducted at each stage of the manufacturing process to ensure the industrial viability of these materials. This included a rheological analysis of suspensions, atomisation, and selection of the optimal sintering atmosphere to identify the method that would provide the best combination of properties and scalability for industrial application.

Subsequently, an in-depth analysis of the mechanical and thermal properties, microstructure, and fractography was performed to validate the suitability of these materials for machining and drilling applications.

6.1.1. Preparation of suspensions

The global demand for elements used in cutting tools, such as W and Co, continues to rise, these have been indeed classified as critical raw materials due to their geostrategic importance and limited availability. Moreover, Co is toxic to aquatic life and poses health risks. Despite their essential role in producing cemented carbides, the supply of these metals is increasingly at risk due to geostrategic dependencies and increasing demand, particularly from the battery market. Consequently, the search for sustainable alternatives to replace Co and even W represents a significant scientific, technological, and industrial challenge.

Powder metallurgy is a widely used method for producing metal components, but it presents limitations when working with ceramics. Colloidal processing offers a promising alternative that addresses these drawbacks. One notable advantage of colloidal processes is the use of water as a solvent, reducing environmental impact and enabling the dissolution of various substances and the incorporation of additives that enhance suspension stability and adjust properties such as pH and viscosity.

PVA is commonly used as a dispersant, stabiliser, and binder in colloidal processing. However, with the aim of using a more sustainable and non-toxic alternative, HPMC was investigated as a substitute for PVA. HPMC is nontoxic, highly soluble in aqueous organic and polar solvents, and demonstrated comparable functionality in colloidal systems.

The rheological analysis of the colloidal suspensions revealed a decrease in viscosity with increasing shear speed, which is characteristic of pseudoplastic fluids. The pseudoplasticity index was determined to be 0.54 for WC-FeNi and 0.42 for Ti(C,N)-FeNi. This variation was attributed to the higher density of the WC particles compared to Ti(C,N) particles. Despite this difference, both suspensions exhibited excellent stabilisation and homogenisation, with minimal agglomeration. These findings confirmed that HPMC functioned efficiently as a dispersant, stabiliser, and binder, achieving stable suspensions with behaviour comparable to those containing PVA.

6.1.2. Selection of sintering atmosphere

Precise control of the sintering atmosphere is essential to obtain materials with superior final properties. However, the selected atmosphere must be compatible with the material and constituents, and economically viable for the industry. To ensure optimal sintering, experiments were conducted in various atmospheres, including N₂H₂ (hydrogenated nitrogen), vacuum (10⁻⁴ mbar), and Ar (argon).

A compressibility study was also performed to determine the optimal compaction pressure, exploring a range from 100 MPa to 1200 MPa. The results indicated that compaction pressures above 500 MPa did not produce further densification of the ceramic matrix, while the metallic matrix exhibited significant deformation. To preserve the integrity of the ceramic particles, the powders were compacted at 500 MPa, achieving a green density of 64 % in both materials.

An extensive microstructural study revealed the geometric characteristics of the materials subjected to liquid phase sintering, consistently showing two clearly differentiated phases in all sintering atmospheres. Additionally, it was observed that the percentage of carbon introduced in the initial composition played a critical role in the precipitation of the FeNi phase. The presence of carbon lowered the liquidus temperature, allowing sintering to occur at reduced temperatures.

Optimisation of the sintering process led to relative densities exceeding 97 % for WC-FeNi in all atmospheres tested. However, Ti(C,N)-FeNi exhibited a more significant variability, with higher porosities: 5 % in Ar, 13 % in a vacuum, and 21 % in N₂H₂. This disparity was attributed to the substantially higher solubility of WC in the liquid FeNi phase compared to that of Ti(C,N), facilitating more substantial dissolution and reprecipitation, which improved densification in WC-based materials.

Phase analysis of both materials confirmed the disappearance of elemental Fe and Ni during sintering, with the formation of a FeNi alloy, a clear indicator of successful sintering.

In materials sintered in the N₂H₂ atmosphere, perimeter layers not observed in other atmospheres were formed. For WC-FeNi, these surface layers showed a decrease in WC in favour of Fe, resulting from the partial disintegration of carbon from the WC. During this process, some carbon dissolved in atmospheric N₂, while another fraction reacted with Ni from the metallic binder to form Ni₃C. This reduced the FeNi phase content in the material, leaving free Fe in the surface layer.

Similarly, increased N₂ activity during sintering promoted FeNi migration into Ti(C,N)-FeNi, partially filling existing porosities. However, this migration left the surface layer of the material with lower content of Fe and Ni. Consequently, the reactions that occurred in N₂H₂ led to the absence of the metallic phase in certain areas, resulting in insufficient densification, heterogeneous sintering, and increased porosity in both materials. These findings ultimately disqualified N₂H₂ as a viable sintering atmosphere for these materials.

Furthermore, WC-FeNi exhibited a hardness higher than Ti(C,N)-FeNi, which correlated with a narrower particle size distribution and a smaller grain size. Predictably, the lowest hardness values were observed in materials sintered under N₂H₂, consistent with their higher porosity and poorer densification.

In conclusion, argon was selected as the optimal sintering atmosphere, offering both materials the best balance between hardness, densification, and grain size. Additionally, the widespread industrial use of argon enhances the marketability of the sintering process without compromising material properties.

Finally, it was verified that the low dimensional changes experienced by both materials during sintering at 1450 °C in argon posed no risk to their structural or dimensional integrity.

6.1.3. Mechanical characterisation

Mechanical characterisation of the materials was a central focus of this study, providing critical information on their behaviour under various loads and temperature conditions. Among the properties evaluated was the density, where the Ti(C,N)-FeNi material did not surpass the reference cermet. The reference material exhibited minimal porosity, with a value of 0.44 %, compared to 4.3 % in the manufactured material.

In contrast, the WC-FeNi material achieved densification nearly identical to that of WC-12Co, representing a significant advancement in sintering.

Analysing mechanical properties was pivotal in assessing the structural integrity and durability of each material under service conditions.

- Flexural strength and fracture toughness as a function of temperature

Tests were conducted across a temperature range from ambient temperature to 800 °C for the longitudinal and transverse sections of each material. The results confirmed that the materials were entirely isotropic, as no variations in measurements related to orientation were observed.

At room temperature, the reference Ti(C,N)-FeNi exhibited the best properties. However, it was concluded that the use of HPMC as a dispersant reduced the properties of Ti(C,N)-FeNi at 25 °C, suggesting that it may not be a suitable substitute for PVA. Unfortunately, comparisons under service conditions were limited because of a lack of data on the behaviour of the reference Ti(C,N)-FeNi at higher temperatures.

The FeNi matrix provided better overall mechanical properties than the Co matrix at temperatures below 200 °C. This behaviour can be attributed to the metal elements in the FeNi matrix undergoing plastic deformation at low temperatures before fracturing, which allowed them to absorb significant amounts of energy during the deformation process. Combined with ceramic materials, this plasticity facilitated stress redistribution within the microstructure, reducing crack propagation, and improving fracture resistance.

However, as the temperature increased above 400 °C, degradation of the FeNi phase was observed, which resulted in the mechanical strength and fracture toughness of FeNi-based materials being surpassed by those of the WC-12Co reference material. At 800 °C, all materials exhibited a sharp decline in properties due to extensive microstructural degradation.

- *Fractographical analysis*

Four distinct fracture mechanisms were identified at low temperatures: ductile fracture in the metallic phase, intergranular and transgranular brittle fracture in the ceramic phase, and detachment between the metallic and ceramic phases. Despite these types of fractures, the adhesion between the phases was strong, contributing to the deviation of the crack path and dispersing energy through the metallic phase. This interaction resulted in an optimised mechanical behaviour and an improved overall material performance.

At 400 °C, the formation of oxides in the FeNi metallic phase surrounding the ceramic particles was evident, with α -Fe₂O₃ being the dominant oxide. From 600 °C, oxidation extended to both the ceramic phase and the Co phase, leading to the formation of WO₃ and CoWO₄.

At 800 °C, extensive degradation affected the metallic matrix and the ceramic phase. The WC phase experienced more rapid and severe degradation than Ti(C,N), accelerating the decline in its properties at elevated temperatures.

- *Thermal diffusivity*

The results of the characterisation revealed two distinct thermal behaviours. In WC-based composite materials, the thermal diffusivity decreased by nearly 50 % as the temperature increased. In contrast, the Ti(C,N)-FeNi material maintained its thermal conductivity almost constant, regardless of the rise in temperature.

The specific heat values of the materials analysed aligned closely with those reported in the literature for WC and Ti(C,N), highlighting the influence of the Fe and Ni alloys. These elements caused a slight increase in the specific heat of the Ti(C,N)-FeNi compound, which mirrored the slight decrease observed in WC-FeNi.

Furthermore, the alloys had a notable impact on thermal conductivity. Thermal conductivity in the Ti(C,N)-FeNi system increased, while in WC-FeNi, it decreased. It was also observed that the ceramic phase predominantly governed the thermal conductivity at lower temperatures. However, as the temperature increased, the metallic phase became dominant.

- *Hardness and wear resistance depending on temperature*

The hardness results demonstrated a clear relationship between grain size and material hardness: smaller grain sizes corresponded to higher hardness values, as predicted by grain refinement hardening. However, the hardness decreased linearly with increasing temperature as a result of the formation of oxides on the surface of all materials. This effect was more noticeable in materials with a Fe-Ni metallic phase. In contrast, the alloying elements in the WC-12Co reference material provided better hardness retention throughout the entire temperature range.

Tribological tests at 25 °C revealed the superior performance of the manufactured materials compared to the reference cemented carbide. The manufactured materials exhibited a lower coefficient of friction, although their wear rates were comparable to those of the reference material. Significant wear to the Al₂O₃ counter body balls led to a material exchange between the specimens and the ball, resulting in overlapping wear mechanisms. The observed wear mechanisms included abrasive, adhesive, and oxidation-induced wear.

As the temperature increased, variations in the coefficient of friction and wear rate were attributed to the formation of oxides on the material surfaces. In the WC-12Co reference material, the formation of CoWO₄ at 400 °C imparted superlubricity, significantly reducing friction. However, at 600 °C, this property decreased due to the formation of WO₃, a tungsten oxide that significantly contributed to the degradation of WC-FeNi. At this temperature, both the metallic and ceramic phases of WC-FeNi were oxidised, leading to rapid deterioration.

In contrast, Ti(C,N)-FeNi demonstrated superior oxidation resistance. At 400 °C, it formed a lubricating and protective oxide layer that inhibited the formation of more volatile oxides, thus reducing wear and maintaining structural integrity.

The tribological results were closely related to the thermal conductivity of these materials. High thermal conductivity, combined with a low coefficient of friction, indicates good wear resistance. This behaviour was evident in the WC-12Co and WC-FeNi materials, which exhibited lower wear rates than Ti(C,N)-FeNi, positioning them as more favourable options for applications requiring wear resistance.

6.2. Future Work

This thesis has laid the groundwork for a novel methodology for manufacturing advanced materials for industrial applications employing innovative colloidal processes. Through meticulous planning and execution, an exhaustive characterisation of the thermal, mechanical and tribological behaviour of two materials as a function of temperature has been achieved. This work represents a step forward in material science, offering sustainable alternatives to conventional cemented carbides and cermets, which are indeed industrially viable.

The decision to focus on a limited number of materials stemmed from the necessity to ensure precision and depth in the analysis. Expanding the scope indiscriminately would have introduced variables that could obscure critical insights, compromising the clarity and reliability. Developing these materials is also resource intensive and requires significant time, energy, and expertise. This research provided a robust understanding of their performance and an insightful comparison with well-established reference materials by prioritising two ceramic phases.

Moreover, the precise characterisation of thermal properties, particularly the specific heat, remains a key area for optimisation. As a fundamental parameter influencing a material's capacity to store and transfer thermal energy, specific heat directly impacts thermal conductivity, a critical property for many industrial applications. Developing more accurate models and measurement techniques for specific heat in uncharacterised materials would enable absolute reproducibility and precision in thermal studies. This effort would validate the current results and

ensure compatibility with future advances in material design and testing methodologies.

- *A Vision for Material Innovation*

The results pave the way for further exploration of novel combinations to enhance and balance mechanical, thermal, and tribological properties while maintaining sustainability. For instance, fine-tuning the composition of the metallic and ceramic phases with the addition of secondary elements, such as iron or yttrium, could lead to improved high-temperature stability or increased resistance to oxidation. Similarly, these secondary phases would optimize grain size distribution and phase homogeneity, enhancing with it the hardness, toughness, and thermal conductivity. Therefore, future studies should investigate the interplay between microstructure, rheology, and mechanical performance of each composition.

This approach could lead to a deeper understanding of how processing parameters influence the final properties of the material, opening new pathways for tailor-made solutions in cutting tools and other high-performance applications.

- *Towards a Sustainable Future*

This research has demonstrated the potential of sustainable material systems, such as WC-FeNi and Ti(C,N)-FeNi, to serve as viable alternatives to traditional hardmetals. These alternatives align with global efforts to reduce the dependence on critical raw materials, such as W and Co, and address pressing concerns about environmental sustainability and resource scarcity. By integrating green chemistry principles, such as water-based colloidal suspensions and nontoxic additives such as HPMC, this work has contributed to the broader movement towards eco-friendly manufacturing practices.

The results underscore the feasibility of combining sustainability with performance, a crucial step in bridging the gap between academic research and industrial application. The methodologies and insights developed in this thesis are not endpoints but rather catalysts for continued innovation. Future research can leverage these findings to explore new material compositions, refine manufacturing processes, and adapt these technologies to emerging industrial challenges.

By continuing to explore and expand upon the methodologies outlined in this work, the material science community has the opportunity to address global challenges with innovative solutions. These efforts will undoubtedly create a sustainable, resilient, and technologically advanced future where performance and environmental stewardship go hand in hand.

- *Final Words*

The journey undertaken in this doctoral thesis is a testimony to the potential of interdisciplinary and international collaboration (Instituto de Cerámica y Vidrio (ICV-CSIC), Czech Technical University in Prague (CTU), Universidad Politécnica de Madrid (UPM) and scientific curiosity). As we move forward, the challenge is to embrace this spirit of innovation and sustainability, ensuring the industry needs and the principles of environmental responsibility to guide future developments in Material Science and Engineering.

References

- [1] A. A. Krimpenis and D. M. Iordanidis, “Design and Analysis of a Desktop Multi-Axis Hybrid Milling-Filament Extrusion CNC Machine Tool for Non-Metallic Materials,” *Machines* 2023, Vol. 11, Page 637, vol. 11, no. 6, p. 637, Jun. 2023, doi: 10.3390/MACHINES11060637.
- [2] ASTM, “F2792 Standard Terminology for Additive Manufacturing Technologies, (Withdrawn 2015).” [Online]. Available: <https://www.astm.org/f2792-12a.html>
- [3] MITSUBISHI MATERIALS CORPORATION, “¿Qué es el Carburo?” [Online]. Available: https://www.mmc-carbide.com/mx/technical_information/tec_guide/tec_guide_carbide
- [4] S. Kalpakjian, S. Schmid, and V. Sekar, *Manufacturing engineering and technology in SI units*. 2021. Accessed: Oct. 21, 2024. [Online]. Available: </content/one-dot-com/one-dot-com/se/en/Nordics-Higher-Education/subject-catalogue/engineering/ManufacturingEngineering-and-Technology-7th-SI-Edition.html>
- [5] T. Kagnaya, C. Boher, L. Lambert, M. Lazard, and T. Cutard, “Microstructural analysis of wear micromechanisms of WC–6Co cutting tools during high speed dry machining,” *Int J Refract Metals Hard Mater*, vol. 42, pp. 151–162, Jan. 2014, doi: 10.1016/J.IJRMHM.2013.08.017.
- [6] A. Mohamed Akeel, R. Kumar, P. Chandrasekhar, A. Panda, and A. Kumar Sahoo, “Hard to cut metal alloys machining: Aspects of cooling strategies, cutting tools and simulations,” *Mater Today Proc*, vol. 62, pp. 3208–3212, Jan. 2022, doi: 10.1016/J.MATPR.2022.04.053.
- [7] B. Boswell and M. N. Islam, “Sustainable cooling method for machining titanium alloy,” *IOP Conf Ser Mater Sci Eng*, vol. 114, no. 1, p. 012021, Feb. 2016, doi: 10.1088/1757-899X/114/1/012021.
- [8] Tungaloy Ibérica, “Mecanizado a alto avance de acero templado, material sinterizado, fundición e Inconel con plaquitas Tungaloy CBN.” Accessed: Sep. 17, 2024. [Online]. Available: https://tungaloy.com/es/whats-new/blogs_pcbn-inserts/

- [9] A. S. S S and M. B, “Review on 3D printing techniques for cutting tools with cooling channels,” *Heliyon*, vol. 9, no. 12, p. e22557, Dec. 2023, doi: 10.1016/J.HELIYON.2023.E22557.
- [10] H. M. Ortner, P. Ettmayer, H. Kolaska, and I. Smid, “The history of the technological progress of hardmetals,” *Int J Refract Metals Hard Mater*, vol. 49, no. 1, pp. 3–8, Mar. 2015, doi: 10.1016/J.IJRMHM.2014.04.016.
- [11] Sandvik Coromant, “Celebrando 100 años del carburo cementado,” *EFEcomunica*, 2023. Accessed: Sep. 17, 2024. [Online]. Available: <https://efecomunica.efe.com/celebrando-100-anos-del-carburo-cementado/>
- [12] R. Komanduri, “Cutting-tool Materials,” *Encyclopedia of Materials: Science and Technology*, pp. 1–13, Jan. 2001, doi: 10.1016/B0-08-043152-6/00353-3.
- [13] Sandvik Coromat, *Mecanizado moderno : manual práctico*. Sandvik Coromat, 1994. Accessed: Sep. 09, 2024. [Online]. Available: <https://libreriacaJonDesastre.com/tecnicos/el-mecanizado-moderno-manual-practico-27277>
- [14] P. Ettmayer, H. Kolaska, and H. M. Ortner, “History of Hardmetals,” *Comprehensive Hard Materials*, vol. 1, pp. 3–27, Jan. 2014, doi: 10.1016/B978-0-08-096527-7.00001-5.
- [15] E. M. . Trent, “Metal cutting,” p. 245, 1991.
- [16] J. García, V. Collado Ciprés, A. Blomqvist, and B. Kaplan, “Cemented carbide microstructures: a review,” *Int J Refract Metals Hard Mater*, vol. 80, pp. 40–68, Apr. 2019, doi: 10.1016/J.IJRMHM.2018.12.004.
- [17] S. N. Monteiro, A. L. D. Skury, M. G. De Azevedo, and G. S. Bobrovnitchii, “Cubic boron nitride competing with diamond as a superhard engineering material – an overview,” *Journal of Materials Research and Technology*, vol. 2, no. 1, pp. 68–74, Jan. 2013, doi: 10.1016/J.JMRT.2013.03.004.
- [18] V. Kanyanta, “Microstructure-property correlations for hard, superhard, and ultrahard materials,” *Microstructure-Property Correlations for Hard, Superhard, and Ultrahard Materials*, pp. 1–239, Jan. 2016, doi: 10.1007/978-3-319-29291-5/COVER.
- [19] L. W. Crane and A. P. Bigg, “Fracture toughness of high speed steels,” *Materials Science and Technology*, vol. 6, no. 10, pp. 993–998, Oct. 1990, doi: 10.1179/026708390790189470.

-
- [20] B. V. Cockeram, "Fracture toughness testing and toughening mechanisms of some commercial cobalt-free hardfacing alloys," *Surf Coat Technol*, vol. 108–109, pp. 377–384, Oct. 1998, doi: 10.1016/S0257-8972(98)00600-8.
- [21] N. Chawla and K. K. Chawla, "Metal matrix composites," *Metal Matrix Composites*, vol. 9781461495482, pp. 1–370, Nov. 2013, doi: 10.1007/978-1-4614-9548-2/COVER.
- [22] E. Chicardi Augusto, "Desarrollo de cermets basados en soluciones sólidas mediante procesos mecanoquímicos," Universidad de Sevilla, Sevilla, España, 2014. [Online]. Available: <https://idus.us.es/handle/11441/53975;jsessionid=D6E4DA1A9BFCB17D7CE02D90A7FEA82E?>
- [23] N. J. Petch, "The Cleavage Strength of Polycrystals," *Journal of the Iron and Steel Institute*, vol. 174, pp. 25–28, 1953.
- [24] W. Schubert, E. Lassner, and W. Böhlke, "Cemented Carbides – A Success Story," 2010.
- [25] P. Alvaredo, S. A. Tsipas, and E. Gordo, "Influence of carbon content on the sinterability of an FeCr matrix cermet reinforced with TiCN," *Int J Refract Metals Hard Mater*, vol. 36, pp. 283–288, Jan. 2013, doi: 10.1016/J.IJRMHM.2012.10.007.
- [26] G. Li, Y. Peng, L. Yan, T. Xu, J. Long, and F. Luo, "Effects of Cr concentration on the microstructure and properties of WC-Ni cemented carbides," *Journal of Materials Research and Technology*, vol. 9, no. 1, pp. 902–907, Jan. 2020, doi: 10.1016/J.JMRT.2019.11.030.
- [27] F. Zhang, J. He, K. Chen, Y. Qin, C. Li, and F. Yin, "Microstructure evolution and mechanical properties of TiCN-Cr nano/micro composite coatings prepared by reactive plasma spraying," *Appl Surf Sci*, vol. 427, pp. 905–914, Jan. 2018, doi: 10.1016/J.APSUSC.2017.08.121.
- [28] J. Xiong, Z. Guo, B. Shen, and D. Cao, "The effect of WC, Mo₂C, TaC content on the microstructure and properties of ultra-fine TiC_{0.7}N_{0.3} cermet," *Mater Des*, vol. 28, no. 5, pp. 1689–1694, Jan. 2007, doi: 10.1016/J.MATDES.2006.03.005.
- [29] N. Li, W. Zhang, P. Zhou, J. Lv, and Y. Du, "Effect of the combined addition of TaC and NbC on the dispersity of cubic phase in ultra-fine WC–10Co–

- 0.5Cr cemented carbides,” *Mater Res Express*, vol. 7, no. 10, p. 106505, Oct. 2020, doi: 10.1088/2053-1591/ABBD5D.
- [30] X. Duan, Y. Huang, W. Liu, Q. Cai, W. Liu, and Y. Ma, “Effect of Ta on the microstructure and mechanical properties of WTa alloys prepared by arc melting,” *Mater Charact*, vol. 188, p. 111823, Jun. 2022, doi: 10.1016/J.MATCHAR.2022.111823.
- [31] W. Wan, J. Xiong, Y. Li, Q. Tang, and M. Liang, “Erosion-corrosion behavior of Ti(C,N)-based cermets containing different secondary carbides,” *Int J Refract Metals Hard Mater*, vol. 66, pp. 180–187, Aug. 2017, doi: 10.1016/J.IJRMHM.2017.03.018.
- [32] S. Zhang *et al.*, “Effect of Ta Content on Microstructure and Properties of (Ti,W)C-Based Cermets,” *Metals 2022, Vol. 12, Page 1282*, vol. 12, no. 8, p. 1282, Jul. 2022, doi: 10.3390/MET12081282.
- [33] M. Naidoo, O. Johnson, I. Sigalas, and M. Herrmann, “Influence of tantalum on the microstructure and properties of Ti(C,N)-Ni cermets,” *Int J Refract Metals Hard Mater*, vol. 42, pp. 97–102, Jan. 2014, doi: 10.1016/J.IJRMHM.2013.08.008.
- [34] A. G. P. da Silva, W. D. Schubert, and B. Lux, “The role of the binder phase in the WC-Co sintering,” *Materials Research*, vol. 4, no. 2, pp. 59–62, 2001, doi: 10.1590/S1516-14392001000200003.
- [35] S. Kim, S. H. Han, J. K. Park, and H. E. Kim, “Variation of WC grain shape with carbon content in the WC–Co alloys during liquid-phase sintering,” *Scr Mater*, vol. 48, no. 5, pp. 635–639, Mar. 2003, doi: 10.1016/S1359-6462(02)00464-5.
- [36] “Machine Tools Market Size.” Accessed: Sep. 17, 2024. [Online]. Available: <https://www.precedenceresearch.com/machine-tools-market>
- [37] “Metal Cutting Tools Market - Global Industry Analysis and Forecast.” Accessed: Sep. 17, 2024. [Online]. Available: <https://www.maximizemarketresearch.com/market-report/global-metal-cutting-tools-market/35510/>
- [38] P. Alves. Dias, Darina. Blagoeva, Claudiu. Pavel, and Nikolaos. Arvanitidis, “Cobalt: demand-supply balances in the transition to electric mobility,” Nov. 2018, doi: 10.2760/97710.

-
- [39] I. Energy Agency, “Global Critical Minerals Outlook 2024,” 2024. [Online]. Available: www.iea.org
- [40] I. Energy Agency, “Critical Minerals Market Review 2023 – Analysis - IEA,” 2023. Accessed: Sep. 17, 2024. [Online]. Available: <https://www.iea.org/reports/critical-minerals-market-review-2023>
- [41] H. Margareth, “Study on the Critical Raw Materilas for the EU 2023,” *European Council*, p. 32, 2023, Accessed: Oct. 22, 2024. [Online]. Available: <http://www.europa.eu>
- [42] M. Cera *et al.*, “Trends and perspectives in the use of organic acids for critical metal recycling from hard-metal scraps,” *Int J Refract Metals Hard Mater*, vol. 114, p. 106249, Aug. 2023, doi: 10.1016/J.IJRMHM.2023.106249.
- [43] B. Zeiler, A. Bartl, and W. D. Schubert, “Recycling of tungsten: Current share, economic limitations, technologies and future potential,” *Int J Refract Metals Hard Mater*, vol. 98, p. 105546, Aug. 2021, doi: 10.1016/J.IJRMHM.2021.105546.
- [44] “Reciclaje de carburo cementado Tamaño del mercado, participación, alcance, tendencias y pronóstico para 2030,” 2023. Accessed: Sep. 07, 2024. [Online]. Available: <https://www.verifiedmarketreports.com/es/product/cemented-carbide-recycling-market/>
- [45] R. P. Singh Gaur, “Modern hydrometallurgical production methods for tungsten,” *JOM*, vol. 58, no. 9, pp. 45–49, 2006, doi: 10.1007/S11837-006-0082-0/METRICS.
- [46] G. Kücher, S. Luidold, C. Czettl, and C. Storf, “Successful control of the reaction mechanism for semi-direct recycling of hard metals,” *Int J Refract Metals Hard Mater*, vol. 86, p. 105131, Jan. 2020, doi: 10.1016/J.IJRMHM.2019.105131.
- [47] W. Lengauer, L. Zhang, J. L. Johnson, and A. Bose, “Preface to the special issue on 100 years of hardmetals,” *Int J Refract Metals Hard Mater*, vol. 119, p. 106553, Feb. 2024, doi: 10.1016/J.IJRMHM.2024.106553.
- [48] O. Eso, X. Wang, S. Wolf, and T. Puzz, “Property correlations of WC-Co with modified binders,” *Int J Refract Metals Hard Mater*, vol. 118, p. 106482, Jan. 2024, doi: 10.1016/J.IJRMHM.2023.106482.

- [49] B. Zhou *et al.*, “WC-Co-TiNbZr composite with simultaneously high hardness and fracture toughness,” *Int J Refract Metals Hard Mater*, vol. 116, p. 106332, Nov. 2023, doi: 10.1016/J.IJRMHM.2023.106332.
- [50] R. Sadangi and A. Bose, “Some aspects of solid solution grain growth inhibitors in cemented tungsten carbides,” *Int J Refract Metals Hard Mater*, vol. 119, p. 106474, Feb. 2024, doi: 10.1016/J.IJRMHM.2023.106474.
- [51] S. J. Fudger, T. L. Luckenbaugh, B. C. Hornbuckle, and K. A. Darling, “Mechanical properties of cemented tungsten carbide with nanocrystalline FeNiZr binder,” *Int J Refract Metals Hard Mater*, vol. 118, p. 106465, Jan. 2024, doi: 10.1016/J.IJRMHM.2023.106465.
- [52] M. de Nicolás-Morillas *et al.*, “Processing of WC with Fe-based alternative binders: Adjustment of C content and effect of Cr addition,” *Int J Refract Metals Hard Mater*, vol. 118, p. 106444, Jan. 2024, doi: 10.1016/J.IJRMHM.2023.106444.
- [53] R. de Oro Calderon, M. Lunzer, I. Wodak, and R. Steinlechner, “Fundamental aspects of phase formation in WC-based cemented carbides containing FeMn-based binders,” *Int J Refract Metals Hard Mater*, vol. 117, p. 106411, Dec. 2023, doi: 10.1016/J.IJRMHM.2023.106411.
- [54] M. Fürst, W. Lengauer, R. Wartbichler, J. M. Tarragó, C. Beltz de Arancibia, and S. Moseley, “Microstructural analysis and ASTM B611-21 wear testing of novel binder hardmetals for future percussive drilling applications,” *Int J Refract Metals Hard Mater*, vol. 118, p. 106440, Jan. 2024, doi: 10.1016/J.IJRMHM.2023.106440.
- [55] Y. Wu, Z. Lu, Y. Qin, Z. Bao, and L. Luo, “Ultrafine/nano WC-Co cemented carbide: Overview of preparation and key technologies,” *Journal of Materials Research and Technology*, vol. 27, pp. 5822–5839, Nov. 2023, doi: 10.1016/J.JMRT.2023.10.315.
- [56] G. H. Ha and B. K. Kim, “Synthesis of ultrafine WC/Co powder by mechanochemical process,” <https://doi.org/10.1179/003258902225001506>, vol. 45, no. 1, pp. 29–32, Feb. 2002, doi: 10.1179/003258902225001506.
- [57] S. Park and S. Kang, “Toughened ultra-fine (Ti,W)(CN)–Ni cermets,” *Scr Mater*, vol. 52, no. 2, pp. 129–133, Jan. 2005, doi: 10.1016/J.SCRIPTAMAT.2004.09.017.

-
- [58] K. Das, T. K. Bandyopadhyay, and S. Das, "A review on the various synthesis routes of TiC reinforced ferrous based composites," *J Mater Sci*, vol. 37, no. 18, pp. 3881–3892, Sep. 2002, doi: 10.1023/A:1019699205003/METRICS.
- [59] G. S. Upadhyaya, *Powder Metallurgy Technology*. Kanpur, India: Cambridge International Science Publishing, 2002.
- [60] C. C. DeMerlis and D. R. Schoneker, "Review of the oral toxicity of polyvinyl alcohol (PVA)," *Food and Chemical Toxicology*, vol. 41, no. 3, pp. 319–326, Mar. 2003, doi: 10.1016/S0278-6915(02)00258-2.
- [61] K. Deshmukh, M. Basheer Ahamed, R. R. Deshmukh, S. K. Khadheer Pasha, P. R. Bhagat, and K. Chidambaram, "Biopolymer Composites With High Dielectric Performance: Interface Engineering," *Biopolymer Composites in Electronics*, pp. 27–128, Jan. 2017, doi: 10.1016/B978-0-12-809261-3.00003-6.
- [62] S. E. Bianchi *et al.*, "Evaluation of the solubility of the HPMC: PVA blends in biological fluids in vitro," *Materials Research*, vol. 14, no. 2, pp. 166–171, 2011, doi: 10.1590/S1516-14392011005000033.
- [63] M. Monschke and K. G. Wagner, "Impact of HPMCAS on the Dissolution Performance of Polyvinyl Alcohol Celecoxib Amorphous Solid Dispersions," *Pharmaceutics*, vol. 12, no. 6, pp. 1–17, Jun. 2020, doi: 10.3390/PHARMACEUTICS12060541.
- [64] O. W. Guirguis, M. T. H. Moselhey, O. W. Guirguis, and M. T. H. Moselhey, "Thermal and structural studies of poly (vinyl alcohol) and hydroxypropyl cellulose blends," *Nat Sci (Irvine)*, vol. 4, no. 1, pp. 57–67, Dec. 2011, doi: 10.4236/NS.2012.41009.
- [65] L. Montes, C. M. Rosell, and R. Moreira, "Rheological Properties of Corn Starch Gels With the Addition of Hydroxypropyl Methylcellulose of Different Viscosities," *Front Nutr*, vol. 9, p. 866789, Mar. 2022, doi: 10.3389/FNUT.2022.866789/BIBTEX.
- [66] Y. Yin *et al.*, "Effect of Hydroxypropyl methyl cellulose (HPMC) on rheology and printability of the first printed layer of cement activated slag-based 3D printing concrete," *Constr Build Mater*, vol. 405, p. 133347, Nov. 2023, doi: 10.1016/J.CONBUILDMAT.2023.133347.
- [67] M. Dios, Z. Gonzalez, P. Alvaredo, R. Bermejo, E. Gordo, and B. Ferrari, "Novel colloidal approach for the microstructural improvement in

- Ti(C,N)/FeNi cermets,” *J Alloys Compd*, vol. 724, pp. 327–338, Nov. 2017, doi: 10.1016/J.JALLCOM.2017.07.034.
- [68] M. de Dios Pérez, D. Elena Gordo Odériz Dra Begoña Ferrari Fernández, and D. Elena Gordo Odériz, “Synthesis, Processing and Mechanical Characterization of Ti(C,N)-based cermets through the combination of Colloidal and Powder Metallurgy techniques,” 2017.
- [69] E. Macarena García Ayala, A. Javier Sánchez Herencia, and P. D. in Chemistry José Ygnacio Pastor Caño, “Aqueous colloidal processing of W and WC-based composites, sintering and mechanical properties at high temperature,” 2021. doi: 10.20868/UPM.thesis.69337.
- [70] G. Bertrand, C. Filiatre, H. Mahdjoub, A. Foissy, and C. Coddet, “Influence of slurry characteristics on the morphology of spray-dried alumina powders,” *J Eur Ceram Soc*, vol. 23, no. 2, pp. 263–271, Feb. 2003, doi: 10.1016/S0955-2219(02)00171-1.
- [71] N. Ricardo and R. Reyes, “Modelación de la ecuación constitutiva de suspensiones de caolín en función de la energía libre superficial del mineral,” 2013, Accessed: May 29, 2024. [Online]. Available: <https://repositorio.unal.edu.co/handle/unal/20320>
- [72] I. Martín, R. Salcedo, and R. Font, “Mecánica de Fluidos. Tema1-Flujo interno,” Alicante, 2011.
- [73] E. Molero Romero and D. Begoña Ferrari Fernández Antonio Javier Sánchez Herencia, “Aditivos de procesamiento en el conformado de estructuras porosas: relevancia de la sinergia partícula-gel,” Jan. 2016, Accessed: May 29, 2024. [Online]. Available: <https://repositorio.uam.es/handle/10486/671252>
- [74] ASTM, “E384-Standard Test Method for Microindentation Hardness of Materials.” doi: 10.1520/E0384-17.
- [75] ASTM, “C1327-Standard Test Method for Vickers Indentation Hardness of Advanced Ceramics.” [Online]. Available: www.astm.org,
- [76] F. P. Beer, E. R. Johnston Jr., J. T. DeWolf, and D. F. Mazurek, *Mechanics of Materials*, 7th ed. McGraw-Hill, 2019.
- [77] ASTM, “C1161-Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature.” [Online]. Available: www.astm.org

-
- [78] ASTM, “C1211-Standard Test Method for Flexural Strength of Advanced Ceramics at Elevated Temperatures 1.” [Online]. Available: www.dodssp.daps.mil.
- [79] ASTM, “C1421-Standard Test Methods for Determination of Fracture Toughness of Advanced Ceramics at Ambient Temperature.” doi: 10.1520/C1421-16.
- [80] ASTM, “E1820-Standard Test Method for Measurement of Fracture Toughness.” doi: 10.1520/E1820-20E01.
- [81] A. Villalobos, “Tenacidad a la Fractura. Método para obtener el K_{1c},” Universidad de los Andes, Bogotá, 2003. [Online]. Available: <chrome-extension://efaidnbmnnnibpcajpcglefindmkaj/https://repositorio.uniandes.edu.co/server/api/core/bitstreams/176f1ea4-45f4-4e2c-8f26-5bc4dea7b525/content>
- [82] H. Tada, P. C. Paris, and G. R. Irwin, “The Stress Analysis of Cracks Handbook, Third Edition,” *The Stress Analysis of Cracks Handbook, Third Edition*, Jul. 2000, doi: 10.1115/1.801535.
- [83] G. V. Guinea, J. Y. Pastor, J. Planas, and M. Elices, “Stress intensity factor, compliance and CMOD for a general three-point-bend beam,” *Int J Fract*, vol. 89, no. 2, pp. 103–116, 1998, doi: 10.1023/A:1007498132504/METRICS.
- [84] ASTM, “G99-Standard Test Method for Wear Testing with a Pin-on-Disk.” doi: 10.1520/G0099-17.
- [85] ASTM, “G133-Linearly Reciprocating Ball-on-Flat Sliding Wear.”
- [86] W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, “Flash Method of Determining Thermal Diffusivity, Heat Capacity, and Thermal Conductivity,” *J Appl Phys*, vol. 32, no. 9, pp. 1679–1684, Sep. 1961, doi: 10.1063/1.1728417.
- [87] S. Lee and D. Kim, “The evaluation of cross-plane/in-plane thermal diffusivity using laser flash apparatus,” *Thermochim Acta*, vol. 653, pp. 126–132, Jul. 2017, doi: 10.1016/J.TCA.2017.04.011.
- [88] E. J. Carr, “Rear-surface integral method for calculating thermal diffusivity from laser flash experiments,” *Chem Eng Sci*, vol. 199, pp. 546–551, May 2019, doi: 10.1016/J.CES.2019.01.014.

- [89] M. Akoshima, H. Abe, and T. Baba, “Thermal Diffusivity of Carbon Materials as Candidate Reference Materials,” *Int J Thermophys*, vol. 36, no. 10–11, pp. 2507–2517, Nov. 2015, doi: 10.1007/S10765-014-1624-2/FIGURES/8.
- [90] ASTM, “E1461-Standard Test Method for Thermal Diffusivity by the Flash Method.”
- [91] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*. Oxford University Press, 1959. Accessed: May 22, 2024. [Online]. Available: <https://global.oup.com/academic/product/conduction-of-heat-in-solids-9780198533689>
- [92] D. A. Watt, “Theory of thermal diffusivity by pulse technique,” *British Journal of Applied Physics*, vol. 17, no. 2, p. 231, Feb. 1966, doi: 10.1088/0508-3443/17/2/311.
- [93] K. B. Larson and K. Koyama, “Correction for Finite-Pulse-Time Effects in Very Thin Samples using the Flash Method of Measuring Thermal Diffusivity,” *J Appl Phys*, vol. 38, no. 2, pp. 465–474, Feb. 1967, doi: 10.1063/1.1709360.
- [94] R. E. Taylor and J. A. Cape, “Finite Pulse-Time Effects In The Flash Diffusivity Technique,” *Appl Phys Lett*, vol. 5, no. 10, pp. 212–213, Nov. 1964, doi: 10.1063/1.1723593.
- [95] T. Azumi and Y. Takahashi, “Novel finite pulse-width correction in flash thermal diffusivity measurement,” *Review of Scientific Instruments*, vol. 52, no. 9, pp. 1411–1413, Sep. 1981, doi: 10.1063/1.1136793.
- [96] T. Re and C. LM III, “Finite Pulse Time Effects In Flash Diffusivity Method,” *High Temperature - High Pressure*, 6, vol. 65, 1974.
- [97] L. M. Clark and R. E. Taylor, “Radiation loss in the flash method for thermal diffusivity,” *J Appl Phys*, vol. 46, no. 2, pp. 714–719, Feb. 1975, doi: 10.1063/1.321635.
- [98] J. A. McKay and J. T. Schriempf, “Corrections for nonuniform surface-heating errors in flash-method thermal-diffusivity measurements,” *J Appl Phys*, vol. 47, no. 4, pp. 1668–1671, Apr. 1976, doi: 10.1063/1.322790.
- [99] J. A. Koski, “Improved data-reduction methods for laser-pulse-diffusivity determination with the use of minicomputers,” Jan. 01, 1981.

- [100] A. Degiovanni and M. Laurent, “Une nouvelle technique d’identification de la diffusivité thermique pour la méthode «flash»,” *Revue de Physique Appliquée*, vol. 21, no. 3, pp. 229–237, Mar. 1986, doi: 10.1051/RPHYSAP:01986002103022900.
- [101] M. González Miquel, “Disolventes verdes: apostando por nuevas soluciones para una industria química sostenible | Escuela Industriales UPM Madrid,” *Comunicaciones ETSII*, 2021. Accessed: Jun. 18, 2024. [Online]. Available: <https://www.escuelaindustrialesupm.com/investigacion/disolventes-verdes-apostando-por-nuevas-soluciones-para-una-industria-quimica-sostenible/>
- [102] I. Gonzalo-Juan, B. Ferrari, M. T. Colomer, and A. J. Sánchez-Herencia, “Colloidal processing and sintering of porous percolative Ni-YSZ layers,” *J Memb Sci*, vol. 352, no. 1–2, pp. 55–62, Apr. 2010, doi: 10.1016/J.MEMSCI.2010.01.060.
- [103] R. G. Neves, J. A. Escribano, B. Ferrari, E. Gordo, and A. J. Sanchez-Herencia, “Improvement of Ti Processing through Colloidal Techniques,” *Key Eng Mater*, vol. 520, pp. 335–340, 2012, doi: 10.4028/WWW.SCIENTIFIC.NET/KEM.520.335.
- [104] E. Molero, B. Ferrari, A. J. Sanchez-Herencia, E. Gordo, and P. Colombo, “Ti/Ti₃SiC₂(/TiC) Bulk and Foam Composites by Pyrolysis of Polycarbosilane and TiH₂ Mixtures,” *Adv Eng Mater*, vol. 19, no. 6, p. 1600700, Jun. 2017, doi: 10.1002/ADEM.201600700.
- [105] M. Dios, Z. Gonzalez, P. Alvaredo, R. Bermejo, E. Gordo, and B. Ferrari, “Novel colloidal approach for the microstructural improvement in Ti(C,N)/FeNi cermets,” *J Alloys Compd*, vol. 724, pp. 327–338, Nov. 2017, doi: 10.1016/J.JALLCOM.2017.07.034.
- [106] E. M. Garcia-Ayala, L. Silvestroni, J. Yus, B. Ferrari, J. Y. Pastor, and A. J. Sanchez-Herencia, “Colloidal processing and sintering of WC-based ceramics with low Ni content as sintering aid,” *J Eur Ceram Soc*, vol. 41, no. 3, pp. 1848–1858, Mar. 2021, doi: 10.1016/J.JEURCERAMSOC.2020.10.038.
- [107] M. J. Choi, M. R. Woo, H. G. Choi, and S. G. Jin, “Effects of Polymers on the Drug Solubility and Dissolution Enhancement of Poorly Water-Soluble Rivaroxaban,” *Int J Mol Sci*, vol. 23, no. 16, Aug. 2022, doi: 10.3390/IJMS23169491.

- [108] P. Kraisit, S. Limmatvapirat, J. Nunthanid, P. Sriamornsak, and M. Luangtana-Anan, "Preparation and Characterization of Hydroxypropyl Methylcellulose/Polycarbophil Mucoadhesive Blend Films Using a Mixture Design Approach," *Chem Pharm Bull (Tokyo)*, vol. 65, no. 3, pp. 284–294, Mar. 2017, doi: 10.1248/CPB.C16-00849.
- [109] J. Zhang, M. Guo, M. Luo, and T. Cai, "Advances in the development of amorphous solid dispersions: The role of polymeric carriers," *Asian J Pharm Sci*, vol. 18, no. 4, p. 100834, Jul. 2023, doi: 10.1016/J.AJPS.2023.100834.
- [110] J. H. Lee *et al.*, "Enhanced dissolution rate of celecoxib using PVP and/or HPMC-based solid dispersions prepared by spray drying method," *J Pharm Investig*, vol. 43, no. 3, pp. 205–213, Jun. 2013, doi: 10.1007/S40005-013-0067-2/FIGURES/8.
- [111] K. L. Christensen, G. P. Pedersen, and H. G. Kristensen, "Preparation of redispersible dry emulsions by spray drying," *Int J Pharm*, vol. 212, no. 2, pp. 187–194, Jan. 2001, doi: 10.1016/S0378-5173(00)00596-2.
- [112] J. Z. Li, L. J. Zhao, X. Lin, L. Shen, and Y. Feng, "Co-spray Drying with HPMC as a Platform to Improve Direct Compaction Properties of Various Tablet Fillers," *AAPS PharmSciTech*, vol. 18, no. 8, pp. 3105–3115, Nov. 2017, doi: 10.1208/S12249-017-0794-1/TABLES/7.
- [113] J. C. Soriano Rodríguez and J. de la Fuente Feria, "Características reológicas de dispersiones coloidales en transición Sol-Gel," Universidad de Sevilla, Sevilla, 2014. Accessed: Jul. 07, 2024. [Online]. Available: <https://idus.us.es/handle/11441/50259>
- [114] E. Molero Romero and D. Begoña Ferrari Fernández Antonio Javier Sánchez Herencia, "Aditivos de procesamiento en el conformado de estructuras porosas: relevancia de la sinergia partícula-gel Memoria presentada por," 2016. [Online]. Available: <http://hdl.handle.net/10486/671252>
- [115] J. C. Soriano Rodríguez and J. de la Fuente Feria, "Características reológicas de dispersiones coloidales en transición Sol-Gel," Universidad de Sevilla, Sevilla, 2014. Accessed: Jul. 07, 2024. [Online]. Available: <https://idus.us.es/handle/11441/50259>
- [116] M. de Dios Pérez, D. Elena Gordo Odériz Dra Begoña Ferrari Fernández, and D. Elena Gordo Odériz, "Synthesis, processing and mechanical characterization of Ti(C,N)-based cermets through the combination of

- colloidal and powder metallurgy techniques,” 2017. Accessed: Jun. 24, 2024. [Online]. Available: <https://hdl.handle.net/10016/27083>
- [117] G. Bertrand, C. Filiatre, H. Mahdjoub, A. Foissy, and C. Coddet, “Influence of slurry characteristics on the morphology of spray-dried alumina powders,” *J Eur Ceram Soc*, vol. 23, no. 2, pp. 263–271, Feb. 2003, doi: 10.1016/S0955-2219(02)00171-1.
- [118] A. Stunda-Zujeva, Z. Irbe, and L. Berzina-Cimdina, “Controlling the morphology of ceramic and composite powders obtained via spray drying – A review,” *Ceram Int*, vol. 43, no. 15, pp. 11543–11551, Oct. 2017, doi: 10.1016/J.CERAMINT.2017.05.023.
- [119] J. I. Tsubaki, H. Yamakawa, T. Mori, and H. Mori, “Optimization of Granules and Slurries for Press Forming,” *Journal of the Ceramic Society of Japan*, vol. 110, no. 1286, pp. 894–898, Oct. 2002, doi: 10.2109/JCERSJ.110.894.
- [120] M. I. Zainuddin, S. Tanaka, R. Furushima, and K. Uematsu, “Correlation between slurry properties and structures and properties of granules,” *J Eur Ceram Soc*, vol. 30, no. 16, pp. 3291–3296, Dec. 2010, doi: 10.1016/J.JEURCERAMSOC.2010.07.004.
- [121] K. Ramabulana, M. Tambani, C. Machio, and M. E. Makhatha, “Effect of particle size distribution on green properties and sintering of Ti-6Al-4V,” *IOP Conf Ser Mater Sci Eng*, vol. 655, no. 1, p. 012020, Oct. 2019, doi: 10.1088/1757-899X/655/1/012020.
- [122] R. M. German, *Sintering theory and practice by Randall M. German / Biblioteca Abierta*. Wiley-Interscience, 1996. Accessed: Jul. 07, 2024. [Online]. Available: https://openlibrary.org/books/OL787893M/Sintering_theory_and_practice
- [123] M. N. Rahaman, *Ceramic processing and sintering*, Second. CRC Press, 2017. doi: 10.1201/9781315274126.
- [124] W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*. Wiley-Interscience, 1976. Accessed: Jul. 07, 2024. [Online]. Available: <https://www.iberlibro.com/Introduction-Ceramics-Kingery-Bowen-Kent-Uhlmann/30364269815/bd>
- [125] R. M. German, “Coarsening in Sintering: Grain Shape Distribution, Grain Size Distribution, and Grain Growth Kinetics in Solid-Pore Systems,”

- Critical Reviews in Solid State and Materials Sciences*, vol. 35, no. 4, pp. 263–305, Nov. 2010, doi: 10.1080/10408436.2010.525197.
- [126] W. D. Callister and D. G. Rethwisch, *Materials science and engineering: an introduction*, 9th ed. Wiley, 2013. Accessed: Jul. 07, 2024. [Online]. Available: https://books.google.com/books/about/Materials_Science_and_Engineering.html?hl=es&id=8ymtMwEACAAJ
- [127] F. J. Iglesias, C. Martínez, M. T. Cotes, J. M. Ruiz, L. E. García, and F. Corpas, “Influencia de la atmósfera de sinterización en las propiedades mecánicas de los aceros P/M AISI 430L,” *Revista de Metalurgia*, vol. 50, no. 1, 2014, doi: 10.3989/REVMETALM.008.
- [128] ASM Handbook, “ASM Handbook, Volume 7: Powder Metallurgy - ASM International,” in *Powder Metal Technologies and Applications*, vol. 7, P. K. Samal and J. W. Newkirk, Eds., 1998.
- [129] R. Bures *et al.*, “High pressure compaction of soft magnetic iron powder,” *Powder Technol*, vol. 421, p. 118434, May 2023, doi: 10.1016/J.POWTEC.2023.118434.
- [130] R. M. Aranda, F. Ternero, R. Astacio, P. Urban, and F. G. Cuevas, “Consolidation of iron powder by electrical discharge,” *Mater Today Proc*, vol. 67, pp. 330–335, Jan. 2022, doi: 10.1016/J.MATPR.2022.07.186.
- [131] C. S. Kang, S. C. Lee, K. T. Kim, and O. Rozenberg, “Densification behavior of iron powder during cold stepped compaction,” *Materials Science and Engineering: A*, vol. 452–453, pp. 359–366, Apr. 2007, doi: 10.1016/J.MSEA.2006.10.113.
- [132] F. V. Lenel, “Powder metallurgy: principles and applications,” p. 593, 1980.
- [133] X. Liu, P. Tang, and W. Chen, “Development of an ettringite-based low carbon binder by promoting the nucleation and Ostwald ripening process,” *Constr Build Mater*, vol. 427, p. 136282, May 2024, doi: 10.1016/J.CONBUILDMAT.2024.136282.
- [134] A. V. Shatov, S. A. Firstov, and I. V. Shatova, “The shape of WC crystals in cemented carbides,” *Materials Science and Engineering: A*, vol. 242, no. 1–2, pp. 7–14, Feb. 1998, doi: 10.1016/S0921-5093(97)00509-1.

- [135] R. M. German, P. Suri, and S. J. Park, "Review: Liquid phase sintering," *J Mater Sci*, vol. 44, no. 1, pp. 1–39, Jan. 2009, doi: 10.1007/S10853-008-3008-0/FIGURES/36.
- [136] L. Chen, W. Lengauer, and K. Dreyer, "Advances in modern nitrogen-containing hardmetals and cermets," *Int J Refract Metals Hard Mater*, vol. 18, no. 2–3, pp. 153–161, Mar. 2000, doi: 10.1016/S0263-4368(00)00016-0.
- [137] K. Frisk, L. Dumitrescu, B. Sunduman, B. Jansson, and O. Kruse, "Development of a database for cemented carbides: Thermodynamic modeling and experiments," *Journal of Phase Equilibria*, vol. 22, no. 6, pp. 645–655, 2001, doi: 10.1007/S11669-001-0028-8/METRICS.
- [138] H. E. Exner, J. Freytag, G. Petzow, and P. Walter, "Sintering of a WC-12 wt% Co Hard Metal with Varying Binder Phase Composition.[SINTERVERLAUF EINES WC-12 GEW. -% Co HARTMETALLS MIT UNTERSCHIEDLICHER BINDEPHASENZUSAMMENSETZUNG.]," *Planseeber Pulvermetall*, vol. 26, no. 2, pp. 90–104.
- [139] T. M. Shaw, "Model for the Effect of Powder Packing on the Driving Force for Liquid-Phase Sintering," *Journal of the American Ceramic Society*, vol. 76, no. 3, pp. 664–670, Mar. 1993, doi: 10.1111/J.1151-2916.1993.TB03657.X.
- [140] J. Kübarsepp, H. Klaasen, and J. Pirso, "Behaviour of TiC-base cermets in different wear conditions," 2001.
- [141] C. L. Cramer, A. D. Preston, K. Ma, and P. Nandwana, "In-situ metal binder-phase formation to make WC-FeNi Cermets with spark plasma sintering from WC, Fe, Ni, and carbon powders," *Int J Refract Metals Hard Mater*, vol. 88, Apr. 2020, doi: 10.1016/j.ijrmhm.2020.105204.
- [142] J. Kübarsepp, K. Juhani, and M. Tarraste, "Abrasion and erosion resistance of cermets: A review," Jan. 01, 2022, *MDPI*. doi: 10.3390/ma15010069.
- [143] F. J. Paneto *et al.*, "Effect of porosity on hardness of $\text{Al}_2\text{O}_3\text{--Y}_3\text{Al}_5\text{O}_{12}$ ceramic composite," *Int J Refract Metals Hard Mater*, vol. 48, pp. 365–368, Jan. 2015, doi: 10.1016/J.IJRMHM.2014.09.010.
- [144] K. Palanisamy, S. Gangolu, and J. Mangalam Antony, "Effects of HVOF spray parameters on porosity and hardness of 316L SS coated Mg AZ80 alloy," *Surf Coat Technol*, vol. 448, p. 128898, Oct. 2022, doi: 10.1016/J.SURFCOAT.2022.128898.

- [145] A. Petersson and J. Ågren, “Sintering shrinkage of WC–Co materials with bimodal grain size distributions,” *Acta Mater*, vol. 53, no. 6, pp. 1665–1671, Apr. 2005, doi: 10.1016/J.ACTAMAT.2004.12.016.
- [146] L. ZHANG, S. CHEN, Y. jie WANG, X. wang YU, and X. jun XIONG, “Tungsten carbide platelet-containing cemented carbide with yttrium containing dispersed phase,” *Transactions of Nonferrous Metals Society of China*, vol. 18, no. 1, pp. 104–108, Feb. 2008, doi: 10.1016/S1003-6326(08)60019-9.
- [147] M. Dios, Z. Gonzalez, P. Alvaredo, R. Bermejo, E. Gordo, and B. Ferrari, “Novel colloidal approach for the microstructural improvement in Ti(C,N)/FeNi cermets,” *J Alloys Compd*, vol. 724, pp. 327–338, Nov. 2017, doi: 10.1016/J.JALLCOM.2017.07.034.
- [148] M. Dios *et al.*, “Mechanical characterization of Ti(C,N)-based cermets fabricated through different colloidal processing routes,” *J Alloys Compd*, vol. 732, pp. 806–817, Jan. 2018, doi: 10.1016/J.JALLCOM.2017.10.274.
- [149] C. Qian, K. Li, X. yi Guo, B. Liu, Z. yi Long, and Y. Liu, “Effect of WC grain size on mechanical properties and microstructures of cemented carbide with medium entropy alloy Co-Ni-Fe binder,” *J Cent South Univ*, vol. 27, no. 4, pp. 1146–1157, Apr. 2020, doi: 10.1007/S11771-020-4355-5/METRICS.
- [150] S. Bolognini, D. Mari, T. Viatte, and W. Benoit, “Fracture toughness of coated TiCN–WC–Co cermets with graded composition,” *Int J Refract Metals Hard Mater*, vol. 19, no. 4–6, pp. 285–292, Jul. 2001, doi: 10.1016/S0263-4368(01)00025-7.
- [151] L. Z. Mohamed, W. A. Ghanem, O. A. El Kady, M. M. Lotfy, H. A. Ahmed, and F. A. Elrefaie, “Oxidation characteristics of porous-nickel prepared by powder metallurgy and cast-nickel at 1273 K in air for total oxidation time of 100 h,” *J Adv Res*, vol. 8, no. 6, pp. 717–729, Nov. 2017, doi: 10.1016/J.JARE.2017.08.004.
- [152] R. Haugrud, “On the high-temperature oxidation of nickel,” *Corros Sci*, vol. 45, no. 1, pp. 211–235, Jan. 2003, doi: 10.1016/S0010-938X(02)00085-9.
- [153] Z. F. Li, Y. Gao, G. M. Cao, and Z. Y. Liu, “High-efficiency reduction behavior for the oxide scale formed on hot-rolled steel in a mixed atmosphere of hydrogen and argon,” *J Mater Sci*, vol. 55, no. 4, pp. 1826–1839, Feb. 2020, doi: 10.1007/S10853-019-04027-0/FIGURES/14.

- [154] P. Kumar, H. No-Lee, and R. Kumar, "Synthesis of phase pure iron oxide polymorphs thin films and their enhanced magnetic properties," *Journal of Materials Science: Materials in Electronics*, vol. 25, no. 10, pp. 4553–4561, Oct. 2014, doi: 10.1007/S10854-014-2203-9/TABLES/2.
- [155] J. Habainy, S. Iyengar, K. B. Surreddi, Y. Lee, and Y. Dai, "Formation of oxide layers on tungsten at low oxygen partial pressures," *Journal of Nuclear Materials*, vol. 506, pp. 26–34, Aug. 2018, doi: 10.1016/J.JNUCMAT.2017.12.018.
- [156] C. Nilsson and J. Habainy, "Oxidation of Pure Tungsten in the Temperature Interval 400° to 900°C," Lund University, 2013.
- [157] L. J. Cárdenas Flechas, "Síntesis y caracterización de nanoestructuras de Co₃O₄ dopadas con Ni para aplicación en detección de gases," Universidad Nacional de Colombia, Colombia, 2022. [Online]. Available: <https://repositorio.unal.edu.co/handle/unal/82901>
- [158] X. Y. Cheng, J. H. Zhou, X. Xiong, Y. Du, and C. Jiang, "First-principles thermal equation of state of tungsten carbide," *Comput Mater Sci*, vol. 59, pp. 41–47, Jun. 2012, doi: 10.1016/J.COMMATSCI.2012.02.028.
- [159] F. FERNÁNDEZ-ROJAS, C. J. FERNÁNDEZ-ROJAS, K. J. SALAS P, V. J. GARCÍA, and E. E. MARINERO, "Conductividad térmica en metales, semiconductores, dieléctricos y materiales amorfos," *Revista de la Facultad de Ingeniería Universidad Central de Venezuela*, vol. 23, no. 3, pp. 5–15, 2008, Accessed: Sep. 15, 2024. [Online]. Available: http://ve.scielo.org/scielo.php?script=sci_arttext&pid=S0798-40652008000300001&lng=es&nrm=iso&tlng=es
- [160] K. Chen, W. Xiao, Z. Li, J. Wu, K. Hong, and X. Ruan, "Effect of Graphene and Carbon Nanotubes on the Thermal Conductivity of WC–Co Cemented Carbide," *Metals 2019, Vol. 9, Page 377*, vol. 9, no. 3, p. 377, Mar. 2019, doi: 10.3390/MET9030377.
- [161] S. Binder, W. Lengauer, and P. Ettmayer, "THE Ti-C-N SYSTEM AND PROPERTIES OF Ti(C,N)".
- [162] F. Grønvold, S. Stølen, E. F. Westrum, A. K. Labban, and B. Uhrenius, "Heat capacity and thermodynamic properties of ditungsten carbide, W₂C_{1-x}, from 10 to 1000 K," *Thermochim Acta*, vol. 129, no. 1, pp. 115–125, Jun. 1988, doi: 10.1016/0040-6031(88)87202-2.

- [163] J. F. Shackelford, Y.-H. Han, S. Kim, and S.-H. Kwon, *CRC Materials Science and Engineering Handbook*. CRC Press, 2016. doi: 10.1201/B18971.
- [164] Ryo Matsumoto, Tomio Itamochi, and Shoji Mori, “Effects of TiCN Composite Die with Low Thermal Conductivity on Hot Forging Performances,” *Journal of Mechanics Engineering and Automation*, vol. 6, no. 2, Feb. 2016, doi: 10.17265/2159-5275/2016.02.001.
- [165] T. Matsuda, “Effect of C/TiO₂ ratio in raw materials on thermal conductivity of titanium carbonitrides synthesized by carbothermal reduction,” *J Alloys Compd*, vol. 816, p. 152541, Mar. 2020, doi: 10.1016/J.JALLCOM.2019.152541.
- [166] K. Liu, X. P. Li, M. Rahman, and X. D. Liu, “CBN tool wear in ductile cutting of tungsten carbide,” *Wear*, vol. 255, no. 7–12, pp. 1344–1351, Aug. 2003, doi: 10.1016/S0043-1648(03)00061-9.
- [167] H. Wang, T. Webb, and J. W. Bitler, “Study of thermal expansion and thermal conductivity of cemented WC–Co composite,” *Int J Refract Metals Hard Mater*, vol. 49, no. 1, pp. 170–177, Mar. 2015, doi: 10.1016/J.IJRMHM.2014.06.009.
- [168] S. Wen *et al.*, “A new model for thermal conductivity of ‘continuous matrix / dispersed and separated 3D-particles’ type composite materials and its application to WC-M (M = Co, Ag) systems,” *J Mater Sci Technol*, vol. 97, pp. 123–133, Jan. 2022, doi: 10.1016/J.JMST.2021.04.036.
- [169] A. Dadgari, D. Huo, and D. Swailes, “Investigation on tool wear and tool life prediction in micro-milling of Ti-6Al-4V,” *Nanotechnology and Precision Engineering*, vol. 1, no. 4, pp. 218–225, Dec. 2018, doi: 10.1016/J.NPE.2018.12.005.
- [170] T. Polcar, R. Novák, and P. Šíroký, “The tribological characteristics of TiCN coating at elevated temperatures,” *Wear*, vol. 260, no. 1–2, pp. 40–49, Jan. 2006, doi: 10.1016/J.WEAR.2004.12.031.
- [171] R. Harouz, S. Boudebane, A. Lakehal, O. Derdy, and H. M. Montrieux, “Investigation of the tribological behaviour of WC/TiC based cermets in contact with Al₂O₃ alumina under high temperature,” *J Mech Behav Mater*, vol. 27, no. 1–2, Apr. 2018, doi: 10.1515/JMBM-2018-0004/MACHINEREADABLECITATION/RIS.

-
- [172] H. Liu, B. Yang, C. Wang, Y. Han, and D. Liu, “The mechanisms and applications of friction energy dissipation,” *Friction* 2022 11:6, vol. 11, no. 6, pp. 839–864, Aug. 2022, doi: 10.1007/S40544-022-0639-0.
- [173] L. Chen, D. Yi, B. Wang, H. Liu, and C. Wu, “Mechanism of the early stages of oxidation of WC–Co cemented carbides,” *Corros Sci*, vol. 103, pp. 75–87, Feb. 2016, doi: 10.1016/J.CORSCI.2015.11.007.
- [174] K. Akhtar, H. Khalid, I. Ul Haq, N. Zubair, Z. Ullah Khan, and A. Hussain, “Tribological Properties of Electrodeposited Ni-Co₃O₄ Nanocomposite Coating on Steel Substrate,” *J Tribol*, vol. 139, no. 6, Nov. 2017, doi: 10.1115/1.4036450/377898.
- [175] B. Gómez, A. Jiménez-Suarez, and E. Gordo, “Oxidation and tribological behaviour of an Fe-based MMC reinforced with TiCN particles,” *Int J Refract Metals Hard Mater*, vol. 27, no. 2, pp. 360–366, Mar. 2009, doi: 10.1016/J.IJRMHM.2008.10.012.
- [176] F. Díaz del Castillo Rodríguez, “TRIBOLOGÍA: FRICCIÓN, DESGASTE Y LUBRICACIÓN,” CUAUTITLÁN IZCALLI, 2007. Accessed: Sep. 27, 2024. [Online]. Available: <https://www.studocu.com/es-mx/document/tecnologico-de-estudios-superiores-de-ecatepec/derechos-humanos/tribologia/4786841>
- [177] M. Franquès and M. Astrid Gómez Botero, “Caracterización de las propiedades tribológicas de los recubrimientos duros,” 2007. Accessed: Sep. 27, 2024. [Online]. Available: <https://www.tdx.cat/handle/10803/1774>
- [178] D. Coureaux, R. Sagaró, J. Calzadilla, A. Mestra1, and L. Llanes, “Boración de Carburos Cementados WC-Co,” 2012.
- [179] Ó. Luengo López, “Estudio tribológico de fricción y desgaste de capas de aleación NiP,” 2008, Accessed: Sep. 27, 2024. [Online]. Available: <https://upcommons.upc.edu/handle/2099.1/6299>
- [180] F. Cheng, J. Lin, and Y. Liang, “Friction and wear properties of a high Nb-containing TiAl alloy against WC-8Co, Si₃N₄, and GCr15 in an unlubricated contact,” *Intermetallics (Barking)*, vol. 106, pp. 7–12, Mar. 2019, doi: 10.1016/J.INTERMET.2018.11.019.
- [181] P. Pérez-Oviedo and J. Torre-Nieto, “Guia de diseño para calcular el desgaste abrasivo entre componentes no lubricados,” 2015.

- [182] J. Hernando, O. J. Jairo, and A. J. Edgar, “Tribological Behavior of Ni-Based Coatings Deposited via Spray and Fuse Technique,” *Coatings* 2020, Vol. 10, Page 1080, vol. 10, no. 11, p. 1080, Nov. 2020, doi: 10.3390/COATINGS10111080.
- [183] E. P. Superior, F. De, A. Fernández, G.-O. Tutora, and P. A. Olmos, “Propiedades tribológicas en el sistema Fe-TiCN,” 2014. Accessed: Sep. 27, 2024. [Online]. Available: <https://hdl.handle.net/10016/22759>
- [184] W. Song, R. Zhang, X. Bai, Q. Jia, and H. Ji, “Exposed crystal facets of WO₃ nanosheets by phase control on NO₂-sensing performance,” *Journal of Materials Science: Materials in Electronics*, vol. 31, no. 1, pp. 610–620, Jan. 2020, doi: 10.1007/S10854-019-02565-6/FIGURES/10.
- [185] S. Chevalier, F. Desserrey, and J. P. Larpin, “Oxygen transport during the high temperature oxidation of pure nickel,” *Oxidation of Metals*, vol. 64, no. 3–4, pp. 219–234, Oct. 2005, doi: 10.1007/S11085-005-6560-X/METRICS.
- [186] “R120013 - RRUFF Database: Raman, X-ray, Infrared, and Chemistry.” Accessed: Aug. 21, 2024. [Online]. Available: <https://rruff.info/general=R120013/display=default/R120013>
- [187] T. Dennenwaldt *et al.*, “Insights into the structural, electronic, and magnetic properties of Fe_{2-x}Ti_xO₃/Fe₂O₃ thin films with x = 0.44 grown on Al₂O₃ (0001),” *J Mater Sci*, vol. 50, no. 1, pp. 122–137, Jan. 2015, doi: 10.1007/S10853-014-8572-X/FIGURES/11.
- [188] P. Alvaredo, C. Abajo, S. A. Tsipas, and E. Gordo, “Influence of heat treatment on the high temperature oxidation mechanisms of an Fe–TiCN cermet,” *J Alloys Compd*, vol. 591, pp. 72–79, Apr. 2014, doi: 10.1016/J.JALLCOM.2013.12.009.