UNIVERSIDAD POLITÉCNICA DE MADRID
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Fast Mapping of Microstructure and Mechanical Properties in Titanium Alloys by Kinetic Diffusion Multiple Approach

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2019

I would like to dedicate this thesis to my family and friends...

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Chuanyun Wang
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Abstract

Beta titanium alloys are alloyed with sufficient amounts of β -stabilizer elements (Mo, Cr, V, Nb, etc) to suppress the martensitic transformation during quenching to room temperature, thus allowing for the retention under ambient conditions of a single bcc phase. These multicomponent systems are a very versatile class of materials, with an excellent combination of strength, toughness and fatigue resistance, which, when properly processed, can find applications in the aerospace, gas turbine, and oil and gas sectors. However, despite their extraordinary combination of properties, compared to other Ti alloy types, β alloys still have a small market share due to their inherent complexity. In particular, composition optimization in ternary or quaternary β -Ti alloys is a formidable endeavor due to the difficulty of isolating the influence of individual alloying elements. Furthermore, the knowledge about the very wide range of microstructures that can be via thermomechanical treatments is still limited. Substantial efforts on alloy design, enabled by a deeper understanding of the correlations between composition, processing, microstructure and mechanical behavior, are therefore timely.

Alloy design in multicomponent systems by conventional methods is usually a daunting process. First, the large numbers of combinations of elements that must be probed by “trial and error” involve vast amounts of time and large quantities of materials. Second, single crystal studies aimed at determining solute effects or fundamental micromechanical parameters are almost impracticable due to the complexity involved in fabricating single crystals of highly alloyed systems. Clearly more efficient and less time-consuming materials’ exploration and design methodologies would be required to discover, prepare, characterize and optimize β -Ti alloys.

The aim of this work is to investigate the effect of solutes and α precipitates on the micromechanical behavior and slip activity of Ti-xAl-yMo-zCr and Ti-xAl-yMo-zV bcc Ti alloys using an efficient high throughput methodology. With this aim, an approach including the development of a large number of compositions by

the fabrication of a diffusion multiple and micromechanical testing by micropillar compression is put in place. The main findings of this research are described below.

First, the mentioned methodology is applied to evaluate the effect of solutes on the two families of alloys in solid solution. The efficiency of specific β -stabilizers to strengthen quaternary β -Ti alloys is found to vary for different alloy compositions. More specifically, Cr appears to be a more effective strengthener than Mo in quaternary Ti-xAl-yMo-zCr alloys. Molybdenum is, however, a very potent strengthener of Ti-xAl-yMo-zV alloys. Furthermore, in Ti-xAl-yMo-zCr alloys strain is observed to be carried out by the combined activation of several $\{110\}$ slip systems that act cooperatively to accommodate strain; the specific systems that become active are found to be dependent on orientation and on composition. In Ti-xAl-yMo-zV an increase in Mo leads to higher levels of activity of slip systems with low Schmid factors (anomalous slip).

Second, the present work analyzes the effect of solute additions on the strain rate sensitivity (m) of quaternary β -Ti alloys belonging to the Ti-xAl-yMo-zCr and Ti-xAl-yMo-zV systems. While m remains unchanged within a wide range of compositions of the Ti-xAl-yMo-zCr system, it is found to decrease with Mo additions in the Ti-xAl-yMo-zV system. The strain rate sensitivity is related to the number of active slip systems and to the operating dislocation mechanisms.

Third, the influence of a high density of nanoscale α precipitates on the mechanical behavior and the slip activity of the Ti-xAl-yMo-zV system is also investigated. Alloys with record ultrahigh compressive yield strengths are developed via tailored heat treatments. It is shown that α precipitation suppresses anomalous slip in the alloys with high Mo content. This is attributed to a prominent role of the global SF in slip transfer enabled by the presence of a large number of α variants.

Finally, this work demonstrates that diffusion multiples coupled with micromechanical probing constitute an efficient and powerful method for alloy design.

Resumen

Las aleaciones de titanio beta (β) contienen cantidades relativamente elevadas de elementos β -estabilizadores para suprimir la transformación martensítica durante el templeado, permitiendo así la retención de una fase bcc a temperatura ambiente. Estos sistemas multicomponente constituyen una clase muy versátil de materiales estructurales, pues están dotados de una excelente resistencia específica, buena tenacidad y elevada resistencia a la fatiga, lo que los convierte en candidatos ideales para aplicaciones en los sectores del transporte, la fabricación de turbinas, y otros. Sin embargo, a pesar de este extraordinario conjunto de propiedades, las aleaciones de titanio β poseen todavía una cuota de mercado limitada. Esto es debido, en parte, a que la optimización de composiciones en sistemas ternarios o cuaternarios es compleja debido a la dificultad de aislar el efecto de elementos aleantes individuales. Por otro lado, el conocimiento del amplio abanico de microestructuras que es posible desarrollar en estos materiales mediante tratamientos térmicos es aún limitado. Por todo ello, la optimización de las aleaciones de titanio β requiere una mayor profundización en las relaciones composición-procesado-microestructura-propiedades.

El diseño de aleaciones en sistemas multicomponente mediante métodos convencionales es una tarea que entraña gran dificultad. En primer lugar, dado el elevado número de combinaciones de elementos que se debe ensayar mediante prueba y error, este tipo de estudios conllevan la utilización de grandes cantidades de material y largos tiempos de desarrollo. En segundo lugar, la fabricación de monocristales es complicada debido a la inestabilidad promovida por el elevado contenido en elementos aleantes. Es, por tanto, necesaria la aplicación de estrategias más eficaces para diseñar aleaciones de titanio β con mejores propiedades.

El objetivo de esta tesis doctoral es investigar el efecto de los solutos y los precipitados α en el comportamiento micromecánico y en la actividad de distintos sistemas de deslizamiento en las aleaciones monocriscales Ti-xAl-yMo-zCr and Ti-xAl-yMo-zV utilizando una metodología de alto rendimiento. Para ello, se

ha combinado la fabricación de un elevado número de composiciones mediante la técnica de los múltiplos de difusión con técnicas de caracterización mecánica local como la compresión de micropilares. A continuación se describen los principales hallazgos de esta investigación.

En primer lugar, la metodología mencionada se ha utilizado para estudiar el efecto de los solutos en las aleaciones monocristalinas Ti-xAl-yMo-zCr and Ti-xAl-yMo-zV en solución sólida. Se ha encontrado, por ejemplo, que el Cr es un endurecedor más eficaz que el Mo en el sistema Ti-xAl-yMo-zCr , mientras que el último es un endurecedor muy eficaz en el sistema Ti-xAl-yMo-zV . Además, se ha visto que, en la familia Ti-xAl-yMo-zCr la deformación se acomoda mediante el efecto combinado de varios sistemas $\{110\}$ con valores elevados del factor de Schmid; los sistemas concretos que se activan dependen de la composición y de la orientación cristalina. En cambio, en la familia Ti-xAl-yMo-zV un aumento de Mo da lugar a una mayor actividad de sistemas de deslizamiento $\{110\}$ con bajos valores del factor de Schmid (deslizamiento anómalo).

En segundo lugar, se ha investigado el efecto de los solutos en la sensibilidad a la velocidad de deformación ($\dot{\epsilon}$) de las aleaciones mencionadas. Se ha encontrado que, en la familia Ti-xAl-yMo-zCr $\dot{\epsilon}$ no varía dentro del rango de composiciones estudiadas. Sin embargo, en la familia Ti-xAl-yMo-zV $\dot{\epsilon}$ depende, para una composición dada, del número de sistemas activos y, además, disminuye con un aumento de Mo.

En tercer lugar, se ha analizado el efecto de una elevada densidad de precipitados α de tamaño nanométrico en el comportamiento mecánico y en la actividad de los distintos sistemas de deslizamiento en las aleaciones mencionadas y en un amplio rango de temperaturas. Se ha logrado obtener aleaciones con un límite elástico en compresión cuyo valor supera al de todas las aleaciones comerciales y al de otras aleaciones similares descritas recientemente en la literatura. Además, se ha comprobado que la precipitación suprime la activación del deslizamiento anómalo en las aleaciones con un elevado contenido de Mo.

Finalmente, este trabajo demuestra que la técnica de los múltiplos de difusión combinada con ensayos micromecánicos constituye una metodología eficaz y potente para el diseño de nuevos materiales.

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CHAPTER 1

Introduction

1.1 Titanium and its alloys

Among the metallic materials for structures, titanium alloys primarily stand out because of two properties: high specific strength/stiffness (Fig. 1.1.a) and excellent corrosion resistance [1, 2]. These characteristics also make them attractive for a variety of applications including aircraft, aero-engines (Fig. 1.1.b), biomedical devices and components in chemical processing equipment [3, 4]. So far, over 100 titanium alloys have been developed for various applications in different fields [2, 5]. The wide space provided for alloy design and property optimization in these alloys stems from their multiple allotropic modifications, abundant alloying elements, and the ample possibilities for microstructural development through adequate processing. Understanding the allotropic phases of titanium and the corresponding transformations is of central importance because they make the physical basis for the various properties achieved by this material. Alloying elements affect the stability, physical and mechanical behavior of these phases in titanium alloys simultaneously within a variety of microstructural permutations.

1.1 Titanium and its alloys

Fig. 1.1: (a) Specific stiffness vs. strength in a wide range of materials [6]; (b) applications of titanium alloys in aero-engines [5].

1.1.1 Allotropic phases in titanium

Titanium crystallizes in a hexagonal close packed structure (HCP, α -Ti) under ambient conditions. At high temperatures, it transforms into a body-centered cubic structure (bcc, β -Ti) (the α/β transition temperature in pure Ti is 882 °C). With increasing pressure, the so-called ω phase, of a simple hexagonal lattice, becomes stable. The schematic phase diagram shown in Fig. 1.2 summarizes these major transformations of pure titanium with temperature and pressure and illustrates the corresponding crystal lattices. Besides, some other intermediate phases with orthorhombic structure also occur at extreme pressures, as explained in detail elsewhere [7,8]. During the α/β allotropic transformation, the two phases keep the Burgers orientation relationship (BOR), i.e., $\{110\}_{\beta} // \{0001\}_{\alpha}$, $\langle 1\bar{1}1 \rangle_{\beta} // \langle 11\bar{2}0 \rangle_{\alpha}$, which results in 12 possible crystallographic equivalent variants of the α phase in a single parent β grain. Meanwhile, the orientation relationship between the β and ω phases is $\{0001\}_{\omega} // \{111\}_{\beta}$, $\langle 11\bar{2}0 \rangle_{\omega} // \langle 0\bar{1}1 \rangle_{\beta}$, giving rise to 4 ω variants for a specific β matrix grain.

Fig. 1.2: *P-T phase diagram of pure titanium and the corresponding lattice structures [9].*

1.1.2 Alloying elements

The alloying elements of titanium are classified into neutral elements, α -stabilizers, and β -stabilizers, depending on their influence on the α/β allotropic transformation temperature (or β -transus temperature), which is shown schematically on the binary phase diagrams of Fig. 1.3. Typical neutral elements like Sn, Hf, and Zr have nearly no influence on the α/β phase boundary in the diagram. α -stabilizers, including Al, O, N, and C, extend the α phase field to higher temperatures, and promote the development of a two-phase $\alpha+\beta$ field in the phase diagram. β -stabilizers shift the β phase field to lower temperatures and are classified into β -isomorphous and β -eutectoid elements based on the different modifications that each type provokes in the phase diagram (Fig. 1.3). The alloying elements in the

1.1 Titanium and its alloys

former category, e.g., V, Mo, and Nb, have a much higher solubility in titanium compared to those in the latter one. Sufficient concentrations of these elements enable the stabilization of the β phase at room temperature. Meanwhile, even low volume fractions of β -eutectoid elements such as Fe, Mn, Cr, Co, Ni, Cu, Si, and H, can lead to the formation of intermetallic compounds.

Fig. 1.3: Influence of alloying elements on the phase diagrams of titanium alloys [1].

1.1.3 Classification of titanium alloys

Commercial titanium alloys are classified as α , near- α , $\alpha+\beta$, and β alloys [1, 2]. Fig. 1.4.a is a three-dimensional schematic illustrating the variations of the Ti phase diagram with the addition of α and β -stabilizers (or a combination of both) [1], as well as the domains in this 3D phase space that belong to each alloy type. α titanium alloys include commercially pure (cp) titanium and alloys containing mainly α -stabilizers or neutral elements. The main equilibrium phase under ambient conditions is the hcp α phase. This kind of titanium alloys exhibits excellent corrosion and oxidation behavior as well as moderate strength due to the presence of solutes like O, Al, Zr, etc., and therefore is mostly utilized to fabricate components for chemical processing equipment. Additionally, they are endowed with good creep resistance, good toughness and strength at cryogenic

temperatures, and are easily weldable. With the addition of minor fractions of α stabilizers, near- α titanium alloys are still in the α phase field under ambient conditions and become suitable for high service temperatures.

The $\alpha+\beta$ titanium alloys contain relatively large volume fractions of the α and β phases under ambient conditions. Their microstructure, i.e., the morphology and distribution of these two phases, can be significantly altered by processing, resulting in a wide range of mechanical properties. In general, these alloys exhibit an excellent combination of strength and ductility at room temperature, good creep resistance up to 300 °C, and relatively good corrosion behaviour. Ti-6Al-4V is the most widely commercialized $\alpha+\beta$ alloy, with wide applicability in the fabrication of aircraft structural components.

The so-called β titanium alloys, which can be subdivided into metastable β alloys and fully stable β alloys, are characterized by still larger fractions of β stabilizing elements. The most distinct characteristic of the former alloys is the wide range of microstructures that can be produced upon different processing conditions, some of which are endowed with an excellent combination of mechanical properties. Metastable β titanium alloys are the object of the present research and will be reviewed in more detail in section 1.2. Fully stable β titanium alloys are less interesting for commercial applications because they cannot be strengthened by precipitation [2]. (In general, for the sake of consistency with the literature, the expression ‘ β alloys’ will refer hereafter to metastable β alloys.)

1.2 β titanium alloys

Fig. 1.4: (a) Schematic diagram of titanium alloy classification for different contents of α and β stabilizers [1]; (b) pseudo-binary phase diagram of β titanium alloys [10].

1.2 β titanium alloys

As the most versatile titanium alloy class, β alloys exhibit the highest specific strength and other attractive mechanical properties such as high toughness and excellent fatigue resistance at large cross sections. Other properties of commercial and practical interest have also been developed, such as superelasticity, superconductivity, and shape memory. In addition, the excellent deformability and the high hydrogen tolerance undoubtedly warrant their continuing market share in lieu of $\alpha+\beta$ titanium alloys. One more advantage of β titanium alloys is the confirmed wide variety of properties obtained in a single alloy composition via simple heat treatments, which lead to a manifold of microstructures. To date, several high strength β titanium alloys, such as Ti-10V-2Fe-3Al (wt.%, similarly hereinafter), Ti-5Mo-5V-5Al-1Cr-1Fe (VT22), Ti-5Al-5Mo-5V-3Cr-0.5Fe, Ti-6Al-2Sn-4Zr-6Mo, etc., have been applied successfully to fabricate structural components like landing gears or gas turbine engine components. Because of the tremendous variations in compositions, microstructures, and properties in this class of titanium alloys, establishing a systematic correlation among them is complicated but crucial to their successful application.

The metallurgical foundation for the tremendous variations in the properties of β titanium alloys is the decomposition of the metastable β phase upon different heat treatments. A typical schematic phase diagram is shown in Fig. 1.4.b. The key phase transformations involved in the decomposition of β -Ti are the following: the diffusional transformation $\beta \rightarrow \alpha$, the martensitic transformations $\beta \rightarrow \alpha'$ and $\beta \rightarrow \alpha''$, the displacive shuffle transformation $\beta \rightarrow \omega$, and the phase separation $\beta \rightarrow \beta'$. These transformations, as well as the crystallographic features of the resulting phases, are discussed in more detail below.

1.2.1 Diffusive $\beta \rightarrow \alpha$ phase transformation

The analysis of the morphology, orientation, volume fraction, and distribution of α phase within the β matrix has been the major focus of worldwide investigations due to the considerable influence of such microstructural features on the mechanical properties of β titanium alloys [1, 3–5, 10, 11].

Fig. 1.5 illustrates several examples of the typical microstructures that can be obtained by different thermomechanical processing methods [1]. Solid solution of β titanium alloys above the β -transus temperature followed by quenching leads to the retention of the coarse equiaxed β grains in the microstructure (Fig. 1.5.a). The α phase tends to precipitate from the metastable β matrix when the alloys are soaked in the $\alpha+\beta$ field for sufficient time. Several processing methods have been devised in order to generate the wide range of available microstructures in β alloys: (a) beta annealing followed by slow cooling and aging (BASCA) [14]; (b) $\alpha+\beta$ annealing (Fig. 1.4.b) in combination with different hot working treatments [1]; (c) β solution treatment and aging (STA, Fig. 1.4.b) [14]. Upon slow cooling from the β phase field the α phase first nucleates preferentially at β grain boundaries and results in a film-like continuous α layer, called grain boundary α (α_{GB}). The α_{GB} layer favors cracking and is thus deleterious to the mechanical properties of titanium alloys. During continued cooling α laths nucleate either at the interface of α_{GB} or at the β grain boundaries and grow into the interior of the original β grains (Fig. 1.5.b); these laths are referred to as sympathetic α [13, 15]. These α laths are

Fig. 1.5: Typical microstructures of beta titanium alloys (a) equiaxed β grains of Ti-7333 alloy after 880 °C solution and water quenching [12]; (b) α_{GB} layer and sympathetic/primary α phase in Ti-7333 alloy slowly cooled from 900 °C to 720 °C and quenched [13]; (c) needle-like primary α (α_P) in Ti-1023 alloy after annealing in $\alpha+\beta$ field; (d) globular α_P in Ti-1023 alloy after $\alpha+\beta$ annealing and hot working treatment; (e) broken α_{GB} layer and globular α_P in Ti-1023 alloy after annealing and mechanical processing in $\alpha+\beta$ phase field; (f) fine secondary α plates in Ti-1023 alloy after low temperature aging [1].

not very effective in strengthening β -Ti alloys due to their relatively coarse size; however, they are crucial to control the ductility of titanium alloys as suggested

by Duerig [10]. Variant selection, as well as the arrangement of the α laths (in triangular (basket weave) or parallel (colony) networks), are highly dependent on the alloy composition and cooling rates, as explained in detail elsewhere [4, 16]. $\alpha+\beta$ annealing in combination with different hot working treatments results in the precipitation of α phase with different morphologies (globular, α_{GB} film, needle-like) (Fig. 1.5.c-e). β solution treatment followed by aging at temperatures typically between 400 and 600°C leads to the precipitation of a fine distribution of α laths (Fig. 1.5.f). They endow β -Ti alloys with exceptional strength when homogeneously distributed throughout the microstructure. During the processing, the volume fraction of coarse α grains and fine α laths are carefully controlled by modifying the solution and ageing temperature to achieve excellent comprehensive mechanical properties of titanium alloys.

1.2.2 Metastable phase transformations

Quenching from the β phase field, or a combination of quenching plus aging, may also lead to the formation of metastable phases (martensitic transformations, $\beta \rightarrow \alpha'$ and $\beta \rightarrow \alpha''$, displacive shuffle transformation, $\beta \rightarrow \omega$, and phase separation $\beta \rightarrow \beta'$, Fig. 1.6), which can, in turn, constitute favourable nucleation sites for fine α precipitates following aging [1, 17]. In this section, the different metastable phases will be reviewed.

The martensite phase in β titanium alloys might have either a hexagonal (α') or an orthorhombic structure (α''), depending on the alloy composition. While the orientation relationship between α' and β matrix is found to be the BOR, the lattice structures of the α'' and β phases are related in the following way: $\{001\}_{\beta} // \{001\}_{\alpha''}$, $\langle 1\bar{1}0 \rangle_{\beta} // \langle 1\bar{1}0 \rangle_{\alpha''}$. More detailed information about titanium martensite may be found in [1, 2, 10].

With increasing content of β -stabilizers, the β phase transforms upon quenching into the athermal ω phase (ω_a) by means of a displacive shuffle transition. This phase has a simple hexagonal lattice in β -Ti alloys but a trigonal structure in heavily stabilized β -Ti alloys [2]. The ω_a phase takes the form of extremely fine

Fig. 1.6: Metastable phases forming in β -Ti alloys: (a) martensite structure in Ti-33Nb-4Sn alloy after solution annealing at 800 °C and quenching [18]; (b) ω phase in Ti-1023 alloy after solution annealing at 900°C and aging at 250 °C [19]; (c) coherent β' particles in Ti-15Zr-20V after aging at 450 °C [2]

particles (2-4 nm) that are uniformly dispersed in the matrix. Upon aging at temperatures below 400 °C, ω_a grows to form a larger isothermal ω particles (ω_{iso}), which have the same crystallographic symmetry but a lower amount of β -stabilizers than the β matrix. With even higher amounts of β -stabilizers, the supersaturated β phase separates upon cooling into the β_1 (lean β -stabilizer) and β_2 (rich β -stabilizer) phases either by nucleation and growth or by spinodal decomposition [2, 20]. Finally, other orthorhombic phases [21–23] or several intermetallics [1, 2, 24] may also form depending on the alloy composition and processing history .

1.2.3 Solid solution strengthening of β -Ti alloys

Solid solution strengthening plays an important role in multicomponent β -Ti alloys, and this is one of the key topics addressed in this thesis. In the following, the fundamentals of solid solution strengthening will be reviewed and, later, the difficulties associated to the quantification of this effect in the studied materials, both by simulation and experimentally, will be highlighted.

Solution strengthening arises from the complicated interactions between mobile dislocations and solutes in the crystal lattice. These elementary interactions, according to whether the dislocation core structure is changed topologically upon

the addition of solutes or not, are divided into two categories. In the former class, the strengthening effect depends on the specific structural interaction between solute atoms and dislocation cores, as demonstrated in titanium, magnesium [25], iron [26], and molybdenum [27] alloys. In the latter, the elastic interactions stemming from the local lattice modifications induced by solute atoms dominate the strengthening behavior [28–30].

As suggested by Mott [31, 32] and Fleischer [28, 29, 33, 34], the parameters involved in solution strengthening are the size misfit strain (ε_b) and the modulus misfit strain (ε_G), respectively. The size misfit strain arises from the difference in the atomic radii of solute and solvent atoms. It provides a measure of the fractional change in lattice parameter per unit concentration of solute atoms, i.e., $\varepsilon_b = \frac{da}{a * dc}$ where a is the lattice parameter and c the solute concentration. This kind of volume distortion, either spherical [29] or tetragonal [35, 36], interacts with edge dislocations significantly. Depending on whether the degree of dilatation (or compressive/tensile distortion) in the dislocation core could be reduced or enhanced by the interaction, the edge dislocation can be either attracted or repelled by solute atoms [35]. On the contrary, owing to the sole shear nature of the screw dislocation core, they are able to move freely from this influence. The modulus misfit is attributed to the modified binding force around the solute atoms [37], i.e., to the presence of regions where the rigidity is locally different from that of the matrix, as suggested by Fleischer [34]. Since the dislocation energy is proportional to the modulus [35, 38], this kind of lattice distortion interacts with all dislocations via modifying their core modulus and energy. It is characterized by the fractional change in shear modulus per unit solute concentration, namely, $\varepsilon_G = \frac{dG}{G * dc}$, where G is the shear modulus. According to Fleischer [34], this quantity makes a better index of the relative hardening when different solute atoms are added to metal.

Based on the aforementioned elementary interactions between solute atoms and mobile dislocations, there are two classic theories for solution strengthening. The strong-pinning theory (Friedel [39], Fleischer [28, 34]) only takes the solute atoms in the slip plane into consideration. They are supposed to serve as repeated independent obstacles for mobile dislocations. In random alloys, the average spacing,

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L, between these obstacles is approximately proportional to the square root of the solute concentration. The strengthening basis is the interaction between the dislocation segment and the solute atom within an $L \times L$ area, neglecting the influence from other nearby solutes. Under stress, the pinned dislocation segment bows out in the area, exerting a counteractive force to the maximum resistive force (F_{max}). The yield stress, τ , of a random alloy at 0 K can be estimated as:

$$\tau_0 = \left(\frac{F_{max}}{2\Gamma} \right)^{\frac{3}{2}} \left(\frac{2\Gamma}{b^2} \right) c^{\frac{1}{2}} \quad (1.1)$$

where Γ is dislocation line tension, and b the magnitude of Burgers vector. Meanwhile, the weak-pinning theory (Mott-Nabarro [32,40], Labusch [41], Nabarro [42]) includes additional solute atoms close to the slip plane. Instead of the maximum pinning force from individual atoms, the predominant strengthening factor is the collective elastic interaction between the mobile dislocation and the surrounding solute atoms. In alloys with a random distribution of solutes, there would be as many repulsive as attractive encounters for mobile dislocations on the average [35]. The actual strengthening is dependent on the variation (trade-off in binding energy and line energy of dislocations) in the energy between dislocation and surrounding solutes during dislocation movement. Therefore, this theory attributes the solution strengthening to the statistical fluctuations in the spatial distribution of solutes within random alloys. Labusch [41] first developed a statistical model to estimate the strength of random alloys at 0 K as:

$$\tau_0 = \left(\frac{F_{max}^4 \omega}{4\Gamma b^7} \right)^{\frac{1}{3}} c^{\frac{2}{3}} \quad (1.2)$$

where ω measures the distance from solute atoms to the slip plane within the range of interest.

At 0 K, the strong pinning theory is the operative strengthening mechanism at low solute concentrations ($\sim 10^{-2}$), while the weak pinning mode dominates this behavior at higher concentrations [43]. Since none of the original two models takes the influence of temperature into consideration, later modifications of the Labusch

model were made, in order to include thermal effects [43–49]. Compared to the collective resistive force in the weak pinning model, the pinning force provided by individual solute atoms is much weaker and more sensitive to the thermal fluctuations. Therefore, the strong pinning strengthening drops rapidly as the temperature increases.

Estimating solute hardening in multicomponent alloys, particularly for β -Ti alloys, is a complex endeavor. Several authors, including Leyson [50,51], Varvenne [43, 52], Gypen [53, 54], Toda-Caraballo [55, 56], and Wang [57] have proposed models for various multicomponent systems. The simulation difficulties on this issue lie in that the parameters required are hard to estimate or measure, especially in the case of commercial multicomponent alloys. Furthermore, there is still a need for the development of physically based models that can capture the complex dislocation-solute interactions in a more realistic manner [58].

Experimentally, gaining fundamental insights into solid solution strengthening of β -Ti alloys is also challenging because one must face the huge difficulty associated to the instability of the bcc structure at room temperature and to the preparation of single crystals of β -Ti alloys. Thus, several basic issues related to the mechanical properties and to the microplasticity of β phase in these alloys remain unclear. More specifically, the individual and combined effects of alloying elements on mechanical properties are still unknown or under debate [59–61]. Furthermore, a complete understanding of the influence on the mechanical properties of β -Ti alloys of solutes necessitates further research on fundamental aspects such as the effects of solutes on the nature of dislocation motion and the resultant slip activity in the β phase, which remain, however, still largely unexplored.

1.2.4 Precipitation strengthening of β -Ti alloys

It is widely accepted that precipitation strengthening is the largest contributor to the high strength of β titanium alloys. In particular, the fine α plates (Fig.1.5.f) formed upon aging at low temperatures exhibit the maximum strengthening power among all the precipitates in these materials. Due to their fine nature, and to the

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fact that they are present in large numbers in the microstructure, it is not clear whether dislocations are able to shear them [62, 63] or loop around them by an Orowan type mechanism [2].

Let us next examine the strengthening effect of α/β phase boundaries. The slip systems of the α and β phases are related by the BOR as depicted in Fig. 1.7.a. In particular, the basal slip plane of a α variant is parallel to a $\{110\}$ slip plane of the β matrix, and there are three $\langle 11\bar{2}0 \rangle_\alpha$ slip directions available for dislocation transfer along the shared slip plane. The different deviations of these three directions with respect to the slip direction of the incoming slip system of the β phase, according to Savage [64], may lead to an anisotropic slip transmission behavior, as depicted in Fig. 1.7.b. While the α/β interface is rather ‘transparent’ to slip transmission into an outgoing system in which the slip direction has a low misorientation with respect to the incoming slip direction, it provides a significant hindrance for dislocation transfer along the other two directions and, therefore, leads to a much higher critical resolved shear stress on the corresponding slip systems. Some of the prismatic and pyramidal slip systems in the α phase are also found to be closely oriented with respect to selected $\{112\}\langle 11\bar{1} \rangle$ and $\{110\}\langle 1\bar{1}1 \rangle$ slip systems in the β matrix respectively, as indicated in Fig. 1.7.a. Besides crystallography, according to Banerjee [4], other factors influencing the ease of slip transfer between the β matrix and α phase are the difference in the lattice constant and modulus, the interfacial stress and the presence of geometrical dislocations at the interface.

Metastable phases make distinct contributions to the strengthening behavior of β titanium alloys. While martensite α' or α'' phases have only a moderate hardening effect [10, 18, 65], ω and β' precipitates possess a noticeable strengthening potential due to their small sizes. However, shearing of the latter by mobile dislocations usually leads to an intense localization of deformation and therefore to low ductility. Finally, intermetallics [24] and ordered β phase particles [20] are considered to be promising strengthening microstructural factors due to the great incoherency of their structures with that of the β matrix. However, their strengthening potency has, to date, been less studied.

Fig. 1.7: (a) Stereographic projection showing the alignment of slip systems between α and β phases [4]; (b) Schematic diagram depicting the formation of residual dislocations upon slip transfer [64]. The Burgers vectors of residual dislocations are indicated by r_{a1} , r_{a2} , and r_{a3} , respectively.

1.3 Dislocation controlled plastic deformation of bcc metals

1.3.1 Thermally activated deformation of bcc metals

Fig. 1.8: (a) Temperature dependence of yielding strength of $[941]$ oriented single crystalline Mo; (b) the corresponding tensile stress-strain curves at different temperatures [66].

Bcc metals are endowed with a strong plastic anisotropy [67, 68], and with a yield strength that is at least one order of magnitude higher than that of fcc or hcp metals. The yield strength decreases, however, sharply, as temperature increases or strain rate decreases [66, 69–72] (Fig. 1.8.a). The temperature beyond which the yield strength becomes constant is called the athermal transition temperature (T_a) [67]. As illustrated in Fig. 1.8.b, the curves below T_a are parabolic and characterized by a high initial yielding strength; in contrast, above T_a , the stress-strain curves exhibit a clearly defined three-stage hardening shape [66, 69], and, as demonstrated by Richter [66], reduced anisotropy. This thermally activated plasticity in bcc metals can be ascribed to the thermally activated motion of screw dislocations, impeded by intrinsic lattice friction, and which will be described in the following sections.

Fig. 1.9: (a) (211) Slip traces on the micropillar of W single crystal compressed along the $[256]$ axis [61]; (b) and (c) single $\{011\}$ slip traces constructing the (211) macroscopic slip trace in (a); (d) $\{110\}$ slip traces on a W micropillar compressed along the $[1\ 5\ 10]$ axis [73].

Another distinct characteristic of bcc metals is that the macroscopic slip traces appearing on the surface of deformed samples are always wavy except at 0 K, and that they align along planes which often do not coincide with one of the $\{011\}$ easy slip planes. Slip system activation also exhibits a significant dependence on temperature. Below T_a , multiple slip system activation has been observed in pure bcc metals and Fe-Si alloys [60, 74, 75]. In the case of single crystals, the specific slip systems that become active, depend on the orientation of the applied stress. For example, the (211) macro slip trace (Fig. 1.9.a) that appears in a W micropillar compressed along the $[256]$ axis is demonstrated to be composed of two elemental slip steps along (101) and (110) planes with high Schmid factors (SFs) (Fig. 1.9.b and 1.9.c) [61], consistent with Chen's model [76]. However, when a W pillar is compressed along a $[1\ 5\ 10]$ axis, a different set of slip traces emerges in the surface. Besides the ones with the highest SFs ($(101)[\bar{1}11]$, $(\bar{1}01)[111]$) (Fig. 1.9.d), an additional slip system ($(0\bar{1}1)[111]$) (Fig. 1.9.d) with a much lower resolved shear stress (i.e., much lower SF) is observed as well (*anomalous slip*) [73, 77]. To date, several models have been proposed to elucidate the occurrence of anomalous slip (slip on systems with low SF). Hsiung [75] and Matsui [78, 79] attributed it

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to the easy glide of dislocation segments on anomalous planes resulting from the hindrance of obstacles like non-shearable particles and jogged dislocations in the primary slip planes. Other studies [80,81] suggested that the interaction between dislocations triggers anomalous slip. However, as Marichal pointed out [73], these mechanisms are short-lived and cannot generate obvious slip traces. Instead, he proposed a model attributing anomalous slip to the cross-kink assisted motion of screw dislocations [73], which depends on the specific core structure of screws and on the related gliding mechanism (explained in the following section). At temperatures above T_a the slip lines become increasingly more undulated, probably due to the enhanced cross-slip during deformation, and anomalous slip is suppressed as the active slip systems are purely determined by their SFs ([66,69,74,82]). The complex slip system activation in bcc metals is further confirmed by the observation of cooperative motion of elongated screw dislocations in different slip systems via ex and in situ TEM observations [69,75,83–88]. To date, the complex slip system activation in bcc metals, and its dependence on composition, is still poorly understood [60,61,89–91].

1.3.2 Screw dislocations in the bcc lattice

To date, the plastic deformation mechanism of bcc metals has been intensively investigated [77,81,92]. Deformed bcc metals contain a high density of $\frac{1}{2}\langle 111 \rangle$ screw dislocations (Fig. 1.10) [85], and they are considered to be the primary strain carrier at low temperatures. The strong thermally activated deformation behavior of bcc metals [71,92], is caused by the high lattice resistance encountered by screw dislocations at temperatures below T_a . Edge dislocations have a smaller Peierls-type barrier and thus move much faster than the screw dislocations as observed via in situ TEM observations [86–88,93]. Early studies attributed the high lattice resistance experienced by screw dislocations to a fcc-like planar splitting core structure, as suggested by Cohen [94]. However, no stable dissociated dislocations in the form of partial dislocations plus a stacking fault have neither been observed by TEM nor predicted by theoretical calculations. Instead, Hirsch [95] suggested

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the core of screw dislocations in bcc metals might spread into several planes belonging to the $\langle 111 \rangle$ zone, and this non-planar core structure, anchoring itself in the lattice, should be responsible not only for the high lattice friction but also for other unusual deformation characteristics [68,96,97]. This model has been firmly established by numerous experimental and theoretical investigations over the past 50 years [68,98,99]. Atomistic simulations further shed light on the details of the screw core structure. The non-planar screw core is demonstrated to fractionally spread into equivalent $\{110\}$ planes in $\langle 111 \rangle$ zones driven by an elastic energy reduction [96]; however, it remains rather compact (Fig. 1.10) because no stable stacking fault could participate in the splitting in bcc metals [68,100,101] .

Fig. 1.10: Dislocation arrangements in Mo single crystal (a) elongated 2 % at 77 K ($[110]$ selected as the reciprocal vector, g , for dislocation observation); (b) elongated 5.8 % at 293 K ($g=[11\bar{1}]$) [85].

In general, two kinds of screw core structures have been reported in the literature (Fig. 1.11). The first kind (Fig. 1.11.a) spreads asymmetrically into $(\bar{1}10)$, $(10\bar{1})$, and $(0\bar{1}1)$ planes which can be perceived as three fractional dislocations. Each fractional dislocation brings in a shift along the original screw dislocation line, i.e., $[111]$ [68,102]. The shift, or polarity in screw core, could take place in either of the two directions along the dislocation line, $[111]$ or $[\bar{1}\bar{1}\bar{1}]$, leading to two energetically equivalent but geometrically distinguishable core variants. As

Fig. 1.11: Dissociated core structures of $\frac{1}{2}[111]$ screw dislocations in Mo: (a) degenerate core; (b) non-degenerate core. The arrangement of atoms is shown via the differential displacement map (DDM). The circles with different colors in the map represent the atomic positions in three successive $\{111\}$ planes. The arrow is constructed in this way: first the atom displacement in each atom column along the Burgers vector (normal to the figure plane) is calculated with respect to the atomic position in perfect lattice; then the displacement difference between neighbouring columns is represented by the length of arrows. The atom column which the arrow points to has a larger displacement than the one at the other end of the arrow.

suggested by Vitek [102], these two variants are symmetric with respect to the $[10\bar{1}]$ axis indicated in Fig. 1.11.a. This kind of core structure is thus called degenerate or polarized. In parallel, the non-degenerate core illustrated in Fig. 1.11.b exhibits higher symmetry by splitting into six fractional dislocations in all the six $\{110\}$ planes in the $\langle 111 \rangle$ zone. According to Vitek [102] and Cai [96], the prevalence of these two core structures in bcc metals depends on the subtle details of the atomic interactions in the core region. Atomistic calculations render contradictory predictions of core structures in the same bcc metal [68, 102], which are attributed to different descriptions of atomic interactions in the different potentials (Finnis-Sinclair type or BOP) employed.

In this context, one question on the difference between the glide behaviors of these two kinds of screw dislocations during deformation arises. According to Vitek [102], such behavior is determined by the variations in the core structures before the dislocation begins to move. Based on the detailed atomistic modelling

Fig. 1.12: (a) Degenerate; (b) non-degenerate core structures of $\frac{1}{2}[111]$ screw dislocations under low shear stress $[102]$.

of $\frac{1}{2} \langle 111 \rangle$ screw dislocations with stress, Ito [103] reports similar responses of the two types of core structure to the shear stress lower than the corresponding CRSS, as illustrated in Fig. 1.12. Both cores attain a configuration akin to the degenerate structure with the maximum extension along the $(10\bar{1})$ plane where the dislocations eventually glide. In such a way, the difference in the two core structures is effectively minimized.

1.3.3 Glide of screw dislocations in the bcc lattice

Fig. 1.13: Schematic diagram of the potential energy of a dislocation in a slip plane [38].

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The potential energy of a dislocation along a slip plane can be qualitatively estimated by the Peierls model. The periodically arranged atoms lead to periodic energy minima and maxima (Fig. 1.13) [38], the difference between which gives a measure of the barrier against the glide of dislocations. Compared to fcc metals, the motion of screw dislocations in a bcc lattice requires a higher stress to transform the whole non-planar core into a planar glissile structure and to surmount the corresponding potential energy barrier at 0 K. At finite temperatures, the probability of thermal assisted atomic vibrations rises, thereby enabling screw dislocations to fractionally bulge (kink) from one energy valley to the next. The resultant double kinks are of edge component and thus can move along the screw line rapidly during deformation [96]. This thermally assisted kink formation and subsequent stress-induced migration [100, 101, 104, 105], illustrated in Fig. 1.14, is believed to be the dominant glide mechanism of screw dislocations in bcc metals, which provides a reasonable description on the thermal activated motion of screws.

Fig. 1.14: Successive steps of the formation and expansion of double-kink on a screw dislocation [104].

Due to the stress-induced degenerate core structure of screw dislocations [103, 106–108], there are different kinds of kink-pair and core defaults, i.e., flips, endowed

with different nucleation energy, to assist the motion of screw dislocations under stress [96, 109–111]. According to Ngan and Wen [112], one particular kink-pair has the lowest nucleation barrier. During deformation, screw dislocations move by nucleating and expanding this kink-pair and cross slip along $\{110\}$ planes, leading to a zigzag path [113]. Besides, as suggested by Cai [96], the secondary core defaults may facilitate the nucleation of other kink-pairs which can compete with the energy-favored kink-pair. Kink interaction gives rise to the cross-kinks which may lead to anomalous slip [73]. Therefore, the motion of screw dislocations during the deformation of bcc metals can proceed by several kinds of kink-pairs contributing in a complex sequence, resulting in the multiple slip activity and ‘composite’ slip traces (Fig. 1.9.a and 1.9.d). At temperatures above T_a , the thermal vibrations of atoms are sufficient for screw dislocations to easily surmount energy barriers [66, 114]. Both edge and screw dislocations are of high mobility, and slide in the slip systems with the highest SFs.

1.3.4 Tuning of dislocation mobility by solute atoms in bcc metals

The research efforts carried out so far to understand the dislocation-controlled plasticity of bcc metals remain mostly confined to pure metals. The influence of alloying elements remains rather unexplored in spite of some recent remarkable efforts in this direction [115–118]. The interaction between individual solutes, solute clusters and screw cores [116, 118, 119] may tune the mobility of dislocations considerably, and thus modify mechanical properties such as the yield strength, and the strain rate sensitivity. The interaction between solutes and dislocations may lead to either softening [27] or strengthening [120]. Caillard [120] reports that kinks along screw dislocations are significantly slowed down by solute atoms, giving rise to collisions of co-existing kinks which may lead to the formation of jogs and considerably alter the time-dependent character. Additionally, the addition of solutes also increases the propensity for kink nucleation along screw lines, as suggested by Rao [116] and Chen [118] which may result in modified slip activity

1.4 High throughput screening methodology for alloy design and property optimization

during deformation. However, the complex influence of solutes on the mechanical behavior and slip activity remains largely unknown for most bcc metals, including β -Ti alloys.

1.4 High throughput screening methodology for alloy design and property optimization

1.4.1 Traditional strategies for the design of advanced materials

The strategies traditionally used to manufacture advanced metallic materials [121–123] include changing the chemical composition, optimizing thermo-mechanical treatments, manufacturing composites and/or different combinations of the previous ones. These strategies allow to modify characteristics such as the solute concentration, the crystalline structure, the size and shape of the grains, the spatial distribution, the size and shape of the second phases or precipitates, the internal stresses, etc. These modifications, in turn, give rise to dramatic variations of the properties (mechanical, magnetic, electrical, etc.). In practice, the application of these strategies is usually implemented in a ‘trial and error’ manner entailing a long development period and great expenses. Particularly, the lack of predictive capacity and flexibility in the development processes of new materials implies that many efforts are wasted in the production of materials that ultimately have no added value compared to those already existing. It is, therefore, urgent to develop new methodologies for designing materials with technological applications that adjust to the rapid pace of change in today’s society.

1.4.2 High throughput screening techniques in materials science

High throughput screening techniques, or combinatorial methodologies, originating from the pharmaceutical industry, have become a promising and powerful paradigm for materials discovery and optimization, and an ideal experimental complement for the simulation predictions [124–128]. These methodologies are normally characterized by the production of material libraries containing samples with wide variations of the material parameters of interest (typically compositions and corresponding properties) and by the efficient characterization of the local microstructures and properties [129–131]. As pointed out by Green [129], the combinatorial methodologies are generally more efficient and less expensive than the traditional approaches. Moreover, since the tests are carried out with the same instruments over a relatively short period of time, the systematic errors are minimized, giving reliable data sets for the validation of modeling [126,129].

Fig. 1.15: Schematic illustration of representative synthesis of (a) discrete library [132]; (b) continuous library (composition spreads) [129]. In (a), the material library is composed of elemental samples in each well simultaneously electrodeposited with the application of counter-electrode array; in (b), the continuous library is produced via selective deposition or sputtering with sample rotation and moving mask system.

Though successful paradigms have been reported over the past decades [133–137], the applications of this approach in materials science are still confined to a

1.4 High throughput screening methodology for alloy design and property optimization

small scale. In general, combinatorial libraries can be divided into two categories: discrete libraries, that is, 1 or 2 dimensional matrices formed by arrays of samples with compositions (or other microstructural parameters) that vary systematically at regular intervals (Fig. 1.15.a), and continuous libraries, in which the variation of composition or some other microstructural parameter is gradient [127]. The generation of thin-film libraries (Fig. 1.15.b) has facilitated the identification of new functional materials for transducers, energy conversion, and optical devices [129,138–141]. However, as suggested by Cahn [125], these thin film libraries cannot be employed to determine the mechanical properties of load-bearing materials. Instead, diffusion multiples are used for advanced structural alloy design and property optimization [133,142–144]. Diffusion multiples are formed by several metal blocks in intimate interfacial contact. This assembly is then subjected to long-term heat treatments and thus soundly bonded by diffusion across the block interfaces. As a result, the interdiffusion regions have graded compositions in which the fraction of a specific alloying species might vary a few weight percent over a distance of a few hundred microns.

Diffusion multiples have been recognized as versatile and efficient tools for metallic alloy design, as sketched in Fig. 1.16 [145]. Coupled with local composition analysis (electron probe micro-analyzer, EPMA) and phase identification (electron backscattered diffraction, EBSD) techniques, diffusion multiples were initially utilized to construct thermodynamic (phase diagram) [142,145] and diffusivity [146–149] databases in multicomponent alloy systems. More recently, microscale thermal conductivity probing and other microscale property measurement tools [130,150,151] have allowed not only to map the thermal, magnetic, optical and other functional properties of new materials, but also to provide insights into the investigation of order-disordering transformations, site preference of intermetallic compounds, conductivity, and point defect density variations with respect to compositions [142,145]. The combination of diffusion multiples and nanomechanics [152,153] allows to assess the mechanical properties of multicomponent alloys within the desired composition range. The profound and lasting influences of solutes [154] on the microstructural constitution (precipitation kinetics) [134,155,156]

Fig. 1.16: Graphic summary of the diffusion multiple approach to the high throughput materials research [145].

and the mechanical properties [157–159] can be directly evaluated, enabling the reasonable selection of alloying elements for alloy design. Furthermore, this strategy has been recently adopted to accelerate the identification of advanced shape memory alloys [160,161]. Diffusion multiples could constitute an excellent tool to investigate the effect of solutes and precipitates on the mechanical behavior and on the active deformation mechanisms in multicomponent β titanium alloys. However, to date, no studies have utilized this combinatorial approach to investigate the complex macro and microplasticity of these alloy systems.

1.5 Research motivation and objective

This thesis aims at revealing the effects of solutes and of α precipitates on the micromechanical behavior of selected quaternary β -Ti alloys belonging to the

1.5 Research motivation and objective

Ti-xAl-yCr-zMo and Ti-xAl-yV-zMo families, whose plasticity is governed, akin to other bcc metals, by the movement of screw dislocations.

Undertaking this endeavor using conventional alloy processing methodologies entails great complexity due to the multiple alloying species that are present in these alloy systems. A first difficulty stems from the fact that the large numbers of combinations of elements that must be probed by “trial and error” involve vast amounts of time and large quantities of materials. The added difficulty of fabricating single crystals of highly alloyed systems [162] severely complicates the realization of fundamental studies aimed at isolating the effect of individual alloying additions on the mechanical behavior. Clearly more efficient and less time-consuming materials’ exploration and design methodologies are required to discover, characterize and optimize β -Ti alloys.

In this work a high throughput methodology, consisting on the production of single crystals with graded compositions of the two quaternary β -Ti alloy systems by the fabrication of diffusion multiples, is combined with site-specific micromechanical property probing. This approach was found suitable to investigate the fundamentals of the effect of solute additions and of α precipitation on the room and high temperature mechanical behavior as well as on the slip activity of the investigated alloys. From this work, guidelines for the design of ultrahigh strength β -Ti alloys are derived. The thesis manuscript is structured in the following chapters:

Chapter 2: Materials and methods.

Chapter 3: Effects of solutes on the mechanical behavior and on the slip activity of solid solution quaternary β -Ti alloys.

Chapter 4: Effects of solutes on the rate sensitivity of solid solution quaternary β -Ti alloys.

Chapter 5: Influence of nanoscale α plates on the mechanical behavior and on the slip activity of quaternary β -Ti alloys.

CHAPTER 2

Materials and methods

2.1 Fabrication of the diffusion multiple

A diffusion multiple composed of blocks of pure Ti and of the ternary Ti alloys Ti-7.7Al-8.4V, Ti-7.7Al-8.1Cr and Ti-13.4 Al-12.4Mo (wt.%), assembled as indicated schematically in Fig. 2.1, was designed.

Fig. 2.1: (a) Schematic drawing and (b) optical image of the diffusion multiple

The three Ti alloy blocks were melted and cast from 99.9% Ti sponge, 99.9% Al, 99.9% Mo, 99.9% V and 99.9% Cr via arc melting in an argon atmosphere. To achieve a homogeneous composition, arc melting was repeated ten times for

2.2 Characterization of composition and microstructure

each alloy, and all the ingots were homogenized at 1200 °C for 12 h. Selected block surfaces were prepared by a standard metallography procedure consisting on grinding with SiC papers with increasingly smaller grit size followed by mechanical polishing. These surfaces were then diffusion-bonded by placing them for 2 h at 850 °C under a compression stress of 15 MPa. Subsequently, the assembly was sealed into an evacuated, and argon-back-flushed capsule, where it was annealed at 1200 °C for 12 h, and finally quenched to room temperature (RT). Different microstructures can be found in different parts of the diffusion multiple after the diffusion annealing treatment, as illustrated in Fig. 2.1.b. With the increase of β stabilizer in different alloy matrixes, the volume fraction of β phase rises in the sequence of pure Ti (pure α), Ti-Al-V and Ti-Al-Mo ($\alpha + \beta$) and Ti-Al-Cr (pure β). The morphology of the α phase also changes dramatically: coarse α is present in pure Ti, acicular α in Ti-Al-V, pyramidal-like α laths in Ti-Al-Mo. Single crystalline, solid solution interdiffusion regions with graded compositions, spanning a few hundred microns, were thus created at the interfaces between these ternary alloy blocks.

The interdiffusion regions of interest for this study will be those developed between the alloys Ti-7.7Al-8.1Cr and Ti-13.4Al-12.4Mo (wt.%), and between alloys Ti-7.7Al-8.4V and Ti-13.4Al-12.4Mo (wt.%). The diffusion directions corresponding to the two regions of interest are denoted as DD (Fig. 2.1), whereas the normal direction to the assembly is termed ND. Due to both the semi-infinite nature and the geometrical configuration of the diffusion multiple, the diffusion along each composing “diffusion pair” is supposed to be uniaxial.

2.2 Characterization of composition and microstructure

The diffusion multiple was sectioned along a plane parallel to all the different diffusion directions and the interdiffusion regions of interest were examined using a combination of complementary techniques (electron probe microanalysis (EPMA),

optical microscopy (OM), scanning and transmission electron microscopy (SEM, TEM), and electron backscattered diffraction (EBSD)). Surface preparation for OM, EPMA, SEM and EBSD consisted on grinding on successively finer SiC papers, manual polishing with 1 μm diamond paste, and, finally, chemo-mechanical polishing using a solution of colloidal silica (OP-S) and hydrogen peroxide (H_2O_2 , 30 %). OM examination required additional etching in a water-based solution of 2 % HF +3 % HNO_3 for 30 s. Great care must be taken to keep the section parallel to the bottom surface during grinding and polishing, in order to avoid errors in the subsequent micromechanical characterization, which will be described in a later section 2.3. The procedure for the preparation of lamellae for TEM examination is described in section 2.2.2.

2.2.1 Analysis of composition

The composition within the interdiffusion regions was measured by EPMA using a JEOL Superprobe JXA 8900 microscope with a voltage of 20 kV and a current of 50 nA. This technique consists on irradiating the sample surface with an electron beam and analyzing the characteristic X-rays generated from the bottom part of interaction volume. Several wavelength dispersive X-ray spectrometers are utilized to record the characteristic X-ray signals and commercial software is used to calculate the alloy composition by comparison with the measured characteristic X-ray signal from standard samples. The EPMA technique allows a measurement accuracy of 0.01 % on the solute content.

2.2.2 Microstructural characterization

First, OM, carried out using an OLYMPUS BX51 microscope, was used to obtain an overall view of the microstructure of the diffusion multiple. The imaging contrast results from the diffuse reflection of visible light at the etched sites (boundaries, precipitates, etc). Due to the relatively large wavelength of visible light, this method cannot provide high resolution imaging.

2.2 Characterization of composition and microstructure

Fig. 2.2: Sketch of the signals due to the interaction between electrons and material [163].

Field emission gun scanning electron microscopy (FEG-SEM) analysis was carried out in a FEI Helios NanoLab 600i FEG-SEM in order to obtain a more accurate view of the finer details of the microstructure. FEG-SEM images are formed from a multiplicity of signals that are originated in the outer sample volume when an incident high energy electron beam hits the specimen surface (Fig. 2.2). Backscattered electrons (BSE) are reflected by elastic scattering interactions with the surface atoms, with little energy loss; secondary electrons (SE) are produced as secondary products, near the surface, within the interaction volume, commonly with lower energy. While BSE contrast reveals the difference in the average atomic number in the scanned area, the SE signal is indicative of the surface topography. Additionally, other signals such as X-rays are also by-products of the interaction between the incident electron beam and the sample; the latter are utilized to analyze the local composition.

Fig. 2.3: (a) Schematic drawing of an EBSD system; (b) typical EBSD pattern of Si [164].

EBSD was utilized to measure the orientation within the interdiffusion regions of the diffusion couple. This method (Fig. 2.3) consists on the scanning of the sample surface, which is tilted approximately 70° with respect to the horizontal, by a high energy electron beam. The backscattered electrons, emerging from a depth of approximately 50 nm, are then collected at each beam position along the rastering pattern. The backscattered electrons are diffracted along the surfaces of cones with very high aperture, in such a way that their intersection with the detector phosphor screen gives rise to lines, termed Kikuchi lines. Since, at each diffraction spot, one diffraction cone is formed for each family of planes, a Kikuchi pattern formed by multiple Kikuchi lines is obtained at each beam location (Fig.2.3.b). A digital camera is used to acquire an image of the Kikuchi pattern and, from the latter, the crystal orientation is identified by a specialized computer software. In this work, EBSD analysis was carried out in the Helios NanoLab 600i FEG-SEM equipped with an HKL NordlysNano electron backscatter detector and the Aztec data acquisition and analysis software package. EBSD measurements were conducted at an accelerating voltage of 25 kV and 0.69 nA.

Examination of very fine microstructural features such as nanoscale precipitates and dislocation arrays was carried out by TEM in a Talos F200X microscope operated at 200 kV. This method allows very high resolution imaging by leveraging the signal of electrons that are diffracted through a very thin specimen. Selected

2.2 Characterization of composition and microstructure

Fig. 2.4: (a) FEI Helios NanoLab dual-beam FIB-FEGSEM used in this work; (b) schematic diagram of the components of the microscope [165].

area diffraction (SAD) patterns were utilized to select dark field imaging conditions of specific precipitates. The appropriate reciprocal lattice vector was chosen for dislocation imaging.

Lamella preparation for TEM examination was carried out by focused ion beam (FIB) milling with high energy Ga^+ ions in the versatile FEI Helios NanoLab dual-beam FIB-FEGSEM (Fig. 2.4). This instrument is equipped with a gas injection system (GIS) that is capable of efficiently and precisely depositing materials like platinum on the sample surface. As shown in Fig. 2.5, the Ga^+ ions strike the cloud of platinum atoms created by the GIS, and cause them to impact on a specific area of the sample surface and to remain there [166]. Lamellae for TEM examination were prepared by a trenching-and-lift-out procedure consisting on the following steps illustrated in Fig. 2.6: a) selection of the area of interest and deposition of a Pt protective layer to avoid implantation of Ga^+ ions; b) rough milling of trenches to remove the surrounding material, thus carving a lamella of $1\sim 1.5\ \mu\text{m}$ in thickness; c) thinning of the lamella with low ion beam currents to decrease the implantation damage; d) performance of bottom and lateral cuts, leaving the lamella attached to the bulk by just one side; e) welding of the lamella

Fig. 2.5: Schematic diagram of an ion beam induced platinum deposition process [166].

to an easy-lift needle via Pt deposition, followed by lamella separation from the bulk; f) lift-out of the lamella; g-h) Pt welding of the lamella to the TEM grid and separation from the needle; i) thinning of the lamella to electron transparency (~ 100 nm thickness).

Fig. 2.6: Procedure for TEM lamella preparation [167].

2.3 Micromechanical property evaluation

The micromechanical behaviour of selected alloy compositions within the interdiffusion regions of interest in the diffusion couple was measured by micropillar compression. Milling of micropillars was performed using the FEI Helios NanoLab dual-beam FIB-FEGSEM at the desired composition sites. Square micropillars were utilized [24, 168–172] because they allow for a more reliable slip trace mea-

2.3 Micromechanical property evaluation

surement on the side surfaces [73,172] while, simultaneously, yielding almost identical mechanical properties as cylindrical pillars [173]. Micropillar side lengths ranging from 2 to 7 μm were selected in order to investigate potential size effects. An aspect ratio between 2:1 and 3:1 (height:side) was used in all pillars with the aim of avoiding buckling effects during compression [174,175]. All the pillars were machined following an efficient annular milling strategy [172,176].

Fig. 2.7: *Micropillar milling procedure.*

Before milling the micropillars, the diffusion multiple was first tilted 52° in order to place the specimen surface perpendicular to the ion beam. The longitudinal edge of the diffusion multiple was oriented horizontally. At the sites of interests, the following successive milling steps were carried out: (i) rough milling for the fast removal of surrounding materials (Fig. 2.7.a); (ii) milling with smaller ion currents (9.3 and 2.5 nA) for a smoother approach to the final dimension of the micropillars (Fig. 2.7.b and Fig. 2.7.c); (iii) taper removal and surface polishing with an 80 pA ion current after tilting the sample to 54° and 50° , respectively; (iv) sample rotation of 90° and repetition of step (iii). A representative $5 \times 5 \times 10$

2.3 Micromechanical property evaluation

μm micropillar thus fabricated is shown in Fig. 2.7.d. One edge of all the square pillars fabricated in this work was made parallel to the longitudinal edge of the diffusion multiple.

The micropillars were compressed at RT and at 450 °C with instrumented nanoindentation platforms equipped with flat punch tips. A nanoindentation system is usually composed of very sensitive loading and X-Y-Z-displacement sensing systems, with an optical camera, an environmental isolation system, and other supporting components. During testing, the load transducers and displacement sensors are capable of measuring forces in the micronewton (μN) range and displacements at sub-nanometer (nm) scale, respectively. Nanoindentation has proven to be a robust technique to determine micromechanical properties and it has been widely utilized in the investigation of bulk materials [177–179], films [180], and diffusion couples [157, 159] in recent years. Since the first exploration by Uchic and his colleagues [153], the combination of micro sample preparation and nanoindentation has facilitated the extraction of local mechanical properties, thus opening a wide and very fertile field of research [181–183].

Fig. 2.8: Two Hysitron TriboIndenter® nanoindentation platforms employed in this work: (a) TI950; (b) PI87.

In this thesis, the Hysitron TriboIndenter® TI950 and PI 87 platforms were utilized to carry out micropillar compression under different testing conditions. RT micropillar compression was performed in the TI950 indentation system. This platform enables site specific micromechanical property extraction within an acoustic enclosure to minimize the amount of acoustic noise, to block air currents and

to act as a thermal buffer to reduce drifts [184]. The loading system set-up is shown in Fig. 2.8.a. The standard load transducer provides a maximum force of 12 mN with a force resolution of 1 nN and a displacement resolution of 0.04 nm; the high load transducer offers a maximum force of 1 N with a force resolution of 0.1 μ N and a displacement resolution of 0.1 nm [184]. The sample was fixed to a magnetic holder by means of mechanical clamps in order to ensure a stiff assembly during testing. A flat-punch diamond tip with a diameter of 10 μ m was utilized. The PI87 picoindenter is a depth-sensing mechanical test platform that was designed to be interfaced with SEM, enabling the in situ observation of microscale deformation at ambient or elevated temperatures. Furthermore, this indentation platform has a piezo-actuated stage with 5 degrees of freedom (X, Y, Z, rotation, and tilt), which allows for alignment correction between the sample and the flat punch indenter (Fig. 2.8.b). In this thesis, high temperature micropillar compression was carried out inside an SEM (EVO MA15, Zeiss) on the PI87 platform coupled with a temperature controller (Model 336, LakeShore). A high load transducer with a maximum force of 150 mN, a force resolution of 1 μ N, and a displacement resolution of 0.1 nm was utilized. More details about the testing conditions are described below in the corresponding chapters.

2.4 Identification of active slip systems

Analysis of the slip traces emerging on the pillar surfaces upon compression allowed determining the active slip systems under different testing conditions. Careful examination of slip traces was performed in FEG-SEM. Slip trace identification was carried out by comparison of the orientation of a given slip trace observed on two adjacent pillar faces with the slip traces of all potentially active systems for a given micropillar orientation. The latter are simulated by calculating the corresponding slip traces in the micropillar coordinate system, which requires the rotation matrix from the standard crystal frame, C_c , to the micropillar reference frame, C_m . First, C_c was transformed into the acquisition frame, C_{ac} , by the rotation matrix R_1 based on the Euler angles corresponding to the micropillar ori-

2.4 Identification of active slip systems

entation, which are measured by EBSD. Then C_{ac} was further rotated to C_m by a second rotation operation, R_2 . In this work, C_{ac} is related to C_m by a rotation of 180° around the surface normal. Therefore, the complete transformation of the reference frame can be summarized in the following equation:

$$C_m = R_2 \cdot R_1 \cdot C_c \quad (2.1)$$

CHAPTER 3

Effects of solutes on the mechanical behavior and on the slip activity of solid solution quaternary β -Ti alloys

3.1 Background and objective

The objective of this chapter is to unveil the effects of solutes on the mechanical properties as well as on the slip activity of single crystal quaternary β titanium alloys using the diffusion multiple approach. To that end, libraries of [134] Ti-Al-Mo-Cr and [113] Ti-Al-Mo-V single crystals with gradient compositions were generated over distances spanning a few hundred microns and their mechanical properties were probed at room temperature by compression of micropillars milled at selected compositions.

Despite their extraordinary combination of properties, β titanium alloys still have a small market share. This may be attributed to the lack of sufficient knowledge about these complicated multicomponent systems, their abundant microstruc-

3.2 Experimental procedure

tures and the unique plastic deformation behavior of the bcc matrix. Substantial efforts on alloy design, enabled by a deeper understanding of the correlations between composition, microstructure and mechanical behavior, are still needed.

3.2 Experimental procedure

Fig. 3.1 is a composition of optical micrographs that illustrates the microstructure of the diffusion multiple. Among the four interfaces, the single β crystal interdiffusion regions of interest for this study, β_1 and β_2 , spanning a few hundred microns, are those developed between the alloys Ti-7.7Al-8.1Cr and Ti-13.4Al-12.4Mo, and between the alloys Ti-7.7Al-8.4V and Ti-13.4Al-12.4Mo, respectively.

Fig. 3.1: Macrostructure of the diffusion multiple, illustrated by a composition of optical micrographs.

3.2 Experimental procedure

The diffusion directions corresponding to the β_1 and β_2 regions are denoted as DD_{β_1} and DD_{β_2} , respectively, whereas the normal direction to the assembly is termed ND. Due to both the semi-infinite nature and the geometrical configuration of the diffusion multiple, the diffusion along each composing ‘diffusion pair’ (i.e., alloy pair) is supposed to be uniaxial and the sites aligned perpendicular to the diffusion directions, DD_{β_1} and DD_{β_2} , are of identical compositions.

Fig. 3.2: Composition gradients, measured by EPMA, across (a) β_1 ; (b) β_2 regions.

Fig. 3.2 illustrates the graded composition across the β_1 and β_2 interdiffusion regions, measured by EPMA. It can be seen that both have a single crystalline β -Ti structure, as indicated by the corresponding $\{100\}$ pole figures, measured by EBSD, and added as insets to Fig. 3.2. The directions parallel to ND are,

3.2 Experimental procedure

respectively, [134] and [113]. Due to the lower diffusivity of Mo compared to that of Cr and V, respectively, the gradient of Mo content within both interdiffusion regions is greater than that of the other two elements. The specific areas, within the interdiffusion regions, where the micropillars were milled, are shaded in pink and yellow, respectively, in Fig. 3.2.a and 3.2.b. Seven different compositions were probed at interdiffusion region β_1 (each schematically depicted by a horizontal line traversing the corresponding pink shaded area in Fig. 3.2.a and hereafter termed C_{1-7}). C_{1-7} compositions are summarized in Table 3.1. It can be seen that, while there is relatively little variation of the Al content, the amounts of Cr and Mo vary significantly. Three compositions were probed at interdiffusion region β_2 (each schematically depicted by a horizontal line traversing the corresponding yellow shaded area in Fig. 3.2.b and hereafter termed C_{1-3}). The exact C_{1-3} compositions are listed in Table 3.1 as well. The variations of Al and V are small compared to the relatively large change in Mo content.

Table 3.1: Selected alloy compositions in β_1 and β_2 regions

		Cr (wt.%)	Mo (wt.%)	Al (wt.%)	Ti (wt.%)
β_1	C_1	6.39±0.01	1.19±0.01	9.22±0.02	Bal.
	C_2	5.83±0.01	1.86±0.02	9.36±0.01	Bal.
	C_3	5.28±0.01	2.95±0.01	9.63±0.01	Bal.
	C_4	4.70±0.01	4.12±0.01	9.81±0.01	Bal.
	C_5	4.29±0.01	5.72±0.01	9.79±0.01	Bal.
	C_6	3.58±0.01	7.19±0.01	10.03±0.01	Bal.
	C_7	2.19±0.01	9.91±0.01	10.53±0.01	Bal.
		V (wt.%)	Mo (wt.%)	Al (wt.%)	Ti (wt.%)
β_2	C_1	2.94±0.02	5.70±0.08	9.86±0.05	Bal.
	C_2	2.31±0.03	9.57±0.12	10.47±0.06	Bal.
	C_3	1.85±0.16	11.74±0.09	11.35±0.04	Bal.

Fig. 3.3 illustrates the rectangular grids of micropillars milled within interdiffusion regions β_1 and β_2 , as well as their compositions. The micropillars were machined following an efficient annular milling strategy described in section 2.3. The compression tests were carried out at a strain rate of $1.25 \times 10^{-3} s^{-1}$, in the displacement control mode, up to a total engineering strain of 12.5 %. A few pillars

were compressed to lower strain in an attempt to capture the successive activation of different slip systems with increasing strain. All the measured experimental load-displacement curves were first corrected by applying the Sneddon correction in order to account for the extra compliance resulting from the elastic deflection of the matrix material below the micropillars [185]. The corrected curves were then transformed into engineering stress-strain curves taking into account the initial cross section and the height of the micropillars right after milling. From these curves, the yield stress was measured as the 0.5 % offset yield stress.

Fig. 3.3: SEM image of the micropillars milled at selected C_i compositions within interdiffusion regions (a) β_1 ; (b) β_2 .

3.3 Results

3.3.1 Size effect study

Ideally, micropillars' cross sections should be as small as possible in order to avoid significant composition gradients within one single pillar while, simultaneously, they should be large enough to ensure that the measured flow stresses are free of size effects and are thus representative of the bulk behavior. Size effects in bcc micropillars have been comparatively less studied than in fcc micropillars.

3.3 Results

The extent of size strengthening has been found to be dependent on the particular material as well as on the crystallographic orientation of the pillar [186–188]. With the aim of determining the optimum micropillar size for the current study, pillars with side-length of 2, 5, and 7 μm were milled and tested. Figs. 3.4.a-g illustrate, as an example, the engineering stress-engineering strain curves corresponding to pillars with different sizes milled at all the C_{1-7} compositions within interdiffusion region β_1 . Evident size effects are present in the smallest pillars (2 μm), which exhibit significantly higher flow stresses than the rest. However, pillars with sides 5 and 7 μm long appear to have relatively comparable mechanical responses. Fig. 3.4.h depicts the yield stress values corresponding to the three pillar sizes investigated and confirms that pillars with sides of 5 μm or larger are representative of the bulk behavior. No appreciable effect of composition on the size strengthening can be appreciated within the composition ranges investigated. On the light of these findings, a minimum pillar size of 5 μm was chosen for the current study.

The variation of Mo, Al, and Cr within a 5 μm pillar in region β_1 would amount to approximately 0.12 wt.%, 0.02 wt.%, and 0.06 wt.%, respectively. The variation of Mo, Al, and V within a 5 μm pillar in region β_2 would be approximately 0.10 wt.%, 0.01 wt.%, and 0.015 wt.%, respectively. These very small intrapillar composition variations are not expected to have a significant effect in the mechanical properties.

3.3.2 Micromechanical response of quaternary β -Ti alloys

Fig. 3.4.h reveals additionally that, within the composition ranges investigated at the β_1 interdiffusion region, negligible changes in the yield stress are observed, despite the large existing variations in Mo and Cr contents. These data allow us to infer qualitatively the relative strengthening potency of selected alloying elements. For example, let us compare alloys C_1 and C_4 . It is remarkable that they exhibit similar yield strength values despite the lower overall alloying content of the former ($\Delta C_{C_1-C_4} = -1.8$ wt.%). More specifically, C_1 is richer in Cr ($\Delta Cr_{C_1-C_4} = 1.7$ wt.%) but significantly poorer in Al and Mo ($\Delta Al_{C_1-C_4} = -0.6$ wt.%; $\Delta Mo_{C_1-C_4} = -$

Fig. 3.4: Engineering stress-strain curves corresponding to (a) C₁, (b) C₂, (c) C₃, (d) C₄, (e) C₅, (f) C₆, and (g) C₇ micropillars within interdiffusion region β_1 ; (h) plot illustrating the influence of pillar size on the yield strength of C₁–C₇ micropillars.

2.7 wt.%). Therefore, it appears that the overall reduction in Al and Mo in C₁ ($\Delta\text{Al} + \text{Mo}_{\text{C}_1-\text{C}_4} = -3.3$ wt.%) is compensated by an increase in Cr of just 1.7 wt.%. This suggests that Cr has, comparatively, a higher strengthening potency in this alloy system. The yield strength values obtained are close or even exceed those

3.3 Results

measured from micro-compression tests in precipitation hardened commercial β -Ti alloy single crystals with similar orientation [19].

Fig. 3.5: (a) Engineering stress-strain curves corresponding to C_1 - C_3 micropillars within interdiffusion region β_2 ; (b) plot illustrating the influence of pillar size on the yield strength of C_1 - C_3 micropillars.

Fig. 3.5 illustrates the engineering stress-engineering strain curves corresponding to C_1 - C_3 micropillars with side length of 5 and 7 μm within the interdiffusion region β_2 (Fig. 3.5.a), as well as the corresponding yield strength values (Fig.3.5.b). For a specific composition, the similarity between the curves and yield strength values corresponding to both pillar sizes corroborates that their mechanical response is representative of the bulk behavior. Dramatic differences can be clearly identified between the mechanical behavior corresponding to composition C_1 and those belonging to the other two investigated compositions. First, the yield strength of C_1 is significantly smaller (423 MPa) than those of C_2 and C_3 (1339 and 1395 MPa, respectively). Second, the stress-strain curve of C_1 has a concave-up shape, starting with a plateau after yielding that is followed by rapid hardening, while the curves corresponding to C_2 and C_3 have concave-down shapes, exhibiting very high yield strengths but comparatively low strain hardening. The drastic increase in the yield strength value between C_1 and C_2 alloys must be attributed to the increase of Mo (from 5.7 to 9.6 wt.%), since the Al and V contents remain relatively similar (Table 3.1).

3.3.3 Slip activity of quaternary β -Ti alloys

Fig. 3.6: SEM images of compressed $[134]$ micropillars within interdiffusion region β_1 : a) C_1 , (b) C_2 , (c) C_3 , (d) C_4 , (e) C_5 , (f) C_6 , and (g) C_7 ; (h) schematic plot of the (211) trace on a $[134]$ oriented micropillar.

Figs. 3.6.a-g display SEM images of the $[134]$ C_{1-7} micropillars within interdiffusion region β_1 following compression testing at RT up to a total engineering strain of 12.5 %. It is apparent that, irrespective of composition, the same slip trace pattern appears at the surface of all pillars. At first sight, it seems that the

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observable sharp slip traces are parallel to a (211) plane, indicated schematically in Fig. 3.6.h.

Fig. 3.7: High resolution SEM images illustrating the slip traces present in the $[134]$ C_4 micropillar within interdiffusion region β_1 : (a) 25000 $\times$, (b) 200000 $\times$ (c) 400000 $\times$; (d) schematic drawing of the following slip planes on a $[134]$ oriented micropillar: $(101)[\bar{1}11]$ in blue, $(211)[\bar{1}11]$ in red, $(110)[\bar{1}11]$ in purple and $(10\bar{1})[111]$ in gray.

However, closer inspection of the slip traces by high resolution SEM imaging (Fig. 3.7) reveals that the slip trace is wavy and presents several bulges, as a consequence of a more complex slip activation. The seemingly sharp (211) traces are in reality formed by elementary steps on $\{110\}$ planes with high Schmid factors (SFs). Table 3.2 summarizes the SFs of $\{110\}$ and $\{112\}$ slip systems when a compression stress is applied along a $[134]$ direction, as in the micropillars of interdiffusion region β_1 . The highest SFs correspond to the slip systems $(211)[\bar{1}11]$ (SF=0.486), $(101)[\bar{1}11]$ (SF=0.472), $(10\bar{1})[111]$ (SF=0.374), and $(110)[\bar{1}11]$ (SF=0.370). Fig.3.7.c shows the traces of these four slip systems super-

imposed to the pillar side parallel to the ND_{β_1} - DD_{β_1} plane; Fig. 3.7.d illustrates schematically the four slip planes in a $[134]$ pillar. Comparison of Figs. 3.7.c and d reveals that the wavy nature of the analyzed slip trace is due to alternating visible steps on the three $\{110\}$ planes with the highest SFs: (101) and (110) , with occasional transfer to the $(10\bar{1})$ plane, which causes the appearance of bulges.

Table 3.2: $\{110\}$ and $\{112\}$ slip systems and their corresponding SFs when a compression stress is applied parallel to direction $[134]$ (interdiffusion region β_1). The two slip systems of highest SF are highlighted in bold.

Slip plane	Slip direction	Schmid factor
(110)	$[1\bar{1}1]$	0.137
(110)	$[\bar{1}11]$	0.370
$(1\bar{1}0)$	$[111]$	0.234
$(1\bar{1}0)$	$[11\bar{1}]$	0.01
(101)	$[\bar{1}11]$	0.472
(101)	$[11\bar{1}]$	0.003
$(10\bar{1})$	$[111]$	0.374
$(10\bar{1})$	$[1\bar{1}1]$	0.101
(011)	$[1\bar{1}1]$	0.238
(011)	$[11\bar{1}]$	0.004
$(01\bar{1})$	$[111]$	0.140
$(01\bar{1})$	$[\bar{1}11]$	0.102
(112)	$[11\bar{1}]$	0.004
$(\bar{1}12)$	$[1\bar{1}1]$	0.196
$(1\bar{1}2)$	$[\bar{1}11]$	0.333
$(11\bar{2})$	$[111]$	0.296
(121)	$[1\bar{1}1]$	0.216
$(\bar{1}21)$	$[11\bar{1}]$	0.003
$(12\bar{1})$	$[\bar{1}11]$	0.154
$(1\bar{2}1)$	$[111]$	0.055
(211)	$[\bar{1}11]$	0.486
$(2\bar{1}1)$	$[11\bar{1}]$	0.001
$(21\bar{1})$	$[1\bar{1}1]$	0.020
$(\bar{2}11)$	$[111]$	0.351

Figs. 3.8.a-c are SEM images of the $[113]$ C_{1-3} micropillars within interdiffusion region β_2 following compression testing at RT up at a total engineering strain of

Fig. 3.8: SEM images of compressed micropillars within interdiffusion region β_2 : (a) C_1 , (b) C_2 , (c) C_3 .

12.5 %. Several observations can be made from this figure. First, although, for this crystal orientation, traces corresponding to multiple slip systems become apparent at all alloy compositions investigated, it seems that fewer traces are observed at composition C_1 than at C_2 and C_3 . Table 3.3 summarizes the SFs of the different $\{110\}$ and $\{112\}$ slip systems in a bcc $[113]$ single crystal tested in compression along ND. The highest SF (0.445) corresponds to two $\{110\}$ systems that do not share a $\langle 111 \rangle$ direction, $(\bar{1}0\bar{1})[1\bar{1}\bar{1}]$, and $(0\bar{1}\bar{1})[\bar{1}1\bar{1}]$. The second highest SF (0.425) corresponds to the $(11\bar{2})[\bar{1}\bar{1}\bar{1}]$ slip system. Next, two $\{110\}$ slip systems with equal SFs (0.367) share a common $\langle 111 \rangle$ slip direction: $(10\bar{1})[\bar{1}\bar{1}\bar{1}]$, and $(01\bar{1})[\bar{1}\bar{1}\bar{1}]$. It can also be observed in Fig. 3.8 that slip traces in many cases are not sharp straight lines, but appear to be bent and exhibit a wavy, zig-zag nature, hinting that they are the result of the combined activation of several slip systems. In the following,

Table 3.3: $\{110\}$ and $\{112\}$ slip systems and their corresponding SFs when a compression stress is applied parallel to direction $[113]$ (interdiffusion region β_2). The $\{110\}$ slip systems with the highest SF are highlighted in bold.

Slip plane	Slip direction	Schmid factor
$(\bar{1}\bar{1}0)$	$[\bar{1}1\bar{1}]$	0.225
$(\bar{1}\bar{1}0)$	$[1\bar{1}\bar{1}]$	0.225
$(\bar{1}10)$	$[\bar{1}\bar{1}\bar{1}]$	0.002
$(\bar{1}10)$	$[\bar{1}\bar{1}1]$	0
$(\bar{1}0\bar{1})$	$[1\bar{1}\bar{1}]$	0.445
$(\bar{1}0\bar{1})$	$[11\bar{1}]$	0.144
$(10\bar{1})$	$[\bar{1}\bar{1}\bar{1}]$	0.367
$(10\bar{1})$	$[\bar{1}1\bar{1}]$	0.220
$(0\bar{1}\bar{1})$	$[\bar{1}\bar{1}\bar{1}]$	0.445
$(0\bar{1}\bar{1})$	$[11\bar{1}]$	0.143
$(01\bar{1})$	$[\bar{1}\bar{1}\bar{1}]$	0.367
$(01\bar{1})$	$[1\bar{1}\bar{1}]$	0.219
$(\bar{1}\bar{1}\bar{2})$	$[11\bar{1}]$	0.166
$(1\bar{1}\bar{2})$	$[\bar{1}\bar{1}\bar{1}]$	0.384
$(\bar{1}1\bar{2})$	$[1\bar{1}\bar{1}]$	0.383
$(11\bar{2})$	$[\bar{1}\bar{1}\bar{1}]$	0.425
$(\bar{1}\bar{2}\bar{1})$	$[\bar{1}\bar{1}\bar{1}]$	0.388
$(1\bar{2}\bar{1})$	$[11\bar{1}]$	0.082
$(\bar{1}\bar{2}1)$	$[1\bar{1}\bar{1}]$	0.003
$(\bar{1}2\bar{1})$	$[\bar{1}\bar{1}\bar{1}]$	0.214
$(\bar{2}\bar{1}\bar{1})$	$[1\bar{1}\bar{1}]$	0.386
$(\bar{2}1\bar{1})$	$[11\bar{1}]$	0.083
$(\bar{2}\bar{1}1)$	$[\bar{1}\bar{1}\bar{1}]$	0.04
$(2\bar{1}\bar{1})$	$[\bar{1}\bar{1}\bar{1}]$	0.211

the slip traces corresponding to compositions C_1 , C_2 and C_3 will be analyzed in detail.

As illustrated in Fig. 3.5, the mechanical response of the C_1 alloy exhibited a first stage of very low hardening followed by a second stage of rapid hardening. In order to investigate the slip activity at these two stages, microcompression of a $[113]$ C_1 pillar was carried out up to an intermediate engineering strain of 4.5%, which corresponds to the beginning of rapid hardening. Fig. 3.9.a illustrates

Fig. 3.9: (a) Engineering stress-strain curve corresponding to the $[113]$ C_1 micropillar within interdiffusion region β_2 deformed up to a strain of 4.5 %. Two SEM images of the compressed C_1 micropillar illustrating the presence of one main slip trace are included as insets; (b) high magnification image of the main slip trace; (c) schematic representation of (101) (light blue) and $(01\bar{1})$ (yellow) planes on a $[113]$ oriented micropillar.

the corresponding engineering stress-strain curve as well as an SEM image of the compressed micropillar and a second image of the single most distinct slip trace observed after straining, which is formed by several steps. Fig. 3.9.b presents a high magnification micrograph illustrating that those steps are the result of slips in two systems. Comparison of Figs. 3.9.b and 3.9.c reveals that the two slip planes are (101) and $(01\bar{1})$, which, indeed, contain slip systems with high SFs ($(\bar{1}0\bar{1})[1\bar{1}\bar{1}]$ (SF=0.445) and $(01\bar{1})[\bar{1}\bar{1}\bar{1}]$ (SF=0.367) (Table 3.3)). It appears that

the strain on each plane are qualitatively proportional to the ratio of SFs. The presence of a low hardening regime at small strains in the stress-strain curves of C_1 micropillars (Fig. 3.5) suggests that an amount of 5.7 wt.% Mo is not enough to severely hinder the combined activation of the mentioned two slip systems, which, therefore constitute a relatively easy glide mode. The activation of only one of the two $\{110\}$ slip systems with the highest SF (SF=0.445, Table 3.3) at the early stages of deformation may be caused by the lack of a perfect alignment of the indenter axis with the pillar axis.

Fig. 3.10: (a) SEM micrograph depicting an overview of the slip traces present in the $[113]$ C_1 micropillar within interdiffusion region β_2 after deformation to an engineering strain of 12.5 %; a schematic drawing of the main $\{110\}$ plane traces has been included as an inset. The two main slip traces, oriented parallel to the two systems with the highest SFs, are labeled as A and B. (b, c) High magnification images of trace A where the traces corresponding to different slip planes have been overlaid; (d, e) high magnification images of trace B where the traces corresponding to different slip planes have been overlaid; (f) schematic representation of the following planes on a $[113]$ oriented micropillar: $(10\bar{1})$ in purple, (110) in green, (011) in red.

Fig. 3.10.a is a SEM micrograph of the C_1 micropillar following compression up to a strain of 12.5 %. Two main slip traces, labeled A and B, can be observed, which are parallel to the two $\{110\}$ systems with the highest SFs. Most of the strain appears to be accumulated at trace A, which was already observed at the earlier stages of deformation (Figs. 3.9.a, b) and that is now much more

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distinct. A closer observation of trace A (Figs. 3.10.b-c) reveals, first, that the steps along the slip trace shorten with increasing deformation and, second, that, those steps are now a result of the activation of additional $\{110\}$ slip systems. More concretely, besides the two slip planes that were already activated during the first stages of deformation ((101) and $(01\bar{1})$), both corresponding to systems with high SFs), and which are drawn schematically in light blue and yellow in Fig. 3.10.a, the following slip planes have been identified: (a) $(10\bar{1})$ (corresponding to a slip system with $SF=0.367$), and drawn schematically in purple in Fig. 3.10.f; (b) $(\bar{1}\bar{1}0)$, that corresponding to two coplanar systems with equal and relatively low SF ($SF_{max}=0.225$), and which is depicted schematically in green Fig. 3.10.f. A closer inspection of trace B (Figs. 3.10.d-e), which is clearly less well defined than trace A, suggests that it is also formed by steps, corresponding in this case to the combined activation of plane $(0\bar{1}\bar{1})$, containing the second slip system with the highest SF, $(0\bar{1}\bar{1})[\bar{1}1\bar{1}]$ ($SF=0.445$), and drawn schematically in red in Fig. 3.10.f, as well as of $(10\bar{1})$, with $SF_{max}=0.367$, (purple in Fig. 3.10.f), and of low SF planes such as $(\bar{1}\bar{1}0)$ ($SF_{max}=0.225$) (red in Fig. 3.10.f). The slip system with the highest SF appears to carry a larger amount of strain (as evidenced by larger steps), and periodic slip transfer into the other systems is observed to take place. The rapid hardening stage following the initial low hardening deformation in the C_1 alloy (Fig. 3.5), thus, seems to result from the activation of the second $\{110\}$ slip system with the highest SF (trace B), which leads to enhanced dislocation interactions between all the active systems. The increase in the stress levels leads to the activation of planes in which both coplanar slip systems have low SFs (anomalous slip) which carry a comparatively small strain. Therefore, the major slip traces on the micropillar are preferentially aligned with the planes having the highest SFs [60].

C_2 and C_3 micropillars exhibit similar slip trace patterns (Fig. 3.8), which are characterized by the presence of multiple traces exhibiting straight, bent and/or zig-zag contours. Fig. 3.11 depicts, as an example, an SEM image of the C_2 pillar where several $\{110\}$ slip traces have been superimposed using the same color coding as in Figs. 3.9 and 3.10. Fig. 3.11.a reveals that, macroscopically, traces parallel

to planes containing slip systems with the highest SF (light blue), with the second highest SF (yellow), as well as with low SF (anomalous slip) (green) are visible. Also, some traces, pointed by an arrow in Fig. 3.11.a, do not appear to be parallel to any $\{110\}$ plane. A more detailed slip trace analysis of selected traces, such as that shown in Fig. 3.11.b, confirms the profuse activation of planes containing only systems with low SFs; i.e., it appears that increasing the Mo content results in a higher incidence of anomalous slip. The presence of bent slip traces reveals that the contributions of the many $\{110\}$ active slip systems vary at different locations within the micropillars, due probably to heterogeneities in the stress distribution.

Fig. 3.11: (a) SEM micrograph depicting an overview of the slip traces present in the $[113]$ C_2 micropillar within interdiffusion region β_2 after deformation to an engineering strain of 12.5 %; a schematic drawing of the main (110) plane traces has been included as an inset; (b) a high resolution SEM image of one of the traces present, in which the traces corresponding to different slip planes have been overlaid.

The origin of the dramatically different mechanical response of C_1 and C_2 - C_3 micropillars, depicted in Fig. 3.5, may then be rationalized in the following way. First, it seems clear that an increase in the Mo content from 5.7 (C_1) to 9.6 (C_2)wt.% gives rise to a large increase of the CRSS of $\{110\}$ systems. Thus, at low Mo contents (C_1), slip would start on a plane containing the system with the highest SF, which could carry out a relatively large amount of strain without significant hardening by periodical slip transfer into another system with the second highest SF. However, at higher Mo contents (C_2 and C_3), this combined system would harden rapidly immediately following yielding, thus triggering the activa-

tion of multiple slip. Further additions of Mo, up to 11.7 wt.% (C₃), do not seem to have any distinct strengthening effects on the {110} slip systems, as evidenced by the similar mechanical responses of C₂ and C₃ pillars.

3.4 Discussion

3.4.1 Role of β -stabilizers as solute strengtheners in quaternary β -Ti alloys

The very high strengthening observed in the β -Ti alloys under study can be rationalized in the following way. It is well known that, in bcc metals, the lattice offers a resistance mainly to screw dislocations due to the complex spatially extended nature of their cores, while the resistance to edge dislocations is much smaller. Therefore, at low temperatures, solid solution strengthening emerges mostly from the interactions of solute atoms with screw dislocations [116]. Plasticity of β -Ti alloys, as in many bcc metals, is accomplished via the formation of double kinks and the subsequent motion of such kinks along the screw dislocation line under sufficient loading. In dilute solid solutions, kink motion is hindered mainly by the modified Peierls potential, which is usually small, as kinks can readily overcome individual solute atoms [119,189]. However, in highly alloyed systems, such as the β -Ti alloys under study, the increasing amount of solutes results in enhanced kink formation [73] and, furthermore, kink mobility becomes progressively more difficult due to pinning by atom clusters [116] and by kink-interaction [120]. A large fraction of alloying additions leads to variations of the core of screw dislocations along their dislocation lines associated with concentration fluctuations, as demonstrated recently by Rao et al. [116] using atomistic simulations. Such variations give rise to changes in the local stacking fault energies on different slip planes, which ultimately increase the likelihood of kinking on a wider variety of planes at different locations along the dislocation line; some of those planes might have relatively low SF and might thus be relatively immobile. The presence of such

concentration variations along screw dislocation lines might thus also contribute to the observed elevated strength in the β -Ti alloys of the present investigation.

The influence of β -stabilizers on the mechanical behavior of multi-component (ternary and quaternary) β -Ti alloys is generally unknown. It is widely recognized that measuring the strengthening potency of solutes in these materials is not trivial and contradictory evidence, mostly obtained from binary alloys, has been presented in the literature [2, 92, 190]. In particular, some studies based on the analysis of the variation of the lattice parameter with increasing solute additions, claim that Cr is a more effective strengthener than Mo [2, 92], while others affirm the contrary [190]. Our results support the comparatively higher strengthening potency of Cr versus Mo (in MPa/wt.%) in the Ti-Al-Cr-Mo quaternary alloy under study, at least within the ranges of Cr and Mo additions investigated. Additionally, our study reveals that Mo is indeed a potent strengthener of Ti-Al-V-Mo alloys.

3.4.2 Influence of β -stabilizers on slip activity in quaternary β -Ti alloys

Slip in bcc metals is recognized to be complex [60, 191]. In general, it is believed that it mainly occurs in the closest packed $\langle 111 \rangle$ direction along $\{110\}$ and $\{112\}$ planes, the former being more commonly cited as the dominant deformation mode at low temperatures [77, 192, 193]. However, a large body of seemingly contradictory evidence on the active deformation mechanisms has been provided by studies based on optical slip trace analysis, electron microscopy and X-ray Laue diffraction [73, 192].

Most studies on bcc micropillar compression have to date focused on pure metals, and have dealt mainly with size effects rather than with the direct observation of slip traces [59, 73, 186, 192, 194]. Kim et al. [187] analyzed slip traces in $[100]$ Nb single crystal micropillars tested at RT under uniaxial compression and tension and identified them as $\{110\}$ planes. Han et al. [194] also identified the slip traces emerging in $[001]$ V single crystal micropillars tested at RT in compression

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as $\{110\}$ slip. In a recent study on bcc W single crystal micropillars, Marichal et al. [61] observed $\{112\}$ traces and they utilized in-situ X-ray Laue diffraction experiments during micro-compression to analyze their origin. They demonstrated that for a $[155]$ single crystal orientation where a $\{112\}$ plane had the highest SF (0.50) and two 110 planes containing the same slip direction had very similar, and also high, SFs (0.44 and 0.43), the sharp slip traces that were observed on a $\{112\}$ plane could be attributed to alternating elementary steps on the two mentioned $\{110\}$ planes. However, for a $[256]$ orientation, where the pair of $\{110\}$ planes sharing the same slip direction are differently stressed (SFs = 0.45 and 0.39), macroscopic strain was measured on these two individual planes and collective cross-slip between them took place to ensure the fulfillment of mechanical boundary conditions, resulting in a zig-zag shaped slip trace on the sample surface. Very few studies [195] have analyzed slip activity in bcc alloys, including β -Ti alloys, via direct observation of slip traces following micropillar compression. In fact, the influence of alloying elements in multicomponent bcc alloys on slip activity is still an open issue.

In the present work we analyzed the nature of the slip traces appearing after micro-compression of single crystalline quaternary β -Ti alloy micropillars. Our results reveal, first, that all the traces observed can be explained in terms of different contributions of $\{110\}$ slip systems, confirming that this is the main deformation mechanism at room temperature for all the compositions investigated. In particular, for the β -Ti alloys with $[134]$ orientation (interdiffusion region β_1), which is relatively close to the $[256]$ pure W single crystal orientation analyzed by [61], the $\{112\}$ slip traces appearing during RT deformation can be ascribed to a combination of elementary steps in the two most highly stressed $\{110\}$ slip systems sharing a common $\langle 111 \rangle$ direction. Additionally, we give conclusive evidence of the contribution of a third $\{110\}$ slip system, which has the same SF as one of the former two (Table 3.2). Changes in Mo and Cr content (Table 3.1) did not affect the mentioned slip behavior.

A second open issue in the plasticity of bcc metals is the occurrence of anomalous slip, including the experimental observation of slip traces which do not coincide

with a single crystallographic plane and which vary with the orientation and sense of the applied stress [191], or the occurrence of plastic slip on planes with a much lower resolved shear stress (i.e., much lower SFs) than that of the primary slip systems [61, 73, 191]. These anomalies are ascribed to the non-planar nature of screw dislocation cores, which split into several non-parallel planes of the $\langle 111 \rangle$ zone, a significant number of which belongs to the $\{110\}$ family [68, 97, 103, 196]. Matsui and Kimura [78, 79] attributed the occurrence of anomalous slip traces to the easy glide of dislocation segments on anomalous planes resulting from the deflection of screws near free surface due to image forces; other theoretical [80] and experimental studies [81] have proposed that the interaction between two screw dislocations triggers anomalous slip. Recently, based on sophisticated in-situ X-ray laue micro-diffraction and discrete dislocation dynamics modelling, Marichal et al. [73] suggested that anomalous slip could be attributed to cross-kinks formed by interactions of dislocations on different slip planes which can generate highly mobile mixed dislocation segments that cross the entire specimen and produce clear slip traces on the surface. The effect of alloying additions on the incidence of anomalous slip on multicomponent bcc metals has not been clarified to date.

Our results reveal that, within interdiffusion region β_2 , the incidence of anomalous slip in C_2 and C_3 micropillars, with alloying contents of 22.3 % and 25 %, respectively, is higher than that of C_1 pillars, where the alloying content is 18.5%. As suggested by Rao et al. [116], it appears here that the increasing amounts of alloying additions may lead to a higher probability of finding local composition fluctuations along the screw dislocation lines, thus promoting local variations of the dislocation core structure. Therefore, increasing the alloying additions would result in a higher probability of kinking on different planes, including those with low Schmid factors. As a consequence, it seems reasonable that the incidence of anomalous slip would increase with increasing alloying content, and lead to the slip traces deviating from the slip plane having the highest SF.

3.5 Summary

The design of advanced β -Ti alloys requires deeper knowledge on the influence of composition on the mechanical response. This work aims to investigate the effect of solutes on the micromechanical behavior, including slip activity, of quaternary β -Ti alloys, using a high throughput approach. The efficiency of specific β -stabilizers to strengthen quaternary β -Ti alloys is found to vary for different alloy compositions. More specifically, Cr appears to be a more effective strengthener than Mo in quaternary Ti-Al-Cr-Mo alloys. Molybdenum is, however, a very potent strengthener of Ti-Al-V-Mo alloys. Additionally, it has been found that strain in the β -Ti alloys investigated is accommodated at room temperature by $\{110\}$ slip. Multiple slip in different $\{110\}$ planes is observed for all the orientations and compositions investigated. The specific combination of $\{110\}$ slip systems that act cooperatively to accommodate strain is, however, found to be dependent on orientation and on composition. In particular, increasing amounts of Mo in Ti-Al-Mo-V alloys favor the activation of an increased number of $\{110\}$ slip planes. The incidence of anomalous slip has also been investigated. It has been found that anomalous slip does take place in β -Ti alloys, as observed commonly in pure bcc metals. The incidence of anomalous slip in β -Ti alloys depends on orientation and on composition. In particular, an increase in Mo in Ti-Al-V-Mo alloys appears to enhance anomalous slip. Finally, the high throughput technique of diffusion multiples is shown to be very effective to probe and elucidate the individual and combined effects of solutes on the mechanical properties of multicomponent alloys as well as to investigate more fundamental aspects of their physical metallurgy.

CHAPTER 4

Effects of solutes on the rate sensitivity of solid solution quaternary β -Ti alloys

4.1 Background and objective

The strain rate sensitivity (m) of a metallic material gives a measure of the dependence of its flow stress (σ) on external testing conditions such as the temperature (T) or the applied strain rate ($\dot{\epsilon}$) [197]. Its value may vary between 0 and 1 (Newtonian fluid). When a material's response is strain rate sensitive, a considerable delay in necking may occur [198]. Superplastic materials, with m values higher than 0.3, are able to withstand elongations of several hundred percent before failure and, thus, constitute a very evident case of the influence of m on ductility [199]. The strain rate sensitivity can be written as [199]:

$$m = \frac{\partial(\log \sigma)}{\partial(\log \dot{\epsilon})} \quad (4.1)$$

or, in terms of the activation volume (v^*), as [200]:

4.1 Background and objective

$$m = \frac{\sqrt{3}kT}{\sigma v^*} \quad (4.2)$$

The plasticity of body centered cubic (bcc) metals has been less studied than that of face centered cubic (fcc) metals and research efforts on this area remain mostly confined to pure metals. The influence of alloying remains rather unexplored in spite of some recent remarkable efforts in this direction [116,117]. Single crystals and coarse grained polycrystals of pure metals with bcc structures have, in general, higher strain rate sensitivity than those with fcc lattices [201]. This is due to the fact that plasticity in bcc metals, at least in the early stages of deformation, is governed by slip of screw dislocations, which dissociate onto three different planes belonging to the $\langle 111 \rangle$ zone [202], rendering a very complex dislocation core with very limited mobility. The movement of such screw dislocations is believed to be controlled by the nucleation of double kinks, a thermally activated process [100,101,105,193]. In fcc metals, on the contrary, dislocations may dissociate into two partials on one slip plane, and they can glide easily, with little need for thermal assistance. A reduction in grain size from the microcrystalline to the nanocrystalline range gives rise to a decrease in the m value in bcc metals [200]. Different explanations have been put forward to rationalize this observation. Earlier works [203] have assumed that the double kink nucleation mechanism would still be rate controlling in nanocrystalline bcc metals, rendering v^* constant for sufficiently high stress levels, and attributed the lower m values observed to the increase in strength due to the Hall-Petch effect (Eq. 4.2). More recently, Cheng et al. [204] have reported a gradual replacement of screw dislocations by edge and mixed dislocations with decreasing grain size in pure Mo; the strain rate sensitivity decrease would then be related to the easiness of glide of the latter. The effect of solute additions on the strain rate sensitivity of bcc metals remains still a rather unexplored subject.

β -Ti alloys constitute excellent systems to investigate the effect of multicomponent alloying additions on m in bcc metals. These alloys, which contain large amounts of alloying additions, are a very versatile class of materials, which may

achieve very high strength after proper heat treatments due to both solute and precipitation strengthening effects [205]. Comprehensive data about the high temperature rate sensitivity of β -Ti alloys has been published [206, 207]. However, relatively little work has been carried out to date to understand the effect of alloying additions on the room temperature strain rate sensitivity of these materials. Recent research [195], combining pillar compression and crystal plasticity modelling, determined indirectly the strain rate sensitivity of the β Ti phase (bcc) in a duplex Ti-6Al-2Sn-4Zr-2Mo (wt%) alloy, finding it to be much higher than that of the corresponding α phase. Understanding the strain rate sensitivity of β -Ti alloys is reportedly critical to optimize cold dwell fatigue behavior [208].

The aim of this work is to utilize the high throughput technique of diffusion multiples to investigate the effect of solute additions on the room temperature strain rate sensitivity of the quaternary Ti-xAl-yMo-zCr and Ti-xAl-yMo-zV alloy systems. The obtained m values have been related to the active deformation mechanisms and to the nature of the dislocations present.

4.2 Experimental procedure

In this part, the same single crystalline interdiffusion regions, β_1 and β_2 , analyzed in Chapter 3, are investigated. Several alloy compositions were selected, respectively, within β_1 and β_2 , in order to evaluate solute effects on the rate sen-

Table 4.1: Alloy compositions selected in β_1 and β_2 regions

		Cr (wt.%)	Mo (wt.%)	Al (wt.%)	Ti (wt.%)
β_1	C ₁	6.39±0.01	1.19±0.01	9.22±0.02	Bal.
	C ₂	5.28±0.01	2.95±0.01	9.63±0.01	Bal.
	C ₃	4.29±0.01	5.72±0.01	9.79±0.01	Bal.
	C ₄	2.19±0.01	9.91±0.01	10.53±0.01	Bal.
		V (wt.%)	Mo (wt.%)	Al (wt.%)	Ti (wt.%)
β_2	C ₁	2.94±0.02	5.70±0.08	9.86±0.05	Bal.
	C ₂	2.31±0.03	9.57±0.12	10.47±0.06	Bal.
	C ₃	1.85±0.16	11.74±0.09	11.35±0.04	Bal.

4.2 Experimental procedure

Fig. 4.1: (a) Schematic drawing of the diffusion multiple where the selected β_1 and β_2 interdiffusion regions are indicated; (b), (c) composition of the selected alloys within β_1 and β_2 interdiffusion regions.

sitivity of β -Ti alloys. These compositions (a total of 4 in β_1 and 3 in β_2), are summarized in Table 4.1 and are labelled C_i in Fig. 4.1. Within β_1 , Al remains relatively unchanged, while the content of Mo and Cr changes noticeably ($\Delta_{Mo} \approx 9$ wt.% and $\Delta_{Cr} \approx 5$ wt.%); within β_2 , the Mo content increases between 6 and 12 wt.%, while the variations of Al and V remain within 1.5 wt.%.

Square micropillars were machined at the selected alloy compositions within β_1 and β_2 interdiffusion regions following the pillar milling procedure described in section 2.3. Micropillars with a side length of $5 \mu\text{m}$ and an aspect ratio of ~ 2.4 , were milled, as it was demonstrated earlier (Chapter 3) that this geometry yields mechanical properties that are free of size effects. A representative pillar array in the β_2 region is shown in Fig. 4.2.

Fig. 4.2: SEM image illustrating the micropillars milled within region β_2 .

Two types of tests were performed in order to investigate the effects of composition on the rate sensitivity. On the one hand, strain rate jump micropillar compression (SRJMC) tests were used to measure the strain rate sensitivity in all the β -Ti alloy compositions investigated. The strain rate was changed at discrete steps between the values $1 \times 10^{-4} \text{s}^{-1}$, $7 \times 10^{-4} \text{s}^{-1}$, $5 \times 10^{-3} \text{s}^{-1}$ and $1 \times 10^{-2} \text{s}^{-1}$ and the corresponding flow stresses were recorded. The strain rate sensitivity (m) was then calculated as the slope of the log (stress)-log (strain rate) plot. Each test was repeated at least 3 times. To reduce the influence of thermal drift between the flat punch indenter and the micropillars, all compression tests were performed after a long contact period of up to 600 s. In order to minimize the stress drops originated by dislocation avalanches, which could lead to a misinterpretation of the stress data, micropillars with a taper of about 4° were used in the SRJMC tests. Additionally, several constant strain rate tests at $1 \times 10^{-4} \text{s}^{-1}$, $7 \times 10^{-4} \text{s}^{-1}$, $5 \times 10^{-3} \text{s}^{-1}$ and $1 \times 10^{-2} \text{s}^{-1}$ were performed in C₁ alloy within inter-diffusion region β_2 . These tests were carried out in micropillars without tapers.

All the tests described above were performed in the displacement control mode on TI950 TriboindenterTM (Hysitron, Inc., Minneapolis, MN, USA) equipped with flat punch tips. A thermal drift correction [208] and the Sneddon correction [185] were applied after compression. Further, the dislocation structure of selected micropillars (C_1 and C_3 of interdiffusion region β_2) was examined by TEM. Foils parallel to the primary slip trace were prepared via a trenching-and-lift-out focused ion beam (FIB) technique and they were then examined in a Talos F200X microscope operated at 200 kV.

4.3 Results and discussion

Fig. 4.3 illustrates representative stress-strain curves corresponding to all the alloys investigated. In particular, Fig. 4.3.a depicts the curves corresponding to SRJMC tests of the C_{1-4} alloys of interdiffusion region β_1 . Fig. 4.3.b shows the curves corresponding to constant strain rate tests of the C_1 alloy of interdiffusion region β_2 . As demonstrated in Chapter 3, the low yield point and the following rapid hardening observed in this figure are due to the transition from single slip to multiple slip. The single slip stage is shaded in orange. It can be clearly seen that the flow stress at the single slip stage increases with increasing strain rate. Fig. 4.3.c illustrates the curves corresponding to SRJMC tests of the C_{1-3} alloys of interdiffusion region β_2 . The change in the shape of the curves with increasing Mo content is due to the activation of a larger number of slip systems with increasing Mo content, as explained in detail in Chapter 3.

The work hardening that is apparent in Figs. 4.3.a and c is in reality a geometrical artifact due to the micropillar taper. Thus, a correction on the steady plastic deformation segment was implemented to remove the geometrical contribution, as suggested by Mohanty et al. [209]. As an example, Fig. 4.3.c illustrates both the measured and corrected stress-strain curves corresponding to the C_3 alloy of interdiffusion region β_2 . The strain rate sensitivity values were measured in all cases from the corrected curves.

Fig. 4.3: Representative stress-strain curves corresponding to the following alloy compositions: (a) C_{1-4} of β_1 ; (b) C_1 of β_2 ; (c) C_{1-3} of β_2 .

Fig. 4.4: Strain rate sensitivity values corresponding to the following alloy compositions: (a) C_{1-4} of β_1 ; (b) C_{1-3} of β_2 .

4.3 Results and discussion

Fig. 4.4 summarizes the strain rate sensitivity values corresponding to the seven quaternary β -Ti alloys investigated. In the Ti-xAl-yMo-zCr system (β_1), the rate sensitivity remains basically unchanged for all the composition range investigated (Fig. 4.4.a). This is consistent with the fact that, as demonstrated in Chapter 3, the four alloys under study have similar flow stress levels because the increase in Mo is compensated by a decrease in Cr and also because, in all of them, the same $\{110\}$ slip planes, namely (101) and (110), with occasional slip transfer to the $(10\bar{1})$ plane, become active. Thus, under these circumstances, the denominator in Eq. 4.2 should remain constant for the four alloy compositions under scrutiny.

Fig. 4.4.b illustrates the strain rate sensitivity values corresponding to the three quaternary Ti-xAl-yMo-zV alloys selected within the β_2 interdiffusion region. Several trends can be inferred from this figure. First, in the C₁ alloy the value measured in the single slip (low strain, low flow stress) regime ($m \approx 0.05$) is significantly larger than the value obtained in the multiple slip (high strain, high flow stress) regime ($m \approx 0.02$). The ratio between both m values ($m_{single\ slip}/m_{multiple\ slip}$) is approximately 2.5. Simultaneously, the average ratio between the flow stress values corresponding to both regimes ($\sigma_{single\ slip}/\sigma_{multiple\ slip}$) is approximately 0.33. Thus, according to Eq. 4.2, ($v_{single\ slip}^*/v_{multiple\ slip}^*$) must be approximately 1.2, i.e., the activation volume becomes smaller in the high strain, high flow stress regime. This may be explained as follows. Fig. 4.5.a illustrates the dislocation structure corresponding to the C₁ alloy pillar, deformed up to an engineering strain of 12.5%. An array of long, serrated screw dislocation segments, with $\frac{1}{2}a[1\bar{1}1]$ Burgers vector, is visible, indicating that double kink nucleation is the rate-controlling mechanism in this alloy, even at such relatively high strains. Under such conditions the activation volume can be written as [201]:

$$v^* = b \times \xi \times l^* \quad (4.3)$$

where b is the Burgers vector of the screw dislocation, ξ is the critical unzipping distance for a screw dislocation, which is a function of the junction strength [210], and l^* is the critical span between two kinks in a kink pair [211]. The critical span

is a decreasing function of the applied stress, indicating a great influence of stress on the core structure of screw dislocations [108, 112, 212]. In particular, it follows an inverse square root dependence, and levels off at very large applied stress. The value of ξ should be roughly constant at a given temperature [210]. Therefore, according to the above, the increase in flow stress in the C_1 alloy pillar with increasing strain, due to the activation of multiple slip systems, is fully consistent with the observed decrease of the activation volume.

Fig. 4.5: TEM examination of the dislocation structure of alloys (a) C_1 (engineering strain=12.5 %) and (b) C_3 (engineering strain=12.5 %) of the β_2 region in bright field mode with $g=\bar{2}00$. The corresponding selected area diffraction patterns, illustrating the direction of the Burgers vector of screw dislocations, are included as insets. In (a), parallel serrated screw dislocation segments are shown; (b) is composed of three sections taken with slightly different tilts in order to better highlight the presence of dipoles, which are pointed out by arrows.

Fig. 4.4.b also reveals that, in the Ti-xAl-yMo-zV system (β_2), an increase in the Mo content results in a slight decrease of the strain rate sensitivity measured at high strain (when multiple slip is operative). In particular, the m value decreases from approximately 0.02 in the C_1 alloy (high strain, high stress regime) to 0.015 in the C_3 alloy, where the Mo content is approximately 6 wt.% higher. The ratio between both m values (m_{C_1}/m_{C_3}) is approximately 1.3. Since, as shown in Fig.

4.4 Summary

4.3, the flow stress values corresponding to the C_1 (high strain) and C_3 alloys are similar, the observed decrease in strain rate sensitivity with increasing Mo content must be attributed to an increase of the activation volume. This might be rationalized as follows. In Chapter 3, it was demonstrated that an increase in Mo within the Ti-xAl-yMo-zV system resulted in the activation of a larger number of $\{110\}$ planes, as well as in a higher incidence of anomalous slip. This is reportedly caused by structural fluctuations in the screw dislocation cores due to local variations in the solute distribution [116,118]. The collision of kinks on different slip planes, which is facilitated by the sluggish motion of kinks in the presence of a high volume fraction of solutes, leads to the formation of superjogs [120]. The latter are well known to act as strong pinning points for dislocations and, in turn, cause the formation of dipoles [120,211–213]. Fig. 4.5 illustrates that, while such dipoles are absent in the C_1 alloy deformed up to a strain of 12.5% (Fig. 4.5.a), they are widely abundant in the deformed C_3 micropillar, deformed to the same strain level (Fig. 4.5.b). The above evidence attests to a change in the rate controlling mechanism, from kink pair nucleation (C_1 alloy) to screw dislocation pinning by superjogs (C_3 alloy). It seems, therefore, reasonable that the activation volume may change with increasing Mo content, thus yielding the observed decrease in the strain rate sensitivity.

4.4 Summary

The present work analyzes the effect of solute additions on the strain rate sensitivity of quaternary β -Ti alloys belonging to the Ti-xAl-yMo-zCr and Ti-xAl-yMo-zV systems. A high throughput approach, combining alloy fabrication by the technique of diffusion multiples and micromechanical testing methods, allows to probe a relatively large array of compositions without significant material consumption. Our results show that, firstly, the strain rate sensitivity remains unchanged throughout the whole range of compositions analyzed within the Ti-xAl-yMo-zCr system since these alloys have similar strength levels and, in them, the same $\{110\}$ slip systems become active. Secondly, in Ti-xAl-yMo-zV with low

Mo content, a transition from single to multiple slip of screw dislocations with strain is accompanied by a significant decrease in the m value due to increasing strength levels originated by work hardening. The rise in the flow stress also contributes to reducing the activation volume as it leads to a decrease in the critical span between the two kinks forming kink pairs in screw dislocations. In the same alloy system, under multiple slip deformation conditions, an increase in the Mo content leads to a further decrease of m , as it promotes screw dislocation pinning leading to the formation of dipoles.

CHAPTER 5

Influence of nanoscale α plates on the mechanical behavior and on the slip activity of quaternary β -Ti alloys

5.1 Background and objective

As the most important strengthening agent in β -Ti alloys, the α phase has been evidenced to exhibit profound effects on the mechanical properties of these materials and therefore has been the subject of major research endeavors in recent years [4,10]. Great efforts have, in particular, been devoted to achieving a uniform dispersion of intragranular fine α laths via the ω -assisted α heterogeneous nucleation process [17,214–218] and exceptional strength (over 1600 MPa) has thus been gained in several typical β titanium alloys [219,220]. The strengthening power of α precipitates has been observed to be dependent on their geometry, morphology, distribution, size and density [4, 10, 221], as well as on the deformation temperature [222]. However, pushing the strength limits achieved so far in these alloys

5.1 Background and objective

to still higher values would require a deeper understanding on the interaction of matrix dislocations and α plates.

Earlier studies have analyzed the factors affecting slip transfer across grain boundaries in titanium [223, 224]. Both the geometrical alignment of incoming and outgoing slip systems, as well as the corresponding global SFs, have been considered, as they determine the magnitude of the resolved shear stress acting on a given system [223, 225]. In general, the reported results suggest that the geometrical alignment dominates over the SF in the slip transfer criterion in α Ti alloys [223, 226] and in $\alpha+\beta$ Ti alloys [64, 227]. While slip in bcc Ti takes place by the activation of $\{110\}\langle\bar{1}\bar{1}1\rangle$ systems, in the hcp α phase it is mostly dominated by prismatic slip, as the latter exhibits the lowest critical resolved shear stress (CRSS) [228, 229]. Basal slip may also occasionally be active depending on the lattice orientation and on composition. Some investigations on slip transfer across α/β interphase boundaries have been carried out in single α/β colonies where only one kind of α BOR variant with respect to the β matrix is present [64, 195, 226]. Suri et al. [226] tested single crystals of a near- α Ti-5-2.5-0.5 alloy formed by a α matrix oriented for prismatic slip and fine β laths; they then utilized TEM to investigate slip transmission across β laths (α - β - α slip transfer). Their research shows that the resistance of α/β interfaces increases with the misalignment between the incoming prismatic plane and the active slip plane in the β phase. Savage et al. [64] compressed individual α/β colonies of the near- α Ti-6242 alloy in which the α phase was favorably oriented for basal slip. Again, their careful TEM analysis of slip transfer across α/β interfaces suggests that the lattice provides little hindrance to slip for the basal slip system with the smallest misorientation with respect to the active slip system in the beta phase, thus leading to a reduced critical resolved shear stress. More recently, Zhang et al. [195] analyzed slip transfer across α/β boundaries in the Ti-6242 alloy by a combined approach including compression of micropillars with different α matrix crystallographic orientations and containing one β lamella. Their research further corroborates that slip transfer across α/β interfaces is predominantly favored by close alignment of incoming and outgoing slip systems, and that global SFs influence less critically the mentioned transfer. To

date, little is known about slip transfer across nanoscale α laths dispersed on a β -Ti alloy matrix, probably due to the complexity inherent to analyzing slip transfer when several α variants are present. In particular, the effect of alloy composition, temperature, and particle density on such dislocation-particle interactions is currently unknown.

The aim of this work is to investigate the effect of a very high density of nanoscale α precipitates on the room and high temperature mechanical behavior and slip activity of the Ti-xAl-yMo-zV β -Ti alloy system. An experimental methodology including alloy design using a high throughput diffusion multiple approach, as well as a combination of in-situ micromechanical testing, EBSD-assisted slip trace analysis, and TEM characterization, is put in place to achieve the mentioned goal. The output of this research includes guidelines to develop very strong β -Ti alloys, with strength values that exceed those exhibited by all commercial β -Ti alloys currently known. The dislocation-particle interactions that give rise to such superior strength values are analyzed and discussed in the frame of the existing literature.

5.2 Experimental procedure

The section of the diffusion couple composed of the two ternary Ti alloy blocks (Ti-7.7Al-8.4V, Ti-13.4Al-12.4Mo, wt.%) was considered for this work. A thin specimen containing the single crystalline interdiffusion region, β_2 , (represented schematically in Fig. 5.1 as the region bounded by red dashed lines) was machined from the well-polished as-processed couple. The normal direction (ND), perpendicular to the diffusion direction (DD) and to the constant composition direction (TD, Fig. 3.1), was identified as [113] via EBSD analysis (Fig. 5.1). The interdiffusion region in the as-processed state is a solid solution. The composition gradient across the selected interdiffusion region was measured by EPMA.

Three solid solution alloy compositions were selected within the β_2 interdiffusion region in order to evaluate the α aging response and the corresponding

5.2 Experimental procedure

Fig. 5.1: Single crystalline interdiffusion region of interest. The $\{100\}$ EBSD direct pole figure is added as an inset; DD stands for diffusion direction and TD for constant composition direction. The micropillars milled at the C_{1-3} alloy compositions are also shown.

influence of α plates on the mechanical properties and on the slip activity. These compositions, labeled C_{1-3} (Fig. 5.1), are summarized in Table 3.1. The Mo content increases from 6 wt.% in C_1 to 12 wt.% in C_3 , while the variations of Al and V remain smaller than 1.5 wt.%.

Square micropillars were milled at the selected alloy compositions within the interdiffusion region using a focused Ga^+ ion beam (FIB), with an accelerating voltage of 30 kV, in a FEI Helios NanoLab 600i dual-beam field emission gun scanning electron microscope (FEI-FEGSEM). A micropillar side-length of 5 μm and an aspect ratio of 2.4 were chosen in order to avoid size effects [230, 231]. A range of ion beam currents were employed at different milling stages; a current of 80 pA was used for the final milling step to minimize the surface damage due to Ga^+ ion implantation and to remove the taper.

The thin specimen containing the micropillars was then fixed to a self-heating stage on a Hysitron PI87 picoindenter using high temperature carbon paste. A clip with screws was also utilized to minimize the compliance during micropillar compression at high temperature. An additional thermocouple was linked to one screw to monitor the temperature. The assembly was later inserted into a scan-

ning electron microscope (EVO MA15, Zeiss). The heat treatment sequence and testing schedule are illustrated schematically in Fig. 5.2. The following micropillar compression tests were performed. First, the initial C_{1-3} single crystalline solid solution alloys were compressed at RT after several hours in vacuum for stabilization. Subsequently, the thin specimen containing the whole interdiffusion region was heated up to 300 °C using a heating rate of approximately 15-20 °C/min, kept at this temperature for 20 min, then heated further to 450 °C, and aged for about 2 h at this temperature. Micropillar compression tests were then carried out at 450 °C at the selected alloy compositions without any intermediate cooling step. Up to three tests per composition were performed. The total high temperature testing time took approximately 2 more hours and then the sample was cooled to RT. Upon cooling, additional micropillar compression tests were carried out at RT. The microstructure at this point (before testing) is referred throughout this chapter as “heat treated microstructure”. All the tests were performed to a total engineering strain of up to $\sim 15\%$ and at a strain rate of $1 \times 10^{-3} s^{-1}$ in the displacement control mode. The compressive yield strength (CYS) was measured as the 0.5% offset strength. In-situ observation of micropillar compression tests, both at room and at high temperature, was carried out in order to investigate the influence of temperature on the deformation behavior.

Fig. 5.2: Heat-treatment sequence and testing schedule.

The microstructures of the three alloys investigated were examined in the heat treated state and after testing at RT and at 450 °C by TEM. Foils parallel to the $(1\bar{1}0)$ plane were prepared via the trenching-and-lift-out FIB technique from the untested area surrounding the micropillars (as-heat treated state) and from the compressed micropillars, respectively. After deformation, the surfaces of micropillars of all the tested alloys were also carefully examined using the FEI-FEGSEM in order to detect the presence of slip traces, which were subsequently assigned to the corresponding slip system following the method described in [176,230], and more briefly in Chapter 2.

5.3 Results and discussion

5.3.1 Room temperature behavior

Fig. 5.3 illustrates the microstructure of the C_{1-3} alloys in the heat treated stage. The three alloys present a similar microstructure, formed by an extremely high density of very fine α lenticular precipitates. The dark field TEM images shown were recorded by selecting the $a/2[112]_\beta$ spot in the selected area diffraction (SAD) pattern corresponding to a $[1\bar{1}0]_\beta$ zone axis. The spots with the highest intensity in the SAD patterns in Fig. 5.3 correspond to the single crystalline β -Ti matrix while those at $a/2[112]_\beta$ (indicated by an orange ring) correspond to the α phase [17,217,218]. It is apparent from Fig. 5.3 that most laths have a thickness that is smaller than 20 nm. It must be noted that alloy C_1 contains a few thicker precipitates, which are less present in the other two alloys. Irrespective of composition, the α variants are dispersed forming a triangle pyramid structure which, as described in [17,218,219], favors hardening due to a reduction of the dislocation mean free path in the constrained β matrix volume. Fig. 5.4 illustrates, as an example, such a structure in the C_3 alloy, where different variants have been isolated using different colors.

Fig. 5.3: Dark field TEM images of the (a, d) C_1 , (b, e) C_2 , and (c, f) C_3 alloys in the heat treated state. The micrographs were obtained using the $a/2[112]$ spot, highlighted using an orange ring in the corresponding diffraction patterns. The zone axis is $[1\bar{1}0]_\beta$.

Since α laths are effective strengthening agents in β -Ti alloys, major efforts have been placed in controlling their size and distribution [17, 219, 220, 232]. The finest lamellae, which exhibit the highest strengthening potential, have been obtained by invoking ω -assisted heterogeneous nucleation in two ways: either via an intermediate heat treating stage at temperatures slightly below the ω solvus before aging at the bottom of the α phase field [218, 219], or via a single α aging treatment using very slow heating rates (smaller than 20 °C/min) [17, 217]. For example, Mantri et al. [219] utilized the first heat treatment sequence to fabricate a β -21S (Ti-15Mo-3Nb-2.7Al-0.2Si, wt.%) alloy endowed with a record ultimate tensile strength (~ 1800 MPa). In particular, they precipitated ultrafine α lamellae with thicknesses smaller than 20 nm by performing a first heating stage at 350 °C for 150 h and a final annealing at 600 °C for 1 h. Zheng et al. [17, 217] utilized the second route to generate a very high density of ultrafine α laths in a Ti-5553 (Ti-5Al-5Mo-5V-3Cr, wt.%) alloy. More specifically, they carried out an aging treatment at 600 °C for 2 h using a heating rate of 5 °C/min. Both proce-

5.3 Results and discussion

dures allowed for a first precipitation of ω particles, which then acted as effective precursors to α precipitation.

Fig. 5.4: TEM observation of the spatial distribution of selected α variants in the C_3 alloy within interdiffusion region β_2 ; (a) isolation of one single variant; (b) three different variants forming a triangle pyramid network. The zone axis is $[\bar{1}11]_\beta$.

In the current study an intermediate heat treatment at 300 °C for 20 min is followed by a second treatment at 450 °C for about 4 h without any cooling stage in between. The heating rate was 15-20 °C/min. Our results confirm that ultrafine laths can thus be obtained in all three Ti-xAl-yV-zMo alloys investigated. Moreover, the particle densities, irrespective of alloy composition, are dramatically larger than those described earlier. For example, Zheng et al. [17], reported a maximum precipitate density of 35 laths per μm^2 . It is evident in Figs. 5.3.a-c that the precipitate densities achieved during the heat treatment carried out in the present study are at least one order of magnitude higher. Our study thus suggests that the relatively low temperature of the intermediate heat treatment (300 °C) facilitates the nucleation of effective ω precursors, leading to a higher precipitate density. The effect of such a dense distribution of ultrafine precipitates on the mechanical properties and on the slip activity is discussed below.

Fig. 5.5: Representative engineering stress-strain curves corresponding to RT micropillar compression of (a) C_1 , (b) C_2 , and (c) C_3 alloys in the heat treated state.

Fig. 5.5 displays representative engineering stress-strain curves of the heat treated C_{1-3} pillars compressed at RT. The compressive yield strength values amount, respectively, to 1800, 1940, and 1940 MPa. These extremely high values represent increases with respect those measured earlier in the same alloys in the solid solution state (Chapter 3) of 330 %, 45 % , and 40 %, respectively, thus attesting to the tremendous strengthening potential of the precipitate distribution attained. Following yielding, no work hardening is observed. The comparatively lower CYs of the C_1 alloy is consistent with the smaller content of solutes and with the presence of thicker precipitates. The dark field TEM images of the compressed

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micropillars (of 15 % strain), illustrated in Fig. 5.6, evidence the stability of the microstructure after deformation.

Fig. 5.6: Dark field TEM images corresponding to heat treated (a) C_1 , (b) C_2 , and (c) C_3 micropillars compressed at RT up to a strain of 15%. The selected $a/2[112]$ spot is highlighted using an orange ring in the corresponding diffraction patterns. The zone axis is $[1\bar{1}0]_\beta$.

5.3.2 High temperature behavior

Fig. 5.7 illustrates the engineering stress-strain curves corresponding to the aged C_{1-3} pillars compressed at 450 °C. The high temperature behavior of the investigated alloys is characterized, first, by very high CYS values (1530, 1720, and 1715 MPa, respectively), which confirm the effective strengthening ability of the ultrafine α plates at elevated temperatures. Fig. 5.8 evidences that deformation at 450 °C does not lead to significant changes in the microstructure of the C_{1-3} micropillars.

Fig. 5.7: Engineering stress-strain curves corresponding to the aged (a) C_1 , (b) C_2 , and (c) C_3 micropillars compressed at 450 °C.

Additionally, our results evidence the presence of pronounced strain bursts during micropillar compression of the aged samples at 450 °C, irrespective of com-

Fig. 5.8: Dark field TEM images corresponding to aged (a) C_1 , (b) C_2 , and (c) C_3 micropillars compressed at 450 °C. The selected $a/2[112]$ spot is highlighted using an orange ring in the corresponding diffraction patterns. The zone axis is $[1\bar{1}0]_{\beta}$.

position (Fig. 5.7), while a maximum of two bursts is apparent in the room temperature tests (Fig. 5.5). Fig. 5.9 illustrates the variation of the strain rate with time for the three alloys investigated during compression at room temperature in the solid solution state (black line), as well as during compression at room (blue line) and high (red line) temperature after precipitation. The multiple strain

bursts appearing during compression at 450 °C of the three alloys can be clearly identified as clear discontinuities in the strain rate evolution with time.

Fig. 5.9: Strain rate-time curves during micropillar compression of (a) C_1 , (b) C_2 , and (c) C_3 alloys. The compression data of single crystalline pillars at RT, pillars with precipitates at RT, and pillars with precipitates at HT are colored in black, blue, and red, respectively. One inset is inserted in Fig. 5.9.a to show details.

In-situ testing was carried out in order to investigate the origin of the increase in the number of strain bursts with increasing temperature. Figs. 5.10 and 5.11 illustrate the stress-strain curves corresponding to in-situ compression tests performed at room (Fig. 5.10) and high (Fig. 5.11) temperature in the C_2 alloy containing precipitates. Figs. 5.10 and 5.11 also include four SEM micrographs (Figs. 5.10.b-e and 5.11.b-e) illustrating the surface of the micropillars at different

Fig. 5.10: (a) A representative stress-strain curve of C_2 micropillar compressed at RT up to a strain of 15 %; (b-e) SEM images showing micropillar surface at the strain as indicated by the arrows in the curve of Fig. 5.10.a.

strains, which are marked in the curve. It can be clearly seen that the strain bursts coincide with the formation of surface steps along $(110)_\beta$ planes. The increase in the number of bursts with temperature is therefore attributed to the promotion of collective dislocation movements by temperature. Thus, at 450 °C, the energy barriers imposed by the presence of α plates decrease and dislocation avalanches can occur more frequently.

5.3.3 β -Ti alloys with ultrahigh strength

Fig. 5.12 compares the room and high temperature compressive yield strength of the C_{1-3} alloys of the present study with the RT CYS values of more than one hundred bulk commercial β -Ti alloys. The latter range from 800 to 1370 MPa according to the MatWeb database (including 111 alloys) [233]. This range is represented by a shaded band in Fig. 5.12, which also includes CYS values extracted from some recent micropillar studies on CP Ti [234], on the $\alpha + \beta$ Ti 6242 alloy [195], and on the β -Ti alloy Ti-1023 alloy [19]. It can be clearly seen that the alloys investigated here present an outstanding compressive yield strength, which exceeds dramatically the values reported earlier. In particular, the RT and 450 °C CYS of the C_{1-3} alloys are, respectively, 25-30 % and 10-20 % higher than the RT CYS of the strongest commercial β -Ti alloy included in the MatWeb database. The RT CYS values of the C_{1-3} alloys are also larger than the highest tensile yield strength values reported in the same database for commercial alloys (1520 MPa) [233], as well as in the recent literature [219, 220].

5.3.4 Influence of α precipitates on the slip activity

The slip traces present at the surfaces of C_{1-3} deformed micropillars were analyzed in order to investigate the interaction between dislocations and α lamellae. As a reference, Fig. 5.13 displays SEM images of two adjacent sides of solid solution C_{1-3} micropillars compressed at RT up to a total engineering strain of 15 %. The observed macroscopic traces, which are formed by distinct $\{110\}$ slip steps at

Fig. 5.11: (a) A representative stress-strain curve of C_2 micropillar compressed at 450°C up to a strain of 15 %; (b-e) SEM images showing micropillar surface at the strain as indicated by the arrows in the curve of Fig. 5.11.a.

the microscale (see inset on Fig. 5.13.a), are in agreement with those described in Chapter 3. In short, in the solid solution C_1 alloy (Figs. 5.13.a,b) the two observed

Fig. 5.12: Comparison of the room and high temperature CYS of the C_{1-3} alloys investigated here with the CYS of one hundred and eleven commercial β -Ti alloys [233] and of CP-Ti [234], Ti 6242 ($\alpha + \beta$) [195] and Ti 1023 (β) [19] micropillars.

macroscopic traces are parallel to the two planes with the highest Schmid factors (SF) (Table 3.3), (101) and (011) (yellow and red traces, respectively). This is consistent with a dominant activity of these systems at the microscale. However, in the C_2 and C_3 alloys (Figs. 5.13.c,d and 5.13.e,f), containing larger amounts of Mo in solid solution, most of the “macroscopic” traces are not parallel to any $\{110\}$, $\{112\}$ or $\{123\}$ plane [60]. This was attributed earlier to a higher contribution of anomalous slip (i.e., of $\{110\}$ slip systems with low SFs) at the microscale. As demonstrated in Chapter 3, the presence of frequent slip steps on $\{110\}$ slip

Fig. 5.13: Slip trace analysis on two adjacent faces of micropillars of the C_1 (a,b), C_2 (c,d), and C_3 (e,f) alloys tested at RT in the solid solution state. The colored lines indicate the “macroscopic” slip traces.

systems with low SFs leads to a deviation of the macroscopic traces from those parallel to high SF slip planes. The increasing activation of anomalous slip in C_2 and C_3 alloys was justified in Chapter 3, on the basis of the computational work by Rao et al. [116], who demonstrated that the presence of higher solute content promotes structural variations in the dislocation cores, leading to kinking on a multiplicity of planes, and ultimately boosting anomalous slip.

Fig. 5.14: Slip trace analysis on two adjacent surfaces of the micropillars of the C_1 (a,b), C_2 (c,d), and C_3 (e,f) alloys compressed at RT in the heat treated state. The colored lines depict the planes parallel to the “macroscopic” slip traces.

Figs. 5.14 and 5.15 illustrate SEM images of two adjacent sides of aged C_{1-3} micropillars compressed at room temperature (Fig. 5.14) and at 450 °C (Fig. 5.15). It is apparent that, irrespective of alloy composition, and irrespective of temperature, the macroscopic slip traces are always parallel to the slip planes with the highest Schmid factors, namely (101) and (011), which are indicated using yellow and red solid lines, respectively. Comparison with the slip trace

5.3 Results and discussion

patterns observed in the corresponding solid solution alloys (Fig. 5.13) leads to the conclusion that the influence of α plates on the microscopic slip activity of β -Ti alloys is highly dependent on composition. Indeed, while the slip trace pattern in the C_1 alloy is not altered by precipitation, in the C_2 and C_3 alloys the incidence of anomalous slip at the microscale appears to decrease in the presence of α lamellae, leading to a shift of the slip traces, which become parallel to the planes with high SF in the precipitated samples. Our results thus evidence that, within the temperature range investigated, α plates act as selective barriers for slip, “filtering out” low SF (anomalous) slip.

Earlier studies [64, 195, 226] have reported that slip transfer across interphase α/β boundaries is predominantly determined by the degree of alignment of incoming and outgoing slip systems, and that global SFs influence less critically the mentioned transfer. These works have been performed in near- α or in α/β alloys, and slip transfer has been analyzed in microstructures containing only one α variant. However, in β -Ti alloys, like the ones investigated in the present work, multiple α variants are present. This might have an effect in the slip transfer, which has to date not been investigated. Our results, indeed, point out that the global SF has a key influence in slip transfer in our Ti-xAl-yMo-zV alloys with high Mo content (C_2 and C_3), in such a way that the activity of low SF slip systems is suppressed (or severely limited) by α precipitation.

In the following, we will analyze whether the presence of multiple variants makes the influence of the geometrical alignment of incoming and outgoing planes less critical. Table 5.1 illustrates the geometric compatibility factor, defined as $m' = \cos\kappa \cdot \cos\Psi$ (where κ is the angle between the two slip directions and Ψ is the angle between the normal directions of the two slip planes) [223, 224], for slip transfer between the β phase and the 12 α variants. The following $\{110\}_\beta$ systems are considered: two with high SF, that remain active after precipitation ($(011)[\bar{1}\bar{1}1]$ and $(101)[\bar{1}\bar{1}1]$, SF=0.445), and two with low SF that are suppressed after precipitation ($(110)[\bar{1}\bar{1}1]$ and $(110)[\bar{1}\bar{1}1]$, SF=0.225). In the α phase, only prismatic slip (P_{1-3}) is considered as there is general agreement that prismatic systems have the lowest critical resolved shear stress values in the hcp α -Ti structure [235] (P_1 :

Fig. 5.15: Slip trace analysis on the micropillars of C_1 (a,b), C_2 (c,d), and C_3 (e,f) alloys compressed at 450°C after aging. The colored lines depict the planes parallel to the “macroscopic” slip traces.

$(01\bar{1}0)[2\bar{1}\bar{1}0]_\alpha$, P_2 : $(10\bar{1}0)[\bar{1}2\bar{1}0]_\alpha$, P_3 : $(1\bar{1}00)[\bar{1}\bar{1}20]_\alpha$). We will assume that, given the high density of α plates that are present in the alloys investigated, an individual dislocation will have equal probability of finding any of the 12 variants. Different colors have been used to highlight the low (gray), medium (yellow), and high (orange) m' values in Table 5.1. The distribution of m' values is identical for all $\{110\}_\beta$ systems considered, irrespective of the corresponding SF. In particular,

5.3 Results and discussion

for each $\{110\}_\beta$ incoming system, two variants have 0 m' values for all P_i outgoing systems, four variants have m' values smaller than 0.4 for all P_i outgoing systems, two variants have m' values of about 0.6 for one outgoing system, and, finally, four variants have m' values higher than 0.8 for one outgoing system. Therefore, when only geometrical criteria are considered, and when a high density of α laths are present, $\{110\}_\beta$ slip systems with both high and low SFs encounter, on average, the same resistance to slip transfer, making the influence of geometrical alignment of incoming and outgoing systems less critical.

It seems therefore reasonable that in β -Ti alloys containing a high density of α precipitates, such as the ones investigated here, the global SF plays an important role in slip transfer. The observation of the suppression of anomalous (low SF) slip with α precipitation in the Ti-xAl-yMo-zV alloys with high Mo content (C_2 and C_3) may be rationalized on the basis of this increasing influence of SF on slip transfer.

Table 5.1: Geometrical compatibility factor (m') for slip transfer between the β phase and the 12 α variants. The following $\{110\}_\beta$ systems are considered: two with high SF, that remain active after precipitation ($(011)[1\bar{1}1]$ and $(101)[\bar{1}11]$), and two with low SF that are suppressed after precipitation ($(110)[1\bar{1}1]$ and $(110)[\bar{1}11]$). In the α phase, only prismatic slip is considered (P_{1-3}) (P_1 : $(01\bar{1}0)[2\bar{1}\bar{1}0]_\alpha$, P_2 : $(10\bar{1}0)[\bar{1}2\bar{1}0]_\alpha$, P_3 : $(1\bar{1}00)[\bar{1}\bar{1}20]_\alpha$).

β	$(011)[1\bar{1}1]$ SF=0.445			$(101)[\bar{1}11]$ SF=0.445		
α	P_1	P_2	P_3	P_1	P_2	P_3
α_1	-0.2165	0.8660	-0.165	0.8371	-0.0962	0.3657
α_2	-0.3657	0.0962	-0.8371	0.2165	-0.8660	0.2165
α_3	0	0	0	0.3235	0.0962	0.2057
α_4	0	0	0	-0.1046	-0.2887	0.2489
α_5	-0.2057	-0.0962	-0.3235	0	0	0
α_6	-0.2489	0.2887	0.1046	0	0	0
α_7	0.1046	0.2887	-0.2489	0.1046	0.2887	-0.2489
α_8	-0.3235	-0.0962	-0.2057	-0.3235	-0.0962	-0.2057
α_9	0.5725	-0.1925	0.1011	-0.2165	0.8660	-0.2165
α_{10}	0.1011	-0.1925	0.5725	-0.8371	0.0962	-0.3657
α_{11}	0.3657	-0.0962	0.8371	-0.5725	0.1925	-0.1011
α_{12}	0.3657	-0.0962	0.8371	-0.5725	0.1925	-0.1011
β	$(110)[1\bar{1}1]$ SF=0.225			$(110)[\bar{1}11]$ SF=0.225		
α	P_1	P_2	P_3	P_1	P_2	P_3
α_1	0	0	0	0	0	0
α_2	0	0	0	0	0	0
α_3	0.2165	-0.8660	0.2165	-0.2489	0.2887	0.1046
α_4	-0.8371	-0.0962	0.3657	-0.2057	-0.0962	-0.3235
α_5	-0.1046	-0.2887	0.2489	-0.2165	0.8660	-0.2165
α_6	0.3235	0.0962	0.2057	-0.3657	0.0962	-0.8371
α_7	-0.1011	0.1925	-0.5725	-0.1011	0.1925	-0.5725
α_8	-0.5725	0.1925	-0.1011	-0.5725	0.1925	-0.1011
α_9	0.2489	-0.2887	-0.1046	-0.2165	0.8660	-0.2165
α_{10}	0.2057	0.0962	0.3235	-0.8371	0.0962	-0.3657
α_{11}	0.3657	-0.0962	0.8371	-0.3235	-0.0962	-0.2057
α_{12}	0.3657	-0.0962	0.8371	-0.3235	-0.0962	-0.2057

5.4 Summary

In this work, the influence of α plates on the mechanical behavior and slip of Ti-xAl-yMo-zV alloys have been investigated at both RT and 450 °C. The following conclusions can be drawn from the present study:

1. A homogeneous and very dense distribution of nanoscale α plates are achieved in the Ti-xAl-yMo-zV system via a heat treatment at low temperature (300 °C), followed by a second α -aging treatment. It is concluded that the first low temperature heat treatment is very effective to promote a high density of α -precursors.

2. The investigated Ti-xAl-yMo-zV alloys exhibit an exceptional compressive yield strength at RT and elevated temperature, which is attributed to the high density of nanoscale α plates. The CYS attained at RT and 450 °C are larger than those corresponding to all commercial alloys included in the MatWeb database and to those reported in the literature for other alloys tested by micropillar compression.

3. Within the composition ranges investigated, the influence of different amounts of alloying additions on the CYS was negligible in comparison with the effect of α precipitation.

4. The anomalous slip activity in the alloys with high Mo content is reduced by the presence of nanoscale α plates irrespective of deformation temperature. This is attributed to the presence of a high density of α variants, which contribute to homogenizing the geometrical factors affecting slip transfer for all $\{110\}_\beta$ slip systems. In this instance, the global SF plays a critical role in slip transfer and therefore anomalous systems, which have low SFs, are filtered out by α laths.

CHAPTER 6

Conclusions

This thesis constitutes an investigation on the influences of solute atoms and α precipitates on the micromechanical behavior and slip activity of selected quaternary β titanium alloys under different deformation conditions. With this aim, a high throughput approach including the efficient fabrication of a large number of compositions using a diffusion multiple, and the local characterization of composition, microstructure, and micromechanical behavior has been put in place. The main conclusions drawn from this work may be summarized as follows:

1. Effects of solutes on the strengthening and on the slip activity of selected Ti-xAl-yMo-zCr and Ti-xAl-yMo-zV alloys in solid solution.

1.1. The efficiency of β -stabilizers to strengthen the quaternary single crystalline β -Ti alloys is found to vary for different alloy compositions. Cr appears to be a more effective strengthener than Mo in quaternary Ti-xAl-yMo-zCr alloy system. Meanwhile, Mo is manifested to be a very potent strengthener for Ti-xAl-yMo-zV system.

1.2. The plastic strain of the investigated single crystalline β -Ti alloys is accommodated by multiple slip in $\{110\}\langle 1\bar{1}1 \rangle$ systems at room temperature, irrespective of orientation and composition. The specific combination of elemental

$\{110\}\langle\bar{1}\bar{1}1\rangle$ slip systems that act cooperatively to accommodate strain is , however, attested to be dependent on orientation and on composition.

1.3. Increasing amounts of Mo in Ti-Al-Mo-V alloys favor the activation of an increased number of elemental slip systems having relatively low Schmid factors (anomalous slip). The incidence of anomalous slip, as observed commonly in pure bcc metals, depends on the crystal orientation and on the alloy composition.

2. Effects of solutes on the rate sensitivity of selected Ti-xAl-yMo-zCr and Ti-xAl-yMo-zV alloys in solid solution.

2.1. The strain rate sensitivity remains unchanged throughout the whole range of compositions analyzed within the Ti-xAl-yMo-zCr systems since these alloys have similar strength levels and, in them, the same elemental $\{110\}\langle\bar{1}\bar{1}1\rangle$ systems become active.

2.2. In the Ti-xAl-yMo-zV alloy with low Mo content, a transition from single to multiple slip of screw dislocations with strain is accompanied by a significant decrease in the strain rate sensitivity value due to the increasing strength levels originated by work hardening. The rise in the flow stress also contributes to the reduced activation volume as it leads to a decrease in the critical span between the two kinks forming kink pairs in screw dislocations.

2.3. In the Ti-xAl-yMo-zV alloy system, an increase in the Mo content leads to a further decrease of strain rate sensitivity under multiple slip deformation conditions, as it promotes the formation of dipoles.

3. Influence of nanoscale α plates on the mechanical behavior and on the slip activity of quaternary Ti-xAl-yMo-zV alloys.

3.1. A homogeneous and very dense distribution of nanoscale α plates are developed in the Ti-xAl-yMo-zV system via a heat treatment at low temperature (300 °C), followed by a second α -aging treatment. It is concluded that the first low temperature heat treatment is very effective to promote a high density of α -precursors.

3.2. The investigated Ti-xAl-yMo-zV alloys exhibit exceptional compressive yield strength at RT and elevated temperature, due to the high density of nanoscale α plates. The CYS attained at RT and at 450 °C are larger than those corresponding to all commercial alloys included in the Matweb database and to those reported in the literature for other alloys tested by micropillar compression.

3.3. Within the composition ranges investigated, the influence of different amount of alloying additions on the CYS was negligible in comparison with the effect of α precipitation.

3.4. The anomalous slip activity in the alloys with high Mo content is reduced by the presence of nanoscale α plates irrespective of deformation temperature. This is attributed to the presence of a high density of α variants, which contribute to homogenizing the geometrical factors affecting slip transfer for all $\{110\}_\beta$ slip systems. In this instance, the global Schmid factor plays a critical role in slip transfer and therefore anomalous systems, which have low Schmid factors, are fittered out by α laths.

The diffusion multiple methodology is evidenced to be an effective high throughput approach to investigate the individual and combined effects of solutes and precipitates on the mechanical properties and microplasticity of β -Ti alloys. This method constitute a key tool for effective alloy design.

CHAPTER 7

Future work

The current research has constituted a step forward in the understanding of β -Ti alloys and, simultaneously, has opened new avenues for further work that may be pursued in the near future. They are the following:

1. Study of the influence of the collective effects of α variants on the strengthening and slip transfer mechanisms of β -Ti alloys. Analysis of the effect of the presence of different numbers of α variants, of variants with different degrees of alignment with respect to the bcc matrix, and of variants with different morphologies, on the transmission of slip across α/β interphase boundaries.
2. Evaluation of the effects of solutes and precipitates on the fracture toughness of β -Ti alloys. The high throughput methodology utilized in the present study could be used to measure this critical mechanical property. In particular a microcantilever bending technique could be utilized for micromechanical property evaluation.
3. Extension of the high throughput methodology used in the current work to the optimization of other β -Ti alloy systems for different applications. For example, biocompatible β -Ti alloys with optimum values of the elastic modulus could be a potential candidate alloy system, among others.

4. Design of β -Ti alloys with ultrahigh strength for additive manufacturing. The knowledge gained regarding the relationship between the composition and heat treatment schedule and the mechanical strength of the alloys investigated could be applied to tailor alloy compositions for additive manufacturing.

APPENDIX A

List of publications

1) Papers in peer-reviewed journals

The work in this thesis has been already published or under preparation in the following papers:

1. **C.Y. Wang**, L. Yang, Y. Cui, M. T. Pérez-Prado. High throughput analysis of solute effects on the mechanical behavior and slip activity of beta titanium alloys. **Materials & Design**, 2018(137):371-383; DOI: 10.1016/j.matdes.2017.10.029. (Chapter 3).
2. **C.Y. Wang**, N. Li, Y. Cui, M. T. Pérez-Prado. Effect of solutes on the rate sensitivity in Ti-xAl-yMo-zV and Ti-xAl-yMo-zCr β -Ti alloys. **Scripta Materialia**, 2018(149):129-133; DOI: 10.1016/j.scriptamat.2018.02.028. (Chapter 4).
3. S. Mao*, **C.Y. Wang***, N. Li, J. Wang, Y. Chen, G. Xu, Y. Guo, Y. Cui. Kinetic diffusion multiple: A high-throughput approach to screening the composition-microstructure-micromechanical properties relationships. **Calphad**, 2018(61):219-226; DOI: 10.1016/j.calphad.2018.04.001. (*equivalent first author) (Methodology).

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4. **C.Y. Wang**, M. A. Monclús, Y. Cui, M.T. Pérez-Prado. Microplasticity of β titanium alloys with ultrahigh strength. (in preparation).

2) Conference contribution

This work has been reported at several international conferences.

1. M.T. Pérez-Prado, **C.Y. Wang**, Y. Cui. Exploiting diffusion multiples for efficient alloy design. DARE Annual Symposium 2016. September 1st, 2016, Sheffield, UK. (Invited talk)
2. **C.Y. Wang**, Y. Cui, M.T. Pérez-Prado. High throughput investigation of solute effects in beta Ti alloys. EUROMAT 2017. September 5th, 2017, Tesalónica, Greece. (Invited talk)
3. **C.Y. Wang**, Y. Cui, M.T. Pérez-Prado. Effect of solutes on the plastic deformation of β -Ti alloys: a high throughput investigation. SES 2018 Society of Engineering Science. October 11th, 2018, Madrid, Spain.

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