Scripta Materialia 158 (2019) 62–65

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular article

A semi-empirical approach to the prediction of deformation behaviors of β-Ti alloys

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ARTICLE INFO

Article history:
Received 2 July 2018
Received in revised form 19 August 2018
Accepted 19 August 2018
Available online xxxx

Keywords:
Titanium alloys
Plastic deformation
Twinning
Stress-induced martensite

ABSTRACT

A semi-empirical approach based on the compositional average electron-to-atom ratio ($\overline{e/a}$) and atomic radius difference ($\overline{\Delta r}$) was proposed to refine the "d-electron method". The $\overline{e/a}-\overline{\Delta r}$ diagram shows that Twinning/Stress-Induced Martensite (SIM) activates when $\overline{\Delta r} > -2.5$, and a low $\overline{e/a}$ or absolute value of $\overline{\Delta r}$ favors Twinning/SIM by reducing the resistance of lattice shear. In addition to the phase stability, it suggests that the valence electron number and atomic radius of alloying element also determine the deformation mechanism in body-centered cubic Ti alloys. This alloy design method was verified by the tensile results of Ti-4Mo-4Co and Ti-6Mo-4Zr (at.%) alloys.

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Body-centered cubic (β) Ti alloys have attracted increased attention due to their good hardenability, low elastic moduli, and shape memory properties [1,2]. β-Ti alloys are defined as those Ti alloys with enough concentration of β stabilizing elements to retain 100% of the β phase at room temperature (RT) upon quenching from temperatures above β transus [3]. The mechanical properties of β-Ti alloys in a solution-treated condition have been reported to depend significantly on the deformation modes, such as stress-induced martensite (SIM), mechanical twinning, and dislocation slip [4]. The occurrence of martensitic transformation or mechanical twinning results in low yield strength and large uniform elongation through significant work hardening, while the dislocation slip induces high yield strength and poor uniform elongation [5]. The dominant deformation mechanism of β-Ti alloys evolves from martensitic transformation to mechanical twinning then to dislocation glide as the β phase stability increases [6]. Thus, altering the β phase stability by adding various β-stabilizing elements is one of the most common methods to design β-Ti alloys. The β phase stability of Ti alloys is commonly evaluated by the molybdenum equivalent (Mo_{eq}), an equivalent concentration that combines the effects of the various β-stabilizing elements [3]. However, the Mo_{eq} is empirically based on binary systems and is problematic in multi-component systems due to the complex interactions among multiple elements [7].

A "d-electron method" has been proposed to reveal the relationship between plastic deformation behavior and β phase stability based on two parameters, *Bo* and *Md* [8]. *Bo*, the bond order, which measures the covalent bond strength between Ti and a particular alloying element, and *Md* being related to the metal d-orbital energy level, can be calculated based on the discrete-variational (DV)-Xα cluster method [9]. The compositional averages of *Bo* and *Md* are denoted as $\overline{Bo}$ and $\overline{Md}$, respectively. According to the "d-electron method", a $\overline{Bo}-\overline{Md}$ diagram was drawn to distinguish different phase zones [10], as shown in Fig. 1. In a sequence from the lower right to the upper left, the diagram is divided into α, α + β, and β phase regions corresponding to the increase of β phase stability. A continuous Twinning/SIM region shows up beside the boundary of β and α + β phases when the $\overline{Bo}$ value is higher than 2.77, implying that deformation by Twinning/SIM requires a low β phase stability. Many β-Ti alloys with compositions located at the Twinning/SIM region were designed by the "d-electron method" and confirmed the formation of SIM and/or twins during deformation [11–13]. Nevertheless, there were also some reported mismatches between the locations in the $\overline{Bo}-\overline{Md}$ diagram and the discovered deformation mechanisms. For example, the Ti-10V-3Fe-3Al (wt%) alloy lies within the twinning region, but in reality shows stress-induced α″ martensite in the microstructure after room temperature deformation [4]. Talling et al. [14] substituted Nb with V to produce a Ti alloy with the exact same $\overline{Bo}$ and $\overline{Md}$ of the original composition, however, the V-based alloy showed a contrasting deformation behavior comparing to the base one. Therefore, problems still exist in the use of the "d-electron method" and the $\overline{Bo}-\overline{Md}$ diagram. Whether all the β-Ti alloys with a low β phase stability exhibit Twinning/SIM-dominant deformation behavior remains

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https://doi.org/10.1016/j.scriptamat.2018.08.035
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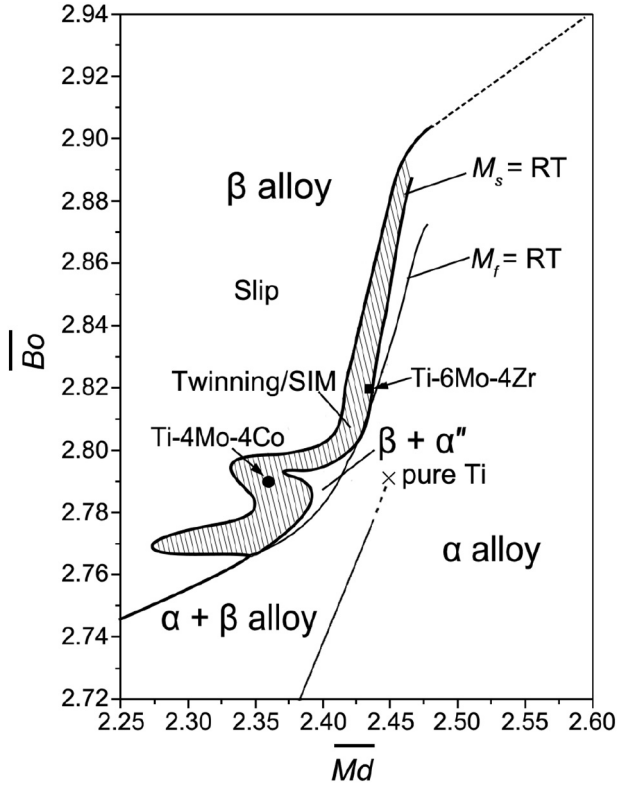

Fig. 1. The $\overline{Bo}-\overline{Md}$ diagram showing that both Ti-4Mo-4Co and Ti-6Mo-4Zr alloys lie within the Twinning/SIM region.

unclear and needs to be investigated by more experimental and theoretical work.

In the present work, two β-type Ti-Mo-based alloys, Ti-4Mo-4Co and Ti-6Mo-4Zr (at.%) with compositions located within the Twinning/SIM region ($\overline{Bo}$ = 2.79, $\overline{Md}$ = 2.36 for Ti-4Mo-4Co, and $\overline{Bo}$ = 2.82, $\overline{Md}$ = 2.44 for Ti-6Mo-4Zr) were designed in order to achieve significant work hardening and superior ductility. However, the experimental results indicate the failure of the existing "d-electron method". Thus, a new approach based on the average electron-to-atom ratio ($\overline{e/a}$) and atomic radius difference ($\overline{\Delta r}$) is proposed in this paper as a supplement to the "d-electron method".

Ingots corresponding to the designed compositions were fabricated from 99.99% pure Ti, Mo, Co and Zr by levitation melting under an Ar atmosphere in a water-cooled Cu crucible. Subsequently, the ingots were cold-rolled to a thickness reduction of 70%. The cold-rolled sheets were sealed in quartz capsules evacuated to a pressure of ~1×10^{-3} Pa and solution treated at 1273 K for 30 min followed by water quenching. The phase constitutions were determined by a D/MAX-3C X-ray diffractometer (XRD) using Cu Kα$_1$ radiation (λ = 1.541 Å). Tensile specimens with gauge dimensions of 3 × 1 × 14 mm were cut by electrical-discharge machining. Room temperature tensile tests were performed on a MTS C40 electronic universal testing machine with an Epsilon 3442 electronic extensometer at a cross-head speed of 2×10^{-3} mm s^{-1}.

The engineering stress-strain curves of the Ti-4Mo-4Co and Ti-6Mo-4Zr alloys tested at room temperature are shown in Fig. 2. As this figure shows, the two alloys exhibit distinctly different tensile properties and deformation behaviors. The Ti-6Mo-4Zr alloy displays a yield strength of 475 MPa, followed by extensive work hardening, resulting in a large tensile elongation of 28%. In contrast, the Ti-4Mo-4Co alloy shows a high yield strength of 980 MPa and a low ductility of 8% elongation, which are the characteristics of dislocation slip. Fig. 3 displays the XRD diffractograms of the Ti-4Mo-4Co and Ti-6Mo-4Zr alloys before and

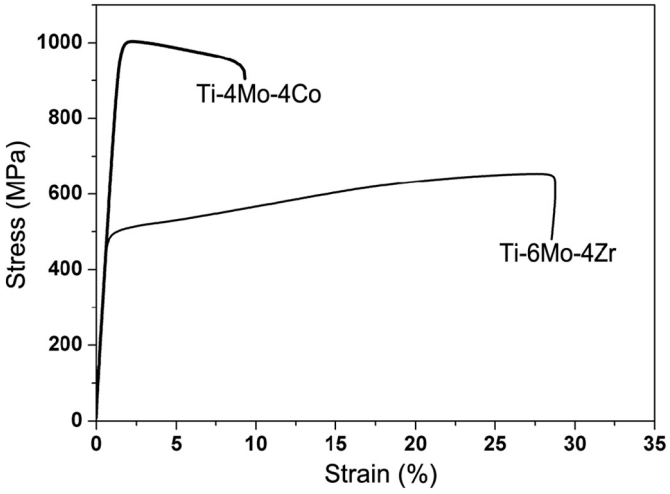

Fig. 2. Engineering tensile stress-strain curves of Ti-4Mo-4Co and Ti-6Mo-4Zr alloys.

after tensile deformation. Both alloys display single-phase β phase before tension. From the strongest (110) β peaks, the lattice parameters of β phases can be calculated to be a = 3.236 Å for the Ti-4Mo-4Co alloy, and a = 3.265 Å for the Ti-6Mo-4Zr alloy. No significant difference is observed in the XRD diffractogram of Ti-4Mo-4Co alloy after tensile testing. However, the XRD diffractogram of Ti-6Mo-4Zr alloy after tension shows the appearance of orthorhombic α″ martensite, which proves the formation of stress-induced α″ martensite during tension.

The tensile and XRD results reveal that the two alloys deform by different mechanisms, although both their compositions lie within the Twinning/SIM region of the $\overline{Bo}-\overline{Md}$ diagram. The $\overline{Bo}-\overline{Md}$ diagram fails to predict the deformation mechanism of Ti-4Mo-4Co alloy, which actually shows a slip-dominant behavior. The Mo_{eq} of Ti-4Mo-4Co alloy is about 14, which is close to that of Ti-6Mo-4Zr alloy (Mo_{eq} ≈ 11) considering the enhanced β-stabilizing effect of Mo by the addition of Zr [15]. Both alloys belong to the metastable β-Ti alloys (Mo_{eq} ≈ 8–24), suggesting that the different deformation behaviors may result from other influencing factors.

Martensitic transformations are diffusionless phase transformations characterized by a homogeneous shear of the parent lattice [16]. SIM transformation could be regarded as a special kind of martensitic reaction in which the driving force is an externally applied stress.

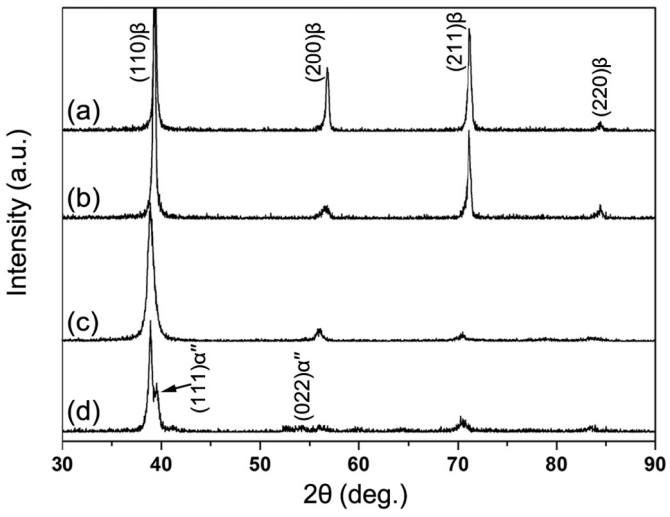

Fig. 3. XRD diffractograms of Ti-4Mo-4Co alloy (a) before and (b) after tension, and Ti-6Mo-4Zr alloy (c) before and (d) after tension.

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