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Phase formation, microstructure and deformation behavior of heavily alloyed TiNb- and TiV-based titanium alloys

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ABSTRACT

The effect of chemical composition on microstructure and mechanical properties of heavily alloyed beta-titanium Ti-Nb(V)-Cu-Co-Al alloys was studied. The alloys were fabricated by casting into a water-cooled copper crucible employing relatively high cooling rates. The microstructure of these alloys consists of primary micrometer-sized bcc-structured (bcc – body centered cubic) dendrites surrounded by a minor amount of intermetallic phases. The morphology and volume fraction of the intermetallic phases are strongly affected by the alloys' chemical composition. Particularly, the solubility of Cu and Co in the bcc dendrites of Ti-V-Cu-Co-Al is lower compared to that of Ti-Nb-Cu-Co-Al leading to a higher volume fraction of the intermetallic phase in the latter alloy. The high mechanical strength of the Ti-Nb(V)-Cu-Co-Al alloys (yield strength up to 1430 MPa) is mainly attributed to their multiphase nature and solid solution hardening of the supersaturated bcc-structured dendrites. Moreover, the large compressive plastic deformability supported by pronounced strain-hardening reaches several tens of percent. The alloys exhibit a significant strength asymmetry between compressive and tensile loadings, namely, they are weak and brittle under tensile loading. The tensile brittleness is associated with the lattice distortion in the bcc-structured dendrites as well as crack initiation at the interdendritic precipitates.

1. Introduction

Common structural materials are at their limits in many applications and there is a demand on new high-performance materials. The performance of materials can be improved by designing composite materials exhibiting better properties than a single constituent does [1–5] or using novel fabrication methods for common materials [6–10] or tailoring non-equilibrium microstructures [11–15] or designing complex microstructural architectures [16–18]. Among others, the heavily alloyed bcc-structured titanium alloys demonstrate an outstanding strength characteristics similar to those found for metallic glass matrix composites [19,20]. These bcc-structured titanium alloys typically exhibit fracture stresses higher than 2 GPa and reach plastic strains larger than 15% under room temperature compression [21–23]. These multicomponent alloys consist of five and more constituent elements. The concentration of each component is typically not less than 5 at%. The as-cast microstructure of such alloys exhibits a dendritic morphology. The dendrites are surrounded by eutectic structures or intermetallics [19,24,25]. The high strength is mainly due to solid solution strengthening of the bcc-structured dendrites [26] and fine interdendritic precipitates or eutectic structures [27]. Above a critical volume fraction of the interdendritic precipitates, these alloys become brittle under tensile loading while being highly deformable under compression [27,28]. Therefore, volume fraction optimization for the interdendritic precipitates is required to reach a combination of high strength and tensile ductility in these alloys [19,29,30].

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In this work, we have developed two heavily alloyed bcc-structured titanium alloys: $Ti_{66}Nb_{13}Cu_8Co_{6.8}Al_{6.2}$ and $Ti_{66}V_{13}Cu_8Co_{6.8}Al_{6.2}$ (at%). The alloys were designed using the principles of microstructure adjustment to reach high yield strength [29] and based on recently reported high-strength Ti-Nb-Cu-Co-Al titanium alloys exhibiting large tensile ductility [19,30]. The alloying elements in these alloys can be divided into two types: elements that preferentially dissolve in the dendrites – dendritic elements, and elements that are mostly present in the interdendritic regions – interdendritic elements. Upon solidification, the primary dendrites mainly contain elements such as Nb, V, and Al, while such elements as Ni, Cu, and Co partially segregate to the interdendritic region to form intermetallic phases [19,25,27]. We have substituted Nb by V to tune the chemical composition of the primary dendrites and to study the effect of the resulting microstructure on the mechanical behavior of these alloys.

2. Materials and methods

The alloys ingots were fabricated from pure elements (99.9 wt%) by arc-melting under argon atmosphere. At first, Ti and Nb as well as Ti and V were alloyed to produce intermediate alloys and then the remaining pure metals were added and melted together. The ingots were remelted at least three times to obtain chemical homogeneity. As next, the master alloys were cast into a water-cooled Cu crucible (12 mm in diameter) to obtain 100 mm rod samples that were used for the subsequent investigation.

X-ray diffractometry (XRD) (STOE STADIP) with Mo-$K_{\alpha 1}$ radiation together with the X'Pert High Score Plus software was used for structural investigation of samples. XRD patterns were analyzed by a combination of Rietveld (for bcc phases) and LeBail (for TiCo-type intermetallics) refinements using FullProf. Peak profiles were modeled using the asymmetric pseudo-Voigt function implementation proposed by Finger, Cox and Jephcoat [31] superimposed on a stepwise linear background. Bcc phases were set up as random solid solutions with site occupancies fixed based on the EDX results. For all phases, the isotropic (coherent scattering domain) size and isotropic (long range) lattice strain were obtained from Bragg reflection profile broadening. To this end, the observed profile breadths were corrected for instrumental broadening using a Si-powder standard. To accurately model the Bragg intensities of the bcc phases at high diffraction angles, it was necessary to introduce the isotropic Debye-Waller factor into the refinements [32]:

$$T = \exp\left[-8U_{iso}\left(\frac{\pi \sin\theta}{\lambda}\right)^2\right] \quad (1)$$

θ is the semi-angle between incident and diffracted beam, λ the X-ray wavelength and U_{iso} is the overall isotropic atomic displacement parameter representing the mean-square displacement. Both thermal atomic motion, which is always present, and static displacive disorder contribute to U_{iso} [32]. This disorder relocates all the atoms away from their mean positions and produces diffuse scattering similar to that of thermal motion, with a corresponding reduction in the integrated intensity of Bragg reflections [33,34].

The bcc reflections in the experiment were tested for preferred orientation during the Rietveld refinements and showed only insignificant orientation effects for all patterns. Taking this into account, the isotropic displacement parameter (1) is needed to accurately model the intensity attenuation at large angles and to reach a good fit of simulated and experimental patterns.

The microstructure before and after tensile deformation was investigated by scanning electron microscopy (SEM) (Zeiss Leo Gemini 1530) coupled with energy-dispersive X-ray analysis (EDX) (Bruker Xflash 4010). For SEM observation, samples were mounted with conductive Cu-based resin and ground with silicon carbide polishing paper in the sequence 600, 1200, 2500 and 4000 grit with a Struers Rotopol

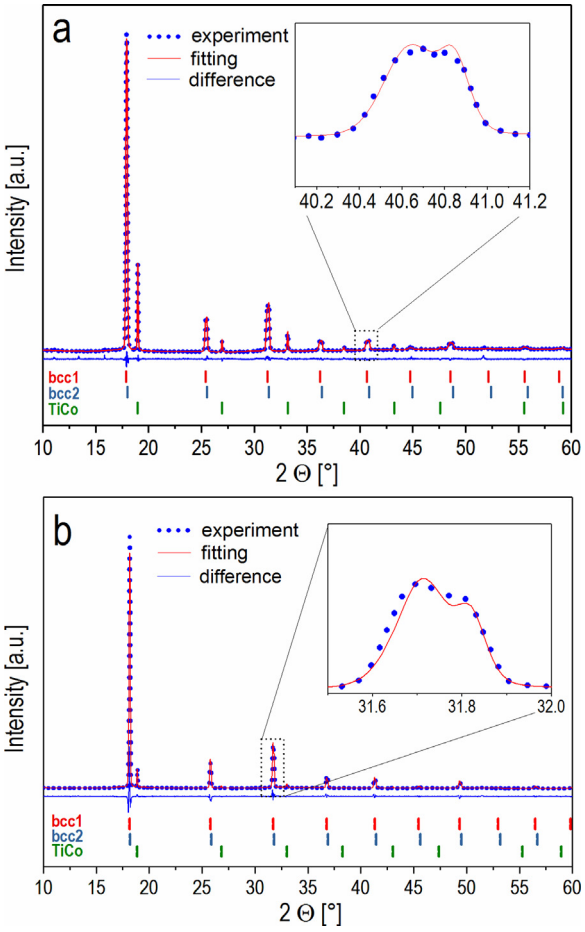

Fig. 1. Calculated and measured X-ray diffraction patterns of (a) $Ti_{66}Nb_{13}Cu_8Co_{6.8}Al_{6.2}$ and (b) $Ti_{66}V_{13}Cu_8Co_{6.8}Al_{6.2}$ alloys.

machine. Finally, specimens were polished around 5 min with the solution of silica colloidal and 10 vol% of H_2O_2 (OP-S, particle size 0.04 μm) and cleaned in the ultrasound bath for 5 min. The ImageJ image software was used to analyze size and volume fraction of phases. Flat tensile test samples with 8 mm gauge length and 1 mm thickness as well as cylindrical compression samples were probed at room temperature using an Instron 8562 testing machine at an initial strain rate of 10^{-4} s^{-1}. The strain was measured by a laser extensometer (Fiedler Optoelektronik).

3. Results and discussion

Fig. 1 presents the experimental and refined XRD patterns of the $Ti_{66}Nb_{13}Cu_8Co_{6.8}Al_{6.2}$ and $Ti_{66}V_{13}Cu_8Co_{6.8}Al_{6.2}$ alloys. In both alloys 3 phases are present, namely two bcc-structured (later bcc, space group: *Im-3 m*) Ti phases of different unit cell size and a simple cubic TiCo-type intermetallic phase (later TiCo, space group: *Pm-3m*) (Fig. 1). Formation of the TiCo intermetallic phase in Ti-Nb-Co-Cu-Al alloys was previously reported in [19,30].

The differing bcc unit cell sizes (relative difference of lattice parameters < 0.6%) give rise to discernible individual profile maxima despite their strong overlap (see the magnified insets in Fig. 1). In addition, all phases exhibit size and/or strain broadening, the broadening being stronger in the Nb containing variety than in the V containing one. This implies smaller grains (coherent scattering domains) and larger strains in the Nb alloy. Table 1 compares the microstructural parameters obtained by refining the XRD patterns for both alloys. While size broadening is absent in the V alloy (indicating grains > ca. 500 nm), the bcc phases in the Nb alloy have a mean grain size of