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Significant tensile ductility and toughness in an ultrafine-structured $Ti_{68.8}Nb_{13.6}Co_6Cu_{5.1}Al_{6.5}$ bi-modal alloy

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ABSTRACT

An important and effective strategy for ductility improvement of ultrafine-structured metallic materials is the development of multi-scale grain structures. Here we report about a new bi-modal $Ti_{68.8}Nb_{13.6}Co_6Cu_{5.1}Al_{6.5}$ alloy with significantly improved tensile ductility and high static toughness. The alloy consists of an ultrafine-structured eutectic (B2 TiCo+bcc β-Ti) and coarse bcc β-Ti dendrites. The microstructure alteration upon tensile loading was studied *in-situ* by means of scanning electron microscopy. It is found that the ultrafine-structured eutectic exhibits a "slip"-like deformation behavior to accommodate the intensive plastic deformation of the dendrites. A detailed study of the microstructure by means of transmission electron microscopy revealed that this is due to a cube-on-cube orientation relationship of the eutectic (B2 TiCo+bcc β-Ti) and dendritic (β-Ti) phases.

1. Introduction

In the case of metallic materials, the grain size is one of the most significant parameters influencing the mechanical properties. This is due to the increasing effect of grain boundaries on the mechanical behavior by lowering the grain size into the nanometer regime [1,2]. As a result, the materials with nano-grained (NG) and ultrafine-grained structure (UFG) exhibit attractive mechanical properties for technological applications [3,4]. However, the high strength of NG and UFG alloys (according to the Hall–Petch relationship) is typically accompanied by low ductility. The latter is attributed to a premature onset of plastic instabilities caused by a low strain-hardening capability. To overcome this obstacle, by hindering the widespread application of NG and UFG materials, the important strategy of creating multi-scale materials was developed [3,5–7].

The introduction of coarse grains, providing the adequate hardening, into NG or UFG metals can improve plasticity of the aggregate while keeping high strength [5]. There are several techniques to produce a multi-scale grain structure: annealing of NG or UFG metals [5,8,9], consolidation of multi-scale powder particles [6,7,10] and casting of alloys having a certain chemical composition [11,12]. The experimental results on former two methods are summarized and discussed elsewhere [3]. It is shown that some multi-scale metals obtained by these techniques exhibit a positive deviation from the rule-of-mixtures relationship or, in other words, an extra gain of toughness when compared with their uni-mode counterparts [3].

The casting technique contains a lower number of processing steps than the previous two and, therefore, is attractive as an energy-saving method. Novel Ti-based alloys (Ti-based DNUS composites (DNUS – dendrites+nano-/ultrafine structures)) having a bi-modal grain size distribution in the as-cast state were firstly reported by He [11]. The strong interest in these alloys is due to their high static toughness. The high static toughness is related to a multi-phase and multi-scale microstructure, which consists of tough micrometer sized β-Ti dendrites surrounded by strong NG or UFG intermetallics. This microstructure forms because of local microsegregation during solidification [13] and, therefore, the chemical composition of the alloy has a significant effect on its parameters [12,14]. In turn, such parameters as volume fraction, distribution, morphology and crystallography of the phases highly affect the deformation behavior of these alloys [12,13,15].

The present manuscript reports about an *in-situ* study of the deformation process of a new as-cast $Ti_{68.8}Nb_{13.6}Co_6Cu_{5.1}Al_{6.5}$ (at%) bi-modal alloy which exhibits significant tensile plasticity in combination with high static toughness.

2. Experimental

The bi-modal $Ti_{68.8}Nb_{13.6}Co_6Cu_{5.1}Al_{6.5}$ (at%) alloy was developed for the present investigations using the principles of microstructure adjustment to improve the tensile ductility [13,15]. The

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ingots were prepared from pure elements (99.9 wt%) by arc-melting. At first, Ti and Nb were alloyed to produce an intermediate alloy and then the remaining pure metals were added and melted together. The ingots were re-melted three times to obtain chemical homogeneity. Cylindrical samples (100 mm length and 12 mm diameter) were prepared from the ingots by casting into a water-cooled Cu-crucible under pure argon atmosphere (99.999%).

The composition of the rods determined by inductively-coupled plasma optical emission spectroscopy (ICP-OES, Thermo Fisher Scientific IRIS Intrepid II XUV) agreed with the nominal composition within a tolerance of about 0.5 at%. The microstructure of the rods was characterized by X-ray diffractometry (XRD, STOE STADI P with Mo-$K_{\alpha 1}$ radiation), scanning electron microscopy (SEM, Zeiss Leo Gemini 1530) and transmission electron microscopy (TEM, FEI TECNAI T20, operated at 200 kV) both coupled with energy-dispersive X-ray analysis (EDX, Bruker Xflash 4010 and Oxford Instruments, respectively). TEM specimens were cut and thinned by a focused ion beam in a FEI HELIOS NanoLab 600i. The X'Pert HighScore Plus software was used to determine the lattice parameters from the measured patterns. The volume fraction of the phases was analyzed by the ImageJ image analysis program.

Flat tensile test samples with 8 mm gage length and 1 mm thickness were prepared by electro-erosive machining according to the DIN 50125 standard [16]. The mechanical properties were investigated with an Instron 8562 testing machine at an initial strain rate of $1\times10^{-4}\,s^{-1}$ at room temperature. The strain was measured by a laser extensometer (Fiedler Optoelektronik). The *in-situ* microstructure alteration during the tensile testing was investigated by a mechanical testing device (Kammrath and Weiss) built in the scanning electron microscope.

3. Results and discussion

3.1. Microstructure

The XRD pattern obtained from the cross-section of the as-cast $Ti_{68.8}Nb_{13.6}Co_6Cu_{5.1}Al_{6.5}$ alloy is presented in the inset of Fig. 1a. $Ti_{68.8}Nb_{13.6}Co_6Cu_{5.1}Al_{6.5}$ is a two-phase alloy consisting of predominant bcc β-Ti (space group *Im-3m*) and minor B2 TiCo (space group *Pm-3m*). The lattice parameter of the β-Ti phase is $a_0=0.3235\pm0.0001$ nm, which is lower than the value $a_0=0.3282$ nm for pure β-Ti at 25 °C (as obtained by extrapolation) [17]. This may indicate that the β-Ti phase is a solid solution. The lattice parameter of the B2 TiCo phase is $a_1=0.3043\pm0.0001$ nm. As already reported in former investigations [13,15], the β-Ti phase is stabilized at room temperature due to a sufficient amount of β-stabilizers (Nb, Co) [18] and high cooling rates of about 10^2 K/s during casting [19].

To reveal the homogeneity of the microstructure throughout the entire length, bottom, middle and top parts of the as-cast rods were studied by SEM. Three microstructural zones were identified on the cross-sections of the rods: a dendritic zone (Fig. 1a), a surface-near zone (Fig. 1b) and a central dendritic zone with interdendritic porosity (not shown here).

The surface-near zone consists of columnar grains and forms a ring along the outer surface with a typical width of 750 ± 250 μm (Fig. 1b). It abuts to the pore-free dendritic zone forming a ring of 4 ± 0.5 mm (Fig. 1a). The region close to the rod axis is occupied by the central dendritic zone with interdendritic porosity. To avoid negative porosity effects on the mechanical properties, the tensile specimens were taken from the intermediate region, which has dendritic morphology and is defect-free. The microstructure of this zone was analyzed in detail.

The microstructure of the dendritic zone of the $Ti_{68.8}Nb_{13.6}Co_6Cu_{5.1}Al_{6.5}$ alloy consists of β-Ti dendrites surrounded by an ultrafine-structured eutectic network (Fig. 1c). The volume fraction of the β-Ti dendrites is 92 ± 2 vol%. The dendrite cell size and arm spacing deduced from SEM images is 58 ± 7 μm and 7 ± 1 μm, respectively. The elemental distribution is shown in Fig. 1d. Distinct microsegregation is observed, namely, Cu and Co are segregated to the dendritic periphery. The average composition of the dendrites is $Ti_{68.2}Nb_{18.9}Co_{3.1}Cu_{2.4}Al_{7.4}$, which confirms that the β-Ti phase is a solid solution. Therefore, the observed shift of the lattice parameter can be explained by the large amount of dissolved elements in the β-Ti phase.

TEM investigations were carried out on the ultrafine eutectic to identify the constituent phases and determine the elemental distribution. It was found that the eutectic structure consists of two phases arranged in lamellae of 200 ± 50 nm thickness (Fig. 2). The eutectic component which appears dark when using the BF-STEM mode (Fig. 2) was identified with the B2 TiCo phase by selected area electron diffraction (SAED) patterns and, it is embedded into the bcc β-Ti phase (appearing bright using the BF-STEM mode). SAED revealed that both eutectic phases exhibit the same crystallographic orientation throughout the entire eutectic region. In addition, the B2 and β components maintain a specific orientation relationship with respect to each other as demonstrated by the SAED patterns in Fig. 2a; the relative orientation of B2 and β inside the eutectic is such that the unit cell axes of both lattices lie parallel to each other, *i.e.* $\langle100\rangle_\beta /\!/ \langle100\rangle_{B2}$. The same orientation relationship is found for the B2 component and one of the β-dendrites neighboring the eutectic (Fig. 2b), but it is broken for all other dendrites (as demonstrated by Fig. 2c). We point out here that the lower left and lower right parts of the BF-STEM image in Fig. 2 belong to the same dendrite. For the eutectic region shown, it is this dendrite that maintains the described orientation relationship of $\langle100\rangle_\beta /\!/ \langle100\rangle_{B2}$ with the eutectic B2. Having a closer look at the eutectic region, it shows that large parts of the eutectic β component are directly connected to the same β-dendrite. Hence, it can be assumed that the eutectic region shown started forming from this dendrite thereby inheriting its crystallographic orientation. As will be shown later in Section 3.3 this orientation relationship significantly influences the deformation behavior of the present alloy.

The elemental distribution within the eutectic was investigated by EDX coupled to TEM (Fig. 3). It was found that the eutectic β component contains more Ti, Co and Cu but less Nb and Al than the β-dendrites, but by contrast, the eutectic B2 component is almost entirely formed by Ti, Co and Cu without detectable amounts of Nb.

Estimates for the chemical compositions were obtained by averaging at least 30 EDX point scans of each component giving values of $Ti_{77}Nb_5Co_6Cu_6Al_6$ (at%) for the eutectic β and $Ti_{48}Co_{29}Cu_{21}Al_2$ (at%) for the eutectic B2 component. Since the typical sizes of the B2 and the β components are similar compared to the specimen thickness (*i.e.* about 100 nm) inhomogeneities across the specimen thickness may occur. The X-ray signal recorded by the EDX detector represents an integration of all rays emitted across the entire specimen thickness and hence the given values are rough estimates for the true chemical composition; nevertheless, they allow assessment of tendencies.

The compositional differences between the β phase inside the eutectic and in the dendrites indicate that during solidification of the primary dendrites the melt became enriched in Ti, Co and Cu. In the case of B2 component, the ratio of Ti atoms to the sum of Co and Cu atoms gives approximately 1, hence a B2-type chemical ordering with Ti atoms occupying one primitive cubic sublattice and a random distribution of Co and Cu atoms on the other primitive cubic sublattice can be realized.

Based on the microstructural investigations presented above the potential solidification process can be schematically illustrated, as shown in Fig. 4. The primary phase, which crystallizes from the melt, is a bcc β-Ti phase with high contents of Nb and Al, and low contents of Co and Cu, relative to the melt. So the remaining melt will be continuously enriched in Co and Cu as