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Single crystal growth of TIMETAL LCB titanium alloy by a floating zone method

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ABSTRACT

The methodology of single crystal growth of metastable β-Ti alloy TIMETAL LCB in an optical floating zone furnace is presented in this paper. Chemical compositions of both precursor material and single crystals were checked. It was found that the concentration of base alloying elements did not change significantly during the growth process, while the concentrations of interstitial elements O and N increased. DSC measurement determined that this concentration shift has a slight impact on ongoing phase transformations, as in the single-crystalline material peak associated with α phase precipitation moves by a few degrees to a lower temperature and peak attributed to diffusion controlled growth of ω particles shifts to a higher temperature. X-ray reciprocal space maps were measured and their simulation showed that the single crystal has a mosaic structure with mean size of mosaic blocks of approximately 60 nm.

1. Introduction

At room temperature and standard pressure, pure titanium crystallizes in a hexagonal close-packed (hcp) structure, which is known as the α phase. This phase is stable up to 883 °C. Above this temperature the structure transforms to a body-centered cubic (bcc) β phase. The stability ranges of α and β phases can be altered and two phase regions or even new phases can be introduced by adding alloying elements. Titanium alloys are attractive materials for aerospace, automotive and biomedical applications due to their outstanding mechanical properties such as high strength in combination with low density. Particularly metastable β-Ti alloys remain of significant interest because of their excellent corrosion resistance, toughness and good hardenability through ageing treatment [1]. Metastable β-Ti alloys have enough β stabilizer content to retain the high temperature β phase in a metastable state upon quenching. In other words, the martensitic decomposition to the low temperature hexagonal α phase is prevented [2]. Moreover, metastable ω phase with hexagonal structure is formed in metastable β-Ti alloys with certain content of alloying elements. The ω phase is observed as uniformly dispersed submicron particles which are coherent with the β-Ti matrix. The ω phase is formed during quenching by a diffusionless displacive transformation, which was first described in detail by de Fontaine et al. [3]. The particles of ω phase further evolve and grow during ageing. This process is accompanied by rejection of β stabilizing elements from the ω phase; thus this reaction is diffusion controlled. The ω phase particles have an important influence on mechanical properties of the alloys. Typically, they increase specific strength and hardness but they can also embrittle the material [4]. Furthermore, the ω particles play a significant role in the β→α phase transformations during ageing at higher temperatures, acting as nucleation sites for the α phase. Consequently, the resulting distribution, size and volume fraction of the α phase are determined by the preceding ω phase morphology [5,6].

Despite a few decades of intensive research of the characteristics of ω phase particles, there is still doubt about the actual causes of ω phase formation. Some authors report that the initial step in ω formation is spinodal decomposition of β phase [7,8]. Other works also report elastic and structural instabilities as causes for ω particles formation during quenching [9,10].

Since the mechanical properties of metastable β-Ti alloys depend strongly on the type and morphology of the particles of secondary phases (i.e. α and ω), the understanding of ongoing phase transformations, ageing kinetics and their influence on the resulting microstructure is of primary importance. Some experimental methods which study these aspects require single-crystalline material with known orientation. In particular, the topotaxial relation of the ω and β phases (i.e., mutual orientation of their lattices) can be studied by x-ray reciprocal space-mapping only in single crystals.

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Small-angle x-ray scattering measurements of polycrystalline samples indicated a possible self-ordering of the ω-particles in the β matrix; however for a detailed analysis of the self-ordering, single-crystalline samples are required.

The objective of this work is to verify the feasibility of the growth of TIMETAL LCB (Ti-6.8Mo-4.5Fe-1.5Al in wt%) single crystals by a floating zone method in an optical furnace and to characterize the structural properties of these single crystals. TIMETAL LCB ("low cost beta") is an alloy which was designed primarily for application in automotive industry, e.g. suspension springs, engine valve springs and torsion bars [11]. The aim of its development was to produce a low cost alloy by means of selecting less expensive raw materials than typical β titanium alloys (i.e. less expensive ferromolybdenum master alloy is used) [12].

As TIMETAL LCB is a complex alloy containing three alloying elements, the main concern in single crystal growth is the melting and solidification behavior of the alloy. Fe belongs to a group of β eutectoid forming elements which typically cause solidification over a wider temperature range. This may lead to solute segregation during solidification of the material. On the other hand, Mo classifies as a β isomorphous alloying element. Addition of these elements does not result in wider solidification range and they are much less prone to segregation than β eutectoid elements. Al is an α stabilizing element and is known to form Al-rich regions in some cases [2]. Nevertheless, the segregation can be eliminated by homogenization (i.e. solution treatment) of the ingot. To the authors' knowledge, no incongruent melting was reported in metastable β titanium alloys.

The chemical compositions of precursor and grown ingot were checked and compared. Furthermore, the effect of compositional change during crystal growth on phase transformations was studied by differential scanning calorimetry (DSC).

The grown ingots were used for x-ray diffraction studies which investigated the influence of ageing on the evolution of ω particles and examined their lattice misfit. The results of these experiments are also discussed in this paper.

According to the literature, only a few successful attempts to grow metastable β-Ti alloys using the floating zone method were made and published. Lee et al. [13] studied single-crystals of Ti–15Mo–5Zr–3Al alloy and their plastic deformation behavior. Takesue et al. [14] investigated the growth and elastic properties of Ti–Nb–Ta–Zr–O alloy (Gum Metal). Hermann et al. [15] reported the growth and characterization of Ti–45Nb single-crystals which were grown using two-phase radio-frequency heating.

2. Experimental details

In this research, we have attempted to grow a single crystal of a metastable β-Ti alloy, TIMETAL LCB. Polycrystalline rods (diameter of 8 mm and length typically 100 mm) were used as precursors for growth of the crystals. The rods were prepared by arc melting by TIMET Corporation. A series of single crystals of the TIMETAL LCB alloy have been prepared by the floating zone method in a commercial four-mirror optical furnace with halogen lamps 4×1000 W (model FZ-T-4000-VPM-PC, Crystal Systems Corp., Japan). After the growth process, each crystal was solution treated at 860 °C for 4 h in an evacuated quartz tube and subsequently water quenched. This treatment ensured homogenized structure and retention of metastable β phase. The quality of all grown crystals was tested by the Laue method using a dedicated Laue camera equipped with a low-power microfocus source (W white x-ray radiation) and a large two-dimensional solid-state detector. We used the OrientExpress software [16] to determine the orientation of the single crystals.

In order to estimate the compositional changes in the material during a crystal growth process, chemical compositions of both precursor and single crystals were measured. Two complementary techniques were employed. The content of the main alloying elements (Ti, Mo, Fe and Al) was determined by energy dispersive x-ray spectroscopy (EDS) on a scanning electron microscope FEI Quanta 200FEG using software Genesis by EDAX. As titanium and its alloys are prone to interstitial contamination at elevated temperatures, especially by oxygen and nitrogen, the content of these two elements was analyzed using an automatic analyzer LECO TC 500C.

The EBSD analysis was performed on a scanning electron microscope FEI Quanta 200FEG using a DigiView EBSD detector to confirm macroscopic crystallinity of the grown ingots. The analysis of the data was carried out using OIM software.

Differential scanning calorimetry (DSC) runs were performed on a Netzsch calorimeter DSC 404 Pegasus. During the measurement, the sample was held in an inert Ar atmosphere with flow rate of 30 ml/min.

In order to obtain samples of appropriate size and shapes for the above mentioned experimental methods, the single crystals were cut using an automatic precision saw Struers Accutom-50 with Struers wafering blade. The samples were then ground and polished utilizing 500, 800, 1200, 2400 and 4000 grit SiC papers. Final polishing was done using a vibratory polisher and employing 0.3 μm and 0.05 μm aqueous alumina (Al_2O_3) suspensions and 0.05 μm colloidal silica.

3. Details of the single crystal growth process

The quartz chamber of the optical furnace was evacuated by a turbomolecular pump up to 10^{-6} mbar before each crystal growth process to avoid oxidation of the titanium alloy. In order to desorb possible surface oxygen contamination on the precursor, the furnace power was increased gradually up to 30% of maximum power (far from the melting point of the alloy) and the rod precursor was passed through the hot zone while continuously evacuating. Significant deterioration of the vacuum down to 10^{-3} mbar was observed when the precursor warmed up, which indicated desorption of oxygen and other gases from the surface of the precursor. After proper evacuation the quartz chamber was quickly filled with high purity Ar protective atmosphere (6N). The whole growth process was performed with Ar flow of 0.25 l/min and pressure of 2.5 bar. At the beginning of each crystal growth, a neck was created in order to isolate one grain. The pulling rate was 10 mm/h and the rotation velocity of both the upper and the lower shaft was 5 rpm. Throughout the whole crystal growth process, the molten zone was perfectly clear with no signs of oxides or foreign phases on the surface, manifesting very high quality of the precursor.

However, some unusual effects have been observed during the growth of the single crystals. A part of the ingot (up to 10 mm below the hot zone) seemed to be still coated with a thin layer of liquid which solidified unevenly on the surface of the ingot. This resulted in irregularities in cylindrical shape of the crystal ingot (see Fig. 1). Initially we suspected that the hot zone was overheated. Nevertheless, when the power of the furnace was reduced, the effect remained almost unchanged while the upper and the lower rod came into contact, as evidenced by off-centered rotation of the rods and vibrations of the melt. The effect of overheating may be therefore excluded. Another possibility which can be considered is very low thermal conductivity of titanium in comparison to other metals. The poor heat transfer through the ingot could be responsible for surface melting due to the absorption of the scattered light. Another hypothesis which could explain