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Martensitic transformations in Ti-6Al-4V (ELI) alloy manufactured by 3D Printing

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ABSTRACT

In the present investigation, Ti-6Al-4V ELI samples were manufactured by the powder-bed fusion (PBF) process using the laser sintering (LS) technology. Microstructure, chemical and phase constitution, and mechanical properties were studied by means of the transmission electron microscopy, atom probe tomography, X-ray diffraction, nanoindentation and mechanical testing. It was found that the structure of LS samples consisted of two different variants of metastable phases, namely the hexagonal α′ martensitic phase and small amounts of the orthorhombic α″ martensitic phase. The martensitic α′-phase was formed because of the high cooling rates of the LS method. The $\{10\bar{1}2\}\langle\bar{1}011\rangle$ hexagonal martensite tensile twins were observed in the microstructure of the as-build alloy. Small areas with inner twinning martensitic plates, which are typical for the metastable orthorhombic martensitic phase in titanium alloys, were identified by the transmission electron microscopy. Atom probe tomography (APT) confirmed localization of β-stabilizing elements at interfaces, presumably at the twin or lamella boundaries. The structure and origin of the martensitic phases in 3D printed Ti-6Al-4V alloys are discussed with respect to in-situ heat treatment during manufacturing.

1. Introduction

Ti-6Al-4V is a widely used alloy for aerospace and medical applications thanks to its excellent combination of strength, toughness, corrosion resistance and biocompatibility. In conventional Ti-6Al-4V alloy, a variety of microstructure and property combinations can be achieved by a control of temperature and cooling rates at heat treatment [1,2]. After furnace cooling from the β region, conventional Ti-6Al-4V is usually (α + β) alloy. In Ti-6Al-4V alloy, solubility of vanadium, which is the β-stabilizer, is about 2 wt% in the hexagonal close-packed (HCP) α phase [3]. Thus, up to 10 vol% β-phase is stabilized in the microstructure after furnace cooling.

At higher cooling rates, formation of metastable phases has been observed [4,5]. Two types of metastable martensitic transformations were observed in Ti-6Al-4V alloys, namely β → α′ and β → α″. The α′ and α″ metastable phases have crystallographic relationships with the parent β phase: $(110)_{\beta}||(0001)_{\alpha'}$ and $\langle 1-11\rangle_{\beta}||\langle 11-20\rangle_{\alpha'}$ [6] and, $\{001\}_{\alpha''}||\{110\}_{\beta}$ and $\langle 100\rangle_{\alpha''}||\langle 001\rangle_{\beta}$ [7]. The type of the martensite, α′ or α″, that is formed at quenching in Ti-6Al-4V alloy, depends on the starting temperature of the quenching and the concentration of the β-stabilizing elements in the β-phase at solution treatments [8]. At quenching from temperatures above the β-transus, when alloying elements are homogeneously distributed in the β-phase, the α′ hexagonal martensite is usually formed. The saturated α′ martensite is found to be transformed from the β-phase when the concentration of vanadium in the β phase is < 4.27 at.% (4.65 wt%). The HCP α′ martensitic phase (space group $P6_3/mmc$, $a = 0.293$ nm, $c = 0.467$ nm) forms in Ti-6Al-4V alloy under fast cooling [6]. A minimum cooling rate of 20 °C/s is necessary for the formation of the martensite phases. When the cooling rate is higher than 525 °C/s, the entire microstructure can be featured as the α′ martensite [9]. In [9] a schematic diagram showing the dependence of the phase state on the rate of cooling for Ti-6Al-4V is suggested. In this diagram a temperature of the start of the β → α′ martensitic transition is as low as 575 °C, and the β-transus is about 994 °C. The formation of α′ martensite promotes strengthening and lowers the ductility of the alloy [8].

At quenching from the α + β two-phase region, the concentration of alloying elements in the β-phase depends on temperature and varies

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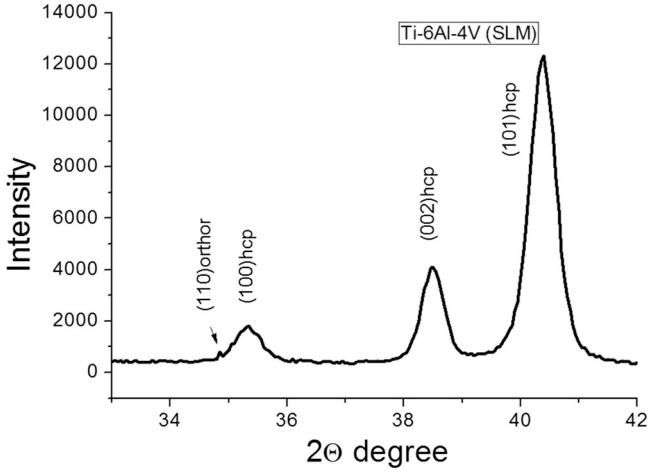

Fig. 1. X-ray diffraction pattern of the LS sample.

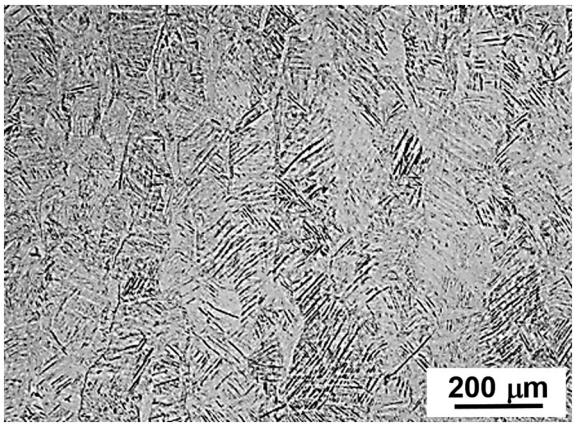

Fig. 2. Microstructure of the studied LS sample, SEM.

between the values mentioned above. Therefore, in dependence on the β-phase composition, α′ or α″ transformation products can be found. Supersaturated α″ phase (5.45–8.0 wt% V) has an orthorhombic crystal structure [5,10]. In Ti-6Al-4V alloy, the α″-phase forms in the localized regions with the vanadium concentration in a range of 9 to 13 wt% [8].

This metastable phase is particularly interesting because of its thermoelastic properties [7]. It is found the super elastic behavior in β-titanium alloys under the reversible stress-induced β → α″ martensitic transformation [11]. The martensitic α″-phase in β-Ti alloys is reported as a base-centered orthorhombic phase, which has a space group of *Cmcm* and lattice parameters of $a = 0.3152$ nm, $b = 0.4854$ nm, and $c = 0.4642$ nm [9]; the lattice parameters vary with alloy composition [12]. The orthorhombic α″ martensite is usually observed with an internal twin structure, which is believed to accommodate the transformation strains under transition from β to α″ [8,12]. The twinning process in the orthorhombic martensitic α″ phase in β–titanium alloys was analyzed in detail in [7,13,14]. Unlike the HCP α′ martensite, the appearance of the orthorhombic α″ martensite leads to softening and its decomposition leads to hardening of the titanium alloys [5,8,15]. Both α′ and α″ martensitic phases decompose at suitable aging to equilibrium α and β phases [8].

Powder-bed fusion (PBF) is the additive technology for 3D printing of the metal alloys. In the PBF process, powder is deposited in a layer-by-layer manner on a substrate. In this study, we used the laser sintering (LS) method [15]. In Ti-6Al-4V alloy manufactured by additive manufacturing, the final structure depends on the method and the process parameters. For instance, in the Ti-6Al-4V alloy manufactured by electron beam melting having lower cooling rates than that of the laser sintering method, the martensitic microstructure depends on the building thickness [16]. The laser powder-bed fusion process includes rapid solidification of the molten alloy from high temperatures, which often substantially exceed the melting point [17]. The microstructure of LS Ti-6Al-4V is formed by martensitic transformation of β-phase at very high cooling rates, about 10^6 K/s. The high cooling rates at laser sintering of Ti-6Al-4V ELI (Extra Low Impurities) alloy do not allow stabilizing of the β-phase enriched with vanadium. During solidification under LS, the metastable α′ martensitic phase in the Ti-6Al-4V is usually found inside of prior β grains [6,18,19]. Nevertheless, formation of the metastable α″ orthorhombic martensite was also observed in Ti-6Al-4V obtained by laser powder-bed fusion [20]. However, the authors of [20] did not study this phase in detail. Thus, the conditions and causes of the formation of the α″ martensitic phase in additive manufactured Ti-6Al-4V alloys are still unclear. The study of the metastable phase transformations in titanium alloys manufactured by additive technologies is an actual scientific and industrial problem. It has a great scientific interest because a formation of the metastable phases influences the mechanical properties of the alloys.

The purpose of this work is the study of the features of the martensitic phase transformations in Ti-6Al-4V (ELI) alloy manufactured by the powder-bed fusion process using the laser sintering technology, in comparison with the conventional titanium alloys.

2. Experimental

Spherical argon-atomized Ti-6Al-4V (ELI) (45 μm) powder from TLS Technik GmbH & Co Spezialpulver KG was used for this study. Samples were produced by the EOSINT M280 (EOS GmbH), equipped with an Ytterbium fiber laser, and operating at 1075 nm wavelength (IPG Photonics Corp.); the laser beam had a Gaussian profile (TEM00 mode) and 80 μm spot diameter. The process parameters for a Ti-6Al-4V alloy are 170 W laser power and scanning speed of 1.2 m/s. A powder layer thickness of 30 μm and a back-and-forth scanning by strips with the hatch distance of 100 μm was applied. The substrate and powder material were similar in chemical composition. Argon was used as the protective atmosphere; the oxygen level in the chamber was 0.07–0.12%.

Structural study was done with the Tecnai G2 30 Twin transmission electron microscope with scanning systems and energy dispersive spectrometer EDAX, GATAN-filter image and scanning electron microscope SEM Hitachi SU70. An X-ray diffractometer DRON-3 with CuK_α radiation was used in this study. Mechanical properties were measured at room temperature with nanoindentor NanoTest; the load time was 10 s, the load F = 32 mN and the size of the indent trace about 2 μm were used the measurement error was 2%. Tensile tests were performed with an Instron 1342 servo-hydraulic testing machine with clip-on extensometer of 12.5 mm and under constant strain rate of $1 \times 10^{-4}\,s^{-1}$. Cylindrical vertical manufactured samples of standard dimension with the gauge length four times the diameter were used for mechanical tests. The initial gauge length was 16 mm.

Preparation of needle-shaped specimens for APT analysis was performed using the standard FIB/SEM lift-out procedure [21]. The samples were analyzed in an Imago LEAP 3000× HR atom probe system. Field evaporation was initiated by laser pulsing with green light ($\lambda = 532$ nm) at a 200 kHz pulse rate, using 0.2 nJ pulse energy. The temperature of the specimens was held at 60 K and the pressure in the chamber was approximately 10^{-9} Pa. APT data was analyzed using the CAMECA IVAS 3.6.10 software. The reconstructions were made using the voltage method with a k-factor of 4.0, image compression factor of 1.65, and an evaporation field of 25 V/nm. The heat map figures are semi-quantitative, and display the variations in V and Al concentrations.