Ageing behavior of Beta-Ti21S produced by laser powder bed fusion

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Beta Ti alloys represent suitable candidates for interesting biomedical applications. The lower elastic modulus compared to alpha-beta alloys (e.g. Ti6Al4V), better matches that of human bones. Furthermore, their composition can be tailored to remove elements like V, detrimental to biocompatibility. Finally, their possibility to reach a fully beta structure after rapid solidification makes them very interesting alloys for additive manufacturing. In this work, the authors considered a beta Ti21S alloy powder (15%Mo, 3.2%Al, 2.8%Nb...) processed by laser powder bed fusion. The mechanical properties in the as-built state are interesting, evidencing a low elastic modulus (53GPa), good mechanical strength (Sy=700MPa, UTS=820MPa), and good fracture elongation (e=21%). The aged alloy shows a distinct strengthening at 650°C, due to the precipitation of the alpha phase, and recovery of the original solidification microstructure. The transformation is accompanied by a reduction in ductility and an increase of the elastic modulus.

INTRODUCTION

Despite the high production costs, Titanium alloys are strategic for specific fields, like aerospace and biomedical ones, due to the high specific mechanical strength, good corrosion resistance, and biocompatibility. The high costs can be justified, considering that for some applications there are very few alternatives (if any) for this alloy. One of the major tasks of metallurgists is to design new alloys or to modify the existing ones to improve their properties. Alpha-beta Ti alloys, as Ti6Al4V, are characterized by a dual-phase equilibrium structure at ambient temperature: alpha shows a hexagonal close-packed (hcp) structure, while beta a body center cubic crystal (bcc) one. On the other hand, the rapid solidification during laser powder bed fusion (LPBF) leads to hard and brittle martensite (α'), which cannot be used without stress relieving and or a full annealing heat treatment, to recover ductility. A possible alternative is to shift to beta Ti alloys, able to stabilize a stable or metastable beta structure during additive manufacturing showing very attractive properties. Molybdenum (Mo), Tantalum (Ta), Niobium (Nb) and Vanadium (V) are the beta isomorphous stabilizer. These elements are expensive, rare and sometimes toxic (in the case of V) which adds more cost and restriction to the end parts. Another main limitation is that the critical

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concentration is needed to stabilize the beta phase although the structure modification utilizing heat treatment might be an advantage in some cases. In the case of Ti-Mo alloys, a series of 15%wt Mo has been proposed. The most relevant is probably beta Ti21S containing15%Mo, 3.2%Al, 2.8%Nb, i.e. 21%wt alloying elements.

Additive manufacturing (AM) seems to be the leader of near net shape and complex shape parts in current decades to overcome and limit some aspects even though it cannot meet all of the demands to cover all aspects. For instance, powder production costs are still very high and the final parts have to be post-processed. Heat treatment is one of the further steps after AM which is combined in most cases to this production method to improve and modify the alloy's properties. Heat treatment of AMed parts is always controversial. On one side, the very fine microstructure produced by AM is unique, due to the high solidification rate. On the other hand, the heat treatment is most of the time unavoidable, because of the need to relieve residual stresses and tuning the mechanical properties. Ti-6Al-4V is the most commonly used alloy in AM. Previous studies demonstrated the need for the heat treatment for this alloy, for the two reasons stated above. Residual stress originating from the large thermal gradients are particularly critical for this material, showing low thermal conductivity so that these have to be reduced to avoid thermal distortions and/or cracking. Although the supports design can improve thermal uniformity, for Ti alloys parts with complex shapes this strategy is not sufficient and heat treatment should be carried out before removing the parts from the building platform. Moreover, Ti6Al4V undergoes martensitic transformation on cooling, responsible for additional stresses in the as-built part.

In a recent paper, the authors showed that it is possible to avoid the martensitic transformation using a metastable Beta-Ti21S alloy (1). The mechanical properties of this alloy in the as-built state are very good, particularly for biomedical applications. Nevertheless, this alloy is also a potential candidate for high strength applications, due to the capability of precipitation hardening.

Previous investigations on the heat treatment of cast and wrought Ti21S alloy have been performed to highlight the optimum parameters. Solution heat treatment, recommended by Timet, consists of short soaking times, around 3-30 min, at supertransus temperatures between 819°C and 899°C (2). Subsequent ageing is performed between 500 and 700°C. Low-temperature ageing (about 500°C) assures the highest strength but insufficient ductility and toughness. Increasing temperature, elongation is recovered on the expenses of strength (3-6). Aging temperature between 400 and 500°C, originates precipitate-free zones close to grain boundaries which localize the plastic deformations; this results in enhanced ductility and loss in strength (3,5).

Two heat treatments are commercially diffused for Ti21S. For low-temperature applications (below 427°C), ageing is performed at 593°C for 8h. When higher thermal stability is required, double ageing is employed (690 ˚Cx8h plus 650 ˚Cx8h); it is also called duplex ageing and has been specifically developed for high-temperature application (2).

A remarkable aspect of ageing for beta alloys is the replacement of the softening behavior with the strain hardening one which removes the adiabatic shear band during plastic deformation. Recent studies have highlighted the role and influence of omega phase over alpha precipitation and distribution; omega phase precipitates during pre-aging, typically performed between 300°C and 400°C, and it is subsequently replaced by alpha once the temperature is raised to the ageing range. This strategy assures a finer alpha distribution and an enhanced strength-to-elongation ratio which cannot be achieved through "conventional" ageing (3,5,7). If the omega phase is not replaced by alpha it dramatically affects the ductility of the alloy causing severe embrittlement, as reported by J. C. Williams et al (8).

As discussed previously (9) the heat treatment process of AMed alloys and their effects on properties can be different from the cast and wrought alloys because of the peculiar microstructure of layered manufactured parts. In this regard, finding the correct heat treatment process needs more effort than other processes. This paper aims to study the direct ageing behavior of Ti21S produced by LPBF.

MATERIALS AND EXPERIMENTAL PROCEDURES

A beta Ti21S prealloyed powder (GKN Hoeganaes Corporation, Cinnaminson, NJ, USA, D10=25 μm, D50=41 μm, D90=60 μm) was used. Cylindrical (D=4 mm, H=10 mm) and dog-bone (ASTM E8M) samples were 3D printed with the main axis parallel to the building direction rotating the beam direction of 90° between subsequent layers. The specimens were fabricated by a laser powder bed fusion (L-PBF) machine model MYSINT100-SISMA, more details of the process parameter can be found in ref (1).

Heat treatment of tensile samples was carried out in a tubular furnace, under a protective Ar/5%H2 flow. After pre-cleaning of the furnace chamber, the samples were heated at 10°C/min up to the target temperature of 350 and 650˚C, soaked for 2h, and slowly cooled back to room temperature inside the furnace (Figure 1).

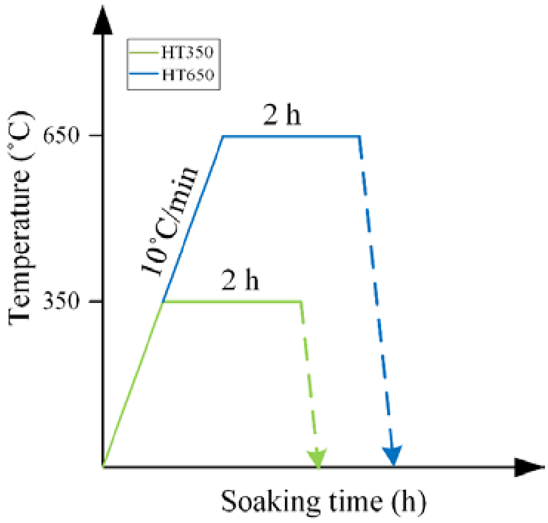

Fig.1 -The two ageing treatments studied in this work HT350 and HT650.

Differential scanning calorimetry (DSC) was used to study phase transformations during ageing. A double scan strategy has been used: assuming that irreversible reactions could go to completion during the first scan, the second one was used as the baseline. The subtracted curve was considered to study the ageing behaviour.

Tensile tests have been carried out according to ASTM E8 at room temperature, at a strain rate of 1 mm/min. Displacements were measured using an extensometer with a 12,5 mm gauge length. Three tests for each condition have been considered. Standard tensile test samples were also printed using the same strategy described for cylindrical samples. They were sandblasted before testing. The microstructural characterization of as-built samples was carried out by optical and scanning electron microscopy. The phase constitution was determined by X-ray diffraction (XRD) using a Co radiation (λ = 0.17889 nm).

RESULTS

AS BUILT MICROSTRUCTURE

The top and lateral views of the as-built material demonstrate the achievement of defect-free microstructure (Figure 2). Beta columnar grains grow for some millimeters along the building direction and grow in the order of a micron in the width, which is close to the hatch spacing (Figure 2a). Planar and epitaxial growth respectively take place from the melting pool interface along with the heating flow (Figure 2b), the identical solidification mechanism can be also observed in the top view (Figure 2c). The cellular substructure inside of each elongated grain configured a very fine and unique microstructure, that should not underestimate in the interpretation of material properties.

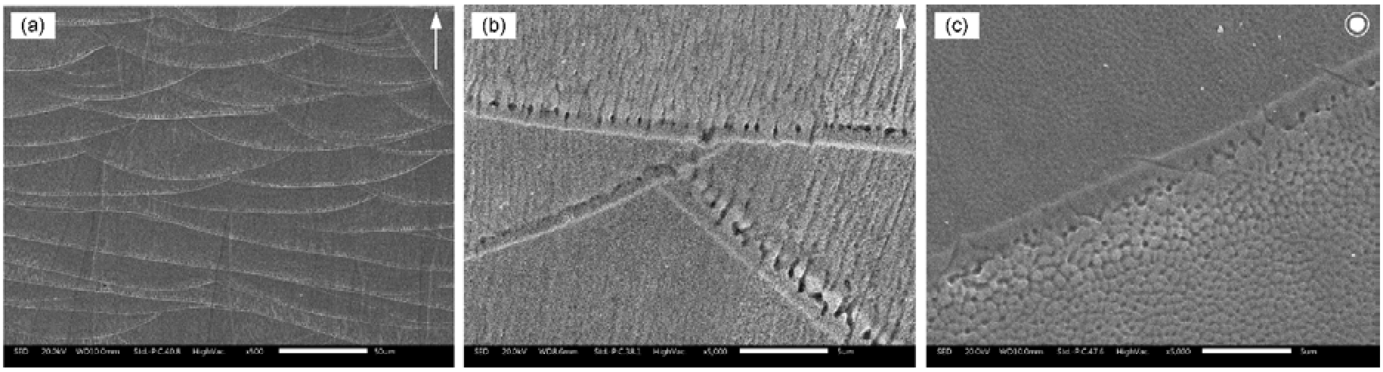

Fig.2 -Micrographs of (a), (b) Lateral and (c) Top views of as-built microstructure. The arrow shows the building direction.

AGEING BEHAVIOR

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

During isochronal heating (10°C/min) the DSC curve of the as-built sample highlights two exothermic peaks at 280 and 588°C (Figure 3). According to the literature, these peaks could be ascribed to the precipitation of i) omega-phase and ii) alpha phase, respectively. The precipitation sequence leads to the ω-assisted β→α transformation: the ω particles precipitating between 200 and 400°C act as nucleation sites for the precipitation of α between 500 and 650°C. A recent work evidences that longer pre-ageing treatments at 350°C (up to 100h) promote finer and finer precipitation of alpha, resulting in higher strength and almost unmodified fracture elongation (10). To confirm phase transformations, further phase detection, microscopic analysis and mechanical tests were performed.

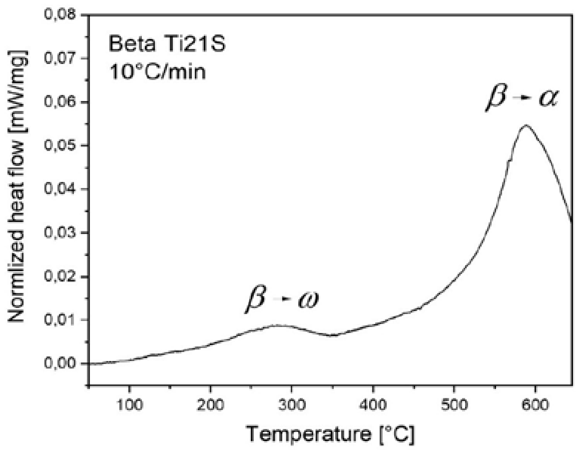

Fig.3 -DSC curve showing the precipitation of ω and α phase.

X RAY DIFFRACTION ANALYSIS (XRD)

XRD analysis confirms the presence of a fully beta structure in the as-built condition (Figure 4). No peaks related to the athermal precipitation of ω can be detected. Similarly, no traces of isothermal ω phase in the samples heat-treated at 350°C, because this phase is too fine to be detected by the XRD. Indeed, the change in the relative intensity of beta peaks evidences a change in crystallographic texture after heat treatment. Alpha phase peaks were detected in the HT650 samples. HT650 samples consist of priory beta phase as matrix and alpha phase as reinforced precipitation.

The strong microstructural texture is accompanied by the crystallographic one (Figure 4b), showing the epitaxial growth beta-bcc phase (Figure 2a). The strong textures in the <100> direction are presented in the top and lateral pole figures surfaces. it can be stated that <100> crystallographic direction oriented in the x, y, and z building directions of the sample. That is to say, the crystals are oriented mostly in this direction, which is the easy growth direction in the bcc crystal (9).

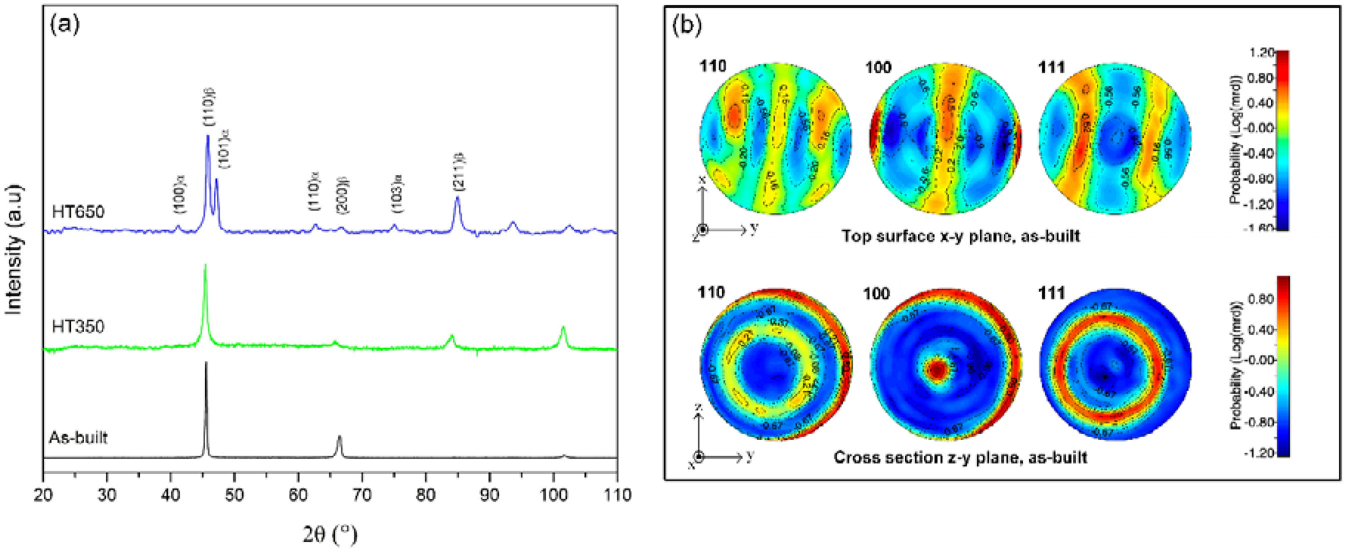

Fig.4 -(a) phase evaluation during heat treatment, alpha precipitations peaks appeared after 650 °C, (b) pole figures projection from the top and lateral sections of the as-built sample.

MICROSTRUCTURAL ANALYSIS

SEM in the high magnification micrograph of lateral and top views dωry electron micrograph of the HT350 samples shows no appreciable difference with the as-built sample, with the columnar solidification microstructure clearly outlined (Figure 5a). Although the omega phase transformation occurs at this temperature, the omega phase precipitants are very fine to be disclosed by the SEM. The HT650 sample has a completely different structure, without traces of the original cellular substructure. Very fine alpha precipitates are now formed from grain boundaries and the interior of beta grains.

Alpha precipitation has four types: first, alpha grain boundary (α_{GB}) that the alpha precipitates at the beta grain boundaries. Second is the alpha Widmanstätten grain boundary (α_{WGB}) which the alpha progress either from the beta grain boundaries or from α_{GB} as parallel colonies. The third one is named alpha Widmanstätten (α_{WM}) that is formed in the interior of the beta grain. The last one is precipitated from the omega phase which is taken under a double ageing regime (α_{WM}-fine). The former one is shown very high strength originates from very fine precipitation (3,5,7,10). As can be seen for HT650 (Figure 5-b), the α_{GB}, α_{WGB}, and α_{WM} were precipitated. α_{WM} is distinguishable in the higher magnification of lateral and top views, Figure 5c and 5d, respectively.

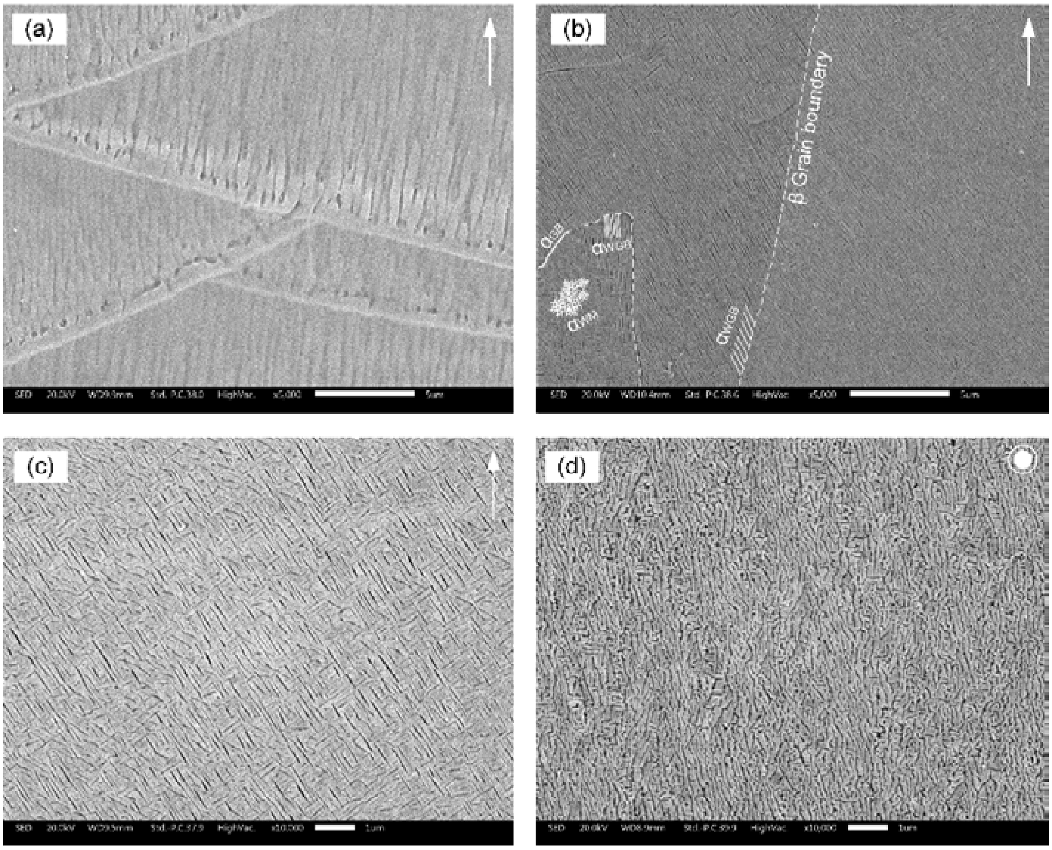

Fig.5 Micrographs of (a) HT350 (b), (c), and (d) HT650 samples, three types of alpha are shown in the (b). α_{WM} is shown from top and lateral sections in the (c) and (d). The arrow shows the building direction.

In AM samples the alpha precipitation (α_{WM}) takes place after only 2h direct ageing, while in the solution heat-treated sample, in the literature (3,5,7), it takes 8h to completely develop. This result might be ascribed by the higher driving force to precipitation in the rapidly solidified alloy. On one hand, the huge cooling rates during LPBF may extend the solubility limits of the beta phase. On the other one, the very fine solidification structure greatly increases the number of potential nucleation sites for alpha precipitation during ageing.

MECHANICAL PROPERTIES

The mechanical properties of AB and HT samples are reported in Figure 6. The as-built material disclosed a low Young's modulus (52 ± 0.3 GPa), good mechanical strength (σy=709±6 MPa, UTS=831±3 MPa), and high fracture elongation (21±1.2%). The strength is in line with that reported in the literature for the same LPBF alloy (1). HT350 does not show significantly different properties compared to the as-built sample: The Young's modulus is slightly higher, the strength too, while the elongation was decreased to 15%±2%. This marginal change can be attributed to the precipitation of isothermal ω. This phase influences the mechanical properties even though it was not detectable in the above analysis methods, known to make the material brittle. In the HT650 sample, the highest strength is associated with the lowest elongation and highest young's modulus. For the heat-treated samples, the strengthening associated with the precipitation of either omega or alpha phase, confirmed by the increased elastic modulus, causes a marked drop in ductility. On the other hand, present data are in good agreement with those reported for single (0.2%YS = 965MPa and UTS = 1034 MPa, el.%=6%) and double aged (0.2%YS = 793 MPa and UTS = 862 MPa, el.%=10%) 4.75mm foils (2).

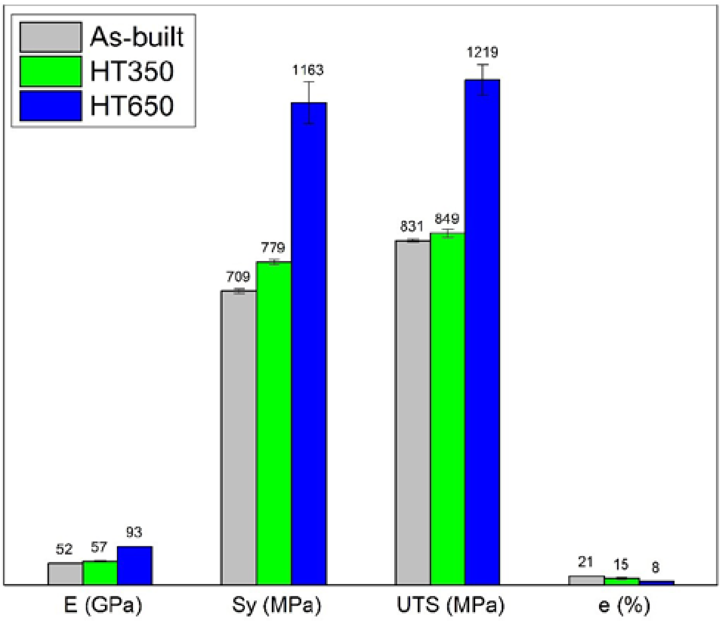

Fig.6 Mechanical properties resulted from the tensile test. Young modulus (E), Sy (yield strength, Ultimate tensile strength (UTS), and elongation (e).

CONCLUSIONS

This study reports a preliminary study on the heat treatment of Beta Ti21S alloy produced by Laser Powder Bed Fusion. The following main conclusions can be drawn:

1. The microstructure and the mechanical properties in the as-built state are very interesting
2. Ageing at 350°C for 2h causes the precipitation of the omega phase, with minor changes in strength and a slight reduction in ductility
3. Ageing at 650°C for 2h promotes a strong precipitation strengthening by alpha-phase and a marked decrease in fracture elongation. The results are in line with those reported for the same wrought alloy.

Further investigations are ongoing to optimize the heat treatment process. The ageing behavior at different temperatures will be considered, as well as the opportunity of double ageing.

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