Beta phase stability of Ti-35Nb-6Ta-7Zr-0.7O beta titanium alloy

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Abstract. Phase stability of metastable beta Ti alloy Ti-35Nb-6Ta-7Zr-0.7O (wt.%) in a beta solution treated condition was studied during annealing at 400°C – 700°C for 1 h – 16 h. Resulting microstructure was characterized by scanning electron microscopy; the samples were also characterized by microhardness measurements. The microhardness did not change in any of the annealed condition. The reason follows from the microstructural observations, the α phase precipitation did occur only at the grain boundaries and only at higher temperatures / longer annealing times. Thus, the β phase stability is high and this fact can be used for designing annealing treatments or the thermo-mechanical processing route.

1 Introduction
Titanium has two main crystallographic structures, hcp α phase and bcc β phase. In pure Ti, α phase is present at low temperatures and transforms into β phase at 882°C. By adding the so-called β stabilizing elements (Nb, Mo, Ta, etc.), pure β phase can be achieved in metastable form by quenching from the β region (β solution treated condition). The metastable β Ti alloys in β solution treated condition can be aged at sub-transus temperatures to promote precipitation of the α phase [1].

Recently developed Ti-35Nb-6Ta-7Zr-0.7O (wt.%) (TNTZO) [2] has promising properties for implant manufacturing – low Young’s modulus of 80 GPa, high strength over 1000 MPa and contains only biocompatible elements [3,4]. The low Young’s modulus is attributed to single β phase condition [5,6] and therefore α phase precipitation should be avoided in final product. High strength is caused by interstitial strengthening by oxygen [7,8].

TNTZO is a high oxygen variant of Ti-35Nb-6Ta-7Zr metastable β alloy [6]. Oxygen is a stabilizing element in terms of increasing β transus temperature [9] (the β transus temperature of TNTZO alloy was not measured, but solution treatment at 820°C / 2h was successful). On the other hand, the effect of oxygen on the precipitation, especially concerning nucleation, of α phase particles in metastable β alloys is unclear.

Currently the most used Ti alloy for implant production is α+β alloy Ti-6Al-4V (wt.%) [10], with extra low interstitial content (ELI) that causes good ductility simultaneously with high strength. In the comparison with Ti-6Al-4V ELI, the TNTZO alloy has similar strength, lower Young’s modulus and does not contain toxic vanadium.

Preparation of the β Ti alloys often comprises of hot working (hot forging or hot rolling) [2,7,11–13] or cold working combined with subsequent annealing [14–16]. It is therefore valuable to study the
kinetics of α phase precipitation in this alloy to successfully design the thermal / thermo-mechanical processing route to avoid the precipitation (and connected rise of Young’s modulus).

2 Materials and Methods

The studied material with nominal composition Ti-35Nb-6Ta-7Zr-0.7O was cast at company Retech Systems LLC by sequential pour melting procedure. Chemical composition shown in Table 1 was analyzed by manufacturer by Inductive Coupled Plasma Atomic Emission Spectroscopy for analyzing content of metals while content of other elements was determined by Combustion Infrared Absorption. A small rod of diameter 10 mm was machined from the cast ingot and beta solution treated at 820°C/2h in pure Ar atmosphere in a quartz tube. The rod was water quenched immediately after finishing the annealing by breaking the quartz tube in water. This condition will be denoted as ST (solution treated).

| Table 1. Chemical composition of Ti-35Nb-6Ta-7Zr-0.7O alloy after casting. |
|-----------------|---------|-------|------|-------|-------|-------|-------|
| Element         | Ti      | Nb    | Zr   | Ta    | O     | N     | C     |
| Composition     | Bal.    | 35.6 ± 0.2 | 7.35 ± 0.04 | 6.0 ± 0.1 | 0.71 ± 0.01 | 0.012 ± 0.002 | 0.010 ± 0.001 |

After solution treatment, the rod was cut into slices 3 mm thick and aged at temperatures 400°C, 500°C, 600°C and 700°C for 1 h, 4 h and 16 h. The samples were water quenched immediately after ageing. To prevent oxidation, the ageing at 400°C and 500°C was done in preheated inert salt baths (potassium nitrate and sodium nitrate mixture). The samples were put directly into salt bath preheated to ageing temperature. Ageing at 600°C and 700°C was done in preheated tube, which was evacuated immediately after inserting the sample. The samples were ground on SiC papers up to 2400 grit and vibratory polished using Vibromet polisher with suspensions Alumina 0.3 µm and 0.05 µm for at least 6 h and Colloidal Silica 0.05 for at least 3 hours. Vickers microhardness measurements were done using automatic Qness Q10 hardness tester with load 0.5 kgf and load time 10 s. Scanning electron microscopy (SEM) observations using back-scattered electrons (BSE) were done at FEI Quanta 200F, equipped with an energy dispersive X-ray spectroscopy (EDS), with accelerating voltage 15 kV.

3 Results and Discussion

3.1 Microhardness measurements

Table 2 shows results from microhardness measurements of aged samples. Within the statistical error, all aged conditions have the same microhardness. The values from aged samples also do not differ from ST condition having microhardness 321 ± 8 HV. Achieved values are comparable to the microhardness of previously prepared TNTZO alloy in laboratory environment [2] and are consistent with the high strength of TNTZO alloy [17]. For comparison with other metastable beta Ti alloy, in Timetal LCB (Ti–6.8Mo–4.5Fe–1.5Al in wt.%) the microhardness grows by 100 HV, compared to ST condition, already after ageing at 400°C / 1 h [18]. The microhardness changes in Timetal LCB are attributed to homogeneous distribution of α and α phases.
Table 2. Microhardness of Ti-35Nb-6Ta-7Zr-0.7O alloy annealed at 400°C – 700°C for 1h – 16h.

| Annealing time | Annealing temperature 400°C | Annealing temperature 500°C | Annealing temperature 600°C | Annealing temperature 700°C |
|----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| 1 h            | 327 ± 7                     | 330 ± 10                    | 332 ± 6                     | 333 ± 11                    |
| 4 h            | 335 ± 7                     | 332 ± 5                     | 331 ± 6                     | 333 ± 9                     |
| 16 h           | 332 ± 6                     | 332 ± 4                     | 332 ± 8                     | 332 ± 4                     |

3.2 SEM observations

Figure 1 shows SEM images of selected conditions at low magnification. All conditions show very large grains with size of approx. 1 mm. There is also porosity in the material and dendritic chemical inhomogeneities, both were created during solidification during casting. The concentration variations of elements with respect to bulk did not exceed 3 wt. %, as proven by EDS. Neither of these features was changed much during ageing. We can observe, that the α phase does not precipitate at the dark areas of chemical inhomonieties – areas with higher amount of Ti. On the other hand, there are α lamellae grown at grain boundary (GB) visible at image of 700°C / 16 h aged condition as black areas.

Figure 1. SEM images of overall microstructure (a) ST condition, (b) 600°C / 1h ageing, (c) 700°C / 16 h ageing. Small square indents originate from microhardness measurements.

Thorough analysis was conducted to determine, at which conditions the GB α starts to precipitate. Figure 2 shows GBs and triple points of selected aged conditions. No α phase precipitation was observed at ageing temperature 400°C. At 500°C, the GB α phase was found only on several GBs after the longest annealing time 16 h. The ageing at 600°C / 1 h was not long enough for α precipitation, same as lower temperatures with shorter annealing times. Figure 2 (a) shows, that even at high magnification, there is no GB α. After 4 h at 600°C, several grain boundaries with α phase were found, similar as in the 500°C / 16 h aged sample. After ageing at 600°C for 16 h, the GB α phase starts to form lamellae growing from the grain boundary into neighboring grains. Similar, but smaller lamellae are observed after 1 h ageing at 700°C. Prolonged ageing at 700°C leads to presence of GB α at majority of grain boundaries and growth of lamellar α phase towards the interior of β grains.
Limited or no precipitation of the α phase in aged samples explains lack of microhardness variations between the conditions. Typical size of the microhardness indent is 50 μm and therefore the distant precipitates do not affect the overall microhardness despite the α phase precipitates are harder than β matrix. The material therefore exhibits β phase stability up to relatively high temperatures. The consequence is that water quenching is not needed to prevent formation of α phase during cooling after using thermo-mechanical processing or any thermal treatment. The downside is that, for practical purposes, this material cannot be strengthened by α phase precipitation in sufficiently short time. This however, is not much limiting as the desired use of this alloy is in biomedical endoprostheses, where the lowest Young’s modulus is desired and α phase would cause the Young’s modulus to rise.

In comparison with other β Ti alloys, the TNTZO has rather high β phase stability. In Ti–29Nb–13Ta–4.6Zr alloy, the α and ω were found after 48 h long ageing at 350°C – 600°C and 300°C – 400°C, respectively. On the other hand, Ti–39Nb–13Ta–4.6Zr with much 10% more Nb had to be aged for 12 days to achieve any α phase precipitation [19]. In the Ti–27Nb–2Ta–3Zr alloy, the α phase precipitates at 500°C already after 0.5 h on GB and after 2 h inside grains [20]. To compare with oxygen-containing alloys, the amount of α phase is raised [12,21] by oxygen content. It is interesting that similar alloy Ti–35Nb–7Zr–5Ta–0.68O with lower amount of Nb (by 0.6%) and Ta (by 1%) shows α phase precipitates both on GB and in grain interiors when aged at temperatures 538°C and 598°C for 8 h [21]. It must be noted that all alloys in the literature were subjected to hot forging before annealing treatment, while in this study, as-cast material was used. Considering that the preferential sites for heterogeneous α phase nucleation are grain boundaries and dislocations, the precipitation is limited to the GBs in the coarse-grained as-cast material. It was already reported that microstructural condition significantly affects alpha phase precipitation [22].

Figure 2. Selected triple points and grain boundaries in TNTZO aged at 600°C for (a) 1 h, (b) 4 h, (c) 16 h and at 700°C for (d) 1 h, (e) 4 h, (f) 16 h.
4 Conclusion

The β titanium alloy with the composition Ti-35Nb-6Ta-7Zr-0.7O (wt.%) after solution treatment and ageing in the temperature range 400°C – 700°C for 1 h – 16 h was characterized by SEM and we can draw following conclusion.

- There is no α phase present in the aged material inside the grains, not even at chemical inhomogenieties, but only on grain boundaries.
- Grain boundary α phase starts to grow after ageing at 500°C / 16 h or 600°C / 4 h. Further ageing yields α lamellae growing from grain boundary into grain.
- Microhardness does not change with ageing, as there was only GB α phase present in aged samples.
- Due to high β phase stability, water quenching from β region may not be required, unless α phase precipitation is not substantially enhanced by microstructural refinement.

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References

[1] Lütjering G and Williams J C 2003 Titanium vol 2 (Springer)
[2] Stráský J, Harcuba P, Václavová K, Horváth K, Landa M, Srba O and Janeček M 2017 Increasing strength of a biomedical Ti-Nb-Ta-Zr alloy by alloying with Fe, Si and O J. Mech. Behav. Biomed. Mater. 71 329–36
[3] Eisenbarth E, Velten D, Müller M, Thull R and Breme J 2004 Biocompatibility of β-stabilizing elements of titanium alloys Biomaterials 25 5705–13
[4] Kopova I, Stráský J, Harcuba P, Landa M, Janeček M and Bačáková L 2016 Newly developed Ti–Nb–Zr–Ta–Si–Fe biomedical beta titanium alloys with increased strength and enhanced biocompatibility Mater. Sci. Eng. C 60 230–8
[5] Tane M, Nakano T, Kuramoto S, Hara M, Niinomi M, Takesue N, Yano T and Nakajima H 2011 Low Young’s modulus in Ti–Nb–Ta–Zr–O alloys: Cold working and oxygen effects Acta Mater. 59 6975–88
[6] Ahmed T and Rack H 1999 Low modulus biocompatible titanium base alloys for medical devices, US patent no. 5,871,595.
[7] Geng F, Niinomi M and Nakai M 2011 Observation of yielding and strain hardening in a titanium alloy having high oxygen content Mater. Sci. Eng. A 528 5435–45
[8] Nakai M, Niinomi M, Akahori T, Tsutsumi H and Ogawa M 2009 Effect of Oxygen Content on Microstructure and Mechanical Properties of Biomedical Ti-29Nb-13Ta-4.6Zr Alloy under Solutionized and Aged Conditions Mater. Trans. 50 2716–20
[9] Welsch G, Boyer R and Collings E W 1993 Materials Properties Handbook: Titanium Alloys (ASM International)
[10] Rack H J and Qazi J I 2006 Titanium alloys for biomedical applications Mater. Sci. Eng. C 26 1269–77
[11] Wei Q, Wang L, Fu Y, Qin J, Lu W and Zhang D 2011 Influence of oxygen content on microstructure and mechanical properties of Ti–Nb–Ta–Zr alloy Mater. Des. 32 2934–2939
[12] Qazi J I, Rack H J and Marquardt B 2004 High-strength metastable beta-titanium alloys for biomedical applications JOM 56 49–51
[13] Hou F Q, Li S J, Hao Y L and Yang R 2010 Nonlinear elastic deformation behaviour of Ti-30Nb-12Zr alloys Scr. Mater. 63 54–7
[14] Kim J I, Kim H Y, Hosoda H and Miyazaki S 2005 Shape Memory Behavior of Ti–22Nb–(0.5–2.0)O(at%) Biomedical Alloys Mater. Trans. 46 852–7
[15] Guo S, Meng Q, Zhao X, Wei Q and Xu H 2015 Design and fabrication of a metastable β-type titanium alloy with ultralow elastic modulus and high strength Sci. Rep. 5
[16] Elmay W, Laheurte P, Eberhardt A, Bolle B, Gloriant T, Patoor E, Prima F, Laille D, Castany P and Wary M 2010 Stability and elastic properties of Ti-alloys for biomedical application designed with electronic parameters EPJ Web Conf. 6 29002
[17] Preisler D, Václavová K, Stráský J, Janeček M and Harcuba P 2016 Microstructure and mechanical properties of Ti-Nb-Zr-Ta-O biomedical alloy Met. 2016 25rd Int. Conf. Metall. Mater. Ostrava TANGER 1509–13
[18] Šmilauerová J, Janeček M, Harcuba P, Stráský J, Veselý J, Kužel R and Rack H J 2017 Ageing response of sub-transus heat treated Ti–6.8Mo–4.5Fe–1.5Al alloy J. Alloys Compd. 724 373–80
[19] Li S, Hao Y L, Yang R, Cui Y and Niinomi M 2002 Effect of Nb on Microstructural Characteristics of Ti-Nb-Ta-Zr Alloy for Biomedical Applications Mater. Trans.-MATER TRANS 43 2964–9
[20] Wang L, Lin Z, Wang X, Shi Q, Yin W, Zhang D, Liu Z and Lu W 2014 Effect of Aging Treatment on Microstructure and Mechanical Properties of Ti27Nb2Ta3Zr β Titanium Alloy for Implant Applications Mater. Trans. 55 141–6
[21] Qazi J I, Marquardt B, Allard L F and Rack H J 2005 Phase transformations in Ti–35Nb–7Zr–5Ta–(0.06–0.68)O alloys Mater. Sci. Eng. C 25 389–97
[22] Gatina S, Semenova I, Janecek M and Strasky J 2014 Effect of high pressure torsion on the aging kinetics of β-titanium Ti-15Mo alloy IOP Conf. Ser. Mater. Sci. Eng. 63 012068