Chapter

Heat Treatment of Metastable Beta Titanium Alloys

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Abstract

Heat treatment of metastable beta titanium alloys involves essentially two steps—solution treatment in beta or alpha+beta phase field and aging at appropriate lower temperatures. High strength in beta titanium alloys can be developed via solution treatment followed by aging by precipitating fine alpha (α) particles in a beta (β) matrix. Volume fraction and morphology of α determine the strength whereas ductility is dependent on the β grain size. Solution treatment in (α + β) range can give rise to a better combination of mechanical properties, compared to solution treatment in the β range. However, aging at some temperatures may lead to a low/nil-ductility situation and this has to be taken into account while designing the aging step. Heating rate to aging temperature also has a significant effect on the microstructure and mechanical properties obtained after aging. In addition to α, formation of intermediate phases such as omega, beta prime during decomposition of beta phase has been a subject of detailed studies. In addition to covering these issues, the review pays special attention to heat treatment of beta titanium alloys for biomedical applications, in view of the growing interest this class of alloys have received.

Keywords: beta titanium alloys, heat treatment, duplex aging, precipitation hardening, intermediate phases, fatigue behavior

1. Introduction

High specific strength and excellent corrosion resistance of titanium-based materials make them an attractive choice for application in various industries such as aerospace, biomaterials, and automotive [1, 2]. Alloying of pure titanium opens a new horizon to develop a variety of products with exceptional properties. Based on the alloying elements and phases present at room temperature, Ti alloys are broadly classified into α, α + β, and β alloys. Compared to α and α + β alloys, β alloys have advantages such as excellent higher specific strength, sufficient toughness, excellent corrosion resistance, better biocompatibility, good fatigue resistance, and good formability.

Mo<sub>eq</sub> is a well-accepted measure to characterize the β-phase stability for a given composition and equation for the deriving the Mo<sub>eq</sub> is shown in Eq. (1) [3, 4].

\[
\text{Mo}_{\text{eq}} = 1.0(\text{wt.}\% \text{ Mo}) + 0.67 (\text{wt.}\% \text{ V}) + 0.44 (\text{wt.}\% \text{ W}) + 0.28 (\text{wt}\% \text{ Nb}) + 0.22 (\text{wt.}\% \text{ Ta}) + 2.9 (\text{wt.}\% \text{ Fe}) + 1.6(\text{wt.}\% \text{ Cr}) - 1.0(\text{wt.}\% \text{ Al}) \] (1)
Beta titanium alloys with a Mo<sub>eq</sub> between 10 and 30 are metastable and hence heat treatable and deeply hardenable [4]. Mo<sub>eq</sub> of the various beta titanium alloys along with their commercial name is shown in Figure 1.

Unlike α + β alloys, in β alloys, higher beta stabilizer content results in complete retention of beta phase upon air cooling or water quenching from solution treatment temperature (above β transus temperature). This difference in transformation can be related to the difference in electron density; the α + β alloys have <4 el/atom, while β alloys have higher electron density, for example, it is 4.148 el/atom for Ti-15-3 alloy [5]. Beta alloys are more workable because of the higher stacking fault energy of the BCC phase, which supports the formation of multiple and cross slips upon deformation, thereby preventing crack formation [6].

In most of the commercial beta alloys, metastable or thermodynamically unstable β phase with BCC crystal structure is formed upon quenching after solution treatment. Hence, subsequent aging leads to the precipitation of the α phase from the beta matrix. To understand the transformation in detail, modeling of precipitation of α by decomposition of β is performed under the framework of Johnson-Mehl-Avrami for Ti-15-3 a metastable beta alloy [7] and Ti-5Mo-2.6Nb-3Al-0.2S/β21s [8], both being β alloys. The transformation of β to α + β upon aging is a slow diffusion-controlled growth of alpha plates in the beta matrix. Hence, the aging time decides the α precipitation fraction [7]. Various microstructures and correspondingly mechanical properties are feasible through heat treatment of β titanium alloys, thereby making them a wide spectrum of candidate materials for a wide range of applications. Beta Ti alloys with less beta stabilizing element were found to have faster precipitation reactions. For example, VT22 alloy exhibited higher precipitation kinetics compared to the Ti-15-3 and Timetal LCB [9]. Devaraj et al. reported that superior strength is achieved through the micro and nanoscale precipitation of α phase in a beta matrix of Ti-1Al-8V-5Fe [10]. As already mentioned, heat treatment of β titanium alloys is comprised of two steps, that is, solution treatment and aging. The solution treatment can be subdivided into α + β and β solution treatment based on the temperature (i.e., α + β solution treatment T < β transus temperature and β solution treatment temperature T > β transus

![Figure 1. Mo<sub>eq</sub> of various beta Ti alloys.](image-url)
temperature). In beta alloys, Ti-6Cr-5Mo-5V-4Al and Ti-5Al-5Mo-5V-3Cr, solution treatment in α + β range followed by aging yielded a better strength–ductility combination compared to solution treatment in the β range followed by aging [11, 12]. Further, if the α + β solution treatment is preceded by rolling in the α + β range even better strength–ductility combination was obtained; this was attributed to the formation of finer β grains in Ti-3.5Al-5Mo-6V-3Cr-2Sn-0.5Fe [13]. Similarly, α + β rolling followed by α + β solution treatment of Ti-10V-2Fe-3Al resulted in improvement of fracture toughness [14]. Deformation or cold working in-between solution treatment and aging could lead a path for obtaining homogeneous precipitation because the dislocations serve as a precursor for precipitation [9]. Zhan et al. also reported that dislocations formed during the high strain rate deformation of the metastable β alloy Ti-6Cr-5Mo-5V-4Al have acted as nucleation sites for the α laths/precipitation at elevated temperature [15]. Similarly, in Ti-15-3 alloy cold working before duplex aging is found to be advantageous in forming finer precipitates [16]. Ti-15-3 alloy exhibits lower precipitation kinetics compared to Timetal LCB and VT22 alloy [17]. Cold working before aging or two-step/duplex aging can be used to increase the precipitation kinetics in Ti-15-3. However, intervening cold work also leads to a significant loss in ductility. Aging of Ti-15-3 alloy with deformed microstructure for prolonged times leads to dislocation rearrangement and formation of subgrains [18]. Grain boundary α and precipitation free zones may occur in aged condition; they play an important role in degrading the tensile and fatigue properties. The authors have reviewed various processing techniques of the beta titanium alloys elsewhere [19]. The heat treatment of beta titanium alloy for biomedical application [20, 21] and heat treatment of additively manufactured beta Ti alloy [22] have also been reported in the literature.

2. Solution treatment

Solution treatment comprises of heating the sample from 20 to 30°C above the beta transus temperature (super-transus) or ~50°C below the beta transus temperature (sub-transus) for a specified time and rapid cooling of the sample to room temperature. Hence, beta transus temperature (β$_{trans}$) plays a vital role in selecting heat treatment temperatures. This beta transus temperature is strongly influenced by the alloying element (i.e., alpha stabilizers will rise the β$_{trans}$, beta stabilizers will lower the β$_{trans}$, and neutral elements will hardly do the changes in the β$_{trans}$). The equation (Eq. (2)) to find the beta transus temperature is given below [23].

$$T_{\beta} = 882 + 21.1 \text{[Al]} - 9.5 \text{[Mo]} + 4.2 \text{[Sn]} - 6.9 \text{[Zr]} - 11.8 \text{[V]} - 12.1 \text{[Cr]} - 15.4 \text{[Fe]} + 23.3 \text{[Si]} + 123 \text{[O]}$$

(2)

Beta transus temperature for some of the important beta titanium alloys is listed in Table 1.

Solution treatment temperature and the cooling rate strongly influence the mechanical properties realized after subsequent aging treatment. Depending on the requirement, metastable beta alloys such as Ti-13V-11Cr-3Al and Ti-15Mo-3Al-3Nb-0.2Si are supplied in the solution-treated condition to ease the down-stream cold working operations [4]. Schematic representation of super- and sub-transus solution treatment and the aging process is shown in Figure 2. Super-transus solution treatment is done above the β$_{trans}$ temperature and sub-transus solution treatment below the β$_{trans}$ temperature. In alloys, such as Ti-5Al-5Mo-5V-3Cr, both super-transus and sub-transus solution treatments were found to be useful in
practice [24]. However, prolonged solution treatment above $\beta$ transus may lead to a remarkable loss of mechanical properties owing to the coarsening of $\beta$ grains [25]. Selection of the solution treatment temperature will also have a strong influence on the morphology and distribution of the alpha precipitation. For example, in Ti-1Al-8V-5Fe (Ti185), sub-transus solution treatment results in higher yield strength and tensile strength and this enhancement is ascribed to the nanoscale $\alpha$ precipitation in the $\beta$ matrix [10].

3. Aging

During age hardening, solution-treated alloy will be heat treated in the temperature range of 480–620°C for 2–16 h. This heat treatment leads to precipitation of fine alpha phase in the beta matrix, and these precipitations hinder the movement of dislocations, making deformation difficult. This phenomenon is referred to as
precipitation hardening. Coherency strains between α precipitates and the β matrix induce a strengthening effect [5]. Comparative examination of the microstructure of solution-treated (800°C/0.5 h) (ST) and microstructure of solution-treated and aged (ST + A) (500°C/8 h) Ti-15-3 samples has clearly revealed the presence of α precipitates in the latter. Precipitation leads to a significant increase in mechanical properties like tensile strength (79%) and hardness (44%) [26]. Age hardening is more effective for beta alloys compared to the α + β alloy owing to the capability of the former to form finer and homogenous α precipitates [27]. The sequence of precipitation of α is dependent on the Mo_eq of the alloy. The sequence of precipitation is given below:

For lower Mo_eq (solute – lean alloy), for example Ti – 10V – 2Fe – 3Al,

\[ \beta \rightarrow \beta + \omega_{iso} \rightarrow \beta + \omega_{iso} + \alpha \rightarrow \beta + \alpha. \]

For higher Mo_eq (solute – rich alloy), for example Ti – 13V – 11Cr – 3Al,

\[ \beta \rightarrow \beta + \beta' \rightarrow \beta + \beta' + \alpha \rightarrow \beta + \alpha. \]

3.1 Single aging

To produce optimum strength–ductility combination, post solution treatment, aging or soaking the material in the temperature range of 200–650°C (well below the \( T_{trans} \) temperature) for a specified time followed by air or furnace cooling is performed [3]. Single aging comprises of heating to the desired temperature, holding for a specified time, and cooling in air or furnace. In Ti-3.5Al-5Mo-6V-3Sn-0.5Fe beta alloy, single-step aging at 440°C for 8 h resulted in high tensile strength of 1637 MPa [28]. In Ti-15-3 alloy, aging at 520°C for 10 h yields a good combination of fatigue life and fracture toughness [29]. Similarly, in the same Ti-15-3 alloy, single-step aging led to a significant increase in the microhardness and fatigue life compared to the solution-treated condition [30].

3.2 Duplex aging

Dual-step aging or duplex aging unlocks the room for further betterment in the mechanical properties through finer and homogeneous α precipitation compared to single-step aging. Many researchers have reported the advantage of duplex aging over single-step aging of beta Ti alloys; most studied is the low-high combination, that is, a low temperature for first step aging and a somewhat higher temperature for second step aging [31–35]. Enhancement of the material behavior during unidirectional and cyclic/fatigue loading could be achieved through duplex aging. In Ti-3Al-8V-6Cr-4Mo-4Zr alloy (also known as Ti 38-644, Beta C), duplex aging resulted in more homogenous alpha precipitation [3]. Precipitates were found to be finer and microstructure was also free of precipitate-free zones (PFZs) and grain boundary α (GBα); this led to a significant improvement in fatigue life of Ti 38-644 [33]. In Ti-15-3 alloy, finer and more homogenous distribution of α precipitates was achieved through duplex aging compared to the single-step aging [34, 36]. In addition to an increase in the mechanical strength (i.e., YS and UTS), increase in ductility was also achieved by duplex aging of Ti-15-3 alloy [17]. Santhosh et al. [37] reported that duplex aging of Ti-15-3 sample leads to (i) a refined and homogenous distribution of the α precipitates in β matrix; (ii) a higher α phase fraction in β matrix; (iii) freedom from PFZs; and (iv) much less GBα, compared to single-aged Ti-15-3 sample. Similarly, duplex aging of the β-C alloy leads to a substantial
increase of fatigue behaviour by producing the completely recrystallized $\beta$ micro-
structure with homogeneously distributed $\alpha$ precipitates and reducing the grain
boundary $\alpha$ [32]. Finer and homogenous $\alpha$ precipitation resulting from duplex aging
enhanced the fatigue limit of beta alloy Ti-5Al-5Mo-5V-3Cr [38]. In a pre-strained
Ti-10Mo-8V-1Fe-3.5Al, two-step aging was found more effective and yielded
higher strength than conventional aging [39]. In contrast to the proceeding
instances, Kazanjian et al. reported that multi-step aging made little difference to
fatigue crack growth compared to the single-step aging [40]. In addition to the
single and duplex aging, triplex aging or aging performed in three steps was
attempted by some researchers on Ti-15-3 beta alloy; they found no significant
benefit in either tensile strength or ductility of the material [41]. Duplex aging was
also found to result in an enhancement of thermal stability during the elevated
temperature application [24].

4. Influence of the rate of heating to the aging temperature

During the heat treatment of metastable beta titanium alloys, heating rate
adopted to attain the desired aging temperature has an influential role in the $\alpha$
precipitation [42–45]. In Timetal LCB, lower heating rate (0.25 ks$^{-1}$) yielded an
optimum combination of strength and ductility with a finer and homogenous $\alpha$
precipitation compared to the faster heating rate (20 ks$^{-1}$) [42]. However, this
heating rate will vary from alloy to alloy. For example, a similar heating rate of
0.25 ks$^{-1}$ produced coarser and non-uniform alpha precipitation in the Ti-15-3 alloy
and the same authors reported 0.01 ks$^{-1}$ as the optimum heating rate for this alloy
[42]. Wu et al. [45] reported a significant increase in microhardness of the Ti-15-3
alloy when a lower heating rate was used. They attributed it to the homogenous
alpha precipitation. In addition, the lower heating rate yielded a microstructure free
of grain boundary $\alpha$.

5. Grain boundary $\alpha$

Grain boundary alpha (GB$_\alpha$) is found detrimental by serving as a nucleus for
crack initiation along $\alpha/\beta$ interfaces during the monotonic as well as cyclic loading.
When the thickness of these GB$_\alpha$ exceeds several microns, ductility and fatigue
crack initiation and propagation are detrimentally affected. Crack is found to
propagate with little resistance along the GB$_\alpha$ in Ti-8Mo-8V-2Fe-3Al [46]. In addition
to tensile ductility, GB$_\alpha$ also has a strong negative influence over the fatigue
behaviour of the $\beta$ titanium alloys [32, 47]. In fatigue loading, the preferred site for
the crack initiation will be the grain boundary decorated with $\alpha$ and inclined at 45°
to the axis of loading [48]. This inclined GB$_\alpha$ provides potential sites for slip
localization as well as fracture initiation. Similarly, subsurface crack initiation
induced by the well-developed GB$_\alpha$ is commonly observed in the highly $\beta$ stabilized
Ti alloy $\beta$-C [32]. One of the strategies to improve the endurance limit is by properly
designing a duplex aging heat treatment step compared to single aging, in order to
facilitate more uniform $\alpha$ precipitation. Duplex aging of Ti-15V-3Al-3Cr-3Sn alloy
at 250°C/24 h + 500°C/8 h resulted in a microstructure almost free of GB$_\alpha$, and this
was also reported as one of the important reasons for the notable increase in fatigue
life in high cycle regime after duplex aging [34]. Presence of GB$_\alpha$ supports the
intergranular fracture and reduces the ductility of the material [25, 28, 49, 50]. In
aged Ti-10V-2Fe-3Al, soft zones were observed along the grain boundaries due to
the GB$_\alpha$; these zones preferentially undergo plastic deformation upon loading [51].
Moreover the fractographic studies have revealed the presence of a band of intense deformation originating from the grain boundary triple point and spreading into the grain interior. This was ascribed to the accommodation deformation required for continuous GB$_\alpha$, which has been stopped at triple point leading to high localized stress concentrations.

6. Precipitation-free zones (PFZs)

Non-uniform distribution of precipitates can occur during certain heat treatment conditions forming regions in microstructure free of precipitates usually near proximity of grain boundary. Uneven precipitation of $\alpha$ upon certain aging conditions may result in such zones where precipitation will not occur, and such zones are termed as precipitation-free zones (PFZs). The preferential $\alpha$ phase nucleation along beta grain boundaries can result in depletion of solute atoms near grain beta boundary region eventually resulting in the formation of PFZs. The hardness of this PFZ is less than the precipitation-hardened surrounding matrix. Hence, PFZs act as sites for strain localization during loading and reduce the tensile strength and ductility as the strength difference between PFZs and aged matrix is higher [34, 50]. In the case of fatigue loading, the presence of PFZs can act as crack nucleation sites imposing a deleterious effect in Ti-3Al-8V-6Cr-4Mo-4Zr [33] and Ti-15-3 [34] by slip localization leading to early crack initiation. To avoid the formation of PFZs and to improve the monotonic and fatigue loading behaviour, duplex aging is developed; results are promising [32–34].

7. Intermediate phases

The intermediate phases, such as isothermal $\omega$ phase and $\beta'$ phase, are formed during low-temperature aging, with the aging temperature generally in the range of 200–450°C [3]. Moreover, the omega phase can also form athermally. The $\omega$ phase provides nuclei for the $\alpha$ precipitation in the subsequent high-temperature aging (second step of duplex aging), thereby promoting the finer and homogenous distribution of the $\alpha$ phase [3]. The above statement is proven in Ti-7333 near beta alloy, isothermal $\omega$ phase formed during aging has assisted the precipitation of the $\alpha$ phase in the beta matrix [52]. During the first step of the dual-step aging of Ti-5Al-5Mo-5V-3Cr-0.3Fe, ~10% volume fraction of $\omega$ phase was reported by Coakley et al. [53] and this $\omega$ phase contributed to a ~15% hike in microhardness compared to the solution-treated or quenched sample. However, the $\omega$ phase leads to the embrittlement/loss of ductility in Ti-Mo alloys due to the inhomogeneous slip distribution caused by the interaction of dislocation and $\omega$ phase/particles upon deformation [54]. Researchers also reported $\omega$ precipitation during low-temperature aging of Ti-15-3 alloy [7, 34]. However, the embrittlement effect of the $\omega$ phase could be efficiently compensated by processing to realize fine $\beta$ grains [51]. Researchers also reported dynamic precipitation of $\omega$ phase under cyclic loading condition [55].

Similarly, stress-induced $\omega$ phase is observed in a metastable beta alloy during the dynamic compression deformation [56]. The $\omega$ phase is hexagonal in leaner beta alloys and trigonal in heavily stabilized beta alloys [56]. Other than the $\omega$ phase, the metastable phase $\beta'$ forms as an intermediate phase during the aging of some beta Ti alloy. $\beta'$ phase with a BCC crystal structure forms if the distortion is less due to the higher concentration of alloy. Similarly, $\omega$ phase with hexagonal crystal structure forms when the distortion in BCC lattice is higher, which is the case with less

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concentrated alloys [27]. In line with the preceding discussions, isothermal $\omega$ is proven to be assisting the alpha nucleation in the Ti-20V [57]. In addition to $\omega$ phase, $\alpha'$ (martensite) phase was also observed in the initial microstructure of the solution-treated Ti-10V-2Fe-3Al and the author reported that stable $\alpha$ could be formed from this $\alpha''$. This is in addition to the $\omega$ phase serving as the nucleus for $\alpha$ formation upon aging [58]. The intermediate martensitic phases $\alpha'$ and $\alpha''$ are suppressed when alloying is done with sufficient beta stabilizer content. This leads to enhancement of the hardenability of the beta alloy [4].

8. Annealing

In general, annealing is performed to eliminate the deleterious residual stress (stress-relieving annealing) and to ease the fabrication process (recrystallization annealing). Schematic representation of the beta alloy and alpha-beta alloy microstructure in annealed condition is shown in Figure 3.

Deleterious tensile residual stresses are induced during various thermo-mechanical processing steps and fabrication techniques like welding. Sources of residual stresses are given in Table 2.

The residual stress gets superimposed on to the service stress, leading to a significant reduction of the life of the component. For example, Ti-5Al-5Mo-5V-3Cr metastable beta alloy was subjected to the stress-relief annealing at 650–750°C for 4 h followed by air cooling [24]. Stress-relief annealing is an intermediate step of thermo-mechanical processing. This annealing is not meant for altering the microstructure. Hence, extreme care should be taken to select the temperature and time combination (i.e., higher temperature annealing should be performed for a shorter time and lower temperature annealing should be performed for a longer time). Post

| Treatment/processes | Remarks                                      |
|---------------------|----------------------------------------------|
| Aging               | Solid-state reactions such as precipitation, phase transformation |
| Quenching           | Non-uniform thermal expansion or contraction |
| Fabrication         | Grinding, polishing, milling, and welding    |

Table 2. Sources of residual stresses.

![Figure 3](image-url)  
*Schematic representation of typical (a) beta (β) alloy and (b) alpha-beta (α-β) alloy microstructures in annealed condition.*
heat treatment, oil/water quenching will not be carried out to avoid insidious residual stress formation. In metastable beta alloys, mostly the heat treatment procedure generally starts with solution treatment and this is followed by aging. In solution treatment, quenching is performed and unwanted residual stresses will get induced due to non-uniformed thermal expansion. Often, the stress-relieving annealing is combined with aging, as the temperature involved is about the same. For example, in Ti-10V-2Fe-3Al, isothermal aging at 495 and 525°C for 8 h leads to precipitation (age hardening) as well as relief of the stresses induced during the solution treatment [24]. In addition to the stress-relieving annealing, recrystallization annealing is also performed to enhance the fabricability of beta titanium alloys, more specifically, if a significant reduction in cross-section is involved, for example sheet formation [4]. Cold workability of Ti-15V-3Cr-3Al-3Sn and Ti-7Mo-5Fe-2A alloys is notably increased by the annealing treatment [59]. In variance to the foregoing discussion, annealing does not increase the cold workability of the Ti-5Mo-5V-5Al-1Fe-1Cr (VT-22) and Ti-7V-4Mo-3Al (TC6) [59]. Cold working is directly related to the formation of sub-grain and cell structure. Little or no influence of the annealing on the cold workability of VT22 and TC6 is attributed to the poorly defined sub-grain and cell structure [59].

9. Mechanical properties influenced by heat treatment

9.1 Tensile, microhardness, and impact properties

The volume fraction of the beta phase in solution-treated alloy plays an important role in determining the tensile strength achieved through heat treatment process [60]. The optimum combination of tensile strength and ductility could be achieved through adequate knowledge of the aging temperature and holding time. For example, in Ti-3.5Al-5Mo-6V-3Cr-2Sn-0.5Fe beta alloy, aging at 440°C for 8 h leads to the peak strength of 1697 MPa with 5.6% of ductility. On the other hand, with the same holding time (8 h), 18% ductility along with a considerable decrease in the tensile strength is obtained by increasing the aging temperature to 560°C; the difference is attributed to the variation in the size of the acicular α precipitates [28]. The influence of aging on Young’s modulus and ductility of Ti-15-3 alloy was clearly brought out by Naresh Kumar et al. [23]. Hardenability of the beta Ti alloy is proportional to the content of the beta stabilizer. For example, the beta alloy Ti-5Al-2Sn-2Zr-4Mo-4Cr possesses an excellent hardenability; it can be hardened uniformly up to 150 mm of thickness [60]. Single-step aging has increased microhardness of Ti-15-3 alloy by 40% compared to the as-received/solution-treated condition [30]. In a similar way, finer precipitation kinetics associated with duplex aging process yields a higher hardness value in Ti-15-3 alloy [36]. In Ti-5Al-5Mo-5V-3Cr-0.3Fe, duplex aging (300°C/8 h + 500°C/2 h) was adopted; a ~15% increase at first stage and 90% increase at second stage in the microhardness was observed. The remarkable increase in the microhardness in the second stage is ascribed to the precipitation of α phase [53]. Aging after α + β solution treatment resulted in a considerable increase in the hardness of β CEZ alloy, but the impact property deteriorated [61].

9.2 Fatigue behavior

In beta alloys, precipitate-free zones and grain boundary α also have control over the fatigue behavior [32]. Precipitation-free zones can be a fatigue crack nucleation site and reduce fatigue life. Similarly, the presence of soft zones associated with
grain boundary $\alpha$ also reduces the resistance to fatigue crack propagation. Hence, duplex aging treatment yielding homogeneous alpha precipitation in beta grains and essential freedom from precipitation-free zone and grain boundary alpha is promising to improve the fatigue life of $\beta$ alloys. In Ti-15-3 alloy, aging at 500°C at 8 h leads to a ~24% of surge in the fatigue strength compared to the solution-treated alloy and the $\alpha$ platelets precipitated during the aging strongly influence the fatigue behavior [26]. Dual-step aging (300°C/2 h + 608°C/8 h) was found to improve the fatigue limit of Ti-5Al-5Mo-5V-3Cr by yielding a microstructure with finer and homogenous alpha precipitation [38]. In Ti-3Al-8V-6Cr-4Mo-4Zr beta alloy, duplex aging led to a loftier hike in fatigue strength and a marginal increase in the fatigue crack growth behavior [32]. Tsay et al. described the prominent influence of the aging temperature upon the fatigue crack growth rate (FCGR); they concluded that the coarser $\alpha$ platelets resulting from longer aging time resist the fatigue crack growth effectively [62]. On the other hand, with a coarser lamellar microstructure, fatigue life in high cycle regime will not be attractive [41].

10. Heat treatment of biomedical beta titanium alloys

Beta titanium alloys are appropriate materials for a wide range of biomedical applications encompassing orthopedic and dental implants, vascular stents, intracranial aneurysms and maxillofacial prostheses. In particular, metastable biocompatible beta titanium alloys have gained substantial interest in this regard and it is highly imperative to tailor the microstructure and properties of these components or devices by suitable thermo-mechanical processing route. The vast majority of the processing routes include a homogenization treatment (for an uniform microstructure without cast dendritic structures), a forming operation (hot/cold rolling or forging), solution treatment, and aging. Since the present context is focusing on heat treatment, the following section will discuss about solution treatment and aging of some relevant metastable beta titanium alloys for cardiovascular stent and orthopedic applications.

10.1 Heat treatment of beta titanium alloys for cardiovascular stent applications

Nitinol is one of the widely used materials for vascular stent applications due to its unequivocal superelasticity properties associated with a reversible stress-induced transformation. However, recently there is a growing distress related with the nitinol implant materials over nickel ion release, which can elicit nickel hypersensitivity, toxicity and carcinogenicity. These mounting concerns have stimulated intensive research for the development of Ni-free biocompatible and corrosion-resistant titanium-niobium (TiNb) based alloy systems for these applications. Titanium-niobium (TiNb) based alloy systems are capable of exhibiting superelasticity functionalities based on the allotropic transformation between parent $\beta$ (disordered bcc) phase and an orthorhombic $\alpha''$ (martensite) phase.

Compared to nitinol alloys, Ni-free TiNb alloys possess inferior superelastic properties at room temperature, particularly in terms of inadequate recovery strain (less than 4%) due to a low critical stress for slip deformation. As depicted in schematic Figure 4a, a material with superelastic property exhibits a two-stage yielding. The initial yield stress corresponds to the critical stress for inducing martensitic transformation leading to superelasticity, whereas the second yield relates to the critical stress for slip-induced plastic deformation. In the case of TiNb alloys, the apparent martensitic yield stress increases with an increase in temperature;
hence higher stresses are required to induce martensite transformation, which can be above the critical slip-inducing stress, leading to plastic deformation with no superelasticity as shown schematically in Figure 4b.

Heat treatment is an efficient strategy to improve the critical stress for slip deformation in TiNb alloys. Stable superelasticity and higher recovery strain (4.2%) were obtained by aging a Ti-26Nb alloy by a low-temperature annealing treatment (600°C) followed by aging (300°C). This was attributed to the precipitation of dense and finer \( \omega \) during aging heat treatment consequently leading to a higher critical stress for slip deformation [63]. A high-temperature, low-duration annealing (900°C/5 min) treatment on a Ti-Zr-Nb-Sn-Mo alloy exhibited nearly perfect superelasticity with a relatively high recovery strain of 6-6.2% [64, 65]. A well-developed \( \{001\} {\beta}_{<110}>{\beta} \) type recrystallization texture due to the presence of Sn resulted in these desirable large recovery strains and solid solution strengthening by Mo addition developed higher tensile strength values. It is also noteworthy to mention here that one of the drawbacks associated with thermal treatment-assisted microstructural evolution is the chemical stabilization of \( \beta \) phase (due to \( \beta \) stabilizer enrichment) adversely affecting superelastic properties. To counteract this, short-duration aging treatments have been developed, which can yield ultra-fine grain \( \beta \) grains (1–2 \( \mu \)m) with concurrent improvement in superelastic properties [66].

10.2 Heat treatment of beta titanium alloys for orthopedic implant applications

The usage of beta titanium alloys for orthopedic implants can be attributed to their inherent biocompatible compositions and lower elastic modulus values compared to conventional orthopedic materials. Compared to conventional CP titanium and Ti-6Al-4V, beta Ti alloys exhibit lower modulus values reducing clinical complications associated with stress shielding. Solution treatment in beta phase often results in a retained beta phase along with non-equilibrium omega (\( \omega \)) or martensitic (\( \alpha'' \)) phase precipitation. As a lower elastic modulus is essential for reducing the clinical complications associated with bone tissue resorption, these metastable phases play a predominant role in determining the implant efficacy. Among these, omega phase precipitation is associated with an increase in strength, reduction in ductility, and in most instances an undesirable increment in modulus values. Moreover, in the case of solution-treated and aged condition, volume fraction, size, and morphology of \( \alpha \) precipitates are dependent on \( \omega \) precipitation. In contrast, orthorhombic \( \alpha'' \) martensite or hexagonal \( \alpha' \) in a beta matrix can significantly reduce modulus values, improve the ductility, even though with a corresponding reduction
in strength. Compared to the low-strength solution-treated conditions, cold working/oxygen content increase/subsequent aging can result in strengthening associated with $\omega$ and/or $\alpha$ precipitation. For example, aging of low-modulus biomedical ternary alloys (Ti-35Nb-7Zr-5Ta and Ti-29Nb-13Ta-4.6Zr) in the temperature range of 300–400°C induced $\omega$, 400–475°C $\omega$-$\alpha$ mixture, and high temperature aging above 475°C revealed $\alpha$ precipitation without any $\omega$ [67, 68]. It should also be taken into account that an increased oxygen content in these alloys suppressed $\omega$ formation while promoting $\alpha$ precipitation.

Heat treatment of newly designed Sn-based $\beta$ titanium alloys (Ti-32Nb-2Sn and Ti-32Nb-4Sn) exhibited a single $\beta$ phase microstructure after solution treatment at 950°C for 0.5 h followed by quenching; subsequent aging resulted in alpha phase precipitation [69]. Higher aspect ratio of precipitated alpha led to age hardening after aging at 500°C for 6 h; aging at 600°C, on the other hand, detrimentally affected mechanical properties due to matrix softening and relatively coarser alpha precipitates. The presence of Sn even in smaller amounts can suppress the $\omega/\alpha''$ precipitation. The abrasion resistance of Ti-10V-1Fe-3Al ($\beta_{\text{trans}} = 830^\circ$C) and Ti-10V-2Cr-3Al ($\beta_{\text{trans}} = 830^\circ$C) was investigated under different microstructures established by various heat treatments [70]. $\alpha + \beta$ solution treatment resulted in near spherical or rod-like $\alpha$, $\beta$ annealing led to metastable $\beta$ grains and acicular martensite phase, $\beta + (\alpha + \beta)$ produced flake $\alpha$ phase or Widmanstatten $\alpha$ phase and aging at a low and medium temperatures generated high density of nano $\omega$ phase precipitates. This study concluded that a dual phase mixture of $\beta$ and flake-shaped alpha is an appropriate microstructure for improving the abrasion resistance.

11. Conclusions

Metastable beta titanium alloys have exclusive properties like the ease of fabrication, excellent biocompatibility, and good corrosion resistance. Hence, a steady progress has been there in the application of these alloys in aerospace industries and other high-technology industrial segments. Metastable beta titanium alloys are evolving as a potential candidate even for biomedical and automotive industries. As the $\beta_{\text{trans}}$ temperature of the metastable beta alloys is significantly lower when compared to $\alpha$ and $\alpha + \beta$ alloys, the cost of processing is considerably lower. Possibility of tailoring the properties through heat treatments based on the requirement is an important and outstanding property of the metastable beta titanium alloys. However, sound knowledge in the process-structure–property correlation is required. Heat treatments should be designed appropriately to avoid embrittlement due to intermediate phases such as $\omega$ and premature failure due to the grain boundary alpha (GB$_\omega$). In this chapter, we have attempted to provide insights into the heat treatment of metastable beta titanium alloys and optimization of the heat treatment parameters to achieve maximized material performance under monotonic and cyclic loading conditions.

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