Article

Examination of Novel Titanium-639 Alloy as a Means of Balancing Strength and Ductility through Molybdenum Addition Rather than Prolonged Aging Heat Treatment

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Abstract: Manufacturing titanium alloys with simultaneous enhancement in strength and ductility has motivated extensive research into various strategies for regulating the arrangement and texture of α and β phases. The present study explores a novel α + β titanium alloy, TIMETAL 639 (Ti-639), produced by replacing a portion of vanadium in Ti-64 with molybdenum. The low diffusivity and β-stabilizing effects of molybdenum help retain bimodal characteristics within solution heat-treated Ti-639 microstructures. EBSD and TEM were used to examine β-phase evolution after thermal processing and recrystallization of new globular α grains within pre-existing colonies in a depleted bimodal microstructure. These depleted bimodal colonies in solution heat-treated Ti-639 also led to lower misorientation spreads and dislocation densities within neighboring primary α grains. Quasi-static compression along the plate normal direction demonstrated the ability of the depleted bimodal microstructure to simultaneously enhance strength and ductility in Ti-639 (~90 MPa stronger, ~6% higher failure strain) versus identically processed Ti-64. Only one solution heat-treatment step (1 h at 900 °C) is needed to achieve these properties in Ti-639, whereas comparable properties in Ti-64 required prolonged aging heat treatment (24 h at 600 °C) after the same solution heat-treatment step, making Ti-639 a viable α + β alloy candidate.

Keywords: Ti alloys; recrystallization; EBSD; microstructure formation mechanism; misorientation

1. Introduction

Owing to their attractive specific strength and high temperature properties as compared to steels, titanium alloys, notably α + β and metastable β grades [1], fulfil a niche market in aerospace applications [2–4]. Simultaneous enhancement of strength and ductility in titanium alloys is a compelling driving force for diminishing weight and improving energy efficiency [5–11]. This, however, is an arduous task due to the notorious trade-off between strength and ductility owing to the presence of the low-symmetry hexagonal close-packed (HCP) α phase and body-centered cubic (BCC) β phase in most commercial alloys [12]. The arrangement of α and β phases, [13,14] along with the crystallographic texture of the HCP α phase, [15–17] are key aspects in the optimization of the trade-off between strength and ductility [18,19]. These microstructural parameters are chiefly regulated by the manufacturing history and chemical composition of the alloy [20]. The optimization of mechanical properties in light of the strength-ductility trade-off is therefore attainable by manipulating the microstructure through appropriate manufacturing processes and heat treatment protocols [21–24].
Microstructure morphologies of titanium alloys can largely be classified into Widmanstätten, equiaxed, and bimodal microstructures [25–28]. Widmanstätten microstructures are capable of delivering enhanced creep strength and fracture toughness along with superior resistance to crack propagation [29,30], while equiaxed microstructures [31–33] can enhance strength, elongation, and resistance to fatigue crack initiation. Bimodal microstructures, however, consist of equiaxed primary \( \alpha \) grains surrounded by colonies of \( \beta \) and secondary \( \alpha \), delivering an optimal balance of strength, ductility, creep, and fatigue [34–36].

Alloy design strategies to promote bimodal microstructures in titanium alloys require successive processing steps in the \( \beta \) and \( \alpha – \beta \) regimes [37,38]. Forging in the \( \beta \) domain encourages the formation of coarse lamellar microstructures that can be further deformed in the \( \alpha – \beta \) domain to generate a bimodal microstructure [39–41]. Maintaining a certain level of ductility while promoting strength can be achieved if heat treatment is conducted in the \( \alpha – \beta \) field to produce a final microstructure of refined globular \( \alpha \) in a matrix of transformed \( \beta \) [41–44]. Such bimodal microstructures have been correlated with shorter effective slip lengths [39,45], greater resistance to adiabatic shear band (ASB) formation [46,47], and higher energy absorption, when compared to equiaxed and lamellar microstructures. The key microstructural parameter to achieve these enhanced mechanical properties is a fine \( \beta \) grain size, leading to diminished colony size during processing [39,48]. Among the currently used \( \alpha + \beta \) titanium alloys, Ti-64 (\( \alpha + \beta \), 6.0 Al, 4.0 V, balance Ti) has received significant attention, given that it accounts for over 50% of all industrially applied titanium alloys by weight [49]. Some key applications include pressure vessels, blades and discs of aircraft turbines and compressors, and surgical implants [50–53]. These alloys show a good balance between physical, mechanical, and corrosion-resistant properties compared to commercial-purity titanium and other titanium alloys [54,55].

Most optimization methods for the enhancement of mechanical properties of Ti-64 and other \( \alpha + \beta \) titanium alloys have relied on manipulation of the main microstructural features such as the sizes of equiaxed \( \alpha \) grains, the presence of continuous \( \alpha \) layers at \( \beta \) grain boundaries, and the sizes of individual \( \alpha \) lamellae [56].

These approaches aim to enhance mechanical properties by utilizing solid-state phase transformations to manipulate the functional characteristics of alloys. Alternatively, the regulation of mechanical properties can be achieved using the combined effects of alloying additions and thermal processing in order to adjust the stability and mechanical behavior of the two phases, both individually and as parts of various microstructural arrangements [18].

The present work studies Ti-639 [57] as a new titanium alloy candidate and examines the effectiveness of a composition-driven strategy in establishing a cost-effective heat-treatment protocol for property enhancement without prolonged aging treatments. The strategy aims to adjust the morphology and texture of \( \alpha \) and \( \beta \) phases, preserving and refining the initial bimodal microstructure. A process-structure-property approach is used to correlate heat-treatment processes and the resultant microstructures using EBSD and TEM analyses, with emphasis on microstructure evolution within the \( \alpha + \beta \) colonies as well as the subsequent effects on compressive performance. In addition, the beneficial effects of the introduction of molybdenum and the adoption of a bimodal microstructure in Ti-639 are contrasted against its widely prevalent Ti-64 counterpart after identical processing.

2. Materials and Methods

The starting materials for heat treatment and analysis were supplied by TIMET [58] and consisted of plates of aerospace grade Ti-64, as well as novel Ti-639 alloy (\( \alpha + \beta \), 6.5 Al, 1.7 Mo, 1.7 V, 0.3 Si, balance Ti) as a relatively new member of the \( \alpha + \beta \) family of titanium alloys [59–62]. Compared to the more commonly used Ti-64, Ti-639 contains a slightly greater amount of aluminum. More notably, a portion of the vanadium is replaced by molybdenum. The objective of synthesizing Ti-639 is to create an alloy that exceeds the strength of Ti-64 while paying the small weight penalty of a 1% increase in density, due to molybdenum’s higher atomic mass. Ti-64 also sees notable use in biomedical applications [63–66] owing to its good corrosion resistance. The introduction
of molybdenum to the alloy composition would not deter the use of the new alloys in similar applications, as molybdenum is also regularly used in biomedical implants due to being relatively biocompatible with low cytotoxicity [67–69]. In addition, molybdenum is a micronutrient found in both plants and animals, and almost all soils globally contain some concentration of molybdenum [70]. Molybdenum is commonly used as a component in refractory metal alloys owing to its resilience at high temperatures [71–75], and the usage of Ti-639 at similar service temperatures to Ti-64 may be acceptable, though beyond the scope of the present study. At the time of submission, the price of molybdenum is ~USD 58/kg [76] while that of vanadium is USD 140/kg [77]. As such, going from 4% vanadium in Ti-64 to 1.7% vanadium + 1.7% molybdenum in Ti-639 can lower the cost of β-stabilizing additives by up to 40% for applications where Ti-639 is deemed appropriate.

The Ti-64 and Ti-639 plates were hot rolled to a final thickness of 0.5 inches, henceforth labeled the as-received condition. Due to limited availability of Ti-639 material, compression was chosen as the preferred method of assessing the mechanical performance of both alloys. Two batches of cylindrical compression samples (0.25 in. diameter, 0.25 in. height) were produced using electrical discharge machining (EDM) with the loading axes oriented along the plate in the normal and rolling directions.

Heat treatment of the compression samples was performed in a muffle furnace. In order to minimize oxygen uptake, the furnace chamber was purged with argon [78,79] for 30 min prior to heat treatment and maintained under a constant flow (~500 mL/min) of argon throughout the entire duration of heat treatment and cooling.

Figure 1 presents a schematic of the heat treatment protocols conducted on Ti-64 and Ti-639 in this study. To avoid the loss of the microstructure imparted during rolling, the solution heat treatment temperature was kept below the β–transus temperatures for both Ti-64 (928–941 °C) and Ti-639 (958–974 °C), as computationally determined by calculation of phase diagram (CALPHAD) methods using ThermoCalc [80] and JMatPro [81]. The temperature and time parameters for heat treatment used in the present study are based on the work of Lütjering et al. [40].

![Figure 1. Time–temperature profile for solution heat-treated and aged Ti-64 and Ti-639.](image)

To study microstructure evolution during heat treatment, samples were prepared by mounting and mechanical polishing. The samples were finished by vibratory polishing using a 0.04 µm colloidal silica suspension for 24 h, before being examined by electron backscatter diffraction (EBSD) using a Zeiss SUPRA 40 (Zeiss, Oberkochen, Germany) field-emission scanning electron microscope (FE-SEM) and analyzed with EDAX orientation.
imaging microscopy (OIM) software [82]. All EBSD scans were conducted along the plate normal direction, with the rolling direction running vertically along the scanned image.

The effects of heat treatment and microstructure modification on mechanical properties were examined through quasi-static compression using an Instron 5882 (Instron, Norwood, MA, USA) load frame. Molybdenum disulfide lubricant was used between the flat faces of the cylindrical samples and the compression platens to mitigate the effects of interfacial friction and avoid specimen barreling. To allay machine compliance effects during testing, the resultant data was processed through a modulus correction program, using a reference modulus of 113 GPa.

3. Results and Discussion

The FE-SEM micrographs in Figure 2 depict the microstructural morphologies of Ti-639 at different processing steps. To produce contrast between the constituent phases, the sample surfaces were etched using a 1% solution of ammonium bifluoride in water. Figure 2a shows that as-received Ti-639 exhibits a distinctly bimodal microstructure, consisting of prominent globular grains of primary $\alpha$ (etched in dark gray), interspersed with colonies of alternating $\alpha$ and $\beta$ lamellae (etched in light gray). Solution heat treatment of Ti-639 is accompanied by coarsening of acicular $\alpha$ and $\beta$ colonies surrounding the primary $\alpha$ grains (Figure 2b), leading to a depleted bimodal microstructure. Subsequent aging of Ti-639 results in the decay of most of the alternating colonies, with marginal retention of the lamellar characteristics (Figure 2c).

![Figure 2. Scanning electron micrographs of etched Ti-639 microstructures. Darker gray regions are primary $\alpha$ grains while lighter regions represent colonies of alternating $\alpha$ and $\beta$ lamellae. (a) As-received micrograph of fully bimodal microstructure. (b) Solution heat-treated microstructure displaying depleted bimodal colonies. (c) Aged microstructure showing major loss of bimodal microstructure. Scale bars in the bottom left correspond to 10 $\mu$m.](image-url)
Figures 3 and 4 show the inverse pole figure (IPF) maps of the α phase and the corresponding IPF contour maps for Ti-639 and Ti-64, respectively. The as-received Ti-639 in Figure 3a portrays large α regions shown in green, corresponding to the prismatic orientation of the HCP phase, also highlighted in the IPF contour in Figure 3d. By comparison, the as-received Ti-64 shows a more equiaxed microstructure, with the α grains exhibiting preferential alignment towards basal orientations (Figure 4a). Solution heat treatment leads to a certain degree of deviation from as-received texture for both Ti-639 (Figure 3b) and Ti-64 (Figure 4b). From Figures 3e and 4e, the microstructure of Ti-639 is more resistant to reorientation than Ti-64, which experiences a significant shift away from the basal-dominated as-received texture, approaching an intermediate distribution between basal and prismatic components. Prolonged aging further promotes the reorganization of grain orientations in both Ti-639 and Ti-64, as shown in Figures 3c and 4c, respectively. The IPF contours in Figures 3f and 4f further illustrate the tendency of both microstructures to drift towards intermediate orientations when supplied with sufficient amounts of temperature and time to do so.

The effect of heat treatment on mechanical properties was examined through quasi-static compression along the plate normal and rolling directions. Figure 5a,b show representative plastic true-stress true-strain curves from three tests for Ti-639 and Ti-64, respectively. Stress–strain curves for the solution heat-treated and aged microstructures compressed in the plate normal direction are accompanied by their corresponding microstructures. As-received Ti-639 has a nominal yield of about 1107 MPa, with a maximum compressive true stress of 1498 MPa occurring at a strain of 33.9% when compressed in the plate normal direction. In contrast, compression along the rolling direction showed a slight increase in yield at 1126 MPa, along with a higher maximum stress of 1529 MPa, but a marked reduction in strain to 16.4%. The significant discrepancy in mechanical performance along the two directions is due to the anisotropy induced by the preferential alignment of large prismatic primary α grains along the plate normal (Figure 3a).
The maximum stress peaks at 1561 MPa at a strain of 28.2%. A similar trend is observed.

Figure 4. Inverse pole figure (IPF) maps and corresponding contour plots obtained from electron backscatter diffraction (EBSD) depicting the progression of α phase in response to heat treatments in Ti-64. The change in the starting basal α texture is shown in (a,d) as-received, (b,e) solution heat-treated, and (c,f) further-aged states. Legend shows the orientation of the scanned surface for each sample, with the rolling direction running vertically along the image. Scale bars in IPF maps correspond to 10 μm.

Figure 5. Representative true stress–true strain curves from quasi static compression of (a) Ti-639 and (b) Ti-64 along the rolling and normal directions at various stages of processing.

When tested along the normal direction, Ti-639 shows an uptick in strength after solution heat treatment, accompanied by a decrease in ductility. This can be attributed to the reduction in the proportion of grains with prismatic texture components (Figure 3b), given that prismatic slip has the lowest critical resolved shear stress (CRSS) in α titanium [42,83]. The maximum stress peaks at 1561 MPa at a strain of 28.2%. A similar trend is observed in the case of samples compressed along the rolling direction, with a stress of 1558 MPa occurring at a strain of 11.5%. Subsequent aging results in a negligible change in yield, along with a drop in the ductility and strength, down to 1519 MPa at 25.2% in the normal direction. Conversely, the mechanical response under compression along the rolling direction shows the opposite trend, with a maximum stress of 1571 MPa at a strain of 11.8%. Both these responses further highlight the effects of texture-induced anisotropy and orientation randomization through recrystallization during the aging phase (Figure 3c,f).
For compression in the normal direction, a smaller fraction of the microstructure is oriented along the most ductile prismatic orientation. The increase in ductility along the rolling direction can also be attributed to the newly formed randomized grains, boosting the capacity of accommodating arbitrary plastic deformation.

The as-received Ti-64 samples show a significantly lower degree of anisotropy, with maximum stresses of 1402 MPa and 1396 MPa at 27.1% and 23.8% strain, when compressed along the normal and rolling directions, respectively. While relatively ductile, the strains achieved by Ti-64 in the normal direction of the as-received case are lower than those seen in Ti-639. EBSD analysis along the normal direction shows a predisposition towards basal orientations (Figure 4a,d), which while moderately ductile, do not share the low CRSS of prismatic deformation at room temperature [42]. Solution heat treatment induces reorientation away from the basal microstructure (Figure 4e), leading to a decrease in ductility along with an increase in strength for both orientations, with peak stresses of 1550 MPa at 15.5% strain in the normal direction, and 1438 MPa at 19.2% strain in the rolling direction.

Aging after solution heat treatment shows divergent results, with the rolling direction becoming stronger but less ductile at 1580 MPa and 16.6%, while the normal direction regains a portion of its ductility at 22.9% with the strength dropping down to 1473 MPa. The aged microstructure shows a significant shift of the grain orientations towards the more ductile prismatic and moderately ductile basal orientations (Figure 4f), as compared to the solution heat-treated microstructure.

To achieve a strength of 1473 MPa while accommodating a true plastic strain of 22.9% in the normal direction, the traditional Ti-64 material needed to undergo a prolonged aging step after solution heat treatment. By comparison, Ti-639 outperforms Ti-64 at 1561 MPa and 28.2% strain while only requiring solution heat treatment. This is further demonstrated by the Vickers microhardness values and converted estimations of tensile strengths [84] for these two cases, shown in Table 1 along with other experimental data.

### Table 1. Summary of quantitative microstructural, mechanical, and microhardness findings for both alloys following different processing conditions.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Processing Condition</th>
<th>Microstructure (EBSD)</th>
<th>Quasi-Static Compression (True Stress–True Strain)</th>
<th>Vickers Microhardness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Avg. Grain Size (µm)</td>
<td>Phase Fraction</td>
<td>Yield Stress (MPa)</td>
</tr>
<tr>
<td>Ti-639</td>
<td>As received</td>
<td>10.2</td>
<td>94% α-6% β</td>
<td>1107 ND</td>
</tr>
<tr>
<td></td>
<td>SHT</td>
<td>9.8</td>
<td>95% α-5% β</td>
<td>1173 1226</td>
</tr>
<tr>
<td></td>
<td>SHT + Aged</td>
<td>8.6</td>
<td>96% α-4% β</td>
<td>1186 1267</td>
</tr>
<tr>
<td>Ti-64</td>
<td>As received</td>
<td>8.2</td>
<td>98% α-2% β</td>
<td>1009 975</td>
</tr>
<tr>
<td></td>
<td>SHT</td>
<td>8.5</td>
<td>97% α-3% β</td>
<td>1195 1074</td>
</tr>
<tr>
<td></td>
<td>SHT + Aged</td>
<td>9.5</td>
<td>97% α-3% β</td>
<td>1082 1237</td>
</tr>
</tbody>
</table>

SHT = Solution Heat Treated, RD = Rolling Direction, ND = Normal Direction.

Variation in material response is linked to the grain morphologies and orientations in each case. In the as-received state, Ti-64 exhibits a primarily equiaxed microstructure, dominated by large α grains with small β regions dispersed along the grain boundaries. On the other hand, the as-received Ti-639 exhibits a bimodal microstructure, comprised of mostly prismatic large primary α grains alongside colonies of alternating lamellae of β and acicular secondary α. The improved mechanical performance of Ti-639 compared to Ti-64 is aided by the propensity of bimodal microstructures to outperform equiaxed ones, resulting in an enhanced balance of strength and ductility [85]. Furthermore, the small increase in the proportion of α-stabilizing aluminum, along with the introduction of molybdenum, caused the bimodal microstructure of Ti-639 to be less susceptible to significant alteration during solution heat treatment by decelerating the rearrangement of the pre-existing bimodal microstructure. In addition to its strengthening effect, molybdenum is also a potent β stabilizer [86] with far lower diffusivity compared to vanadium [87], the conventional...
choice for β stabilization. The formation of new α grains during heat treatment has been shown by Semiatin et al. [87] to occur at the interface between α and β grains. Therefore, β grains stabilized by molybdenum become pinned, and can serve as nucleation sites for new smaller α grains along the periphery of larger prismatic primary α grains.

As a result, the solution heat-treated microstructure has large prismatic α grains whose boundaries are now decorated with randomly oriented refined α grains. To induce greater randomization and departure from the inherited bimodal microstructure, Ti-639 would need to be heat treated for longer, as observed in the aged microstructure for Ti-639 (Figure 4c). By comparison, the absence of molybdenum in the β phase of Ti-64 makes the microstructure less resilient against significant alteration during solution heat treatment. Given that the β grains in bimodal microstructures are confined to colonies of alternating α and β lamellae, the interfaces of these colonies would serve as prime locations for nucleation of new α grains. Consequently, the newly recrystallized α grains would grow at the expense of the β lamellae that reside in the surrounding colonies.

The schematic in Figure 6a describes a mechanism for the nucleation and growth of freshly recrystallized α within a lamellar α-β colony. The process begins with a new globular α grain nucleating near the boundary of an existing lamellar colony. As the recrystallized α grain grows, it consumes the space once occupied by the lamellae and shrinks their length in the process. The presence of shortened lamellae can be used to identify specific locations within the colonies where α recrystallization took place. The scanning electron micrograph in Figure 6b highlights one such region within the microstructure of solution heat-treated Ti-639. The shortened length of the β lamella at the center of the colony is the likely result of encroachment by a recrystallized α grain.

**Figure 6.** (a) Schematic describing the shrinking of β lamella within the colony during heat treatment and (b) SEM image of a colony in solution heat-treated Ti-639 (reduction in β lamella lengths is used as a method for tracking locations of recrystallized globular α inside the colony).
Figure 7 presents EBSD data of the solution heat-treated Ti-639 sample to further investigate the presence of recrystallized α grains at the sites of shortened β lamellae. Figure 7a shows an overlaid phase and image quality map of the solution heat-treated Ti-639, while Figure 7b emphasizes the location where a previous lamellar colony now contains a more equiaxed α grain surrounded by shrunken β lamellae. Figure 7c shows a segment of the IPF map where the α grain is isolated with all its adjacent β grains. Figure 7d compares the pole figure of the α grain relative to its basal orientation of (0001) with the orientation of the surrounding β grains. The agreement of the data with the Burgers orientation relationship of (110) \parallel (0001) [88] corroborates the notion of the α grain being recrystallized within a prior colony, with the orientation being influenced by the pre-existing β.

Figure 8 shows similar analysis of the aged Ti-639 microstructure. The diminishing of β lamellae within the microstructure can also serve as a morphological correlation to estimate the extent of recrystallization in the colonies during heat treatment in the α-β temperature domain. After prolonged aging, the positions of prior colonies become populated with several newly formed α grains, while prior β grains are now confined to the peripheries of prior colonies (Figure 8a). Newly recrystallized α can be found in regions between depleted β lamellae, as demonstrated in Figure 8b. Figure 8c shows an isolated IPF map of the potentially recrystallized α grain, along with any β lamellae that share its grain boundary. Pole figure data in Figure 8d indicates that the α grain does follow the Burgers orientation relationship, confirming recrystallization and growth of the α grain within the colony during prolonged aging.

Figure 7. (a) Combined image quality (IQ) and phase map of solution heat-treated Ti-639. Red regions correspond to α, while β is colored in green. (b) Site of α recrystallization. (c) IPF map of isolated α grain with surrounding β lamellae. (d) Pole figures of isolated grains confirm that the recrystallized α grain obeys the Burgers orientation relationship (110) \parallel (0001).

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To observe the texture of the evolved α grains as a result of each of the heat treatment steps, the microstructure data from EBSD was further analyzed by partitioning the α phase using grain orientation spread (GOS), with a maximum cutoff value of 3° [89]. This partition isolates grains where the lattice has been relaxed and no longer retains a large amount of internal distortion. Relaxation can be caused by recovery within existing α grains or formation of new α grains during recrystallization. Since recrystallized grains tend to be equiaxed, a secondary partitioning step was performed using grain aspect ratio (GAR), with a cutoff value of 0.75 (here, an aspect ratio of 1 corresponds to a perfectly symmetric/equiaxed grain). The resultant crystallographic textures are depicted in Figure 9. For both heat treatments, the texture of the recrystallized portion, corresponding to partition where GOS ≤ 3° and GAR ≥ 0.75, appears to be more random, occupying largely intermediate orientations away from any of the three primary directions. By contrast, the crystallographic texture of the overall relaxed microstructure appears to be dominated by...
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![Figure 9. Inverse pole figure contours showing crystallographic textures in relaxed α microstructures due to recovery and relaxation following solution heat treatment and subsequent aging. (GOS = grain orientation spread, GAR = grain aspect ratio).](image)

Figure 10a and Figure 10b represent IPF maps of the β phase in the solution heat-treated and further-aged conditions respectively. In addition to the reduction in β lamellae due to new α grains nucleating at the interfaces, growing recrystallized α grains can also split the pre-existing β grains in their path, as reported by Semiatin et al. [87].

The solution heat-treated sample preserves some of its bimodal characteristics, highlighted by the encircled regions of successive β lamellae. In contrast, the aged microstructure showed little to no preservation of the β phase morphology. Furthermore, the aged β grains were arranged in lengths of interrupted lines with very similar grain orientations across the span. Figure 10b contains three such lengths with the corresponding unit cell orientations for each of the split segments, confirming that the segments were once part of the same β lamella. The prominence of this splitting phenomenon in the aged microstructure further compounds upon the reduction of β grains due to α recrystallization during aging.

Transmission electron microscopy (TEM) was performed to further observe the splitting of β lamellae in aged Ti-639. Figure 11a captures the interphase region in a colony at the instant of β splitting, indicating that β splitting occurs as a result of encountering recrystallized α grains that grew during prolonged aging. Figure 11b examines the distribution of molybdenum within the selected region using energy dispersive X-ray spectroscopy (EDS). Molybdenum atoms show a propensity to partition along the peripheries of the β lamella.
preferential molybdenum segregation towards the α phase in the present study), shown in Figure 12b. Notably, there is no apparent influence of rolling direction on the orientation or alignment of β lamellae as an indication of preferential molybdenum segregation towards the α phase in Ti-639 in the (a) solution heat-treated and (b) aged conditions. Solution heat-treated β grains preserve some of the lamellar β structures. Further aging leads to an increase in splitting of longer β lamellae, evident by the highlighted segments sharing the same crystallographic orientation.

Figure 11. TEM analysis of interface between α and β in aged Ti-639 showing (a) splitting of a β lamella as an α grain impinges across and (b) EDS elemental map of molybdenum demonstrating preferential molybdenum segregation towards the α-β interface.

Analysis of β lamellae on aggregate over the entire scanned domains further demonstrates the effects of this lateral impingement by α at the expense of the β lamellae. Figure 12a depicts the frequency of β lamellae as a function of their widths. The width of each lamella is defined by the minor axis diameter of the best-fitting ellipse used by OIM software. While many of the β grains with the smallest widths are lost as a result of being consumed during subsequent aging, there is little statistical change in the widths of the thicker lamellae. Further examination of the geometric orientation of these lamellae was performed using their grain shape orientations in OIM, which defines the angle between
the major axis of the best-fitting ellipse and the horizontal axis of the scan (transverse direction in the present study), shown in Figure 12b. Notably, there is no apparent influence of rolling direction on the orientation or alignment of β lamellae. Furthermore, there is also no major change in the distribution of these orientations as a function of aging, showing little additional change in the geometric characteristics of β lamellae during aging, and that the primary changes in β grains occur as a result of recovery, recrystallization, or growth in the surrounding α grains.

Figure 12. Quantitative analysis of changes in geometric characteristics of β lamellae between solution heat treatment and aging using (a) lamella width and (b) major axis orientation.

The impact of solution heat treatment is not limited to the recrystallization of new α grains within the colonies. The globular primary α grains near colonies also experience effects of α recrystallization within the colonies. In particular, globular α grains that are surrounded by significantly recrystallized colonies on multiple sides exhibit recovery of their internal structure. Highlighted in Figure 13 are several primary α grains in the solution heat-treated microstructure. Grains a and b are surrounded on three sides by prior colonies that have experienced substantial recrystallization, evident by the considerably smaller α grains amidst diminished β lamellae. On the other hand, grains c, d, and e, are
located among clusters of larger primary α grains, with the adjoining colonies being less significantly altered by recrystallization. The solution heat-treated sample was preferred for observation because some colonies retained their lamellar β microstructures while other colonies had undergone higher degrees of alteration through recrystallization. Such a microstructure allows for side-by-side analysis of adjacency effects of colonies on primary α within the same sample. To assess the extent of recovery on the isolated primary α grains, a line scan of the misorientation profile across the span of each grain was plotted. The point-to-point misorientation represents variation between successive data points along the scan line, while the point-to-origin data corresponds to the angular deviation between the current point and the first point (farthest left) on the scan line. Grains a and b show a negligible amount of accumulated point-to-first misorientation. In contrast, c, d, and e have significantly greater misorientations between opposing ends of their grains.

**Figure 13.** Misorientation profiles of α grains in solution heat-treated Ti-639. Grains (a,b) are chosen from locations bordered by colonies on three sides, while grains (c-e) are picked from regions surrounded mostly by other primary α neighbors.
The variation is attributed to the fact that recrystallization of colonies is accompanied by the relieving of stored internal stresses from the rolling process. As a result, primary α grains that are surrounded by recrystallized prior colonies now have a relaxed stress field at their boundaries, allowing for recovery to take place more easily. By comparison, grains that are less surrounded by colonies, or whose neighboring colonies have not undergone considerable recrystallization, show lower degrees of recovery, as shown by the more sizable increase in the measured misorientations.

The effects of neighboring colonies on the grain substructures can be quantitatively correlated by using the misorientation within the grain to estimate the underlying dislocation density. Table 2 lists the average misorientation angle across the span of each probed grain, the length of the line scan, and the calculated density of geometrically necessary dislocations (GND) for each grain. The average misorientation for a grain is obtained by computing the area under the point-to-origin misorientation profile using a Riemann sum before dividing the value by the length of the line scan. The formulation used to determine GND density [90] is given in Equation (1):

\[ \rho_{\text{GND}} = \frac{\alpha \cdot \theta \cdot |b| \cdot x}{L} \]  

(1)

The value of \( \alpha \) is taken to be 2, which assumes the simpler case of pure tilt misorientation, requiring only one set of edge dislocations to accommodate the misorientation [90]. The parameter \( b \) is the Burgers vector, which equals the lattice parameter ‘a’ for α titanium and has a value of 2.95 angstroms [91]. \( \theta \) and \( x \) are the angle and distance in radians and meters, respectively, which are used to approximate the lattice curvature.

<table>
<thead>
<tr>
<th>Grain</th>
<th>Avg. Misorientation (deg)</th>
<th>Length of Line Scan (µm)</th>
<th>Dislocation Density ((m^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.83</td>
<td>13.1</td>
<td>(7.5 \times 10^{12})</td>
</tr>
<tr>
<td>b</td>
<td>0.58</td>
<td>11.8</td>
<td>(5.8 \times 10^{12})</td>
</tr>
<tr>
<td>c</td>
<td>14.9</td>
<td>19.2</td>
<td>(9.2 \times 10^{13})</td>
</tr>
<tr>
<td>d</td>
<td>18.5</td>
<td>22.4</td>
<td>(9.8 \times 10^{13})</td>
</tr>
<tr>
<td>e</td>
<td>8.7</td>
<td>22.6</td>
<td>(4.6 \times 10^{13})</td>
</tr>
</tbody>
</table>

The lower dislocation densities of primary α grains located amidst recrystallized colonies in the depleted bimodal microstructure of solution heat-treated Ti-639 further confirm the lattice relaxation effects of recrystallization within the grain. This relaxation, combined with the microstructure-stabilizing effects of molybdenum, allows the solution heat-treated Ti-639 to retain a significant portion of its ductility, despite the gain in strength and nucleation of new α grains within colonies at the expense of β lamellae.

4. Conclusions

The performance of Ti-639 after solution heat treatment and subsequent aging was assessed and compared to identically processed Ti-64, with the objective of establishing Ti-639 as a viable member of the family of α + β titanium alloys. The key findings of this study can be summarized as follows:

1. The depleted bimodal microstructure of solution heat-treated Ti-639 surpassed the aged microstructure of Ti-64 in both compressive strength (1561 MPa vs. 1473 MPa) and failure strain (28.2% vs. 22.9%) along the plate normal direction. This enhanced performance was attained in Ti-639 without requiring the additional prolonged aging step necessary for Ti-64.
2. The introduction of molybdenum in place of a portion of vanadium produced a marked increase in strength in Ti-639, compared to Ti-64. Molybdenum also forestalled the deterioration of bimodal microstructures during heat treatment due to its low
diffusivity and tendency to aggregate at $\alpha$-$\beta$ interphase boundaries, as confirmed by EDS elemental mapping at the interface using TEM.

3. In solution heat-treated Ti-639, colonies displayed shortened $\beta$ lamellae due to recrystallized globular $\alpha$ grains nucleating and growing along the length of acicular $\beta$ grains. EBSD results showed that the newly formed $\alpha$ grains followed the Burgers orientation relationship $(110) || (0001)$ with neighboring $\beta$ lamellae.

4. Further aging of Ti-639 caused the recrystallized $\alpha$ grains to continue expanding. As these $\alpha$ grains tried to grow across the width of the $\beta$ lamellae, they split the $\beta$ lamellae, further compounding the deterioration of the length of $\beta$ grains. This was demonstrated through the identical crystallographic orientation of split segments which were once part of the same acicular $\beta$ grain and was corroborated through TEM imaging.

5. The effects of $\alpha$ recrystallization within colonies also extended to the existing primary $\alpha$ grains located at the peripheries of recrystallized colonies. Primary $\alpha$ grains surrounded by recrystallized colonies showed very small misorientation profiles as well as lower calculated dislocation densities, compared to primary $\alpha$ grains that are mostly bordered by other primary $\alpha$ grains.

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References


44. Tan, C.; Sun, Q.; Zhang, G. Role of Microstructure in Plastic Deformation and Crack Propagation Behaviour of an α/β Titanium Alloy. *Vacuum* 2021, 183, 109848. [CrossRef]


52. Barber, C.C.; Burnham, M.; Ojameruaye, O.; McKee, M.D. A Systematic Review of the Use of Titanium versus Stainless Steel Implants for Fracture Fixation. *OTA Int.* 2021, 4, e138. [CrossRef]


67. Fernandes, C.; Taurino, I. Biodegradable Molybdenum (Mo) and Tungsten (W) Devices: One Step Closer towards Fully-Transient Biomedical Implants. *Sensors* 2022, 22, 3062. [CrossRef]

74. Yan, J.; Lin, Y.Z.; Wang, Y.; Qiu, J.; Fan, F.; Song, C. Refractory WMoNbVTa High-Entropy Alloy as a Diffusion Barrier between a Molybdenum Substrate and MoSi2 Ceramic Coating. *Ceram. Int.* 2022, 48, 11410–11418. [CrossRef]
84. Sente Software—Home. Available online: https://www.sentesoftware.co.uk/ (accessed on 13 July 2024).

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