Titanium Alloys: Thermomechanical Treatment

Thermomechanical treatment (TMT) is commonly used to manipulate the microstructure and properties of titanium alloys. The principles of TMT are general in nature, though the detailed effects may vary from alloy to alloy. The effects of TMT on the properties of titanium alloys are especially pronounced in the case of fracture resistance. The influence of microstructure on toughness and tensile ductility tends to be inverse. This is illustrated by a representative set of data (Table 1) for Ti-6%Al-2%Sn-4%Zr-6%Mo, a high-strength titanium alloy in which this inverse trend is quite pronounced.

Although this article is largely concerned with the techniques and mechanisms of microstructural alteration by TMT, it is essential to emphasize that the principal motive for TMT is manipulation of properties. The particular processing route selected depends heavily on the intended application. For example, fracture-critical structures perform most efficiently when fabricated from materials processed to achieve high fracture toughness. Fatigue-limited structures, on the other hand, are more sensitive to crack initiation and crack growth rate. Other considerations may include the ductility required for applications involving forming or installation, in which case tensile ductility may dominate the processing selection. In general, it is not possible to optimize all these properties simultaneously.

I. Microstructural Development in Titanium Alloys

Most commercially important titanium alloys contained varying amounts of the body-centered-cube (bcc) β phase. The mechanisms and kinetics of transformation of the β phase during cooling dominate the development of titanium microstructure. The principal effect of TMT is to perturb or alter these transformation mechanisms. As a result, TMT provides an additional degree of freedom in controlling or manipulating the microstructure of this class of alloys.

It is important to understand the competition between the nucleation and growth of α phase and the martensitic decomposition of the β phase. To illustrate this point, a schematic vertical section from a titanium-aluminum-X phase diagram is shown in Fig. 1. Here X can be any β isomorphous alloying element such as vanadium, molybdenum, niobium or tantalum. If an alloy is heated above the β transus, (so that it is 100% β phase) and then cooled, the transformation product which is formed depends on the cooling rate. If it is cooled rapidly enough, the β phase transforms by nucleation and shear to a hexagonal-close-packed (hcp) martensitic product which is designated α′. If it is cooled somewhat more slowly, it transforms by nucleation and growth to a colony microstructure comprising hcp α phase and β phase. These two microstructures are shown in Figs. 2a and 2b. If the alloy is heated into the two-phase α + β region and then cooled at different rates, the transformation products which form depend not only on cooling rate but also on the solution treatment temperature. The typical range of products which

<table>
<thead>
<tr>
<th>Condition</th>
<th>Tensile strength</th>
<th>Fracture toughness Kt (MPa mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>β block, β finish, STA</td>
<td>Yield (MPa) 1050</td>
<td>Ultimate (MPa) 1200</td>
</tr>
<tr>
<td>β block, high α + β finish, STA</td>
<td>1100</td>
<td>1210</td>
</tr>
<tr>
<td>α + β block, α + β finish, STA</td>
<td>1120</td>
<td>1210</td>
</tr>
<tr>
<td>α + β block, α + β finish, STOA</td>
<td>1070</td>
<td>1140</td>
</tr>
</tbody>
</table>

Table 1
Typical properties of Ti-6%Al-2%Sn-4%Zr-6%Mo alloy
Figure 1
Schematic vertical section of Ti-Al-X phase diagram (where X is Mo or V), showing the composition dependence of the $M_s$ temperature and the constitution which results from quenching from a range of solution treatment temperatures.

The phase diagram can be formed on quenching from various solution treatment temperatures are shown on the right-hand side in Fig. 1. It should be noted that $\alpha''$ is a second type of titanium martensite having an orthorhombic structure, which tends to form from $\beta$ phase compositions rich in $\beta$ stabilizers.

The competition between the mechanisms of nucleation and growth and of martensitic decomposition of the $\beta$ phase is best illustrated using a continuous cooling transformation (CCT) diagram as shown schematically in Fig. 3a. It can be seen that nucleation and growth “C” curve is intersected during slower cooling, whereas it is bypassed during rapid cooling (quenching), in which case martensite is formed. An important additional factor introduced by mechanical working, which is shown schematically in Fig. 3b, is the acceleration of the $\beta$ decomposition kinetics due to the continuous introduction of heterogeneous $\alpha$ phase nucleation sites. This has the result of broadening the nucleation and growth curve and shifting it to the left (toward the zero time axis). Thus, one effect of TMT is to increase the rate at which the $\beta$ phase decomposes by nucleation and growth.

2. Effect of Mechanical Working (TMT) on Microstructure

The mechanical working of titanium alloys for the purpose of TMT is usually accomplished by hot rolling or hot forging. Other working operations such as extrusion or spinning also can be used for this purpose. It is important to control the deformation rate at any particular temperature to achieve the desired microstructure. The principal effect of working is to alter the morphology of the primary $\alpha$ phase.

Such alterations are shown in Figs. 4a and 4b. To understand the effect of TMT, the globular and elongated $\alpha$ phase should be compared with the platelike $\alpha$ formed by nucleation and growth in the absence of mechanical work. Fig. 2b. The morphological change observed in the mechanically worked alloys is the result both of the formation of $\alpha$ phase by nucleation and growth in the early stages of working and of the effect of subsequent plastic deformation of this $\alpha$ phase during subsequent working. Such plastic deformation of the $\alpha$ phase leads to its recrystallization and globularization, as can be seen in Fig. 4.

The extent to which the $\alpha$ phase morphology is
changed depends directly on the amount of plastic work, which in turn depends on the strain rate and temperature. The strain rate and temperature at which the plastic working is done are critical because there is a dynamic competition between in situ recovery and the storage of plastic work which will subsequently drive the recrystallization reaction. Because the rate of this recovery process decreases with decreasing temperature, smaller amounts of work at lower temperatures can have the same effect as larger amounts at higher temperatures. In other words, the occurrence of this recovery reaction means that there is not usually a unique combination of temperature and time to produce a given microstructure.

In alloys with higher concentrations of β stabilizing elements, the kinetics of the nucleation and growth reaction tend to be slower. As a result, appreciable competition develops between heterogeneous nucleation of α at prior β grain boundaries and intragranular nucleation of α. This competition often results in a continuous or semicontinuous layer of grain boundary α in alloys which have been subjected to thermal treatment alone. The resulting grain boundary α has a deleterious effect on properties, especially tensile ductility. An important benefit of TMT, as previously mentioned, is the acceleration of the nucleation and growth kinetics for intergranular α nucleation. This becomes a useful means of reducing the tendency to form the grain boundary α phase. Moreover, mechanical working tends to break up and recrystallize grain boundary α making it less continuous and less deleterious to properties.

Thus it is clear that the working temperatures and amounts of plastic work appropriate to the production of a given microstructure depend on the alloy composition and must be closely controlled for some types of alloy. For example, strict control over the processing history is important in heavily β-stabilized
A limiting example of this is provided by the metastable β alloys such as Ti-10%V-2%Fe-3%Al. These alloys, α-β working to avoid grain boundary is essential if good tensile ductility is to be obtained. Examples of grain boundary α and an α-β worked structure which can be obtained in Ti-10%V-2%Fe-3%Al are shown in Figs. 5a and 5b.

![Micrographs showing grain boundary α and α-β worked structure](image)

**Figure 5**
Light micrographs showing (a) globular primary α and (b) grain boundary α in the metastable β alloy Ti-10%V-2%Fe-3%Al

3. Effects of Post-TMT Thermal Treatment on Microstructure

Depending on the details of the time, temperature and strain combination in the TMT cycle, the recrystallization and/or recovery processes which occur simultaneously may or may not go to completion. In any case, it is desirable to finish the TMT at low enough temperatures and with sufficient deformation to leave a considerable amount of residual dislocation damage in the material. In such cases, the microstructure can be further altered by thermal treatment after the TMT has been completed. A particular example of this is the subsequent annealing of hot-worked plate after rolling operations have been completed. Figures 6a and 6b illustrate the as-worked structure of Ti-6Al-4V and the recrystallization that has occurred during subsequent annealing. Attendant on this annealing is a substantial improvement in fracture toughness.

To ensure that the recrystallization is complete, heating high into the α + β phase field is necessary. To produce a large volume fraction of globular α, the cooling rate following this high α + β annealing operation must be carefully controlled and relatively slow.

![Micrographs showing recrystallization](image)

**Figure 6**
Light micrographs showing the effect of recrystallization on α morphology in Ti-6%Al-4%V: (a) as hot-worked; (b) given a recrystallization anneal in the α + β region and slowly cooled.
slow. During slow cooling, the α phase regrows epitaxially, whereas separate nucleation and growth of Widmanstätten α in the remaining metastable β phase occurs during cooling at higher rates. Figures 6b and 7 illustrate these microstructural differences. The essential feature is the diffusion length for the outward diffusion of titanium from the β phase during the regrowth of the primary α. If the cooling rate is too high, sufficient undercooling develops for separate nucleation of α within the β regions.

![Figure 7](image1)  
**Figure 7**  
Light micrograph of Ti–6% Al–4% V showing that increased cooling rate from an annealing treatment in the α + β region leads to nucleation of an α + β platelet structure between elongated primary α particles.

Finally, it is important to mention the relationship between the finishing temperature of the TMT operation and the final annealing temperature. If a high volume fraction of globular primary α is desired, the working operation must be finished at a lower temperature than any subsequent annealing operations. That is, once the TMT has ceased during mechanical working in a falling temperature regime, normal nucleation and growth rapidly take over. Thus, relatively coarse Widmanstätten α plates can be interspersed between the globular primary α in the cases where the TMT has been finished at a relatively high temperature in the α-β phase field. The result of this is the so-called duplex or triplex microstructure, in which globular primary α and relatively coarse Widmanstätten α are mixed. An example of a triplex microstructure is shown in Fig. 8. This structure has coarse Widmanstätten α which is formed during cooling after the working operation. Reheating and slow cooling typically do not increase the globular primary α phase volume fraction at the expense of this coarse Widmanstätten α. If very slow cooling rates are used, the globular α grows epitaxially at the expense of the Widmanstätten α, but the resulting primary α grain size is coarse, leading to degradation of a variety of properties. Thus, α alloys which are processed to achieve a high volume fraction of equiaxed primary α, it is important to finish the TMT operation at a relatively low temperature.

4. Effects of TMT on Preferred Orientation (Texture)

Because of the hexagonal structure of the α phase, appreciable anisotropy of properties can be developed in titanium alloys if the α phase has a significant preferred orientation. This preferred orientation manifests itself as directionality in properties, such as modulus, tensile ductility and yield stress, as well as many of the fracture-related properties. The detailed effects of TMT temperature, time and strain on texture are complicated. It is, however, important to mention the presence of texture in most hot-worked products because of its effect on properties. It is also important to note that there seems to be an effect of processing method on the resulting texture. That is to say, uniaxial deformation such as plate rolling produces textures different from those obtained by axisymmetric flow (forging) under the same conditions of time, temperature and strain. Therefore, the texture to be expected is not only very sensitive to working temperature and amount of strain but is also very sensitive to working methods. As a result, users of titanium products which have been subjected to TMT cycles should be aware of the important effects of texture on properties and should allow for such effects in cases where this could make a significant difference in the performance of the material.

*See also:* Titanium: Properties; Titanium and Titanium Alloys: Selection

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highly corrosion-resistant and suitable for medical applications, but widespread usage has been limited to commercially pure titanium and Ti–6%Al–4%V.

The term commercially pure (CP) titanium is applied to unalloyed titanium and designates several grades containing minor amounts of impurity elements, such as carbon, iron and oxygen. The amount of oxygen can be controlled at various levels to provide increased strength. The compositions and properties of the four grades of CP titanium listed in Table 1 illustrate this.

Table 1
Chemical composition (wt%) and minimum mechanical properties of CP titanium

<table>
<thead>
<tr>
<th>Grade</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
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<tbody>
<tr>
<td>Nitrogen, max.</td>
<td>0.03</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Carbon, max.</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Hydrogen, max.a</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Iron, max.</td>
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<td>0.20</td>
<td>0.30</td>
<td>0.50</td>
</tr>
<tr>
<td>Oxygen, max.</td>
<td>0.18</td>
<td>0.25</td>
<td>0.35</td>
<td>0.40</td>
</tr>
<tr>
<td>Titanium</td>
<td>bal.</td>
<td>bal.</td>
<td>bal.</td>
<td>bal.</td>
</tr>
<tr>
<td>Yield strength (MPa)</td>
<td>170</td>
<td>275</td>
<td>380</td>
<td>485</td>
</tr>
<tr>
<td>Ultimate strength (MPa)</td>
<td>240</td>
<td>345</td>
<td>450</td>
<td>550</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>24</td>
<td>20</td>
<td>18</td>
<td>15</td>
</tr>
</tbody>
</table>

a Value for bar products 0.0125, for flat products 0.015

The microstructure of CP titanium is essentially all α titanium (hexagonal-close-packed crystal structure) with relatively low strength and high ductility. The material may be slightly cold-worked for additional strength, but cannot be strengthened by heat treatment.

The addition of aluminum to titanium stabilizes the α phase, while vanadium addition stabilizes the β phase (body-centered-cubic structure). The combination of 6% aluminum and 4% vanadium enables both allotropie modifications to exist at room temperature; therefore, this alloy is classified as a two-phase α–β material. The alloying additions also contribute to increased strength by solid-solution strengthening mechanisms. The complex metallurgical transformations, as well as the relative amounts of α and β phases present in the material, can affect the mechanical properties. For applications where high strength and fatigue resistance are required, the material is annealed. The annealed microstructure corresponds to a uniform distribution of the α and β phases as illustrated in Fig. 1. A coarse α network may embrittle the material and is carefully avoided. Similarly, heat-treated or transformed material is not used, because the slight gain in tensile strength is offset by a reduction in fracture toughness.

The chemical composition of the material selected

I. Physical Metallurgy

Titanium was a laboratory curiosity until 1946, when Kroll developed a process for commercially producing titanium by reducing titanium tetrachloride. Since that time, the availability of titanium has prompted much work on the development of new and improved alloys as well as extensive evaluations of the properties of some 20 alloys. Medical researchers evaluated commercially pure titanium and Ti–6%Al–4%V alloy and found them to be outstanding materials for surgical implant applications. Several other alloys were also found to be