

# HEAT TREATING TITANIUM AND ITS ALLOYS

*How to ensure success in stress relieving, annealing, solution treating and aging, and other heat processing operations.*

*The overview is based on a chapter in the author's new ASM book, Titanium: A Technical Guide.*

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**T**itanium and titanium alloys are heat treated for several reasons:

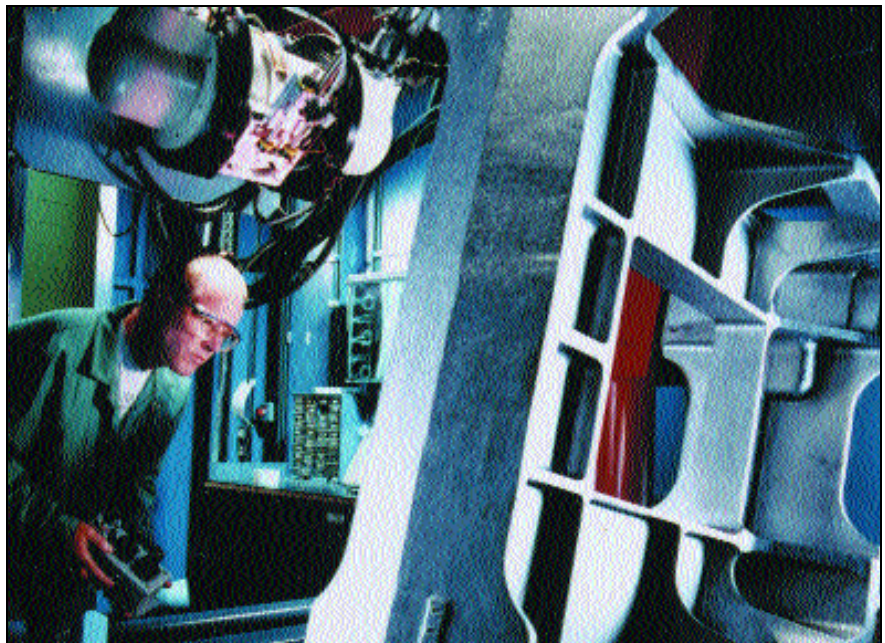
- To reduce residual stresses developed during fabrication (stress relieving)
- To produce the most acceptable combination of ductility, machinability, and dimensional and structural stability, especially in alpha-beta alloys (annealing)
- To increase strength by solution treating and aging
- To optimize special properties, such as fracture toughness, fatigue strength, and high-temperature creep strength

Stress relieving and annealing may

be used to prevent preferential chemical attack in some corrosive environments, to prevent distortion, and to condition the metal for subsequent forming and fabricating operations. Hot isostatic pressing, a specialized heat treatment process (Fig. 1 and 2), can help narrow the fatigue property scatter band and raise the minimum fatigue life of cast components.

Typical stress relieving, annealing, and solution treating and aging cycles are given in the Datasheet in this issue of *Heat Treating Progress*. Beta transus temperatures for commercially pure (CP) titanium and selected titanium alloys also are included.

## Response to heat treatment



*Fig. 1 — Aft engine mount bulkhead for the Pratt & Whitney-powered Boeing 777 aircraft is the first cast titanium alloy component to be used in a fracture-critical aerospace application. It replaced a fabricated assembly after passing a series of FAA-mandated static tests last year. The substitution was enabled by technical developments in the investment casting process combined with advanced hot isostatic pressing (HIP) techniques. Photo courtesy of Howmet Castings.*

The basic alpha, near-alpha, alpha-beta, and beta alloys have heat treatment responses attuned to the microstructure (phases and distribution) that can be produced, which is a function of chemical composition.

**Alpha, near-alpha:** Because alpha alloys undergo little in the way of phase change, their microstructure cannot be manipulated much by heat treatment. Consequently, high strength cannot be developed in the alpha alloys by heat treatment. However, some near-alpha alloys, such as Ti-8Al-1Mo-1V, can be solution treated and aged to develop higher strengths. Both alpha and near-alpha titanium alloys can be stress relieved and annealed.

**Alpha-beta:** The alpha-beta alloys make up the largest class of titanium alloys. Microstructures can be substantially altered by working (forging) and/or heat treating them below or above the beta transus. Compositions, sizes, and distributions of phases in these two-phase alloys can be manipulated within certain limits. As a result, alpha-beta alloys can be hardened by heat treatment, and solution treating plus aging is used to produce maximum strengths. Other heat treatments, including stress relieving, also may be applied to these alloys.

**Beta alloys:** In commercial (metastable) beta alloys, stress relieving and aging treatments can be combined. Also, annealing and solution treating can be identical operations.

**Beta transus:** The beta transus temperature (Datasheet, Part 1) of a titanium alloy — the minimum temperature above which equilibrium alpha phase does not exist — is very significant for heat treating purposes, especially when the heat treatment involves heating near or above this temperature.

When the heat treatment temperature is near the beta transus, the transus of each heat in a lot must be accurately determined, because the value will vary from heat to heat due to small differences in composition, particularly oxygen content. Titanium producers generally certify the beta transus for each heat they supply.

Note that hardness testing is not recommended for checking the effectiveness of heat treating titanium alloys. The correlation between strength and hardness is poor in these materials. Whenever verification of a property is required, the appropriate mechanical test should be used.

### Stress relieving of titanium

Stress relieving is probably the most common heat treatment given to titanium and titanium alloys. It is used to decrease the undesirable residual stresses that result from nonuniform hot forging deformation, nonuniform cold forming and straightening, asymmetric machining of plate (hogouts) or forgings, welding of wrought, cast, or powder metallurgy (P/M) parts, and cooling of castings.

Stress relieving helps maintain shape stability and also can eliminate unfavorable conditions such as loss of compressive yield strength — the Bauschinger effect — that can be particularly severe in titanium alloys. Stress relieving can be performed without adversely affecting strength or ductility.

Typical stress-relief cycles are listed in the Datasheet, Part 2.

**Selection decision:** When symmetrical shapes are machined in the annealed condition, using modest cuts and uniform stock removal, stress relieving may not be required. However, the greater the depth of cut and/or the more nonuniform the cut, the more likely it is that stress relieving will be needed either to successfully complete the machining and fabrication cycle or to ensure maximum service life of the component.

It may be possible to omit a separate stress relief if the manufacturing sequence can be adjusted so that an annealing or hardening operation also serves to relieve residual stresses. For example, forging stresses can be relieved during the annealing operation required prior to machining. Example: Large, thin forged rings have been processed with minimum distortion by rough machining material in the annealed condition. Subsequent operations include solution treating, quenching, partial aging, finish machining, and final aging. The partial aging operation also relieves quenching stresses, while the final aging relieves stresses developed during finish machining.

**Time/temperature and cooling:** More than one combination of time and temperature can yield a satisfactory stress relief. Cooling rate from the stress-relieving temperature is not critical for titanium alloys. However, uniformity of cooling is. This is particularly true in the 480 to 315°C (900 to 600°F) temperature range. Furnace or air cooling is preferred. Oil or water quenching should not be used to ac-

celerate cooling after stress relieving. These faster quenchants can promote nonuniform cooling, which can induce residual stresses.

**Metallurgical response:** The metallurgical response of the alloy involved plays a major role in the selection of stress-relief cycles. To reduce stresses in a reasonable time, the maximum temperature consistent with limited change in microstructure is used.

The treatment involves holding at a temperature sufficiently high to relieve stresses but not cause an undesirable amount of precipitation or strain aging in alpha-beta and beta alloys, or undesirable recrystallization in single-phase alpha alloys that rely on cold work for strength.

Beta alloys and the more highly alloyed alpha-beta compositions rely on microstructural control via heat treatment to optimize strength properties. Consequently, they are best stress relieved using a thermal exposure that is compatible with the recommended annealing, solution treating, stabilization, or aging process. Note, however, that the stress relief treatment per se is not used to control microstructure.

**Quality control:** The only way to nondestructively gage the effectiveness of a stress-relief cycle is by X-ray diffraction. Stress relieving produces no significant changes in microstructure that can be detected by light optical microscopy.

Although X-ray stress measurement can be used to assess the degree of stress reduction, the method is imperfect. Very limited data are available, most of which were generated in the first two decades following the commercial development of titanium. The shapes of residual stress-vs.-time curves at each stress-relief temperature are likely to differ for every alloy. They also are a function of prior processing. Nevertheless, relative stress reduction as a function of time at temperature is routinely treated as an invariant function, and the relative stress curves are applied to alloys for which actual measurements are limited or nonexistent.

### Process annealing methods

“Annealing” is a generic term and may be applied differently by different producers. For example, solution treating is frequently considered an annealing process, and the stress relief heat treatment is often called stress relief annealing. Techniques that serve

primarily to increase toughness, ductility at room temperature, dimensional and thermal stability, and, sometimes, creep resistance are considered “process annealing” or just “annealing” methods.

**Annealing treatments:** Common annealing treatments include mill, duplex, recrystallization, and beta annealing. Selected cycles are listed in the Datasheet, Part 3.

- Mill annealing is a general-purpose treatment given to all mill products. It is not a full anneal, and can leave traces of cold or warm working in the microstructure of heavily worked product (particularly sheet).

- Duplex annealing is an example of the multiple-anneal processes that sometimes are specified. Triplex annealing also has been practiced. Such treatments frequently are used in the context of solution treating and aging.

- Both recrystallization and beta annealing are used to improve toughness. Recrystallization annealing has replaced beta annealing for fracture-critical airframe components. In this method, the alloy is heated into the upper end of the alpha-beta range, held for a predetermined time, and then very slowly cooled.

- Beta annealing is done at a temperature only slightly higher than the beta transus, to prevent excessive grain growth. Annealing time depends on section thickness and should be long enough to permit complete transformation to beta. Time at temperature after transformation to beta should be held to a minimum to control grain growth of the beta phase. Beta annealing can be followed by an air cool, although larger sections may need to be fan cooled or even water quenched to prevent the formation of detrimental alpha phase at grain boundaries.

The cooling method used after higher-temperature annealing can affect tensile properties. For example, air cooling of Ti-6Al-6V-2Sn from the mill annealing temperature results in a tensile strength lower than that obtained by furnace cooling. Regardless of the method used, if distortion is a problem, the cooling rate should be uniform down to 315°C (600°F).

Because process annealing treatments usually are less closely controlled than solution treating and aging, more property variability or “scatter” will occur in annealed alloys. Nevertheless, many titanium alloys are placed in service in the annealed



*Fig. 2 — In hot isostatic pressing, or HIP, elevated temperatures and isostatic pressure are simultaneously applied to components for a precisely controlled time. The heat- and pressure-treating process can be used to reduce or eliminate voids in castings through creep and diffusion bonding. These Ti-6Al-4V seal housings are being loaded into a HIP vessel at Howmet Castings, Whitehall, Mich. HIP'ing will reduce microshrinkage in the castings. Photo courtesy of Howmet Castings.*

condition.

**Phase stability:** In beta and alpha-beta titanium alloys, thermal instability is a function of beta-phase transformations. In alpha-beta alloys during cooling from the annealing temperature, or in isothermal exposure of beta alloys, beta can transform to the undesirable (brittle) intermediate phase, omega.

Beta alloy chemical compositions are controlled to prevent omega formation, and alpha-beta alloys are given a stabilization anneal. This annealing treatment produces a stable beta phase capable of resisting further transformation when exposed to elevated temperatures in service. In the case of alloys that are solution treated and aged, the aging treatment may be able to double as the stabilization heat treatment.

Alpha-beta alloys that are lean in beta, such as Ti-6Al-4V, can be air cooled from the annealing temperature without impairing their stability. Furnace cooling (slow cooling), however, may promote formation of Ti<sub>3</sub>Al, which can degrade the alloy's resistance to stress corrosion.

A duplex anneal is used to obtain maximum stability in the near-alpha alloys Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo. First step is a solution an-

neal at a temperature high in the alpha-beta range, usually 25 to 55°C (50 to 100°F) below the beta transus for Ti-8Al-1Mo-1V alloy, and 15 to 25°C (25 to 50°F) below the beta transus for Ti-6Al-2Sn-4Zr-2Mo. Forgings are held for one hour (nominal) and then air or fan cooled, depending on section size.

The solution anneal is followed by stabilization annealing for eight hours at 595°C (1100°F). The final annealing temperature should be at least 55°C (100°F) above the anticipated use temperature so that no further microstructural changes will occur during service.

Note that maximum creep resistance can be developed in Ti-6Al-2Sn-4Zr-2Mo by beta annealing or beta processing (and by adding silicon).

**Distortion:** Straightening, sizing, and flattening operations are often necessary to correct distortion resulting from annealing, particularly of close-tolerance thin sections. Because titanium alloys exhibit excessive springback, the straightening of bar to close tolerances and the flattening of sheet present major problems for producers and fabricators. Straightening, sizing, and flattening can be stand-alone processes or can be combined with annealing (or stress relief) by use

of appropriate fixtures.

Unlike aluminum alloys, titanium alloys are not easily straightened when cold. Springback and resistance to straightening at room temperature make it necessary to employ an elevated temperature process. Creep straightening is the method of choice.

Creep straightening takes advantage of the low creep resistance of many titanium alloys at annealing temperatures. Thus, with proper fixturing and, in some instances, judicious weighting, many sheet metal fabrications and thin, complex forgings can be satisfactorily straightened during annealing. Again, uniform cooling to below 315°C (600°F) after straightening can improve results.

In creep flattening, titanium sheet is heated while being held between two clean, flat sheets of steel in a furnace containing an oxidizing or inert atmosphere. Vacuum creep flattening, a variation, is used to produce stress-free flat plate for subsequent machining. The plate is placed on a large, flat, ceramic bed that has integral electric heating elements. Insulation is placed on top of the plate, and a plastic sheet is sealed to the frame. The bed is slowly heated to the annealing temperature while a vacuum is pulled under the plastic. Atmospheric pressure creep-flattens the plate.

### Solution treating and aging

Maximum strength in titanium alloys is achieved by solution annealing (commonly called “solution heat treating” or just “solution treating”) followed by quenching and then aging. The process can be used to obtain a wide range of strength levels in alpha-beta and beta alloys. The response of most titanium alloys to solution treating and aging originates in the instability of the high-temperature beta phase at lower temperatures.

In general, solution treating and aging does not mean the same thing

for titanium as it does for traditional age-hardening systems, such as aluminum alloys or nickel-base superalloys. Ti-2.5Cu is a rare exception because a compound (Ti<sub>2</sub>Cu) does precipitate from supersaturated alpha phase upon quenching from a high-temperature solution anneal and then aging at an appropriate temperature. The Ti<sub>2</sub>Cu forms zones (as in aluminum alloys) that increase strength at lower temperatures. Note, however, that Ti-2.5Cu does not produce precipitate particles, such as gamma prime, that characterize nickel-base superalloys, which are true high-temperature alloys.

No titanium alloy of conventional composition is truly age hardenable. However, an addition of silicon to near-alpha and alpha-beta alloys will improve high-temperature strength, presumably by formation of a silicide phase during customary solution treating and aging processes.

Solution treating and aging (or stabilization) usually, but not always, follow working operations to optimize mechanical properties. Heating an alpha-beta alloy to the solution treating temperature produces a higher ratio of beta phase to alpha phase. This phase partitioning is maintained by quenching; on subsequent aging, the unstable beta phase and any martensite that may be present decompose, increasing strength. Commercial beta alloys, generally supplied in the solution-treated condition, need only to be aged.

**Furnace conditions:** After being cleaned, titanium parts are loaded into fixtures or racks that permit free access to heating and cooling media. Thick and thin components of the same alloy may be solution treated together, but the time at temperature (soak time) is determined by the thickest section. The rule of thumb for most alloys: 20 to 30 minutes for every 25 mm (1 in.) of thickness.

A load can be charged directly into a furnace operating at the solution treating temperature. Preheating is not essential, but it can be used to minimize distortion of complex parts. Microstructural changes occurring during heat treating can cause components to “grow.” (Designs for large parts require allowances for growth.) The growth due to heating can be retained after cooling, and it can be increased either by longer hold times at the solution treating temperature or by lower heating rates.

Depending on the alloy, the solution treating temperature is either slightly above or slightly below its beta transus. Solution treating cycles for selected titanium alloys are given in the Datasheet, Part 4.

**Beta alloys:** Solution treating temperatures for beta alloys can be above the beta transus. Beta alloys normally are obtained from producers in the solution-treated condition. If reheating is required, soak times should be only as long as necessary to obtain complete solutioning, because grains can grow rapidly under these conditions (since no second phase is present to prevent it). For near-beta alloys, solution heat treating may have to be carried out below the beta transus (an alpha-beta anneal). The solution-treated product will contain globular alpha plus retained beta. The microstructure after aging will consist of a bimodal alpha distribution (primary alpha plus alpha from aging).

**Alpha-beta alloys:** Alpha-beta alloys are solution treated at a temperature slightly below the beta transus. Close control of temperature is essential. If the beta transus is exceeded, tensile properties (especially ductility) are reduced and cannot be fully restored by subsequent thermal treatment.

Selection of a solution treatment for alpha-beta alloys is made after deciding on the combination of mechanical properties required after aging. A change in the solution treating temperature of an alpha-beta alloy alters the amount of beta phase and, consequently, affects the alloy’s response to aging (Table 1).

To obtain high strength with adequate ductility, it generally is necessary to solution treat at a temperature high in the alpha-beta field, normally 25 to 85°C (50 to 150°F) below the beta transus. If higher fracture toughness or improved resistance to stress corrosion is required, beta annealing or beta solution treating may be desir-

**Table 1 — Effect of solution treating temperature on tensile properties at room temperature of Ti-6Al-4V bars(a)**

Solution treating temperature		Tensile strength		Yield strength(b)		Elongation in 4D(c)
°C	°F	MPa	ksi	MPa	ksi	%
845	1550	1025	149	980	142	18
870	1600	1060	154	985	143	17
900	1650	1095	159	995	144	16
925	1700	1110	161	1000	145	16
940	1725	1140	165	1055	153	16

(a) Properties determined on 13 mm (0.5 in.) in diameter bar after solution treating, quenching, and aging. Aging treatment: 8 h at 480°C (900°F), air cool. (b) 0.2% offset. (c) D = specimen diameter.

able, but, as previously noted, considerable loss of ductility will result.

**Near-alpha alloys:** Similar to the alpha-beta alloys, solution treatment of near-alpha alloys above the beta transus will optimize creep resistance, but at the expense of ductility and fatigue strength. The best combination of creep and fatigue strengths is obtained by solution treating at a temperature very close to, but still below, the beta transus. Only about 10 to 15% of primary (untransformed) alpha should persist at the solution treating temperature.

The need to closely approach the beta transus poses production concerns. In some alloys, the problem is avoided by modifying alloy composition so that a flattened beta approach curve is produced; for example, a carbon addition in Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.3Si (IMI 834).

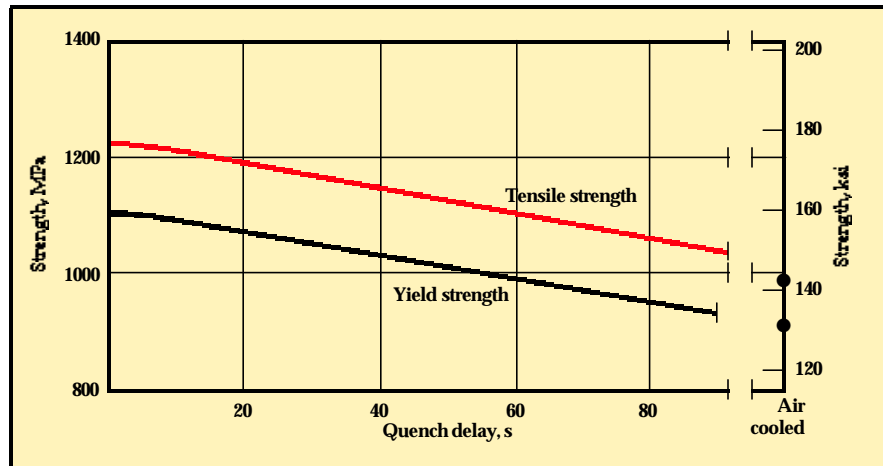
### Quenching and cooling

Beta alloys generally are air cooled from the solution treating temperature. For alpha-beta alloys, the cooling rate has an important effect on strength. Appreciable diffusion can occur if the rate is too low, affecting phase chemistry and/or ratios. As a result, decomposition of the altered beta phase during subsequent aging may not have the desired strengthening effect.

For alpha-beta alloys that have a relatively high beta stabilizer content and for products that have a small section size, air or fan cooling may be adequate. If the mechanical property specification permits, this slower cooling is preferred because it minimizes distortion. However, rapid cooling to prevent decomposition of beta phase and maximize aging response usually is required. Preferred media include water, a 5% brine solution, or a caustic soda solution.

The need for rapid quenching is emphasized by the corollary requirement of a short quench delay time — the time needed to transfer solution treated parts from the furnace to the quench tank. Some alpha-beta alloys can tolerate a maximum delay of only seven seconds, depending on the mass of the sections being heat treated. The more highly beta-stabilized alpha-beta alloys can tolerate delay times of up to 20 seconds. The effect of delay time on the tensile properties of Ti-6Al-4V is shown in Fig. 3.

When the section thickness of a Ti-6Al-4V part exceeds 75 mm (3 in.), it



is difficult to cool the center fast enough to maintain an unstable beta phase for transformation during subsequent aging. This explains why the properties of solution treated and aged Ti-6Al-4V parts having large sections usually are similar to those of process annealed material. On the other hand, alloys such as Ti-6Al-2Sn-4Zr-6Mo and Ti-5Al-2Sn-2Zr-4Mo-4Cr, in which fan or air cooling develops good strength in sections through 100 mm (4 in.), are less sensitive to a delayed quench.

Therefore, it is important to recognize that section size has a significant influence on effectiveness of quenching and, in turn, an alloy's aging response. Two handy guidelines:

- The amount and type of beta stabilizer in an alpha-beta alloy determine depth of hardening or strengthening.
- Unless an alpha-beta alloy is highly alloyed with beta stabilizers, thick sections have lower tensile properties.

The effect of as-quenched section size on the tensile properties of Ti-6Al-4V is shown in Fig. 4.

### Aging for higher strength

The final step in heat treating titanium alloys to high strength is to age or reheat to a temperature between about 425 and 650°C (800 and 1200°F). Aging of alpha-beta or beta alloys causes decomposition of the supersaturated beta phase retained on quenching, and (in alpha-beta alloys) the transformation of any martensite to alpha. The time-temperature combination selected for a given alloy depends on

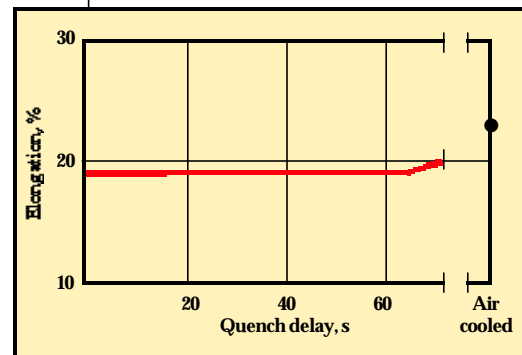


Fig. 3 — Effect of quench delay on the tensile properties of Ti-6Al-4V alpha-beta alloy. Bar, 13 mm (0.5 in.) in diameter, was solution treated one hour at 955°C (1750°F), water quenched, aged six hours at 480°C (900°F), and air cooled.

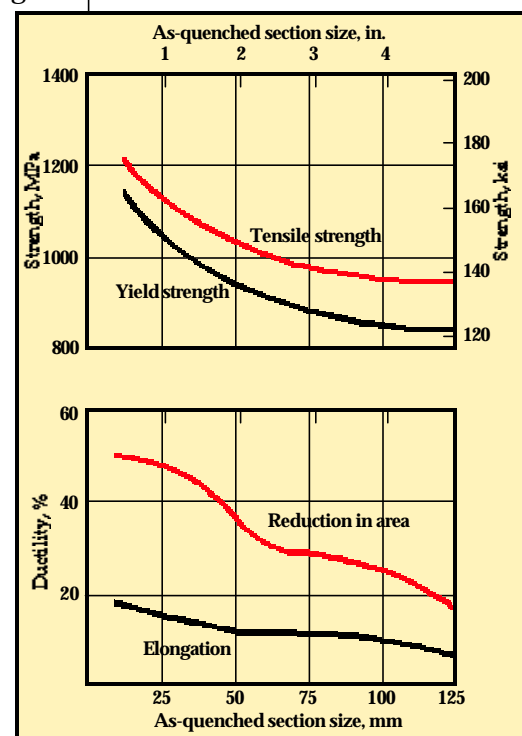


Fig. 4 — Effect of as-quenched section size on the tensile properties of Ti-6Al-4V alpha-beta alloy.

the strength required. Typical aging times and temperatures for selected titanium alloys also are given in Part 4 of the Datasheet.

Aging an alloy above its standard aging temperature, yet still several hundred degrees below the beta transus, results in overaging. The transformation proceeds much farther than normal, producing the solution treated and overaged (STOA) condition. It sometimes is used to obtain modest increases in strength while maintaining satisfactory toughness and dimensional stability. The STOA cycle for Ti-6Al-4V, for example, is heat one hour at 955°C (1750°F), water quench, hold two hours at 705°C (1300°F), and air cool. In this case, STOA improves notch strength and fracture toughness, and provides a creep strength similar to that obtained by regular annealing.

Heat treating of alpha-beta alloys for high strength frequently involves a series of compromises and modifications, depending on the type of service and on special properties that may be required, such as ductility and suitability for fabrication. This is especially true where fracture toughness is important in design and where strength is lowered to lengthen design life. The aged condition is not necessarily one of equilibrium in titanium alloys. However, proper aging will produce high strength with adequate ductility and metallurgical stability.

**Omega phase:** As previously mentioned, the beta phase in highly beta-stabilized alpha-beta alloys or in beta alloys can form omega phase, a metastable transition phase. During aging of some highly beta-stabilized alpha-beta alloys, beta transforms first to omega phase before alpha is produced. Retained omega phase, which imparts unacceptable brittleness, can be avoided by severe quenching and rapid reheating to an aging temperature above 425°C (800°F). Note that a coarse alpha phase forms that may not provide optimum strength properties. Omega phase formation is not a problem today, because aging times and temperatures are chosen to ensure that any omega reaction proceeds to completion.

**Beta alloys:** Metastable beta alloys usually do not require a separate solution treatment prior to aging. Final hot working, followed by air cooling, leaves these alloys in a condition comparable to that of solution treated material. In some instances, however, solution

treating at 790°C (1450°F) can produce more uniform properties after aging.

Short aging times can be used on cold worked material to produce a significant increase in strength over that obtained by cold working alone. Aging hot worked or solution treated, chromium-containing beta alloys for longer times may increase strength but decrease ductility and fracture toughness, due to the formation of titanium-chromium compounds.

### Processing considerations

Titanium components to be heat treated should be clean and dry. Oil, fingerprints, grease, paint, and other foreign matter should be removed from all surfaces. Do not use ordinary tap water for cleaning. Cleaning is required because the chemical reactivity of titanium at high temperatures can lead to its contamination or embrittlement, and can increase its susceptibility to stress corrosion. Oxygen and nitrogen can form a hard, brittle alpha phase on the surface (alpha case).

After cleaning, parts should be handled with clean gloves to prevent recontamination. If a component is to be sized, straightened, or heat treated in a fixture, the fixture also should be free of any foreign matter and loosely adhering scale.

Other key considerations in heat treating titanium alloys include:

- Prevent heat treating temperatures from exceeding the beta transus, unless specified.
- Remove alpha case after *all* heat treating is completed.
- Provide sufficient stock for post-heat treatment metal removal requirements, such as removal of contaminated material.

### Atmosphere reactions

Any heat treatment at approximately 425°C (800°F) or above must be performed in an atmosphere that prevents pickup of oxygen or nitrogen and subsequent and undesirable formation of the hard alpha case. The atmosphere will also help minimize scaling.

Titanium reacts with the oxygen, water, and carbon dioxide normally found in oxidizing heat treating atmospheres. It also reacts with hydrogen formed by decomposition of water vapor. Pickup of oxygen/nitrogen also will occur even in forging operations where coatings are used to protect and lubricate the billet. In some cases, surface contamination can

render a part unfit for use. Therefore, unless the heat treatment is performed in a vacuum furnace or in an inert atmosphere, and unless surface cleanliness is maintained, the atmosphere will have a direct, negative effect on alloy properties.

While it may be possible to recover properties by vacuum heat treating (to remove hydrogen) or by stock removal (of an oxygen/nitrogen enriched surface layer), it usually is more efficient to prevent or minimize atmosphere/alloy interactions whenever possible.

**Alpha case, oxidation:** Oxygen and nitrogen (alpha stabilizers) will react with a titanium surface. Pickup of oxygen or nitrogen during heat treatment results in a surface microstructure of predominantly alpha phase, which, as previously noted, is called "alpha case." Alpha case at 955°C (1750°F), for example, can extend 0.2 to 0.3 mm (0.008 to 0.012 in.) beneath the surface. Of the two alpha case formers, oxygen is the more potent, because it is absorbed at a much higher rate than nitrogen.

Alpha case is brittle and must be removed before the component is put into service. It can be removed by machining, but tool wear may be excessive because the layer is very abrasive to both carbide and high-speed steel cutting tools. Standard practice is to remove alpha case by mechanical and/or chemical methods.

Titanium is chemically active at high temperatures and will oxidize in air, resulting in the formation of scale. Although oxidation may be a problem in sheet forming operations, it is not a primary concern in heat treating.

Oxygen pickup during heat treating can be minimized by spray coating the metal with an antioxidant. The coatings are effective at temperatures up to about 760°C (1400°F). However, their use does not eliminate the need to remove alpha case after heat treating.

Oxidation (scaling) rates of commercial titanium alloys vary widely. Tables have been developed for estimating the minimum amount of metal that must be removed to reach unaffected base metal. It is a function of heat treating temperature and the amount of time that the alloy was exposed to the oxidizing atmosphere.

One way to ensure complete removal of alpha case formed by oxygen pickup is to etch the part in an ammonium bifluoride solution — the etching characteristics of oxygen-en-

riched case differ from those of uncontaminated material. A more sensitive procedure is an etch/anodize process, called "blue etch" for the characteristic color of oxygen-enriched metal. Blue etch anodize was used for years to inspect titanium alloy forgings for oxygen-enriched, surface-connected defects related to melting problems. For other mill products, metallographic examination is preferred.

**Hydrogen:** Current specifications limit hydrogen content to 100–200 ppm max., depending on alloy and mill form. Excess hydrogen embrittles some alloys, reducing impact strength and notch tensile strength and causing delayed cracking and premature failure.

Hydrogen pickup occurs not only during heat treatment but also during pickling or the chemical cleaning operations used to remove alpha case. The amount of pickup can only be determined by chemical analysis — there is no relatively simple etch procedure. If a high hydrogen level is found, vacuum annealing is required. A typical cycle consists of heating at or near the standard annealing temperature for two to four hours in a vacuum of at least 0.01 torr (1.3 Pa, 10 mm Hg).

Except for high vacuum, molten salts, and chemically inert gases such as argon, all heat treating atmospheres contain some hydrogen at the temperatures used to anneal titanium. Hydrocarbon fuels produce hydrogen as a by-product of incomplete combustion, and electric furnaces with an air atmosphere contain hydrogen from breakdown of water vapor. However, because small amounts of hydrogen can be tolerated, and because inert media are expensive, most titanium heat treating is performed in conventional furnaces employing oxidizing atmospheres with at least 5% excess oxygen in the flue gas. The oxidizing atmosphere helps reduce hydrogen pickup in two ways: by reducing the partial pressure of hydrogen in the surrounding atmosphere, and by promoting the formation of a protective surface oxide.

**Other gases:** Nitrogen normally does not present a serious contamination problem because it is absorbed by titanium during heat treating at a much slower rate than oxygen. Dry nitrogen has been used successfully as a lower-cost protective atmosphere for heat treating titanium forgings that are to be fully machined after treatment. Absorption of too much ni-

trogen can, however, result in the formation of alpha case.

Carbon monoxide and carbon dioxide decompose in the presence of hot titanium and produce surface oxidation. They are not recommended for titanium alloy heat treating.

**Chlorides:** Titanium alloys having high levels of residual stress are subject to stress corrosion when exposed to chlorides at temperatures above 290°C (550°F). Salt in fingerprints and the chlorides in some degreasing solutions can cause stress-corrosion cracking at temperatures above 315°C (600°F). Although readily reproduced in the laboratory and known to occur during heat treating, hot-salt cracking in service has not been a significant problem.

Care is required during thermal processing to ensure freedom from chloride contamination.

### Hot isostatic pressing

Hot isostatic pressing (HIP) is an accepted thermal-mechanical method for closing internal solidification shrinkage or gas porosity in titanium castings. It also is used in powder metallurgy (P/M) processing. HIP clearly functions as a heat treatment because parts are exposed to temperatures between 900 and 955°C (1650 and 1750°F) for two to four hours (Fig. 1 and 2).

In HIP, chemically clean components are placed in a heated, argon-filled vessel and subjected to pressures of 70 to 105 MPa (10 to 15 ksi). Higher pressures of 205 MPa (30 ksi) have been used to process some high-temperature titanium alloys. The temperatures used are in the high end of the alpha-beta range for the few alloys (principally Ti-6Al-4V) that are cast + hot isostatically pressed.

Heat treatment after HIP generally is close to, but below, the beta transus. Alloy properties vary with the HIP temperature. A temperature of 955°C (1750°F) formerly was thought to produce a better microstructure and mechanical properties than a cycle at 900°C (1650°F). Today, however, experience and specification consolidation have resulted in a preference for the lower temperature. The cooling rate after HIP also can affect the properties of titanium alloys.

HIP narrows the fatigue property scatter band and raises minimum fatigue life. HIP temperatures can coarsen alpha platelets, causing a slight loss in tensile strength, but the overall benefits of the process

usually outweigh any potential drawbacks. **HIP**

*Alpha case is brittle and must be removed before the component is put into service.*

*Standard practice is to remove alpha case by mechanical and/or chemical methods.*

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