Evaluation of Commercial Titanium Alloys

Robert Loucks

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EVALUATION OF COMMERCIAL TITANIUM ALLOYS

A Report Submitted to
Dr. F. A. Hames
and
Professor W. W. Chance

to fulfill
Requirements of Metallurgy 53
and English 61

by
Robert Loucks

Montana School of Mines
Butte, Montana
December 16, 1956
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Montana School of Mines
Butte, Montana
December 16, 1956
Dr. F. A. Hames  
Department of Metallurgy  
Montana School of Mines  
Butte, Montana

Dear Dr. Hames:

Subject: Metallurgical Plant Study Report

In compliance with your request for a term report, I respectfully submit the following report entitled "Evaluation of Commercial Titanium Alloys".

This report consists mainly of library research on much of the available information compiled on titanium and its alloys. In order to present a clear picture of these alloys and their use, I have outlined the physical metallurgy of titanium. Metallography, phase behavior, and heat treatments were reviewed in this outline, as well as the uses of the alloys, compared to other metals currently available.

Since this report consists only of library research, I have made no recommendations, but have concluded that the future for titanium is very bright. The future will undoubtedly bring many advances in methods for both the preparation and use of the metal and its alloys.

If any further questions arise upon this report or its material, please feel free to present them to me. I shall be very glad to try to answer them for you.

Respectfully yours,

Robert Loucks

Robert Loucks
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ABSTRACT

Uses of titanium and its alloys range from aircraft structures to corrosion-resistance applications. The properties of the metal, including physical metallurgy, naturally dictate the fields of application. The interstitial elements, plus aluminum and tin, preferentially stabilize the alpha phase of titanium. These "alpha" alloys have microstructures similar to martensitic iron. Beta phase stabilizers include manganese, iron, chromium, and vanadium. Alpha plus beta alloys are sub-classified according to their stability at room temperature. More beta-stabilizer gives greater stability. The different classes of alloys have various advantages and disadvantages which regulate the use of the alloys. With future improvements, titanium will be one of the more important constructional materials.
EVALUATION OF COMMERCIAL TITANIUM ALLOYS

I. INTRODUCTION

The advent of titanium metal production brought with it a possible answer to the constant search by industry for a constructional material which is light in weight, but still has a superior strength. Titanium has strength comparable to many steels, with even higher strengths envisioned, and the density of titanium is 0.16 lb per cu in., compared with 0.28 lb per cu in. for iron. Another important property of titanium is its unusual corrosion resistance. Because of these properties, scientists and engineers immediately began planning for prospective uses for the metal. Enthusiasm was such that titanium soon became known as a "wonder metal", but continued research discovered disadvantages not apparent in the first evaluation. Since that time, continued research and development have been applied, and most of the problems are being solved. Although titanium will not be used in all the applications earlier surmised, there are still many fields where it can be used economically and with good advantage.

Titanium has been known since about 1789, when it was discovered in magnetic sands. Shortly after this first discovery, an analysis of rutile by a geologist named Klaproth again produced evidence of this metal. It was named "Titan metal", which was later corrupted to titanium. Separation of titanium from rutile was made by 1825, but it was not until 1906 that enough relatively pure metal was produced to permit proper evaluation of the element's properties.

In 1932, Wilhelm Kroll developed an extraction process for procuring the metal from its ores. This process, still known as the Kroll process, is the basic process for titanium production today. The basic fundamentals of the process are chlorination of the oxide ores to titanium tetrachloride, which is reduced with molten magnesium in an inert gaseous atmosphere.
Titanium is produced in the form of sponge metal, which must be consolidated into a solid form before it can be used as a constructional material.

Consolidation to the solid metal form is impossible by conventional melting procedures because of titanium's exceptional chemical affinity and reactivity with all known refractories, metals, and air at elevated temperatures. This problem is generally solved by either arc melting or induction melting. In arc melting, a water-cooled copper furnace is used, because molten titanium does not adhere to this surface and, in effect, a wall of solidified titanium surrounds the molten charge. Impurities are greatly minimized by this process. Either non consumable carbon or tungsten electrodes or consumable titanium electrodes may be used. An inert atmosphere is maintained over the charge to protect from air contamination.

Induction melting is, as the name implies, the employing of exterior energized induction coils to melt the charge, which is in a graphite crucible. About 1/2 per cent carbon is absorbed by the molten metal, which reduces the ductility and increases the hardness of the metal slightly.

In 1946, a pilot plant operated by the U. S. Bureau of Mines produced 100-lb batches of titanium sponge by the Kroll Process. Because of the properties shown by the metal, several companies became interested in production. Extractive units were constructed as economy and need provided, and production increased from 2 1/2 tons in 1948 to an estimated 13,000 tons for 1956. Even at present, long-range plans are calling for increased production by existing plants and construction of new facilities by many metals-extraction corporations. Incentive has been additionally supplied by government financial and moral support.

As production of the metal increased, different industries were able to begin applying the metal in all feasible ways. The largest consumer of titanium is the aircraft industry. Because of the virtually unlimited
funds set forth by Government contracts for defense systems, the aircraft industry is able to overcome the economical barrier produced by the present high cost of titanium. Private industry is able to use the metal only in isolated cases where its corrosion resistance will be able to show economy, generally over long periods of time.

Physical metallurgy of titanium has progressed simultaneously with all other phases of development. Numerous alloys have been developed in the search for better properties and different applications. These alloys are classified according to their alloying elements, which stabilize the two phases of titanium. The low-temperature phase of titanium is alpha, which has a hexagonal close-packed lattice structure. The high-temperature phase is body-centered cubic beta.

Aluminum, tin, and the interstitial elements stabilize the alpha phase, which gives rise to the name alpha-stabilized alloys for those containing these elements alone. Examples of this class are the commercially pure titaniuums, which have only carbon, oxygen, and nitrogen dissolved interstitially; and the A-110AT alloy, which has a nominal composition of 5% aluminum and 2.5% tin, with the balance titanium.

Elements which stabilize beta include the following: manganese, iron, chromium, vanadium, molybdenum, and tungsten. The beta-stabilized alloys are further subdivided into two classes: the alpha-beta group, and the pure beta group. The alpha-beta group has insufficient beta-stabilizing elements to produce an equilibrium beta structure when such an alloy is quenched from the beta field. These alpha-beta alloys may contain either beta-stabilizing elements alone or a combination of alpha and beta phase stabilizers. Examples of this alpha-beta group are CA110M with a nominal composition of 8% manganese and 92% titanium; and NST 2.5 Fe-2.5 V with 2.5% iron, 2.5% vanadium, and 95% titanium in the simple beta-stabilized division. An
example of an alloy with both beta and alpha stabilizers is the C-120AV alloy. The composition of this alloy is 6% aluminum, 4% vanadium, and 90% titanium.

As yet, no all-beta alloys have been produced commercially, but there have been indications that an alloy with a composition of 30% molybdenum will be used for non military applications, principally for corrosion resistance.

II. DESCRIPTION AND PROPERTIES OF ALLOYS

As stated above, the alloys are divided into three classes: alpha, alpha-beta, and beta alloys.

A. Alpha Alloys

Alpha-stabilized alloys follow a common general type of phase behavior. The transformation range of alpha-stabilized alloys is noted in Figure 1.

![Figure 1. Transformation Range of Alpha-Stabilized System.](image)

From this diagram, it can be noted that the transformation temperature is raised with increased alloy content.

1. Alloying Elements: Elements which stabilize alpha are, as noted previously, aluminum, tin, oxygen, nitrogen, and carbon. The latter three elements dissolve interstitially in the alpha phase, whereas the first two are dissolved substitutionally.

The alpha solubilities of oxygen, nitrogen, and carbon are, respectively, 14.5%, 9%, and 0.43%. Although these elements are highly soluble in
alpha titanium, the practical limit of solution for room temperature ductility and hot workability is approximately 1/25 of the above amounts. Because of this simultaneous affinity for alpha and the production of detrimental effects, the control of these elements is generally quite critical to alloy production.

By dissolution of more than a certain per cent, aluminum also limits the ductility and hot workability of titanium. The effect is not so great, however, because a much larger percentage of aluminum can be dissolved without a serious decrease in the alpha ductility. Tin is unique in its effect on titanium in that it can stabilize either the alpha or the beta phase. It is soluble in the alpha phase to approximately 20%, and the entire alpha range is ductile and hot-workable.

The effect of adding combinations of aluminum and tin as alloying elements is not spectacular. Generally, a better workability is produced by the addition of an optimum percentage of tin to an aluminum alloy. A higher specific strengthening effect has been noticed in aluminum as compared with tin alloying. (6,248)

2. Metallography: The metallography of alpha-stabilized alloys is similar to most common solid solution type of alloys. Such an alloy worked and annealed in the all alpha field will show an equiaxed mosaic structure. Cold working will produce flow lines or structures such as mechanical twins. When an alpha alloy is heated into the alpha plus beta field, it will produce a structure somewhat similar to a hypoeutectoid steel. A structure that resembles pearlite is formed, which is actually alpha platelets transformed from beta upon cooling. Heating into the all-beta field will produce a "basket-weave" structure composed entirely of alpha platelets in acicular form, which have transformed from the high temperature beta grains. In all of these microstructures, the grain boundaries and the matrix are composed
of alpha titanium. The rate of cooling does not affect the microstructures to any extent. In any case, it is impossible to retain the beta phase at room temperature.

Alpha alloys do not respond to heat treatment than that of a simple annealing process. As stated above, it is impossible to obtain a retained-beta structure at room temperature in any alpha alloys; so the alloys are in equilibrium and, as a result, very stable. Although acicular particles are precipitated by quenching much as in the martensitic reactions of steel, virtually no distortion of the hexagonal lattice occurs. As a result of the minimum distortion of the lattice, no strengthening action occurs, and the acicular alpha is not hard and brittle like martensite.

B. Alpha-Beta Alloys

Alpha-beta alloys are subdivided according to: (1) whether or not they contain aluminum and/or tin, and (2) whether they have a single beta-stabilizing element or a complex series of such elements. The beta-stabilizing elements may produce either an isomorphic beta phase or one that decomposes in a eutectoid reaction. The eutectoid reaction occurs very slowly and is not found after normal heat treatments. This eutectoid reaction may tend to go to equilibrium and cause failure with the application of high-temperature stresses. Complexing of the beta alloying elements helps to prevent the eutectoid reaction and, as a result, promotes thermal stability.

Beta-stabilizing elements follow the general type of behavior shown in Figure 2. From this diagram, it can be seen that the transformation temperature is lowered with increasing alloying composition.
1. **Alloying Elements**: The known elements which provide a beta isomorphic system include molybdenum, vanadium, tantalum, and columbium. Elements which produce a eutectoid reaction include (in order of increasing decomposition reactivity) manganese, iron, chromium, cobalt, nickel, copper, and silicon. These elements, in alloys without aluminum or tin, tend to strengthen the alloys with increasing content to a certain limit. This strengthening effect is apparently due to increasing amounts of beta phase being stabilized and retained at room temperature. Since virtually all of the beta stabilizer dissolves preferentially in the beta field, the alpha is left relatively pure and ductile, whereas the beta becomes hard and strong. The strength reaches a limit when beta becomes the continuous phase, which is generally about 30% beta. The specific strengthening effect of certain alloying elements is different, with iron and manganese producing the greatest increase in strength per unit weight at a given annealing temperature (7,25).

Aluminum and tin additions to alpha-beta alloys tend to produce stability at elevated temperature service, and to slow down the undesirable beta to omega reaction. Omega is formed, by certain alloy compositions, as a coherent transition phase between beta and alpha when diffusion rates become too low for proper transformation. Omega is very hard and tends to produce brittleness in the beta phase. During aging of the alloy, omega will break down and form alpha and enriched beta.
2. **Metallography:** Alpha-beta alloys show a variety of microstructures under varying conditions of temperature and composition. For example, a specimen annealed from relatively high in the alpha-plus-beta field will produce a fine-grained combination alpha-beta structure. The composition of the alloy will decide which phase will be the continuous one: low concentration of beta-stabilizer will produce beta in an alpha matrix, whereas higher concentrations will produce alpha islands in a beta matrix. Heating into the beta field and slow cooling will produce a Widmanstatten structure of alpha plates precipitated on beta crystallographic planes. In this case, beta will be the continuous matrix. A higher percentage of beta stabilizer will produce less alpha-precipitated plates. Quenching from the beta field forms alpha needles very similar to a martensitic structure inside the retained beta grains. As before, an increase in beta-stabilizer content will produce less alpha precipitation. With a large enough percentage of beta-stabilizer, a completely beta mosaic structure will be formed, when the metal is quenched.

2. **Heat Treatment:** The presence of a beta phase upon cooling makes possible the production of higher strengths and hardnesses by heat treatment. The reaction which produces the improved properties is precipitation or age-hardening, much the same as the reaction found is the heat treatment of aluminum alloys. Titanium age-hardening differs from aluminum treatment only in that the precipitant is a phase and not an intermetallic compound.

The general form of heat treatment consists of heating the alloy into the alpha-plus-beta field, just below the beta transus, to dissolve the alpha into the beta. Heating into the all beta field will cause the interstitial alpha stabilizers to move into the beta phase, and to accelerate beta-reaction rates, causing beta to alpha, or beta to omega, reactions to occur before aging, with resultant hardening. In many cases, this hardness is undesir-
able, because of forming procedures carried on before aging. When the alloy is quenched from the solution range, a certain amount of beta will be retained, and martensitic alpha will be precipitated in the grains. In the subsequent aging treatment, beta is decomposed to alpha, which forms as a very fine dispersion along the crystallographic planes. This alpha dispersion consequently strengthens and hardens the metal.

Beta titanium transforms to alpha by two mechanisms. With fast cooling, a martensitic reaction occurs, producing a typical martensite acicular structure. When the alloy is cooled slowly, alpha is produced by a nucleation and growth process. If the specimen is quenched from the beta field to the alpha-beta field and isothermally transformed, the alpha produced is in straight, narrow platelets, whereas continuous slow cooling produces a more irregular, almost dendritic structure. Another way of showing the differences in structure produced by different cooling rates is to increase the rate of cooling on a specimen during a given cooling cycle. As the rate of cooling increases, the alpha lamellae become progressively finer to a certain rate, at which coarse lamellae are suddenly formed. It is believed that the sudden coarsening occurs when the critical cooling rate for the martensite reaction is reached.

The solution temperature and alloying elements have specific effects upon the metal properties. In plain alpha-beta alloys with no aluminum or tin, the strength increases and the ductility decreases with increasing solution temperature. With an addition of aluminum to the alloy, the yield strength decreases to a minimum with increasing solution temperature, whereas the ductility decreases as above. This decrease to a minimum in yield strength is due to the retention of a beta structure with no omega formation. Aluminum apparently prevents the formation of quench-formed omega, which is present in alloys that do not contain aluminum. One exception to this
phenomenon is molybdenum alloying, which tends to prevent omega formation at high percentages. Certain beta-stabilizers affect the hardenability of titanium alloys by producing a sluggish beta to alpha transformation. As the alloying additions make this reaction more sluggish, omega will be formed, with a consequent hardening of the metal. However, quenching of Jominy bars will produce a relatively soft martensitic case and an omega-hardened core. The hardness will rise to a maximum at the depth for which the cooling rate best aids beta sluggishness and omega formation.

Aging of the alloy after solution treatment produces a hardening and strengthening effect by reprecipitating alpha in the beta grains. The hardness increases to a maximum, followed by a decrease with overaging. Increasing the temperature decreases the time for the hardening response, and above a certain maximum temperature, no hardening response is obtained. Omega formation is generally responsible for the hardening maximum, and the decrease in hardness during overaging is due to the completing of the beta to omega to alpha reaction. Overaging past this range of omega formation produces the best combinations of strength and ductility. It is also generally advantageous to age the alloy at temperatures above those expected in service. This high-temperature aging will bring about stability and prevent overaging to lower strengths, with resultant service failure.

C. Beta Alloys

Beta alloys have been divided into three classes: unstable or metastable, virtually stable, and stable. Unstable titanium alloys, when quenched, produce an all-beta structure. They have sufficient beta-stabilizing content to prevent omega transformation during the quench, but they will transform upon heat treatment or service at elevated temperatures. Virtually stable alloys have greater amounts of beta-stabilizer, and will,
on slow cooling, retain an all-beta structure. They will not transform to omega or alpha at relatively high temperatures and long times, but they will transform when subjected to temperatures just below the beta transus for a long period of time. Stable beta alloys have not been produced to date, but they would have to have a beta transus below room temperature.

All-beta alloys show a plain, mosaic structure of beta grains. Unstable beta alloys only will respond to heat treatment. The principle of the heat treatment would necessarily be identical to that described above for the alpha-beta alloys. Since the beta alloys are a continuation of the alpha-beta system, the general phase diagram is comparable. The higher alloy content end of that system is applicable to the all-beta alloys.

III. Use Of Alloys

The uses for which the various titanium alloys can be adapted are decided upon by their specific advantages and disadvantages.

A. Alpha Alloys

The advantages in having an all-alpha structure are:

1) Useful strength to higher temperatures,
2) No embrittling heat treatment response, and
3) Good weldability.

The disadvantages are:

1) Poorest bend ductility, and
2) More power required for hot working.

These properties indicate that the alpha alloys can be used for either forging or rolling practices. A specific example is the use of Al-110AT (5Al-2.5Sn) for combustion chamber liners in jet engines. This alloy is a natural choice because it fulfills the stringent requirements of this application. These liners require a material having a yield strength of...
120,000 psi at room temperature and 60,000 psi at 600 F. The material also must be weldable and the resulting welds ductile.

B. Alpha-Beta Alloys

The advantages for alpha-beta alloys are:

1) Doubled strength compared with unalloyed titanium,
2) Good ductility,
3) Easy forming, forging, and rolling compared with alpha or beta alloys,
4) Relative simplicity to produce, and
5) Heat treatable to higher strengths.

The disadvantages are:

1) Poor ductility from uncontrolled heat treatment,
2) Poor weld ductility.

Alpha-beta alloys have been used as both forging and rolling alloys. Specific examples are; airplane fuselage frames and bulkheads forged out of 5 Al, 1.4 Cr, 1.3 Fe, and 1.4 Mn alloy, rivets and other fasteners made from 3 Al-5 Cr alloy, and airplane exterior skins rolled from 8 Mn alloy. Heat treatments are opening new fields for development.

C. Beta Alloys

The advantages of an all-beta structure are:

1) Excellent ductility,
2) No detrimental heat treatment response, and
3) High strength without heat treatment.

The disadvantages are:

1) Large sensitivity to contamination by air, and
2) High content of expensive alloying materials.
Although no all-beta alloys are produced commercially at present, they could and probably will be used for certain applications in the future. Because of its good ductility, all-beta structures in titanium would be a good sheet alloy.

All titanium alloys have good corrosion resistance. Because of this fact, one of the biggest uses of titanium is, and will be, for corrosion-resisting equipment in various process industries. Titanium has very good ability to withstand hot chloride environments which severely attack most other metals. Titanium's corrosion resistance is not accelerated by applied stresses, and a pitting type of corrosion is never found. Welded titanium exhibits the same corrosion resistance as the unwelded metal.

IV. CONCLUSION

Interest in titanium has grown rapidly within the past 10 years from a laboratory curiosity to a widely considered constructional material. Many problems have been encountered in the development of the metal for widespread use, but concentrated research will undoubtedly bring solutions to the remaining problems.

Presently three types of titanium alloys are being investigated; alpha, alpha-plus-beta, and beta. Alpha alloys are those with only alpha-stabilizing elements added, such as carbon, nitrogen, oxygen, aluminum, and tin. Alpha-plus-beta alloys are those which have enough beta-stabilizing elements added to produce an alpha-plus-beta structure at room temperature. Beta alloys contain sufficient beta stabilizer to produce an all-beta structure at room temperature. Elements such as manganese, molybdenum, vanadium, and iron stabilize the beta phase and produce greater hot and cold workability and heat treatability. The alpha stabilizers produce a higher permissible working temperature and a better high-temperature strength.
The ability to be heat treated of alpha-beta alloys has opened new fields of research and promised higher strengths and properties. Most reports tend to predict further growth in the titanium industry and many more uses for this bright, new metal.
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Figure 3 - Comparison of Titanium With Other Constructional Materials
BIBLIOGRAPHY


