Ilmenite ore, main source of titanium, is plentiful. The National Lead Co. takes ore out of huge "benches" like these in New York's Adirondack Mountains.

TITANIUM

It's an old metal, but now that it's been discovered by the engineers its future looks bright

by POL DUWEZ

LAST SEPTEMBER, headlines in a Paris newspaper proclaimed that "a new metal has just been discovered in the United States; it is lighter than aluminum and stronger than steel." This enthusiastic misstatement is typical of the general public relations approach to titanium. As a matter of plain fact titanium is not a new metal; it was not recently "discovered" in the United States; it is not lighter than aluminum; and it is not stronger than steel.

For the record, titanium was first recognized in 1791, and the pure metal isolated in 1911. It is heavier than aluminum, though not as heavy as iron. It has a specific gravity of 4.4 It is strong, but not as strong as steel. Pure titanium has a tensile strength of 80,000 lb/sq in.—and many alloy steels may be heat-treated to much higher tensile strength.

But in spite of the fact that titanium is an old metal for chemists and physicists, it has just been discovered by the engineers. It combines a number of physical properties of special interest to the engineer. It has a great resistance to heat; in spite of its rather low specific gravity, it has a melting point of about 3300 F.—higher than that of iron, nickel, or cobalt. It also has a remarkable resistance to corrosion—better than that of stainless steel. Pure titanium is ductile and can be rolled and forged. On a strength per weight basis, it compares favorably with the two older classes of aluminum and iron base alloys. Titanium is abundant, being the ninth most plentiful element in the chemical composition of the earth, and the fifth most common metal.

With this combination of properties, titanium has a wide field of applications in engineering. It may be substituted for stainless steel in aircraft construction with a substantial saving in weight. Its remarkable resistance to corrosion by sea water makes it an ideal material for ship building. Replacing steel, titanium base alloys can appreciably decrease the weight of engines. But perhaps the most important application, and one for which titanium may be found to be the only successful metal, is in the field of supersonic aircraft. At supersonic speeds, aerodynamic heating of the structure is inevitable, and aluminum alloys may become useless because of their poor mechanical properties at temperatures above 300 or 400°F. Today, steel seems to be the only solution to the problem, but the development of titanium alloys may change the picture radically.

What's holding things up?

Considering all the possibilities of titanium, it is surprising that such a metal has not been more extensively studied in the past. But the preparation of pure titanium is a difficult problem of extractive metallurgy. The ordinary method of thermal reduction of an oxide by carbon does not apply to titanium. At high temperature titanium oxide in the presence of carbon is transformed into a very stable carbide. And this tendency of titanium to form interstitial compounds at high temperature is not limited to the case of carbon, but exists for other elements such as nitrogen, oxygen, and hydrogen. Even minute quantities of these elements exert considerable effect on the mechanical properties of titanium, especially on its ductility. As little as a few hundredths of a per cent of nitrogen renders titanium brittle at room temperatures. Consequently, the various metallurgical operations must be performed in high vacuum or in an atmosphere of purified inert gas, such as helium or argon.

Titanium is now being produced, but in small quantities—and, at $5.00 a pound, its cost is still very high. This is no reason for pessimism. In 1885 aluminum also cost about $5.00 a pound. Only a few years later, after the simultaneous discovery of the electrolytic process by Hall in the United States and Heroult in France, aluminum was produced in large quantity and the price dropped to as low as $0.25 a pound.

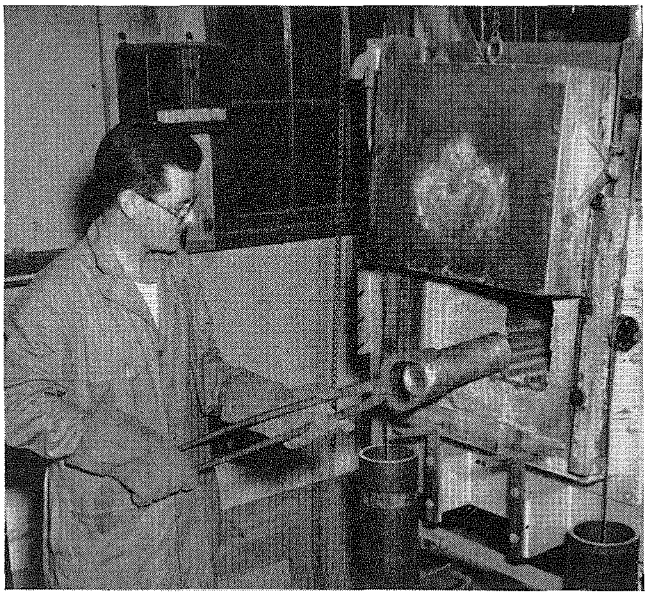
Metallurgy of titanium

Today only two methods are known for the production of titanium. The first consists of reducing titanium tetrachloride by molten magnesium in vacuum or in an inert atmosphere. In the second, titanium iodide is decomposed by heating in vacuum, and pure metallic titanium is deposited from the vapor phase on a heated filament.

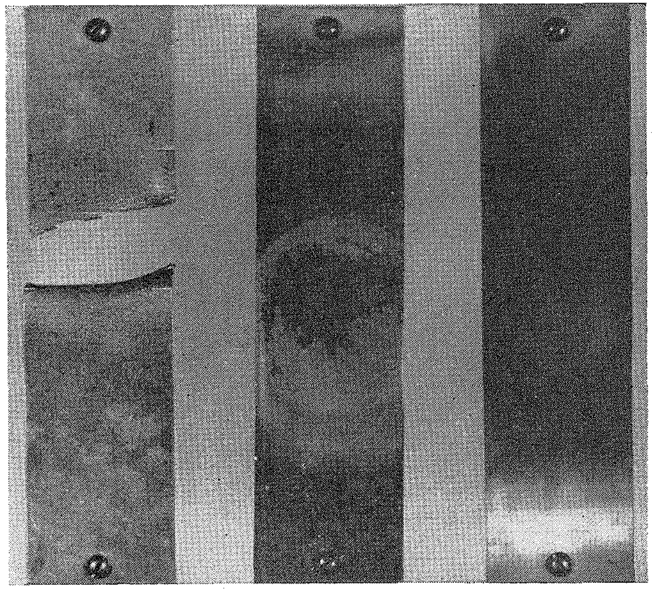
The principle of the first method was discovered in 1910 by Hunter, when he isolated titanium for the first time. His experiment consisted of heating titanium tetrachloride in the presence of sodium in a sealed bomb. Kroll later proposed the substitution of magnesium for sodium and built "production" units capable of treating several pounds of titanium per batch. The Kroll method is the starting point of the U. S. Bureau of Mines development work on the metallurgy of titanium.

In this process, magnesium is melted in a cast-iron reaction chamber heated electrically to a temperature of about 1400°F. The chamber is filled with an atmosphere of carefully purified dry helium. Liquid titanium tetrachloride is slowly added to the melt and immediately reacts to form titanium and magnesium chloride. The reaction being exothermic, the temperature increases slowly during the operation and may reach 1650°F. After the reaction chamber has cooled down, the spongy mass of titanium mixed with magnesium chloride is extracted. A leaching treatment with a dilute solution of hydrochloric acid eliminates the magnesium chloride and pure sponge titanium is separated. The solubility of magnesium in titanium being very limited, the metal produced by this process retains a negligible amount of magnesium, which does not seem to be an objectionable impurity. As a result of the acid treatment, however, some hydrogen is absorbed by titanium; hence the sponge metal is rather brittle. Fortunately, hydrogen can be removed by subsequent heat treatment in high vacuum, and the metal is not permanently contaminated, as it would be in the case of nitrogen or carbon impurities. At the Bureau of Mines, experimental units are operating at present with a capacity of about 100 pounds of titanium per batch. The efficiency of the process may be measured by the weight of titanium produced per pound of magnesium. It is approximately 0.68, and might be increased to about 0.8.

The second method by which titanium may be obtained in the pure ductile state is based on the original work of the Dutch physicist van Arkel, published in 1925. In this process, impure titanium powder is first mixed with a certain quantity of iodine and placed in an evacuated and sealed glass container. When the mixture is heated to about 800°F, titanium iodide forms and vaporizes. On contact with a tungsten filament heated to about 2000°F, the iodine liberated reacts with the impure titanium and the process is cyclic. The metal produced by this method is in the form of a rod about one foot long and about 3/8 inch in diameter. It is made of very large crystals, as much as 1/4 inch across. This titanium has a degree of purity not attainable by any other method. Unfortunately, the vapor deposition



Scores of companies like Remington Arms, Du Pont subsidiary, are now conducting research on melting, alloying, and (above) fabricating titanium metal.



Remington Arms test shows effect of 30-minute exposure to 2,200-degree F. flame of aluminum alloy (left), stainless steel (center), and titanium (right).

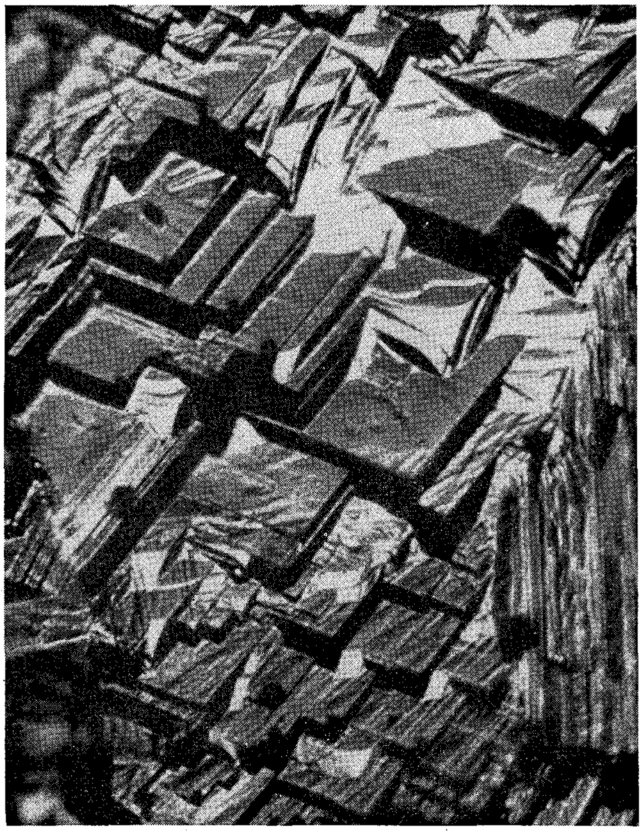
process in its present form produces only small quantities of metal. It is too early to state whether or not future engineering developments will bring this process into the field of large-scale production.

Obviously, the metallurgy of titanium is based on principles entirely different from those encountered in the production of the more usual metals. A striking feature of the metallurgy of titanium is the fact that the metal does not appear in the liquid state at any time during the process. In the Kroll method, the titanium tetrachloride is reduced to solid titanium, which remains solid at the temperature of liquid magnesium. In the van Arkel process, the vapor of titanium iodide decomposes into the solid metal at a temperature much below the melting point.

Preparation of titanium ingots

Transforming either the sponge metal or the van Arkel rods into ingots and then into structural shapes is the next difficult step in the metallurgy of titanium. The obvious reaction of any metallurgist confronted with the problem would be to try to melt the metal in vacuum or purified inert atmosphere. Here again titanium proves to have unusual properties. In the molten state it is chemically so active that it "alloys" with any presently known crucible material. Graphite is readily dissolved and contaminates the melt. Pure oxides of high melting points, such as alumina, beryllia, and thoria, are reduced by molten titanium and the amount of oxygen picked up by the metal is sufficient to promote brittleness. An additional difficulty comes from the extreme wetting power of the molten metal, which penetrates into the most minute pores of the crucible and creeps up along the walls. The crucible may empty itself, even against the force of gravity.

The problem of melting titanium, however, is not a hopeless one. Recently a technique previously used for melting molybdenum has been successfully applied to titanium. It consists of striking an arc between an electrode of the metal and a water-cooled copper crucible in an evacuated chamber. The liquid metal from the electrode flows into the crucible, where it is immediately solidified so that reaction with copper is prevented. The resulting ingot has a normal coarse-grained cast structure, and can be subsequently rolled or forged. This method will probably play an important role in the metallurgy of titanium.

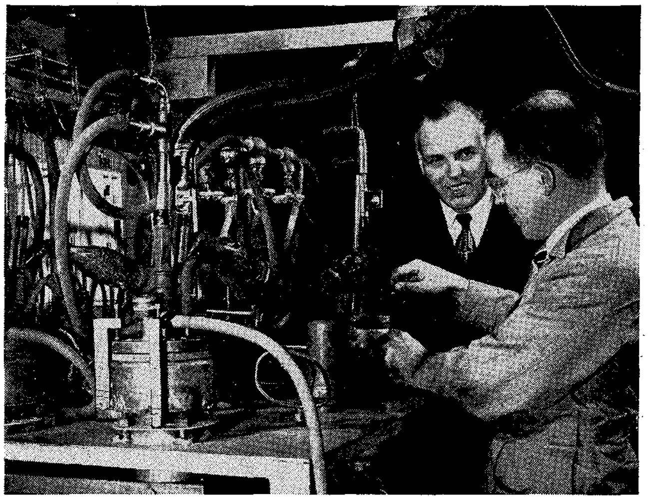


This photomicrograph reveals the crystal formation which is obtained in a titanium-molybdenum alloy by cooling through the allotropic transformation.

When confronted with a problem hard to solve, it is sometimes possible to find a way out by avoiding the problem altogether. This principle finds an application in the case of titanium. It is indeed quite possible to process the metal entirely by powder metallurgy methods, thus avoiding the inherent difficulties of the melting process. The sponge metal obtained by the Kroll process is first ground into a fine powder. This grinding is relatively easy, because the sponge titanium is rather brittle as a result of the hydrogen absorbed during leaching. The powder is then compacted into dies at pressures from 20 to 40 tons/sq in. The compacts are sintered at high temperature (generally above 2000°F) in a vacuum of at least 10^{-4}mm of mercury, during which treatment most of the hydrogen is removed. The sintering could also be carried on in a purified inert gas, instead of a vacuum, if the metal powder could be obtained free of hydrogen. Except for the necessity of sintering in a high vacuum, the powder metallurgy of titanium offers no difficulties. The powder can be considered as a soft powder (like copper or pure iron) and is easily pressed into strong compacts. During sintering, shrinkage proceeds without producing appreciable distortion, and relatively high densities may be obtained with temperatures of the order of 2000°F. The size of ingots produced by powder metallurgy methods depends on the capacity of the hydraulic presses required for compacting the powder.

Processing titanium

Pure ductile titanium obtained by one of the methods described above can be cold-rolled. Intermediate annealing treatments are, of course, necessary to prevent brittleness due to excessive cold working. Annealing can be achieved at a relatively low temperature (1500°F), but it is imperative to perform the heat treatment either in high vacuum or in an atmosphere of purified inert gas. It must be remembered that titanium at high temperature has a great tendency to dissolve ntirogen, oxygen, or hydrogen, with consequent loss of ductility. Although hydrogen can be extracted by subsequent treatment in high vacuum, nitrogen and oxygen are permanently retained. In this connection it should be pointed out that the safe temperature at which titanium can be heated in air may not be higher than about 1000°F. Unless alloys of titanium are developed that are less sensitive to the action of gases at high temperature, titanium will not be the outstanding high-temperature metal which over-enthusiastic promoters have suggested.



Small ingots of titanium alloys are melted and cast in these improvised arc furnaces at Battelle Institute. Coca-Cola bottles are containers for charging materials.

The hot-rolling of titanium brings up the same problem of protecting the metal from atmosphere. A solution to this problem which has proved to be successful on an experimental scale consists of "canning" the piece to be rolled in a sealed iron box. Heating and rolling can then be performed in air and the iron container is removed after cooling.

Alloys of titanium

As with aluminum and iron, it is quite certain that the alloys of titanium will have a much wider use than the pure metal. Iron is perhaps the best example of a metal whose physical properties are improved by alloying. Pure iron has very limited use compared with the ever-increasing applications of carbon and alloyed steels. The extraordinary versatility of alloys of iron is due to the fact that iron is a transition element, and that it has an allotropic transformation. As a transition element, iron forms extended solid solutions with a great number of metals. Having a transformation point, it lends itself to heat treatments by which non-equilibrium structures of infinite varieties can be produced.

These two remarkable features are also found in titanium, and their existence may be the most convincing argument in favor of the future importance of titanium alloys. The field is wide open for the development of alloys that might duplicate in number and versatility the older iron base alloys, with the added advantage of less weight.

Need for fundamental research

The present knowledge of titanium alloys is fragramentary. Only a few phase diagrams involving titanium have been studied. Titanium has generally been considered as a minor alloying element and only the portion of the phase diagrams in which the concentration of titanium is relatively small has been investigated. Furthermore, the few alloy systems for which these portions of phase diagrams exist do not include the most promising ones. On the basis of the modern theory of alloys, it is quite probable that the alloys of titanium with molybdenum, tungsten, vanadium, columbium, and tantalum will be among the most outstanding. At present, only sketchy information is available on these important systems. Additional research work on the phase diagrams of titanium with carbon, oxygen, and hydrogen remains of primary importance, in view of the very marked effect these three elements have on the mechanical properties of titanium.

The need for basic research on alloy systems containing titanium may not be obvious to the practical-minded metallurgist, who may object that many of our present-day alloys were developed and used long before the theoretical metallurgist was able to explain their properties. But the same practical metallurgist is using iron-carbon phase diagrams and data on rates of transformation of austenite in alloy steels without perhaps realizing that they are the result of the type of research he proposes to by-pass in his impatience to obtain new alloys of titanium. Without fundamental research the choice of alloying elements and the conditions of processing will have to be established on a semi-empirical basis—a method frequently costly in effort, time, and money.

In connection with the study of alloy structure, it is interesting to point out that in the past most of the basic work on the phase diagrams of metals has been done in Germany and in England. Even during the war these basic studies seem to have been carried through in spite of more urgent practical problems. In an article entitled "The Designation of Phase Alloy Systems" (*Metal Progress*, January 1949), Tylor Lyman draws attention to the very small contribution by workers in the United States to the origin of phase diagrams. He finds that the United States has originated only about eight per cent of the phase diagrams, while Germany has contributed 45 per cent, and England about 17 per cent. Lyman puts the question, "Who will do this fundamental research now that German science is so largely impoverished?"

This question deserves careful attention. At present, titanium research is oriented toward the rapid development of alloys for immediate use. These efforts will doubtless yield much new information quickly, but they can scarcely provide a sound understanding of the alloy systems. It will take a logically balanced program of scientific research and engineering development to realize the full possibilities of this most promising metal.

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