TITANIUM AND TITANIUM ALLOYS

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by

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PREFACE

In the few years since titanium became a commercial metal, hundreds of papers have been published dealing with the metal. These papers are scattered through the transactions of a number of scientific and technical societies and through many business publications. It is the purpose of this book to present a selective review of the work covered in these publications and to supplement it with information obtained from the producers of the commercial materials.

This book is intended for the engineer or designer interested in the possibilities of applying titanium in the solution of his problems. It is not intended for the producer of titanium. Only sufficient information is included on production to indicate the effects of melting methods on the properties. Neither will this book appeal particularly to those engaged in research and development for it deals almost exclusively with technology. The properties of pure titanium are covered briefly merely to furnish a background for a discussion of commercial materials. It is hoped that this survey will indicate the present state of knowledge of titanium technology and point to some of the directions in which progress can be expected.

Many papers have been read and abstracted in developing this book. Acknowledgment to individual authors is made in the text. However, much of the information on commercial materials has been obtained from company literature. I am indebted to E. I. du Pont de Nemours & Co., Mallory-Sharon Titanium Corp., Rem-Cru Titanium, Inc., Superior Tube Co., and Titanium Metals Corp. of America for supplying data on commercial titanium and its alloys.

Finally, it is a pleasure to acknowledge the assistance of my secretary, Miss Ruby Spector, who typed the manuscript and my wife, Helen, who prepared many of the graphs and helped read the proofs.

Westfield, N. J., February, 1954 — JOHN L. EVERHART

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1. INTRODUCTION

The intense interest in titanium apparent at every technical meeting at which it is discussed, shows that many people believe it has great commercial potentialities. This belief is based on three factors (1) abundance of raw materials (2) location of ores and (3) properties of the metal.

Titanium is the fourth most abundant element having structural possibilities in the earth's crust. Only aluminum, iron and magnesium are more plentiful. The titanium content of the crust is estimated to be greater than the combined totals of copper, lead, tin, zinc, nickel and the precious metals.

Mere abundance, however, does not insure economical availability. Minerals must be concentrated into fairly large deposits containing sufficiently high metal values to permit economical extraction from the earth if they are to be considered ores. Known deposits of high grade titanium are sufficiently plentiful to insure a supply of the metal for many years.

The location of large commercial deposits within the borders of the United States increases the interest in a metal which has high strategic value. It is this fact which has induced the Government to encourage the development of large scale production quickly. Only because of this encouragement and financial assistance has production increased from a mere 2¼ tons in 1948 to about 2300 tons in 1953.

This unusual interest in a metal only about five years old, commercially, is based also on its properties. Titanium lies roughly half way between aluminum and iron in density. On a strength/weight basis, it is superior to all other structural metals. In addition it has excellent corrosion resistance to many environments. Thus it becomes a metal of great commercial and military potentialities.

The future of titanium is largely dependent on the ability of the producers to overcome the handicaps of batch operation leading to nonuniform composition, to produce shapes of uniform quality and to develop suitable fabricating methods. All these must be achieved at prices which will make the metal truly competitive with other constructional materials. Prices will have to be reduced greatly, if titanium is to become a generally useful metal in a civilian as contrasted with a military economy. If relatively low prices are not achieved, titanium will remain a specialty metal.

Developments during the past year have indicated that many of these problems are being overcome. There has been considerable improvement in uniformity, fabrication methods have been improved, suitable machining procedures have been devised which greatly reduce this problem and joining methods are being perfected. Only price has failed to show an improvement. There was no reduction during the year 1953.

Occurrence

Titanium occurs, naturally, chiefly as rutile (TiO_2) or ilmanite ($FeTiO_2$). Most of the rutile is found in beach sands while the ilmanite is generally found in hard rock, although it is found also in sands.

Beach sands containing both of these ores are found throughout the world, the largest known sources being in Australia, India and Brazil. Deposits are found in the United States in various localities but only those in Florida are being operated on a commercial scale.

Hard rock deposits containing ilmanite are found throughout the world also. These vary in size and grade and the mere presence of ilmanite does not indicate usefulness. Large deposits containing at least 30 per cent of ore are necessary if mining is to be profitable. The Bureau of Mines estimates that the world's largest known deposit of titanium in eastern Quebec could be the source of at least 50,000,000 tons of titanium metal. The largest hard rock ilmanite mines in the United States are in upper New York state but other high grade ores have been found in Virginia and North Carolina and lower grade ores occur in at least a dozen states.

Because of the abundance of ores in this country and Canada, titanium is one of the few metals which the United States will not have to import from overseas sources in the event of an all-out war. This is one of the major reasons for the intense interest being exhibited by the Defense Department in the development of metallic titanium. Known deposits of titanium ore in the United States alone can furnish an ample supply for industry far into the future.

Extraction from the Ore

Titanium is a highly reactive element and extraction of a grade sufficiently pure to be ductile is difficult. The metal reacts with the oxygen and nitrogen of the air and in the molten state also reacts with all known refractories. Thus many problems had to be solved in winning it. At present, extraction is a two stage operation.

In the first stage, it is necessary to obtain titanium dioxide either by beneficiation of rutile or by smelting ilmenite to obtain a slag of high titanium content. Subsequently the crude oxide must be purified. In the second stage, metallic titanium is produced from this basic raw material.

Several methods have been suggested for winning metallic titanium from its ores and some have been operated on a laboratory scale. There is only one being operated on a commercial scale at present. Basically, this is the Kroll process, although various modifications are in use by different organizations. The starting material is titanium tetrachloride obtained by heating titanium dioxide, mixed with carbon, in a stream of chlorine. Titanium tetrachloride is obtained as an impure liquid which is purified by redistillation. Generally the purified tetrachloride is reduced by reaction with magnesium although other metals such as sodium can be used. The crude metal must be further treated to obtain a product sufficiently pure to be ductile upon consolidation.

Until quite recently, this reduction was carried on as a batch operation, the quantity produced in a batch was small and there was considerable variation in quality from batch to batch. However, considerable improvement has been achieved and a continuous process has been developed which should further improve the uniformity and quality of the product. The metal obtained by this method is a spongy material which must be consolidated by melting or other means.

The decomposition of titanium iodide has been used also for the production of titanium. Thus far this method has only been employed on a small scale although attempts are in progress to develop a continuous process. Since the method requires the vaporization of the iodide and its subsequent decomposition, a rather slow reaction, it appears that it will always be a high cost operation. The metal produced by this process is the purest obtainable and will probably be used mostly for experimental work. At present iodide titanium costs many times as much as the chloride product.

Other processes based on the electrolysis of a fused electrolyte offer many advantages and have been investigated extensively. One of these has reached the pilot plant stage. However, this is a batch operation, not a continuous process, and therefore will not be as economical as is desirable. Research work aimed at finding a continuous electrolytic process continues. It is probable that a method of this type will be developed but at present, and for the near future at least, a large proportion, if not the major proportion of the commercial titanium produced in the world will probably be obtained by some modification of the Kroll process.

Melting

The spongy product of the reduction process must be consolidated in some manner. Originally, powder metallurgy techniques were employed and these procedures will still find a place in the production of small parts but, for most purposes, melting is required to produce the massive ingots needed for further working. Both arc and induction melting furnaces have been employed. This step has been one of the major stumbling blocks in the process and has been responsible for the production of non-uniform material with widely varying properties.

However, the rapidly developing technology has led to great improvements in the furnaces used. Ingots up to 1200 or 1400 lb are commonly produced and furnaces have been installed which permit the production of 4000 lb ingots. This increase in size of ingots has been particularly advantageous because it has permitted the use of larger scale rolling equipment with a resulting improvement in the physical uniformity of flat products.

Probably the major melting method employed at present is arc-melting in a water-cooled copper crucible using an inert atmosphere which is generally argon. Either nonconsumable electrodes of graphite or tungsten or consumable electrodes of titanium are used, the latter being favored because they reduce the possibility of contamination of the melt. Sponge is introduced into the crucible, an arc is struck between the sponge and the electrode and a pool of molten metal forms. This solidifies rapidly in contact with the crucible walls, more sponge is added and an ingot is built up gradually. The process has been improved by a procedure called skull-melting. In this modification, a layer of titanium is frozen against the copper crucible walls. This layer acts as the crucible in ingot production and improves the purity of the product. The principal disadvantage of this melting procedure is lack of uniformity in the product because the ingot is built up of layers.

One method of improving uniformity has been the blending of selected batches of sponge. Another method, which has been suggested by Van Thyne, Turner and Kessler, particularly for produotion of alloys, is double melting. They point out that in single melting processes, segregation occurs particularly of high density constituents because of the relatively small quantity of metal which is molten at one time and the consequent lack of time to obtain uniform distribution. Two methods are employed in double melting. In one a nonconsumable electrode furnace is used for the first operation and the resulting ingot is forged to rod and used as a consumable electrode in the second operation. Alternately, consumable electrode melting is used for both operations.

Some producers prefer induction melting to arc melting. It is claimed to be the most desirable method because the stirring effect achieved during operation of the furnace assists in producing homogeneous ingots. However, it is necessary to use graphite crucibles and some carbon pick-up from the crucible occurs. Thus induction melted titanium has a higher carbon content than arc-melted and this increase in carbon has undesirable effects on some fabricating properties.

The induction method is also claimed to be the only satisfactory method of remelting heavy as well as light scrap. The reuse of scrap is one of the major problems of the industry and in this application induction melting has a definite advantage over other procedures. Some producers predict that when a suitable refractory is found which will not react with titanium, induction melting will probably supplant arc melting.

It has been suggested that the following carbon contents can be considered typical of the products produced by the different melting procedures (1) Arc-melted ingot produced with a consumable electrode, 0.03 per cent carbon; (2) arc-melted with a tungsten electrode, 0.05 per cent carbon; (3) arc-melted with a carbon electrode, 0.2 per cent carbon; and (4) induction melted, 0.6 per cent carbon.

Production

There have been many predictions of the rate of increase in production of titanium and most of them have been far too high.

Actually progress has been slow but steady. The first commercial metal was melted in 1948 and the

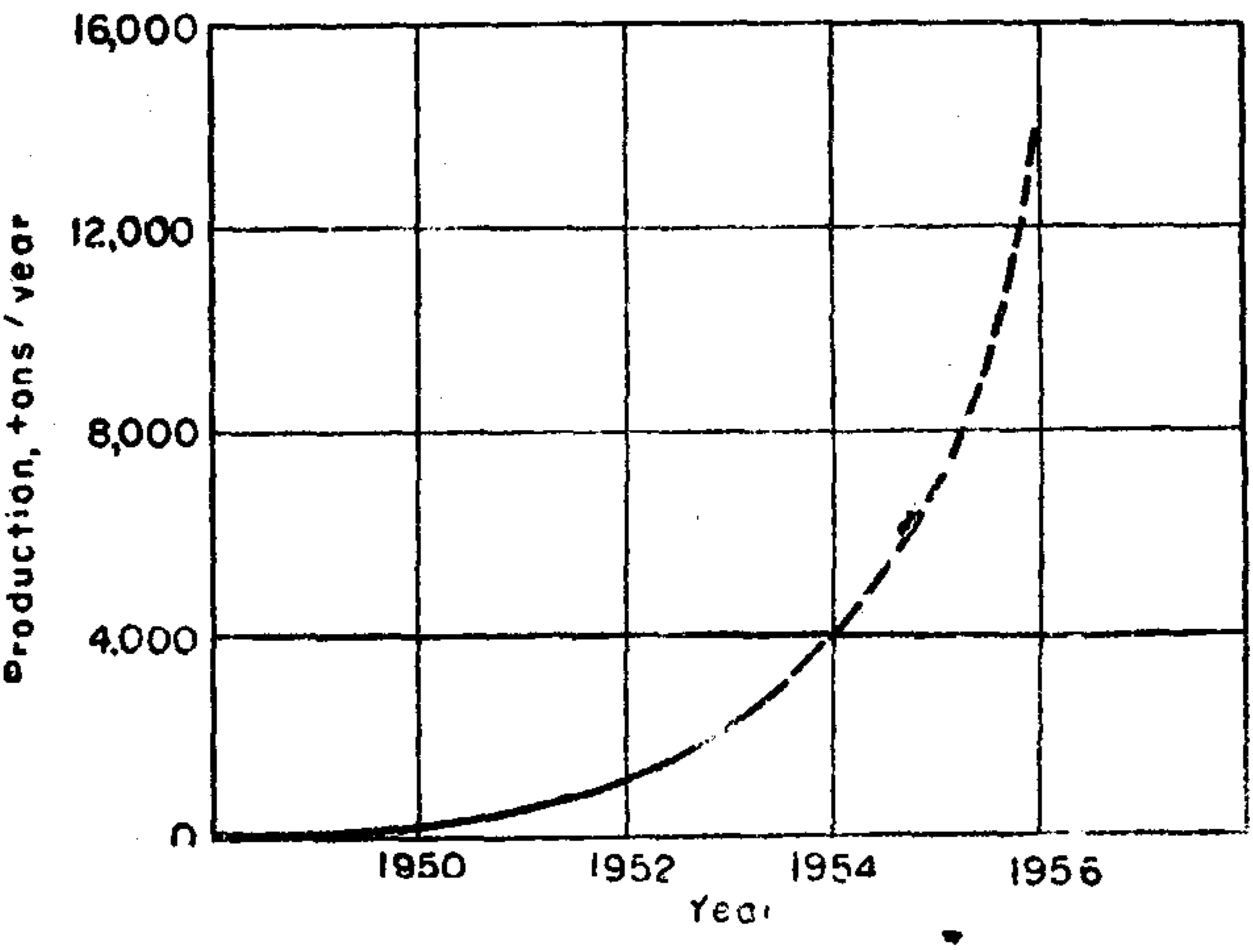

Fig. 1-1. Production of Titanium (Lippert)

output was about 5000 lb. By 1951, production had reached 500 tons and in 1953 this had increased to about 2250 tons. With new capacity both in the production of sponge and in melting about to go into operation, the figures may well be 7000 tons in 1954 and 13,000 tons in 1956. This is considerably below the predicted 22,000 tons by 1955 but is far nearer the output expected by those in close touch with the industry than the higher figure.

In the meantime, demand is increasing and it is probable that titanium will be in extremely short supply until 1956 at least. Although there will be moderate quantities available for civilian aircraft and the development of other civilian applications, most of the material will be employed in the military program.

Production figures do not tell the whole story, either. It is estimated that 2 lb of sponge are required to yield 1 lb of rolled sheet and this high scrap loss reduces the material available for use. Until recently, most of this scrap has been stored because of inability to remelt the material. However, methods of reusing scrap have been devised. It is estimated also that 40 per cent of the titanium produced is scrapped at aircraft manufacturers' plants and much of this material is going to waste because it is not being segregated and returned to the mills.

The problem of scrap accumulations at manufacturers' plants has become so serious that the Business and Defense Services Administration has been requested to issue an order calling for the segregation of scrap since titanium has been declared a scarce material essential to military programs.

The slow rate of increase in titanium production is causing considerable anxiety in the Defense Department because of the lead-time necessary in aircraft design. At a recent meeting of a Senate Committee investigating strategic materials, it was brought out that the 1953 Air Force aircraft program called for 3500 tons of titanium while only about 2300 tons were produced, thus leaving a shortage for this application alone of more than 1000 tons. It was also pointed out that the minimum requirements for the Air Force in 1956 will be 35,000 tons but under the present program, scheduled output is only 25,000 tons, and actual output will probably be half as much.

These requirements cover only the needs of the Air Force. The Army and Navy could also use titanium in considerable quantities if it was available. Thus, the three services could use to great advantage more than 100,000 tons each year and because of civilian applications, it was suggested that the production goal should be 200,000 tons per year.

One of the bottle-necks in the attempts to increase production is the reluctance of producers to expand their production facilities using the high-cost Kroll process when they are hoping that a more economical process will be developed shortly.

In order to break this bottleneck, the Government will advance funds to producers to pay for increased capacity, guarantee to purchase most if not all of the sponge, allow quick tax write-offs and permit each company to cancel its obligation to the General Services Administration if the equipment becomes obsolete during the life of the contract. Theoretically, this expansion should increase the capacity to nearly 35,000 tons by 1957.

Economics

Titanium today is an expensive metal. Domestic sponge carries a price tag of $3 to $5 per lb. This figure when contrasted with the price of a few cents per lb for crude titanium dioxide reflects the cost of the Kroll process. It is claimed that the Japanese are able to produce sponge at a lower figure and they are actually delivering small quantities of the order of 5 tons per month in this country at about $400 per ton under the domestic price. However, the bulk of the sponge produced in this country, and as a matter of fact, in the free world will come from domestic producers for some years. Unless a lower cost process is introduced and brought rapidly into tonnage production, it is doubtful whether prices will fall much below $3 per lb in the near future.

When melting and mill charges are included, the prices of mill products such as sheet and rod range upward from about $10 per pound. One of the reasons for the high prices of mill products has been the inability to reuse scrap. However, two of the producers have developed procedures for remelting varying proportions of scrap and this development should result in a reduction in production costs which will be reflected in lower prices of these products.

Relative prices of Type 302 stainless steel, aluminum alloy 75S, magnesium alloy FS1 and titanium using several different bases are shown in Fig. 1-2. Since these metals are compared so frequently