TITANIUM

Physical Metallurgy Processing and Applications

Edited by
F.H. Froes

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F.H. Froes, editor

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Preface

THE TITANIUM INDUSTRY has been in existence for approximately 60 years, and a great amount of information on the science and technology of this "wonder" metal has been compiled in that relatively short time. This reference book is based on an education course developed by ASM International in the early 1980s, which has been revised several times as new technical information became available, the latest revision in 2014 by F.H. (Sam) Froes, an expert in titanium and titanium alloy technology.

This book is a comprehensive compilation of the science and technology of titanium and its alloys. It details the history of the titanium industry and discusses various extraction processes, including the Kroll and Hunter processes and others. The fundamentals of solidification and phase diagrams are discussed, numerous detailed descriptions of beta (β)-to-alpha (α) transformations are included, and there are extensive discussions on processing, characteristics, and performance of the different classes of titanium alloys, including alpha (α), alpha-beta (α-β), beta (β), and intermetallic compounds. There are chapters devoted to alloying, deformation and recrystallization, mechanical properties and testing, and metallography. The following are also covered: melting and casting; forming of plate, sheet, strip, and tubing; joining; and machining. Practical aspects of primary and secondary processing are given, including a comprehensive description of superplastic forming. Details of expanding powder metallurgy techniques are included. The relationship of microstructure to mechanical properties is addressed in detail. A detailed description of corrosion behavior is included, and a comprehensive section on current applications of titanium and its alloys, documenting why certain alloys are used in various applications as well as their limitations, is also addressed.

Permeating the book are examples of how lowering the cost of titanium can lead to increased use. I believe that this book will be of considerable value to persons new to the industry as well as practitioners, and that it will significantly increase your knowledge of the science and technology of titanium.

Dr. F.H. (Sam) Froes
Tacoma, Washington, August 2014

About the Editor

Dr. F.H. (Sam) Froes has been involved in the titanium field for more than 40 years. After receiving a B.S. from Liverpool University, M.S. and Ph.D. degrees from Sheffield University, he was employed by a primary titanium producer, Crucible Steel Company, where he was leader of the Titanium Group. He spent time at the United States Air Force (USAF) Materials Laboratory, where he was a branch chief and supervisor of the Light Metals Group, which included titanium. While at the USAF Laboratory, Dr. Froes co-organized the landmark TMS-sponsored Conference on Titanium Powder Metallurgy in 1980. This was followed by 17 years at the University of Idaho, where he was director and department head of the Materials Science and Engineering Department. During this tenure, Dr. Froes was Chairman of the World Titanium Conference held in San Diego in 1992. He has over 800 publications, in excess of 60 patents, and has edited almost 30 books, the majority on various aspects of titanium. Recent publications include a comprehensive review of titanium powder metallurgy and an article on titanium additive manufacturing. He has organized more than 10 symposia on various aspects of titanium science and technology, including in recent years co-sponsorship of four TMS symposia on cost-effective titanium. Since the early 1980s, Dr. Froes has taught the ASM International education course "Titanium and Its Alloys." He is an ASM Fellow, a member of the Russian Academy of Science, and was awarded the Service to Powder Metallurgy by the Metal Powder Association.

Contents

CHAPTER 1

History and Extractive Metallurgy*

THE ELEMENT TITANIUM (Ti) is a unique metal. It is the fourth-most abundant structural metal in the Earth's crust (~0.5%). It has a desirable combination of physical, chemical (corrosion resistance, low bioreactivity), and mechanical properties that make it attractive for many aerospace, medical, and industrial applications (Ref 1.1, 1.2). Early use was geared toward the aerospace industry, but later applications included industrial, automotive, sports, and medicine due to its unique characteristics. Titanium is a transitional metal, distinct from other light metals such as aluminum and magnesium. It has a high solubility for a number of other elements and high reactivity with interstitial elements (oxygen, nitrogen, hydrogen, and carbon). Titanium has a relatively short production history, with the first commercial quantities of the metal produced in 1950. By 2011, worldwide annual sponge production increased to 186,000 metric tons (excluding U.S. production) and capacity increased to 283,000 metric tons. Production of titanium ores and concentrates is approaching 10 million metric tons. Current and historic production and data on titanium are maintained by the United States Government (Ref 1.3, 1.4, 1.5).

Historical Background

The element titanium was discovered in England by the Reverend William Gregor in 1790. In 1791, Gregor presented a description and chemical composition of some black magnetic sands found on the southern Cornish coast. His analysis of the black sand corresponded roughly to that of the mineral ilmenite ($FeTiO_3$).

Little interest was shown in the discovery until 1795, when M.H. Klaproth noticed close agreement between Gregor's account and results of his own investigation of oxide extracted from rutile (impure TiO_2) from Hungary. The identity of the two materials was established; Klaproth acknowledged priority to Gregor and applied the name titanium to the new element.

Early attempts to prepare pure titanium from its compounds resulted in the formation of nitrides (TiN), carbides (TiC), or carbonitrides (TiCN), which, because of their metallic luster and appearance, were often mistaken for metal. In 1887, L.F. Nilson and O. Peterson obtained a product of 97.4% purity by reducing titanium tetrachloride with sodium in an airtight steel cylinder.

Another early worker was H. Moissan, who reduced titanium dioxide with carbon in a lime crucible at the temperature of a powerful electric arc. The product contained 5% C, but on reheating with additional TiO_2 this was reduced to 2%.

The first pure titanium metal was prepared in the United States by M.A. Hunter at the General Electric Company in 1906. Hunter followed the methods of Nilson and Peterson and excluded air from the apparatus. He obtained metallic titanium practically free of impurities.

In Holland in 1925, A.C. Van Arkel and J.H. deBoer produced titanium by thermal decomposition of titanium tetrachloride. Titanium made by this procedure was very expensive but pure.

The start of the present large-scale titanium industry can be traced to the work of W.J. Kroll. He produced ductile titanium metal by reacting titanium tetrachloride with magnesium metal in a closed pressureless system with an inert gas (argon) atmosphere. The first display of cold ductile titanium in the United States (produced by Kroll at the Bureau of Mines in Albany, Oregon) took place in October 1938.

*Adapted and revised from Eldon R. Poulsen and Francis H. Froes, originally from Richard A. Wood, *Titanium and Its Alloys*, ASM International.

The Degussa Company was working on titanium at approximately the same time as Kroll. They produced over 400 kg (880 lb) of titanium by sodium reduction of titanium tetrachloride. However, the material contained up to 2% Fe.

In approximately 1940, the United States Bureau of Mines became interested in the characteristics and production of titanium metal. After reviewing all the known processes, the Bureau selected the Kroll process as the one most likely to economically produce ductile titanium, and it set up a series of reactors for making titanium. A Bureau publication in 1946 described a Kroll unit capable of making 7 kg (15 lb) batches of good-quality titanium powder by magnesium reduction, followed by acid leaching to remove the excess magnesium and $MgCl_2$ (Fig. 1.1).

In 1949, the Bureau reported the successful operation of a magnesium-reduction unit for making 40 kg (90 lb) batches of titanium. This unit was similar to the one previously reported, except for the batch size. In 1952, the Bureau reported the removal of magnesium and magnesium chloride from titanium sponge by vacuum distillation.

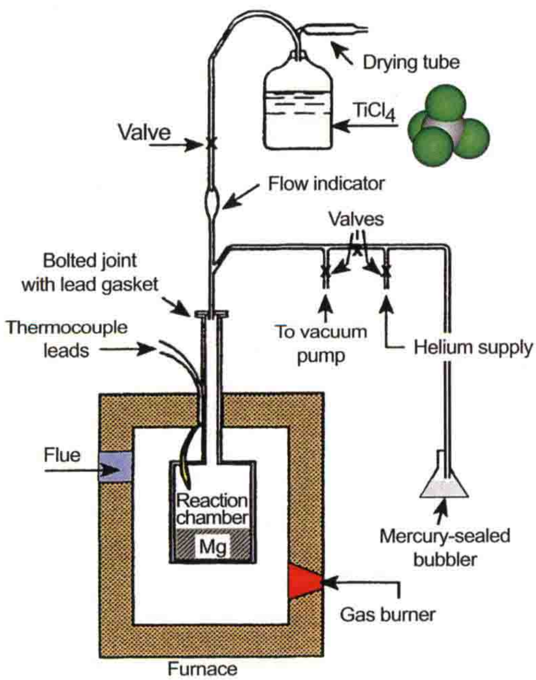

Fig. 1.1 Reaction vessel for making titanium powder using the Kroll process. The equipment was capable of producing 7 kg (15 lb) batches.

The Early Titanium Industry and More Recent Developments

In the early 1950s, a number of large companies helped to meet the challenge to produce titanium. In most cases, new organizations were formed to combine technical expertise with metal production facilities. The companies formed were normally a combination of a pigment company with the chemical expertise and a stainless steel company with the vacuum melting and mill processing capabilities.

In the United States in the late 1940s/early 1950s, a number of companies entered the titanium business, with strong government support. A pilot unit created in 1947 at DuPont expanded production to 800,000 kg (1.8 million lb) of sponge per year by 1952. Remington Arms, a 60%-owned DuPont subsidiary, used iodide titanium and DuPont sponge. Studies by Battelle Columbus and Remington Arms included melting, alloy development, physical metallurgy, and the production of mill products as early as 1948. Powder approaches were evaluated, but vacuum arc melting proved to be most successful. The first titanium for actual flight was ordered from Remington Arms in 1949 by the Douglas Company. Unalloyed (A70) sheet was rolled by Republic Steel and formed into 578 different parts for the Douglas Mach 2 X -3 Stiletto. The technical cadre assembled at Remington Arms later became the nucleus for Rem-Cru Titanium Inc., formed equally by Remington Arms and Crucible Steel in June 1950.

Allegheny Ludlum Steel Corporation started a semicommercial titanium-melting facility in 1949. They and the National Lead Company organized Titanium Metals Corporation of America (TMCA) in January 1950 on an equal basis. Later, TMCA became the first fully integrated company for producing titanium from ore to finished products. National Lead operated the Bureau of Mines sponge plant in 1951 and constructed pilot plants for sponge in 1949 and 1951. Subsequently the name TMCA was changed to TIMET.

P.R. Mallory Company entered the market in 1947 when they began work on the powder metallurgy of titanium under Navy sponsorship. Along with the Sharon Steel Corporation, they organized the Mallory-Sharon Titanium Corporation on an equal basis in 1951 to produce and market the metal. National Distillers and Chemical Corporation started sponge production in 1957. They acquired P.R. Mallory's interest in Mallory-Sharon in 1958, changing the name to

Reactive Metals, Inc. In 1964, U.S. Steel acquired 50% of the company, and the name eventually was changed to RMI Company.

Cramet, Inc. was organized in 1953 as a wholly owned subsidiary of the Crane Company to supply sponge for Republic Steel. Republic organized a titanium division in 1950 to produce mill products. Dow Chemical Company started sponge production in 1954, and the Electrometallurgical Company of Union Carbide began in 1956. All of these companies dropped out of the market during the 1958 downturn, which resulted in large part from the change in emphasis by the U.S. military from the use of manned aircraft to missiles.

However, production in the early and mid-1950s accelerated rapidly, although not as rapidly as the overly enthusiastic predictions that production would reach 180 million kg (400 million lb) by 1960, which would have exceeded the production of stainless steel and magnesium, and approached the production levels of aluminum by 1965. Some early production capacities in the United States are given in Table 1.1.

Other U.S. producers became active at later dates, including Oregon Metallurgical Corporation, Dow-Howmet, International Titanium Incorporated of Washington, Western Zirconium Company, and Albany Titanium Company. Early U.S. sponge producers are listed in Table 1.2 along with capacities.

Numerous other companies became active participants in the titanium industry, including forgers, rollers, extruders, foundries, tube manufacturers, and fabricators.

The development and growth of titanium production also occurred outside the United States. Work in the United Kingdom, for example, centered at Imperial Chemical Industries Ltd. (ICI) where sponge production began in 1948. A few hundred kilograms (pounds) of magnesium-reduced Kroll sponge were produced. Plant capacity was increased to 9000 kg (20,000 lb) per year in 1951, and a 90,000 kg (200,000 lb) per

Table 1.1 Early capacities of major U.S. producers

	Mill product capacity, est. 1956		Ingot melting capacity, est. 1957	
Company	$\times 10^6$ kg/yr	$\times 10^6$ lb/yr	$\times 10^6$ kg/yr	$\times 10^6$ lb/yr
Titanium Metals Corp. of America	2.3	5.0	10.0	22.0
Rem-Cru Titanium Inc.	1.8	4.0	6.0	13.2
Mallory-Sharon Titanium Corp.	1.4	3.0	5.4	12.0
Republic Steel Corp.	0.5	1.1	5.4	12.0

Source: TIMET records

Table 1.2 U.S. titanium sponge producers and capacity, 1947 to 1987

	Approximate capacity, 1000 kg (2000 lb) per year					
Organization	Process(a)	Capacity	Initial year	1958	1984	1987
U.S. Bureau of Mines	Mg, V	1.8 (4)	1947	...	(b)	...
E.I. du Pont de Nemours & Co., Inc.	Mg, V	2.3(5)	1947	6,500 (14,400)	(b)	...
Titanium Metals Corporation of America	Mg, L	3,200 (7,200)	1951	8,200 (18,000)	14,500 (32,000)	14,500 (32,000)
Dow Chemical Company	Mg, L	100 (216)	1954	1,600 (3,600)(b)	(b)	...
Cramet, Inc.	Mg, L	470 (1,034)	1955	5,500 (12,000)	(b)	...
Union Carbide Corp.	Na, L	6,800 (15,000)	1956	6,800 (15,000)	(b)	...
National Distillers and Chemical Corporation(c)	Na, L	4,500 (10,000)	1958	4,500 (10,000)	8,600 (19,000)	8,600 (19,000)
Oregon Metallurgical Corporation	Mg, L	...	1966	...	4,100 (9,000)	4,100 (9,000)
D-H Titanium Company(d)	E, L	90 (200)	1981	...	(b)	...
Teledyne Wah Chang Albany	Mg, V	910 (2,000)	1980	...	1,400 (3,000)	...
Western Zirconium Company	Mg	455 (1,000)	1982	...	5,900 (13,000)(e)	...
Albany Titanium, Inc.	K_2TiF_6	...	1982	...	...	...

(a) Mg = Kroll (magnesium) process; V and L = vacuum distillation or leaching; Na = sodium process; E = electrolytic process. (b) Operations discontinued. (c) Now RMI Company, owned by ND&CC (50%) and U.S. Steel (50%). (d) Pilot plant operation from 1979 to 1982. (e) Estimate. Source: TIMET Records year plant was planned. However, following development of a modified production process, subsequent plants were changed to a sodium-reduction technique, with capacities of 45,000 kg (100,000 lb) per year in 1953 and 1.5 million kg (3 million lb) in 1955. At the same time, ICI Metals Division (subsequently IMI) started melting titanium at a capacity of 150,000 kg (300,000 lb) per year in 1954. By 1955, ICI was producing 1.5 million kg (3 million lb) and became the principal European manufacturer of titanium and titanium alloy mill products.

In continental Europe, ingot melting and fabrication started in approximately 1955 and has continued since at companies in France, Germany, and Sweden. Sponge was manufactured for a few years in France, but the process was discontinued in 1963.

The birth of the Soviet titanium industry occurred in 1950, and Kroll sponge production began in 1954. Major expansions have been made since that date.

Several Japanese firms also became early sponge producers, as shown in Table 1.3, supplying metal to other countries, including the United States.

By 1987, U.S. sponge manufacturers had been reduced to three: TIMET, RMI, and Oremet. The Japanese by then had become major sponge producers, with limited capacity in melting and processing.

Early challenges of production included development of inert double-consumable melting in cold-mold furnace, circumvention of hydrogen embrittlement due to inadequate vacuum melting, chemical cleaning and use of gas furnaces, and hot salt stress-corrosion cracking due to chlorides on stressed specimens above 3000 °C (5400 °F). During the early 1950s, the value of aluminum, manganese, and vanadium as alloy additions was established in alloys such as Ti-8Mn, Ti-4Al-4Mn (1951), and the "workhorse alloy" Ti-6Al-4V (1954), patented by Crucible Steel. The first beta alloy, B120VCA (Ti-13V-11Cr-3Al), was also developed by Crucible Steel and was used extensively on the SR-71 (1955). Silicon additions for elevated-temperature use were introduced in Britain (1956). McDonnell (later McDonnell Douglas) used just 13.6 kg (30 lb) of titanium on the F3H airframe (1951), increasing the use to 136 kg (300 lb) in 1954. The experimental X-15 high-flying supersonic aircraft was composed of 17.5% by weight titanium alloy. Engine use was also established in the mid-1950s, with first use on the PWA J57 in 1954, with an increased use on the GE J73 (6% in 1954). The Rolls-Royce Avon engine used Ti-2Al-2Mn starting in 1954. At the same time, use of titanium in corrosion applications and for orthopedic devices was occurring. In 1957, the U.S. titanium industry had an annual capacity of 20.4 million kg (45 million lb) of sponge and a capacity of greater than 9 million kg (20 million lb) of mill products. (Despite this capacity, only 4.5 million kg, or 10 million lb, were shipped in 1957.) The late-1957 decision by the U.S. military to emphasize missiles over manned aircraft resulted in a thinning out of the titanium industry.

By 1970, space exploration and the launching of a number of new civilian jets during the 1960s resulted in a tripling of mill product shipments in the United States to 13.5 million kg (30 million lb). Over 90% of these shipments went to non-military aerospace systems such as the B747, DC10, and L1011. Engine use also increased the GE4 (slated for use on the U.S. Supersonic Transport, or SST), which was composed of 32% Ti by weight. Advances in quality occurred with the development of triple melting for rotating components and the avoidance of inclusions by more careful cleaning of scrap. Nonaerospace use of titanium also developed; desalination plants, power plants, and other fresh- and saltwater applications made use of corrosion-resistant grades containing small additions from platinum group metals.

Just one year later, in 1971, with the cancellation of the U.S. SST project, the titanium market reached another low, with just 9.26 million kg

Table 1.3 Early Japanese titanium sponge production (1000 kg, or 2000 lb, per year)

Company	1952	1953	1954	1987
Osaka Titanium Manufacturing Company	8.2 (18)	54.4 (120)	307 (676)	18,000 (40,000)
Toho Titanium Industry Company, Ltd.	...	4.5 (10)	239 (526)	12,000 (26,000)
Nippon Soda Company Ltd.	...	5.4 (12)	34 (74)	4,500 (10,000)
Showa Ti	...	...	...	2,700 (6000)
Nippon Electric Metallurgical Company, Ltd.	...	...	25.4 (56)	...
Mitsui Mining and Smelting Company	...	...	6.4 (14)	...
Total	8.2 (18)	64.4 (142)	611 (1346)	37,000 (82,000)

Source: TIMET records