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The Progress of Analysis Technologies for Titanium

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Abstract

The importance of titanium analytical technologies has notably increased with the rise in the demand for titanium and titanium base alloys. This paper describes the progress in the composition analysis method and characterization, such as structure analysis. In recent years, there are many papers that raise attention to trace level analysis in the high purity titanium and characterization.

1. Introduction

Since sponge titanium was first produced in Japan in 1952, analysis methods relating to titanium have advanced as the production of titanium ingots and mill products increased, and advanced analysis methods have come to be practiced in proportion to the progress of standardization of analysis methods and advancements of analysis facilities. Many technical papers worthy of special attention have been presented lately, particularly in relation to the research and development of analysis methods of trace elements in high purity titanium and characterization, such as structure analysis employing physical analysis apparatuses.

This paper gives an overview of the following two aspects related to the titanium-related analysis, namely composition analysis (outline, standard analysis methods, composition analysis methods other than the standard methods, and trace element analysis methods) and the characterization employing physical analysis apparatuses, and, after that, future prospects. The author investigated reference literature publicized mainly since 1985, but those related to the field such as shape-memory alloys and hydrogen-absorbing alloys, have been omitted.

2. Composition Analysis Methods

2.1 Outline of Analysis Methods

The Japan Titanium Society was founded at the same time that commercial production of titanium products commenced in Japan and the society began its activities with the standardization of analysis methods. Its organ, Titanium Japan, has covered many articles to introduce and explain analysis methods developed by its member companies since the first issue. More recent issues of the Titanium Zirconium Magazine include reports to combine titanium refining technologies with analysis technologies[1,2] and those to discuss the then progress and problems of the titanium-related analysis[3]. After many reports on the research of the analysis methods used by titanium producers were publicized in the Titanium Japan and after Toho Titanium and Kobe Steel publicized their own in-house analysis practices of titanium[4-6], Nippon Steel reported on technologies relating to gas and chemical analyses methods and standard samples for analysis developed internally in an article titled "Element Analysis Methods of New Materials" [7]. Ever since, many analysis technologies developed by the titanium producers have been proposed and utilized as drafts for the establishments and revisions of the standards of analysis methods under the Japanese Industrial Standard (JIS).

With respect to the present state of analysis technologies closely

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linked with production of titanium products, in recent issues of the Titanium Japan, the Technical Committee of the Japan Titanium Society wrote a series of articles titled "Titanium Production Technologies." In the Titanium Analysis Method edition[8,9] of the series of articles, explained in detail are a variety of sampling and analysis methods and analysis principles relating to the inspection analysis for raw material control, analysis for process control and analysis of products (including high purity titanium) covering the processes from the raw materials to the final products.

2.2 Standard Analysis Methods

2.2.1 Standardization of Analysis Methods in Japan

Standards of titanium products are provided in Japan under the JIS and the Titanium Industry Standard (TIS) set forth by the Japan Titanium Society, supplementing JIS. JIS stipulates the material standards of sponge titanium, pure titanium and titanium alloys, and specifies analysis methods of 13 elements including all the elements the contents of which are specified in respective material standards and some trace elements. The specified analysis methods include chemical analysis methods, atomic absorption spectrometry, ICP atomic emission spectrometry, gas analysis methods, X-ray fluorescence spectrometry, and spark discharge atomic emission spectrometry.

Table 1 shows historical changes of the analysis methods under JIS. The first meeting of the Analysis Subcommittee of the Japan Titanium Society was held in 1953 to discuss standardization of the analysis methods of Fe, C, Si, N and Mg, important for the export of sponge titanium. The results of the discussion took the shape of a standard in JIS: 1957, the first titanium-related standard under JIS, in which the analysis methods of 7 elements covering the above 5 elements and Mn and Cl were specified. Then, JIS was revised in 1961 to provide one standard for each of the elements and newly establish general rules for sampling and analysis methods and a new standard of an analysis method of H. The titanium-related JIS provisions were intensively revised in 1973, 1988 and around 1995 to incorporate the latest analysis technologies of the time. The revisions in 1988 were characterized especially by a revision of the gas analysis methods and application of the standards to alloys, and those around 1995 by inclusion of the ICP atomic emission spectrometry and expansion of the application to alloys.

The TIS stipulates standards of analysis methods for 15 alloy elements not provided in the JIS material standards. The TIS recently set forth analysis methods (ICP atomic emission spectrometry) for addition elements of the alloys containing Ru, Ni, and Co, the material standards for which were registered in ASTM, and standardization of the analysis methods for the alloys containing rare earth element and S are being discussed at present.

The elements to be analyzed, analysis methods and applicable ranges of the standardized analysis methods are shown in **Table 2**.

2.2.2 Standardization of Analysis Methods in Overseas Countries

In the U.S.A., the analysis methods for 19 elements in the range from trace amounts to high concentrations are specified in the ASTM under E120, E1409 and E1447 as referee methods. The specified methods are, for example, a mixture of what are stipulated under JIS and TIS, but E120 specifies a W analysis method not included in JIS and TIS, while no analysis methods are provided for C and Na. Whereas the material standards of the ASTM stipulates upper limits of individual impurity elements (< 0.1 mass %) and an upper limit of all the impurity elements (< 0.4 mass %), their analysis methods are not specified. Generally, the ASTM's standard system is rather slow in revising analysis methods. Wet chemical analysis methods form the main stream. The ICP atomic emission spectrometry is not included in the ASTM standard system.

In Russia, like in the ASTM, the analysis methods for 19 elements are specified in the GOST standard system, and the standard system is similar to the ASTM in that most of the specified analysis methods are for alloy elements. Most of the methods are wet chemical analysis methods established around 1986. Composition standards of pure titanium are specified in the BS of the U.K. and the DIN of Germany, but because no quotation of analysis method standards under these standard systems have been seen, it seems that no titanium-related analysis methods are specified in either of them.

The applicable ranges of these foreign standards are shown in Table 2 together with the standards under the JIS.

2.3 Composition Analysis Methods Other than Standard Methods

There have been many noteworthy papers related to composition analysis methods other than the standard methods especially in the last few years when high purity titanium products came to be used in the field of electronic materials such as target materials and analysis technologies showed remarkable advancements in response to increased significance of analysis in the fields such as development and control of the high purity titanium products. The purity of titanium targets is mostly determined in the ingot making stage. Alkali metals (Na and K), heavy metals (Fe, Cr, etc.), and soft error-inducing U and Th are harmful elements for the titanium targets and their analysis in trace amounts is of importance.

2.3.1 Chemical Analysis Methods

(1) Titration Methods

There is a paper[10] reporting determination of Al in a Ti-Al-V alloy by the EDTA titration, characterized by determining Al without separating, unlike the method under the JIS.

(2) Spectrophotometric Methods

1) Al: There is a paper[11] reporting determination of 0.1 to 1.0% of Al using a chrome azural S complex, eliminating interference of Ti and alloy elements by masking with H_2O_2 and Zn-EDTA.
2) V: 0.19 to 4.0% of V in alloys containing V was determined through extraction of a 4-(2-pyridyrazo) resorcinal complex[12].
3) Ru: 0.01 to 1.0% of Ru was determined at a relative standard deviation of 1.5%, by transforming Ru in a Ti-Ru-Ni alloy into a thiourea Ru complex[13].
4) P: A spectrophotometric method was reported[14], wherein P in a Ti-Al alloy was transformed into P-molybdenum blue, after separating Ti, Fe and Ni using NaOH and masking with potassium sodium tartrate.
5) Te: 0.01% of Te was determined at a relative standard deviation of 2.3%, by transforming Te in a Ti-Al alloy into tellurium bromide[15].
6) Sb: 0.02% or more of Sb can be determined by transforming Sb in a Ti-Al alloy into a 5-Br-PADAPT complex and extracting it using benzene[16].
7) Si: A detection limit of Si of 0.07 ppm was obtained through the spectrophotometry[17] of Si-molybdenum blue, after separating Si as a fluoride from an acid-decomposed solution by distillation. A similar method is specified in JIS H 1618.
8) Pd: There is a paper reporting a method[18] to extract 0.1 to 0.8% of Pd contained in a Pd alloy as a PAR-XMH complex by the chloroform extraction with EDTA.

(1) Others

1) Nb: There is a paper[19] reporting a reaction rate analysis method to determine 0.1 to 10% of Nb, taking advantage of a catalytic reaction of Nb in a reaction between H_2O_2 and ascorbic acid.

Table 1 Historical Changes of Analysis Methods of Titanium and Titanium Alloys under JIS

JIS No.	Item	Time of establishment and revision in JIS and description					
		1957	1960 - 1969	1970 - 1979	1980 - 1989	1990 - 1999	2000 -
H 1610	Sampling		Established (1961), applicable to sponge Ti only.			Revised (1995) to expand application to ingots and mill products of Ti and alloys.	Revised (2001) to expand application to Ti casting.
H 1611	General rules for analysis method		Established (1961) applicable to Ti only.	Revised (1973) to expand applicable elements.		Revised (1995) to expand application to alloys and applicable elements.	Revised (2001) to expand application to Ti casting.
H 1612	N determination method	Established as H 1601. Distillation- sulfuric acid/ sodium hydroxide back titration method.	Revised (1961) as separate standard H 1612.	Revised (1973) to include distilled separation -Nessler spectrophotometry.		Revised (1993) to expand application to alloys, delete distilled separation-Nessler spectrophotometry and include inert gas fusion thermal conductivity method.	
H 1613	Mn determination method	Established as H 1601. Periodate oxidation spectrophotometry.	Revised (1961) as separate standard H 1613.	Revised (1973) to include atomic absorption spectrometry.		Revised (1996) to expand application to alloys and include ICP atomic emission spectrometry.	
H 1614	Fe determination method	Established as H 1601. Thiocyanate spectrophotometry.	Revised (1961) as separate standard H 1614.	Revised (1973) to include o-phenanthroline spectrophotometry and X-ray fluorescence spectrometry. Revised (1976) to introduce SI units.		Revised (1995) to expand application to alloys and include atomic absorption spectrometry and ICP atomic emission spectrometry.	
H 1615	Cl determination method	Established as H 1601. Silver chloride separation-sodium sulfate spectrophotometry.	Revised (1961) as separate standard H 1615 and include silver chloride gravimetry.	Revised (1973) to delete silver chloride gravimetry and include silver nitrate titrimetry.		Revised (1997) to delete silver chloride separation- sodium sulfate spectrophotometry and include potentiometric titrimetry.	
H 1616	Mg determination method	Established as H 1601. Titan yellow spectrophotometry.	Revised (1961) as separate standard H 1616 and include sodium thiosulfate precipitation separation method.	Revised (1973) to delete sodium thiosulfate precipitation separation method and include atomic absorption spectrometry. Revised (1976) to introduce SI units.		Revised (1995) to expand application to alloys, delete titan yellow spectrophotometry and include ICP atomic emission spectrometry.	
H 1617	C determination method	Established as H 1601. Combustion gravimetry.	Revised (1961) as separate standard H 1617.	Revised (1973) to delete combustion gravimetry and include combustion neutralization titrimetry, combustion conduction method and combustion electricity method.	Revised (1988) to expand application to alloys and include combustion infrared absorption method and combustion thermal conduction method.	Revised (1995) to modify format and introduce tolerances.	
H 1618	Si determination method	Established as H 1601. Gravimetry.	Revised (1961) as separate standard H 1618 and include molybdenum blue spectrophotometry.	Revised (1973) to modify format.		Revised (1995) to expand application to alloys and include silicon tetra fluoride vaporization separation- molybdenum blue spectrophotometry.	
H 1619	H determination method		Established (1961). Vacuum fusion method. Vacuum heating extraction method. Equilibrium pressure measuring method (a) (reference method).	Revised (1973) to include vacuum heating constant volume pressure measurement method (b), high-temperature vacuum fusion constant volume pressure measurement method (c) and vacuum heating gas volume method.	Revised (1988) to expand application to alloys and delete methods (a), (b) and (c), and include vacuum heating gas chromatography and inert gas fusion gas chromatography.	Revised (1995) to delete vacuum heating gas chromatography and introduce SI units.	
H 1620	O determination Method		Established (1968). Vacuum heating constant volume pressure measurement methods A and B.	Revised (1973) to include vacuum heating constant volume pressure measurement method, inert gas fusion electricity method, inert gas fusion conduction method and inert gas fusion gas chromatography.	Revised (1988) to expand application to alloys, delete inert gas fusion conduction method and include vacuum fusion gas chromatography and inert gas fusion infrared absorption method.	Revised (1995) to delete inert gas fusion electricity method and vacuum fusion gas chromatography, and introduce SI units.	
H 1621	Pd determination method			Established (1976). Dimethylglyoxime spectrophotometry. PAN extraction spectrophotometry. X-ray fluorescence spectrometry. P-nitroso-dimethylaniline spectrophotometry (reference method).		Revised (1992) to delete PAN extraction spectrophotometry and p-nitroso-dimethylaniline spectrophotometry and include ICP atomic emission spectrometry.	
H 1622	Al determination method			Established (1976). Alkali separation oxine gravimetric method. Alkali separation EDTA titration method.		Revised (1998) to delete alkali separation EDTA titration method and include ICP atomic emission spectrometry.	
H 1623	Na determination method				Established (1981). Flame photometry. Atomic absorption spectrometry.	Revised (1995) to delete flame photometry.	
H 1624	V determination method					Established (1990). Potassium permanganate oxidation-sulfuric acid 2-ammonium iron (II) titration method.	
H 130	Atomic emission spectrometry			Established (1970) for application to Mn, Mg, Si, Fe.		Revised (1995) to delete Mn, Mg and include C.	

Table 2 Comparison of standard analysis methods of titanium and titanium alloys (JIS, ASTM, GOST and TIS)

Element	Applicable Range (% (m/m)) and Analysis Methods
	0.001 0.005 0.01 0.05 0.1 0.5 1 5 10 50
N	0.002 0.1 JIS H1612 Titration method
	0.005 0.03 JIS H1612 Inert gas fusion thermal conductivity method
	0.005 0.2 ASTM E120 Titration method
	GOST 9863.1 Unclear
Mn	0.003 0.1 JIS H1613 Spectrophotometric method
	0.001 0.05 JIS H1613 Atomic absorption spectrometry
	0.001 0.1 JIS H1613 ICP atomic emission spectrometry
	0.005 0.75 ASTM E120 Spectrophotometric method
	0.1 20 ASTM E120 Titration method
	0.1 3 GOST 19863.7 Spectrophotometric method
	0.5 TIS 7708 Spectrophotometric method
Fe	0.005 2 JIS H1614 Spectrophotometric method
	0.005 2 JIS H1614 Atomic absorption spectrometry
	0.01 3 JIS H1614 ICP atomic emission spectrometry
	0.005 1.6 JIS H1614 X-ray fluorescence spectrometry
	0.01 0.5 JIS H1630 Spark discharge atomic emission spectrometry
	0.2 20 ASTM E120 Titration method
	0.005 1 ASTM E120 Spectrophotometric method
	0.1 0.3 ASTM E539 X-ray Fluorescence spectrometry
	0.1 1.6 GOST 19863.5 Spectrophotometric method
	0.1 1 GOST 19863.5 Atomic absorption spectrometry
	0.002 2 TIS 7811 Spectrophotometric method
	0.5 TIS 7811 Titration method
Cl	0.005 0.2 JIS H 1615 Titration method
	0.02 1 ASTM E120 Gravimetric method
	GOST 9863.4 Unclear
Mg	0.01 0.1 JIS H1616 Atomic absorption spectrometry
	0.001 0.1 JIS H1616 ICP atomic emission spectrometry
	0.02 1 ASTM E120 Gravimetric method
C	0.005 0.2 JIS H1617 Titration method
	0.002 0.2 JIS H1617 Conductivity method, electricity method, thermal conductivity method, infrared absorption method
	0.005 0.1 JIS H1630 Spark discharge atomic emission spectrometry
	GOST 9863.9 Unclear
Si	0.03 1 JIS H1618 Gravimetric method
	0.005 0.15 JIS H1618 Spectrophotometric method
	0.001 0.05 JIS H1618 Spectrophotometric method
	0.006 0.08 JIS H1630 Spark discharge atomic emission spectrometry
	0.005 1 ASTM E120 Spectrophotometric method
	0.05 5 ASTM E120 Gravimetric method
	0.005 0.5 GOST 19863.6 Spectrophotometric method
H	0.0001 0.02 JIS H1619 Vacuum heating constant volume pressure measurement method, inert gas fusion thermal conductivity method
	0.001 0.02 ASTM E1447 Inert gas fusion thermal conductivity method
	0.0006 0.1 GOST 24956 Vacuum heating constant volume pressure measurement method
O	0.005 0.5 JIS H1620 Vacuum heating constant volume pressure measurement method, Inert gas fusion thermal conductivity method, Infrared absorption method
	0.03 0.5 ASTM E120 Vacuum heating constant volume pressure measurement method
	0.004 0.3 ASTM E1409 Inert gas fusion thermal conductivity method, infrared absorption method
	0.02 0.5 GOST 28052 Neutron radiation, inert gas fusion method
Pd	0.01 0.3 JIS H1621 Spectrophotometric method
	0.05 0.4 JIS H1621 ICP atomic emission spectrometry
	0.05 0.25 JIS H1621 X-ray fluorescence spectrometry
	0.1 0.25 ASTM E120 Spectrophotometric method
	0.05 1 GOST 19863.11 Spectrophotometric method
	0.001 TIS 7402 Spectrophotometric method
	0.005 TIS 7402 Spectrophotometric method
Al	0.5 10 JIS H1622 Gravimetric method, ICP atomic emission spectrometry
	1 8 ASTM E120 Gravimetric method
	4.6 7.2 ASTM E539 X-ray fluorescence spectrometry
	0.1 10 GOST 19863.1 Titration method
	1 10 GOST 19863.1 Atomic absorption spectrometry
	0.5 TIS 7403-91 Titration method
	0.5 TIS 7403-91 Gravimetric method
	1 10 TIS 7403-91 ICP atomic emission spectrometry
Na	0.01 0.2 JIS H1623 Atomic absorption spectrometry
V	0.5 15 JIS H1624 Titration method
	0.5 20 ASTM E120 Titration method
	2.6 5.4 ASTM E539 X-ray fluorescence spectrometry
	0.3 6 GOST 19863.2 Titration method
	0.3 5.5 GOST 19863.3 Titration method (simultaneously with Cr)
	1 6 GOST 19863.2 Atomic absorption spectrometry
	0.5 TIS 7606-92 Titration method
	1 15 TIS 7606-92 ICP atomic emission spectrometry
Cr	0.1 20 ASTM E120 Titration method
	0.005 0.1 ASTM E120 Spectrophotometric method
	0.3 10 GOST 19863.3 (simultaneously with V)
	0.3 10 GOST 19863.12
	0.1 3 GOST 19863.12 Atomic absorption spectrometry
	0.05 10 TIS 7810 Spectrophotometric method
	0.1 TIS 7810 Titration method
Nb	0.25 5 ASTM E120 Gravimetric method
	0.1 1.5 GOST 19863.9 Spectrophotometric method
	0.5 5 GOST 19863.9 Atomic absorption spectrometry
	0.5 10 TIS 8321 Gravimetric method, spectrophotometric method
Cu	0.4 1.1 ASTM E120 Spectrophotometric method
	0.001 0.55 ASTM E120 Spectrophotometric method
	GOST 19863.14 Unclear
	0.01 TIS 8117 Spectrophotometric method
	0.5 TIS 8117 Titration method
Mo	0.25 5 ASTM E120 Titration method
	0.04 5 ASTM E120 Spectrophotometric method
	0.005 0.1 ASTM E120 Spectrophotometric method
	0.3 10 GOST 19863.8 Spectrophotometric method
	1 10 GOST 19863.8 Atomic absorption spectrometry
	1 20 TIS 8423 Titration method
Ta	0.25 5 ASTM E120 Gravimetric method
	GOST 19863.15 Unclear
	0.5 10 TIS 8320 Gravimetric method
Sn	0.25 10 ASTM E120 Titration method
	0.5 5 GOST 19863.10
	2 5 GOST 19863.10 Atomic absorption spectrometry
	0.1 TIS 7809 Spectrophotometric method
	0.5 TIS 7809-92 Titration method
	1 12 TIS 7809-92 ICP atomic emission spectrometry
W	1 ASTM E120 Spectrophotometric method
	0.1 1.5 GOST 19863.4 Spectrophotometric method
	1 6 GOST 19863.4 Spectrophotometric method
Zr	1 20 ASTM E120 Gravimetric method
	0.5 12 GOST 19863.13 Gravimetric method
	0.5 12 GOST 19863.13 Titration method
	0.01 0.5 GOST 19863.13 Spectrophotometric method
	1 20 TIS 8422 Gravimetric method
Ru	0.04 0.12 TIS 9632 ICP atomic emission spectrometry
Ni	0.01 1 TIS 9632,9633 ICP atomic emission spectrometry
	GOST 19863.16 Unclear
Co	0.01 0.8 TIS 9633 ICP atomic emission spaectrometry

The method is applied to product analysis as a quick analysis method.

2) C: There is a paper[20)] reporting a determination method of trace amount of C by burning a sample in an electric resistance furnace using Cu as an accelerator and measuring the generated CO_2 by non-aqueous coulometric titration.

2.3.2 Atomic Absorption Spectrometry (AAS)

The flame type AAS includes the following: a method[21)] to determine Cu and Ni in the order of ppm by extracting their APDC complexes with diisobutyl ketone from a strong acid solution; a method[22)] to extract Pb, Bi and Cd as 8-quinolinol complexes with MIBK at a pH of 9.2; a method[23)] to determine Ca using $SrCO_3$ as a matrix modifier and without separating Ti; and a method[24)] to determine Si by decomposing a sample with HF by teflon autoclave. With regard to the high sensitivity electrothermal type AAS, there is a paper[25)] reporting a method to determine Ca, Cu, K, Mg, Mn, Na, Pb and Zn, without using a matrix modifier, and As, Co, Fe, Ni, Sn, Al and Cr, with an addition of carbon powder, through direct heating of a 30-mg solid sample; a detection limit of 0.02 ng/g of Mg was obtained by the method. Another paper[26)] on the electrothermal type AAS reports successful suppression of interference of coexisting elements through use of the L'vov platform-graphite tube after decomposing samples with HF-HNO_3.

2.3.3 ICP Atomic Emission Spectrometry (ICP-AES)

There is a paper[27)] reporting simultaneous determination of Mn, Cu, Ni, Cr, Mo, Al, V, Sn, Zr, Fe and Y in titanium and titanium alloys using Ti as the internal standard. Another paper[28)] reports simultaneous determination of Si, P and Nb in addition to the above elements using a teflon nebulizer with an HF solution. Yet another paper[29)] reports enhancement of detection sensitivity of 18 elements, namely Cu, Fe, Ni, Pb, V, Cd, Co, Zn, Ga, In, Mg, Mn, Sn, Ag, Al, Ba, Ca and Th, through their separation in very small quantities from Ti and condensation using various ion exchangers. The method brings about an improvement by 2 to 3 orders of magnitude in the detection limit, which became 1 to 10 ng/ml of solution concentration thanks to the separation from Ti. Further, there is a paper[30)] reporting determination of 17 elements, i.e. Ba, Bi, Ca, Cd, Cu, Ga, In, Li, Mg, Mn, Na, Ni, Pb, Tl and Zn, at a detection limit of 0.08 µg/g, through their separation using negative ion exchange resins and employing an ultrasonic nebulizer together. With regard to use of coprecipitation, there is a paper[31)] reporting determination of Fe, Ni, Cu, Co and Mg by masking Ti with H_2O_2 and separating and condensing the elements using $In(OH)_3$.

As an activity of the Development of International Standards for Supporting New Industries under the governmental auspices, new technologies are being developed for determining 0.001% or more of 18 impurity elements (Pd, Mn, Fe, Mg, Si, Al, V, Ni, Cr, Sn, Cu, Mo, Zr, Nb, Ta, Co, Y and B) contained in return alloy materials and likely to contaminate pure titanium products[32-34)].

2.3.4 ICP Mass Spectrometry (ICP-MS)

This analysis method is attracting attention owing to its high sensitivity and its capacity to analyze many elements at the same time and easily determine U and Th. It has been applied to determination of B at a detection limit of 0.4 µg/l without separating the matrix, using Be as the internal standard and directly spraying an HF solution using a PTFE sample introduction system[35)]. There is a paper[36)] reporting that U and Th were successfully determined to the level of 0.1 ppb, by forming matrices through the combination of ICP-MS with negative ion exchange separation using 9M hydrochloric acid for U, and with positive ion exchange separation using 1.5M hydrochloric acid for Th. There is a report[37)] that 16 elements were detected in a range of 1 to 10 ng/g through computer control of the ion exchange separation and the determination, in consideration of the fact that Ti interferes with the determination of most elements by the ICP-MS. The computer control is applicable also to the ICP-AES.

2.3.5 Gas Analysis Method

There are detailed study reports[38,39)] regarding a metal bath to improve the extraction ratio of O in the impulse heating-inert gas fusion method. Information useful for material inspection is obtained through analyses of O and N in the form of non-metallic inclusions in a Ti-6Al-4V alloy using EPMA[40)]. 190 to 480 ppm of hydrogen was detected in an analysis[41)] of compressor blades of a destructed jet engine by the application of cold neutrons to prompt gamma activation analysis to Ti alloys, as a method to determine H using a non-destructive analysis method. There is a paper reporting an application of the isotope dilution mass spectrometry to the analysis of H[42)]. According to another paper[43)], application of the atomic emission spectrometry to the gas analysis is being studied, a N-filling optical system is being developed for reducing the background caused by spark light emission, and the detection limit in the analysis of N, O and H is also being examined. Another paper[44)] reports that the influence of the glow discharge atomic emission spectrometry on the spattering speed is estimated and analysis of O and H in the depth direction from the sample surface is being applied to actual practice.

2.3.6 Atomic Emission Spectrometry (AES)

There is a paper[45)] reporting determination of Fe, Ni, Si, Mn and Cu in high purity titanium using the photospectrometry of discharge and emission spectrum of hollow cathode tube discharge. Measurement of Zr, Ru, Pd, Hf, Cu, Y, V, Mo, Nb, Al, Co, Ni, Ta, Bi, Sn Cr and Mn in Ti and Ti alloys in one spectrometric operation was made practicable through the use of carbon powder as a cushioning material and large current arc discharge[46)]. There also is a quick scrap classification method by determination of Al, Mn, V, Sn, Mo, Cu, Cr and Zr using a simplified spectroscope-spectrogram[47)].

The Development of International Standards for Supporting New Industries mentioned in relation to the ICP-AES also covers the AES, and studies are under way[32-34)] aiming at establishing application of the AES to the analysis of C, O, N, and H in addition to the 18 elements mentioned in 2.3.3.

2.3.7 X-ray Fluorescence Spectrometry (XRF)

There are papers[48,49)] reporting determination of Al, V, Cr, Fe, Zr, Mo and Sn by a method applying the fundamental parameter (FP) method using an Au tube for the X-ray emission, and other papers[50,51)] report application of the method to β-alloys, for which no standard sample is provided. Another paper[52)] reports that a high degree of agreement between standard values of standard samples and chemical analysis results has been obtained through comparative examinations of determination values obtained through the FP method and the theoretical α coefficient method using the acid decomposition/glass bead technique. Analysis Technology Committee of the Iron and Steel Institute of Japan reported[53)] the result of its joint experiment using the dj correction method, comparing it with the result of the dj correction method[54)]. Besides these, there are reports of determination of 0.75 to 5.0% of Ta in a Ti alloy by the solution method using the wavelength disperesive XRF[55)] and determination of trace amounts of Fe, Cu and Ni by the XRF combined with coprecipitation and separation of $In(OH)_3$[56)].

2.3.8 Glow Discharge Mass Spectrometry (GD-MS)

There are papers[57,58)] reporting the results of studies of the relative sensitivity factor, which is one of the fundamentals of element determination. A sample preparation method using acid-H_2O_2 etching to avoid contamination during the preparation processes was developed[59] and the new method enabled elimination of contamination in 60 s, curtailing the pre-burn time from 1 h. or more to 20 min. Applications of the method to the impurity analysis of high purity titanium[60] and to the analysis of Sc[61] were reported and in the latter, the detection limit was confirmed through a cross check with the ICP-MS.

2.3.9 Activation Analysis (AA)

Besides the determination of single elements such as the determination of B by the deuteron AA[62], that of Nb by the proton AA[63], etc., a determination lower limit of 25.5 ppt for U and another of 3.1 ppt for Th were obtained in analyses using the neutron AA[64]. Further, with regard to the neutron AA, there are papers reporting determination of 17 elements, namely Na, Cr, Fe, Co, Se, As, Zr, Mo, Sb, Cs, Ce, Tb, Yb, Hf, Ta, W and Th[65], and another determination of 26 elements including Th, U, Cu, Fe, K, Na, Ni, etc.[66] According to these papers, detection limits ranging from Ir: 0.002 ng/g to Zr: 45 ng/g were obtained.

2.3.10 Isotope Dilution Mass Spectrometry (ID)

There is a paper reporting detection limits of U and Th (0.07 ng/g), Cu (1 ng/g), Cd (1.7 ng/g), Ni (4 ng/g), Pb (6 ng/g) and Fe (35 ng/g) obtained through the ID with a thermion type quadrupole spectrometer in combination with various separation methods (ion exchange, extraction, electrolysis, and coprecipitation)[67]. The paper also compares the Cr determination results by the ID and the GD-MS.

2.3.11 Microprobe Analysis

A paper reports a measurement of spattering speed of a Ti-6Al-2.5Sn alloy for the purpose of a depth direction analysis of solid thin film samples by the Auger electron spectroscopy (AES, abbreviation not used herein for avoiding confusion with atomic emission spectrometry)[68]. Other papers report local determination of O, Fe, Ni, Cr, etc. by the secondary ion mass spectrometry[69] and determination of O[70].

3. Characterization

Recent rapid advancement of physical analyzers (surface analyzers, local analyzers, etc.) has carried the role of analysis beyond the realm of composition determination to the field of the so-called characterization such as structure analysis of materials, and analysis has provided this field with much information.

3.1 Analysis of Medical Materials

Studies of the chemical structure of titanium and a Ti-6Al-4V alloy by the X-ray photoelectron spectrometry (XPS) after a series of treatment of the samples revealed that most of the elements were oxidized as a result of their having been exposed to the atmosphere. An analysis of surface structure of TiO_2 films formed by the sol-gel method and the plasma spray method made it clear that, while the sol-gel method was less prone to contamination with water-OH group and the films formed by the method were identified as chemically equivalent to TiO_2, those formed by the plasma spray were strongly contaminated with C, Ca, P and N[71]. There is a paper reporting the results of XPS examination of chemical structure at the surfaces of TiO_2 and $CaTiO_3$ films formed by the sol-gel method[72], and another paper reporting on ion form and formation mechanism of a Ca phosphate formed on Ti oxides in a neutral electrolyte[73].

An oxide film was formed on the surfaces of titanium and Ti-6Al-17Nb and Ti-6Al-4V alloys for implantation in organisms by the electrolytic polarization in a buffer solution of phosphoric acid, and the relation between the oxide film thickness and the film formation potential, initial products, etc. were analyzed by methods such as the Raman spectroscopy (RS), etc. The initial phase of hydroxilapatite ($Ca_{10}(PO_4)_6(OH)_2$) deposited by electrolysis was found to be amorphous through the RS, scanning electron microscope (SEM) and infrared absorption spectrum (IR), and from the result of the anode electrolytic polarization after fixing collagen on the oxide surface, collagen fiber was found to be accumulated in the oxide film or strongly combined with TiO_2[74]. There is also a report of a study, using the element analysis, IR and RS, of the composition and structure of carbonate-hydroxilapatite formed on titanium surfaces by vacuum spray[75].

Titanium and a Ti-6Al-4V alloy for dental and orthopedic implantation use were implanted in a rabbit tibia for 3 months. As a result of application of the particle induced X-ray emission (PIXE) to the detection of Ti dissolved, released or migrated during the period, Ti was detected in surrounding organisms in good accuracy, and it was made clear that the Ti concentration was higher in hard organisms than in soft organisms. The relation between the surface form of the implanted material and corrosion resistance was also clarified[76]. Elution of Ca and Ti from an artificial radix of titanium implanted in an organism was measured and mapped by the XRF. As a result, the elution of Ti was found to be large near the implant and decrease quickly as the distance from the implant surface became larger[77]. Passive films of Ti-6Al-4V, Ti-5Al-2.5Fe and Ti-4Fe alloys, each treated with HIP, were analyzed by the XPS, and it was confirmed that only the Ti-4Fe alloy had good corrosion resistance free from local corrosion[78]. The EPMA, XRS, etc. have also been used for examining baking interfaces between titanium and earthenware materials[79].

3.2 Structure Analysis of Nitrided Layer

Distribution of ^{14}N in the depth direction was measured using the Rutherford back scattering spectroscopy (RBS) for the purpose of clarifying the mechanism by which the hardness and wear and corrosion resistance are improved when a titanium nitride film is formed by the thermal nitriding, ion beam vapor deposition, sol-gel method, ion implantation or similar methods[80]. Distributions of TiN, Ti_2N and α-Ti in the depth direction were made clear using the X-ray microdiffranctometry analysis of titanium surface layer formed by heating the titanium material at 1,000°C for 12 h. in an atmosphere of 80vol%N_2 and 20vol%H_2[81]. Another paper reports analyses, by the XPS and Auger electron spectroscopy, in the depth direction of a nitride layer formed through reactions of Ti with N_2 and NH_3 at 890°C, and studies causes of continuous composition changes[82].

A titanium nitride layer was formed using glow discharge plasma in a N gas atmosphere, and distribution of N up to a depth of 4 to 5 μm was measured by the RBS and NRA, oxygen distribution by the NRA and EPMA, and structural orientation of the film by the X-ray diffraction (XRD)[83]. Mapping of Ti, Al and V by the microbeam PIXE was carried out at surfaces, with and without wear, of a Ti-6Al-4V alloy gear after cold forging and plasma nitriding treatment, and distribution of nitrogen concentration at the surface and along depth was examined using the NRA resonance distribution and micro NRA. As a result, the nitrogen layer was about 17 μm thick and Al and V were found to be depleted at several micrometers from the surface[84].

3.3 Structure Analysis of Oxidized and Carburized Layers

Distribution of ion-injected O in titanium was investigated using the RBS, XRD and XPS and the O/Ti ratio at the top of the trapezoid distribution of O was confirmed to be 1.5[85]. Depth profiles of anode oxidation films of titanium formed under different electrolysis voltages were analyzed, simultaneously applying the elastic rebounding direction analysis (ERDA) and Rutherford front scattering spectroscopy, and it was confirmed that the composition of the oxidation film changed depending on the increase in the electrolysis voltage[86]. Distribution of ion-injected C along depth was also measured using the ERDA and RBS[87].

3.4 Analysis of Absorption, Emission and Diffusion of Hydrogen

The quantity of the glow discharge atomic emission spectrometry (GDS) was made clear using titanium samples on which hydrides were formed by immersing them in an NaCl-HCl solution, and it was made clear that hydrogen penetration in a corrosive environment occurred after the destruction of a passive film and that the thickness of the penetration layer was governed mainly by the corrosion speed[88]. A β-alloy was heated to 482 to 650°C in a mixed gas of H_2-O_2 and temperature-dependency of hydrogen absorption amount was estimated using the thermogravimetry method and capacity testing method[89]. As a means of in-situ measurement of hydrogen behavior in a high stress area, the nuclear reaction analysis was applied to the measurement of hydrogen concentration change in a β phase Ti-13Mn alloy and a Ti-31V alloy under a uni-axial stress gradient[90]. The influence of the content of H on tensile characteristics, the relation between the content of H and plastic deformation and the relation between H emission speed and strain were made clear by imposing, using a tensile tester, plastic deformations of a strain range from 0 to 16% to samples of a Ti-5Al-2.5Sn alloy after vacuum annealing[91]. The ERDA was employed for measuring electrical behavior of hydrogen and deuterium, and data analysis and sample preparation methods were studied based on the obtained result[92]. The AE frequency analysis method was applied to the analysis of the propagation process of hydrogen embrittlement of a Ti-15V-3Al-3Sn-3Cr alloy[93].

3.5 Analysis of Worked Materials, etc.

Surfaces of titanium foils and an extrusion-formed Ti-48Al alloy were observed by Auger electron spectroscopy. It was discovered with the foil that the majority of the oxides on the surface was TiO_2 and that a layer at least 30 nm of the surface was contaminated with free C and carbides. With regard to the alloy, it became clear that the amount of C was large in the $\alpha_2+\gamma$ dual phase zones, that O existed in a somewhat large amount in the γ single phase zones as Ti_2O_3 and inside the samples as lower level oxides[94]. Durability of bonding joints between pure titanium and a Ti-6Al-4V alloy was examined by wedge cleavage tests, and the interdependency between bonding pre-treatment and the durability was correlated with measurement results obtained by the XPS. As a result, it was found out that NaOH anode treatment offered the best durability thanks to the fact that Ti shifts to the high molecular weight side[95]. Corroded and sound surfaces of a Ti alloy formed in normal atmosphere at a high temperature were analyzed to a depth of 10 μm or so by the hollow cathode tube discharge atomic emission spectrometry to measure Al distribution in the depth direction, and Al concentration was found high at the lower cinder layer but roughly the same as in the alloy itself at deeper layers[96].

4. Future Prospects

Wider application of the ICP atomic emission spectrometry is being promoted in the JIS and TIS systems. In consideration of the fact that the analysis methods are not yet established as international standards, proposals are made to include the determination technologies developed in the activity of the Development of International Standards for Supporting New Industries[32-34] as analysis standards of the ISO system. In the field of analysis of titanium, on the other hand, only a very small number of standard materials guaranteeing analysis values are supplied. For this reason, standard materials for analyses of C, N, O, H and Fe in industrially pure titanium are being prepared as a part of the "Investigation Commission for Quick Preparation of Intellectual Infrastructure"[97], and a joint experiment to confirm accuracy of high purity titanium analysis methods typically such as the ICP-MS and preparation of high purity titanium standard materials are being promoted[98]. In the field of the research of analysis technologies, composition analysis methods for production of new alloys, analysis methods of high purity titanium and new analysis technologies for the characterization related to materials research and development will continue being developed.

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