Determination of Metal Impurities in Tantalum Diboride after Acid Dissolution by Inductively Coupled Plasma Atomic Emission Spectrometry

Fumiaki YOKOTA,* Tatsuo NAKANO,* Akiko SHIMIZU,* Toshio ISHIZUKA,**
and Hisashi MORIKAWA***

*Material Department, Industrial Research Institute, Aichi Prefectural Government,
Hitotsugi, Kariya, Aichi 448-0003, Japan

**Faculty of Science, Niigata University, 8050, Ikarashi 2, Niigata 950-2181, Japan

***Chemistry Department, National Industrial Research Institute of Nagoya,
Hirate, Kita, Nagoya 462-8510, Japan

(Received August 26, 1999; Accepted October 22, 1999)

Tantalum diboride (TaB_2) is a non-oxide ceramic that has the properties of good corrosion resistance (chemical stability), high melting-point, good hardness (Mohs hardness ≥ 8) and high heat conductivity. Because of these attractive properties, new uses are anticipated in addition to uses hitherto described. However, the superior properties of TaB_2 ceramics are markedly affected by impurities (some metals, carbon, *etc.*).^{1,2} Metal impurities in TaB_2 ceramics affect some properties such as hardness, sintering, chemical stability and heat conductivity. Therefore, the determination of metal impurities is very important in the characterization of TaB_2 .

Metal impurities in TaB_2 powder have rarely been determined because the importance of trace metal impurities influencing the physical-chemical properties of the ceramics has not been recognized. Recently, the direct solid sample introduction techniques using inductively coupled plasma atomic emission spectrometry (ICP-AES) have been applied to the analysis for advanced ceramics.^{3,4} These methods, however, require certified standard samples in order to obtain accurate results. Unfortunately, certified TaB_2 standard samples could not be obtained. On the other hand, ICP-AES is a superior technique for the determination of trace elements in solution and has been applied to the determination of impurities in non-oxide advanced ceramics.⁵⁻⁹ In the absence of the certified samples, the solid sample must be brought into solution for ICP-AES methods.

It has been reported that TaB_2 was quite insoluble in any acid¹⁰ and decomposed upon only fusion with a mixture of sodium carbonate and calcium oxide.¹¹ In our preliminary fusion experiment carried out in accordance with the above literature, TaB_2 could not be brought into solution. Fusion methods with fluxes are not suitable for the determination of impurities because of contamination from fluxes and decomposition vessels (*e.g.*, platinum crucibles), and chemical and physical interferences caused by fluxes. Hence, acid decomposition methods are preferable to fusion methods for the determination of impurities. In this study, metal impurities (Ca, Co, Cr, Fe, Mg, Nb, Ti and W) in TaB_2 powder samples have been determined by ICP-AES following an acid decomposition which was developed in our laboratories. Sample decompositions using several acids in an open and a closed system (a PTFE pressure vessel), a sample decomposition procedure,

matrix effects on the determination of impurities in TaB_2 , detection limits, calibration graphs and recovery tests for the 8 elements are described. The results obtained for commercial TaB_2 powder samples are also presented.

Experimental

Apparatus and operating conditions

A Seiko (Model SPS 1200A) sequential spectrometer with an ICP source was used. The details have been described elsewhere.⁹ The nebulizer and torch applied were suitable for high salt concentrations. Wet argon (saturated with water vapor) was used as carrier gas.

In the qualitative analysis of TaB_2 powder samples, the 8 elements were detected by dc arc emission spectrography and secondary ion mass spectrometry. The analytical lines of each element listed in Table 1 were selected considering the detection limits and the spectral interferences by concomitant elements available from lists of prominent lines in ICP-AES,^{12,13} and examinations of the experimental wavelength scans of each element, Ta and sample solutions. The operating conditions used have been described elsewhere.⁷

A Hitachi (Model 180-80) atomic absorption spectrometer was applied to determine several elements (Ca, Co, Fe and Mg). A PTFE pressure vessel (San-ai Science; Type HUT-25, inner volume 25 ml) was used to dissolve TaB_2 powder samples under pressure. A PTFE beaker (100 ml), a PTFE funnel, a plastic pipette and a plastic calibrated flask were also used. Following each sample decomposition, the PTFE beaker and pressure vessel were thoroughly cleaned by boiling with *aqua regia* for several hours.

Reagents and samples

Stock standard solutions for AAS (Wako Pure Chemicals, 1 mg ml^{-1}) were used for all the elements. Hydrofluoric acid (Merck, Suprapur, about 40% pure, sp.gr=1.13) and nitric acid (Wako Pure Chemicals, Super Special Grade, about 61% pure, sp.gr=1.38) were used to dissolve TaB_2 . Other acids and hydrogen peroxide were produced by Wako Pure Chemicals having super special grade and special grade quality, respectively. Tantalum pentoxide (Johnson Matthey, Specpure)

Table 1 Analytical lines, detection limits and concentration ranges for calibration

Element	Analytical line/ nm	Detection limit		Concentration range/ $\mu\text{g ml}^{-1}$
		In solution/ ng ml^{-1}	In sample/ $\mu\text{g g}^{-1}$	
Ca	II 393.366	0.18	0.07	0.1 - 0.5
Co	II 228.616	3.6	1.4	1.0 - 5.0
Cr	II 267.716	2.8	1.1	0.2 - 1.0
Fe	II 239.562	2.5	1.0	1.0 - 5.0
Mg	II 279.553	0.07	0.03	0.05 - 0.1
Nb	II 322.548	7.8	3.1	1.0 - 5.0
Ti	II 336.121	0.8	0.32	0.2 - 1.0
W	II 209.475	15	6.3	0.1 - 0.5

Table 2 Decomposition results for TaB₂ powder samples by wet acid decomposition in an open vessel (sample: 0.25 g)

HF (1+1)	Aqua regia	Added acid / ml			Percentage of decomposition ^b
		HNO ₃ (1+1)	H ₂ SO ₄ (1+1)	H ₂ O ₂	
10 - 20 ^a	10 - 20	10 - 20			○
		5 - 10	10		◆
		10 - 20		2 - 4	◆
5 - 10			2 - 4		●
5 - 10		2 - 4			◎
5 - 10				2 - 4	◎

a. Reagent volume added to each 0.25 g sample (ml). b. ◎, > 99%; ○, 80 - 90%; ●, 60 - 80%; ◆, almost insoluble.

was used as a matrix component for Ta after decomposition with hydrofluoric acid in a PTFE pressure vessel, and possible impurities in Ta₂O₅ were determined by ICP-AES. Boric acid (Merck, Suprapur) was used as a masking agent for fluoride ion in sample solution, and as a matrix component. High purity water with a metered resistivity of 18 M Ω cm, which was purified by a Milli-Q purification system (Japan Millipore, Labo type), was used to prepare all sample and standard solutions.

Tantalum diboride powder samples manufactured by Nippon Shin Kinzoku (average particle size; 1.65 μm , free carbon content; 0.1%) and Johnson Matthey were analyzed.

Recommended acid decomposition procedure

A 0.25 g amount of TaB₂ powder sample was taken in a PTFE pressure vessel, 2 ml of hydrofluoric acid (1+1) and 5 ml of nitric acid (1+4) were added. The vessel was closed by capping and kept at 160°C for 16 h in a drying oven. After cooling, the solution was filtrated to remove the free carbon residue. The filtrate was transferred to a 100 ml calibrated flask with 20 ml of 4% boric acid, and then diluted with high-purity water. The quantities of these acids used could be minimized so as to decrease the blank values from acids, and the decomposition temperature (160°C) was the lowest one at which the TaB₂ sample decomposed perfectly.

Each piece of filter paper (Toyo Roshi, class 7, ϕ =70 mm) was successively washed several times with hydrofluoric acid (1+9) and high-purity water before filtration so as to reduce contamination from itself.

Results and Discussion

Sample dissolution

From our studies for refractory boride compounds, we have decided that the compounds are first decomposed by an oxidizing acid, and then the decomposed compounds are dissolved by the acid which can dissolve the metal element and its compounds. It has been reported that tantalum (metal) and its compounds such as Ta₂O₅ and TaC dissolve in hydrofluoric acid.^{10,14} Therefore, wet acid decomposition procedures by use of hydrofluoric acid and/or several oxidizing acids were examined in an open system. These experiments were carried out in a quartz beaker or in a PTFE beaker by occasionally heating on a sand bath. The main decomposition results are shown in Table 2. The decomposition ratio was calculated as mentioned hereunder: After the reaction of TaB₂ with these acids almost ceased, the mixture was filtrated through a filter paper (Toyo Roshi, class 7). The filter papers containing the residues were ashed in a platinum crucible and the decomposition rates were calculated from the residue's weight and/or the amount of Ta in the filtrate determined by ICP-AES. Each treatment time taken for the decomposition was about 4 h except for the hydrofluoric acid treatment. The treatment time for hydrofluoric acid amounted to about 2 days due to the very slow reaction. As can be seen in Table 2, TaB₂ powder sample could not be decomposed by any oxidizing acid. However, it was found that, even in an open vessel, the sample could be dissolved only in hydrofluoric acid. In addition to this result, by use of a mixture of hydrofluoric and nitric acids or a mixture of hydrofluoric acid and hydrogen peroxide, the reaction was accelerated. The decomposition rate was above 99%, and the ashed residues consisted of Ta and metal

Table 3 Analytical results for commercial TaB₂ powder samples and recoveries of metal impurities

Element	Nippon Shin Kinzoku		Johnson Matthey			
	Concn./ $\mu\text{g g}^{-1}$		Concn./ $\mu\text{g g}^{-1}$	Added/ $\mu\text{g g}^{-1}$	Found/ $\mu\text{g g}^{-1}$	Recovery, %
Ca	124 $\pm$ 1 ^a	(117) ^b	12.5 $\pm$ 0.3 ^a	39.6	52.3	101 ^c
Co	1860 $\pm$ 2	(1830)	341 $\pm$ 3	(341) ^b	724	97
Cr	266 $\pm$ 3		314 $\pm$ 2	396	713	101
Fe	1120 $\pm$ 10	(1170)	1070 $\pm$ 10	(1090)	2050	100
Mg	15.2 $\pm$ 0.1	(14.9)	1.56 $\pm$ 0.04	(2.0)	40.4	98
Nb	539 $\pm$ 6		33.5 $\pm$ 2.0	397	432	100
Ti	352 $\pm$ 2		73.3 $\pm$ 0.7	397	473	101
W	16900 $\pm$ 180		3510 $\pm$ 20	3970	7600	103

a. Mean content $\pm$ SD for five determinations. b. Values in parentheses were obtained by AAS. c. Average of three times.

impurities such as W and Ti which were confirmed by X-ray fluorescence analysis.

Considering the wet acid decomposition results described above, we examined acid decomposition procedures under pressure in a PTFE vessel using these acids. In the case of decomposition under pressure (160°C, 16 h) using a mixture of hydrofluoric and nitric acids or a mixture of hydrofluoric acid and hydrogen peroxide [2 ml of HF (1 + 1) and 5 ml of H₂O₂(1+4)], TaB₂ powder sample could be dissolved perfectly. However, the sample solution decomposed under pressure contained a small amount of a black residue which was supposedly free carbon. In order to identify this residue, the mixture was filtrated through a piece of filter-paper (Toyo Roshi, class 7), and then the filter-paper was ashed in a platinum crucible. There was hardly any residue in the crucible by visual observation and no increase of weight. After ashing, a 1 g amount of sodium carbonate or potassium nitrate was added into the crucible and fused in an electronic furnace. The fused melt was dissolved in diluted hydrochloric or nitric acid, followed by ICP-AES measurement for the 8 elements investigated. The concentrations of these elements except for Ca and Fe, which resulted from contaminations from the crucible and/or each flux, were below detection limits, and the concentrations for Ca and Fe detected were almost the same as those obtained from the blank fusion test. This suggests that the TaB₂ sample, except for free carbon which existed in the sample itself, could be decomposed perfectly by the two kinds of acid mixtures. However, even on adding diluted hydrogen peroxide dropwise to the powder sample in the presence of hydrofluoric acid, the sample often (about once in three times) reacted vigorously with hydrogen peroxide, and was scattered from the vessel, the inner volume of which was 25 ml. Because of this, the procedure by use of a mixture of hydrofluoric and nitric acids under pressure could be selected as the recommended acid decomposition procedure.

ICP-AES measurement

[Matrix effects]

The sample solution prepared as described in the Experimental contained 0.25% TaB₂, 0.84% nitric acid, 0.45% hydrofluoric acid and 0.80% boric acid as matrix components. The effects of the TaB₂ matrix on the background levels and the emission intensities of each element were studied before the analysis of the commercial samples. These experiments were carried out by use of two kinds of matrix-matched standard solutions for each element. One was matched to the matrices of the sample solution (0.25% TaB₂, 0.84% HNO₃, 0.45% HF and

0.80% H₃BO₃) and the other was matched to those of the reagent blank solution (0.84% HNO₃, 0.45% HF and 0.80% H₃BO₃).

The sample matrix increased the background levels of all the elements studied from 3% for Ti to 170% for Co, compared with the background levels in the reagent blank matrix. On the other hand, the sample matrix decreased the emission intensities of Co, Cr, W and Mg by 3–5%, compared with the intensities in the reagent blank matrix. The intensities of the other elements in the sample matrix were almost the same as those of the reagent blank matrix. The interferences from the TaB₂ component are caused by many factors, such as spectral line broadening, radiative electron-ion recombination processes, various forms of stray light, *etc.* The reference solutions for the calibration were matched to the matrices of the sample solution using tantalum pentoxide, nitric acid, hydrofluoric acid and boric acid so as to avoid such interferences.

[Calibration graphs and detection limits]

The calibration graphs for the 8 elements were constructed in the concentration ranges shown in Table 1. The Ta₂O₅ used for matrix-matching contained Ca and Mg as impurities. The net line intensities that were used to construct the calibration graphs were obtained by subtracting the blank signals. The concentrations of other impurities in the Ta₂O₅ were almost negligible. The number of the reference solutions of each element was four, of which one was the blank, and the relative standard deviations at each concentration ranged from 0.2 to 1.9% depending on the element and the measured concentration (five measurements). Each calibration graph was linear over the concentration range given in Table 1. For sequential determinations by a sequential slew scanning system, the reference solutions for the 8 elements were divided into two groups: one was for W, the other was for the remaining seven elements, considering the stability of the solution. The reference solutions for calibrations were stable for several weeks.

The detection limits of the 8 elements were determined using the solutions matched to the matrices of the sample solutions. A signal-integration method (5s) was used to obtain the lowest detection limits. Each detection limit (3 σ) given in Table 1 was calculated on the basis of five measurements.

Analysis of samples

The proposed method was applied to the determination of the 8 metal impurities in commercial TaB₂ powder samples. The analytical results are shown in Table 3, in which the results for some of the same elements (Ca, Co, Fe and Mg) obtained by

atomic absorption spectrometry (AAS) are also listed. The other four elements could not be determined by AAS because of chemical interference caused by Ta and/or the low sensitivity of AAS. The concentration values determined by ICP-AES were in good agreement with those obtained by AAS.

In order to check the accuracy of the proposed method, it would be necessary to determine the impurities of a certified TaB₂ sample and/or compare the results obtained by other established procedures such as fusion methods. However, a certified standard sample could not be obtained, unfortunately, and our TaB₂ powder sample could not be brought into solution by the procedure reported.⁹ Hence, the recovery study for the 8 elements was examined. Known amounts of standard solutions of each element were spiked into Johnson Matthey's powder sample before acid decomposition, and the recoveries were examined. The recovery results obtained are also shown in Table 3. The mean recoveries for the 8 elements from the sample ranged from 97% for Co to 103% for W. Blank values through the whole proposed procedure were less than the detection limits except for Ca. The contamination resulting from the proposed procedure for Ca was very slight (less than 1 µg g⁻¹). This might be caused by a PTFE vessel and/or the decomposition procedure itself. These suggest that the proposed method is suitable for the sensitive and precise determination of metal impurities in TaB₂ powder samples.

A part of this work was reported at the 47th Annual Meeting of the Japan Society for Analytical Chemistry, Gifu, October 6-8, 1998.

References

1. K. Shinozaki and A. Tsuge, "Seramitukusu no kyarakutarizeishon gijutu (Characterization Technique for Ceramics, in Japanese)", ed. The Ceramics Society of Japan, **1991**, Gihoudou, Tokyo, 266.
2. D. W. Richerson, *Am. Ceram. Soc. Bull.*, **1973**, 52, 560.
3. X. Liu and G. Horlick, *J. Anal. At. Spectrom.*, **1994**, 9, 833.
4. B. Docekal, J. Broekaert, T. Graule, P. Tschöpel, and G. Tölg, *Fresenius' J. Anal. Chem.*, **1992**, 342, 113.
5. F. Yokota, T. Nakano, T. Ishizuka, and H. Morikawa, *Bunseki Kagaku*, **1998**, 47, 721.
6. F. Yokota, T. Ishizuka, and H. Morikawa, *Bunseki Kagaku*, **1997**, 46, 395.
7. F. Yokota, T. Ishizuka, and H. Morikawa, *Analyst* [London], **1995**, 120, 2823.
8. F. Yokota, H. Morikawa, and T. Ishizuka, *Bunseki Kagaku*, **1995**, 44, 123.
9. F. Yokota, H. Morikawa, and T. Ishizuka, *Analyst* [London], **1994**, 119, 1023.
10. R. E. Droegkamp, M. Schussler, J. B. Lambert, and D. F. Taylor, "Kirk-Othmer Encyclopedia of Chemical Technology", ed. H. F. Mark, D. F. Othmer, C. G. Overberger, and G. T. Seaborg, **1983**, 3rd ed., Vol. 22, Wiley, New York, 559.
11. L. N. Kugai and T. N. Nazarchuk, *Zavod. Lab.*, **1971**, 37, 1053.
12. P. W. J. M. Boumans, "Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectrometry", **1984**, 2nd ed., Pergamon Press, Oxford.
13. F. M. Phelps III, "M. I. T. Wavelength Tables", **1982**, Vol. 2, M. I. T. Press, Cambridge, MA, USA.
14. C. R. Hammond, "CRC Handbook of Chemistry and Physics", ed. D. R. Linde, **1992**, 72nd ed., sect. 4-104, CRC Press, Boca Raton.

1. K. Shinozaki and A. Tsuge, "Seramitukusu no