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1 Introduction

In recent years fine ceramics have received remarkable attention as materials for engineering, electronics and cutting tools because of their superior properties such as high-toughness, high-temperature strength and corrosion resistance. Unlike conventional ceramics, fine ceramics is highly purified for further improvement of properties, and needs strict control of the raw materials and the products. Thus, not only at the stage of commercial production, but also at the starting point for developing the product, analytical characterization technique has an important role for the selection of the raw

materials and the examination of the production process. At the first stage of investigation, the relation between impurities and the properties of the product is not clear; therefore, many elements must be analyzed. Conventional chemical analysis or atomic absorption spectrometry, which can analyze elements only one at a time, cannot keep up with the rapid advances of product development. On the other hand, the inductively coupled plasma atomic emission spectrometry (ICP-AES) has a high sensitivity and can determine many elements simultaneously; hence, this technique is very useful. Although there are few standard samples available for advanced materials including fine ceramics, it is another advantage of the ICP-AES that synthesized standard solutions can be used for calibration.

Since ceramics has the property of corrosion resistance, the complete decomposition of raw materials, intermediate, and final products cannot be achieved easily. In addition, conventional decomposition methods used for chemical analysis cannot be directly applied to ICP-AES. In the analysis of highly purified fine ceramics, it is important to take extreme care to control contamination during the decomposition stage and to select the most suitable decomposition method for each type of ceramic. Furthermore, the problems characteristic of ICP-AES, such as suppression of the effects of co-exsistent elements and background correction, must be resolved.

This paper describes the impurities determination

method using an ICP-AES, taking BN, AlN and ZrO_2, as example as already performed at Kawasaki Steel.

2 Experimental

2.1 Apparatus

The ICP-AES measurements were conducted by using a Shimadzu ICPQ100 (atomospheric-polychrometer) and/or an ICPS100V (vacuum-monochrometer). **Table 1** shows the operating conditions. For decomposition of a sample, the acids method under the pressure was performed in a PTFE vessel (Parr, inner volume of 30 m*l*), and a TR-Autobead 1000 M glassbead preparing machine was used for the fusion of ZrO_2.

Table 1 Operating conditions of ICP-AES

	ICPQ 100	ICPS 100V
RF power (kW)	1.2	1.2
Coolant gas flow (*l*/min)	11	15
Plasma gas flow (*l*/min)	1.0	1.5
Carrier gas flow (*l*/min)	1.0	1.0
Purge gas flow (*l*/min)	—	4.0
Observation height (mm)	16	13

2.2 Reagent

Standard stock solutions for AAS (Wako Pure Chemicals, $1000\ \mu g \cdot ml^{-1}$) were used for each element. Boric acid and sodium carbonate (suprapure, Merck) and sodium borate (spectromelt, Merck) were used as fusion agents. ZrO_2 from Johnson Matthey was used for background correction. All other acids and reagents used were an analytical-reagent grade.

2.3 Introduction of Samples Solution

For BN and AlN, the introduction of sample solution to the ICP-AES was carried out by the ordinary continuous nebulizing method. For ZrO_2, which contains large amounts of fusion agents, a micro-injection technique, as described elsewhere,[1] was used because of the high salt content of the solution. As shown in **Fig. 1**, an aliquot of sample solution was transferred by a micropipette into a PTFE sampling cup. The whole solution in the cup was then fed to the nebulizer through a PTFE capillary tube. An air gap was placed between the sample and the carrier water so that the sample solution may not diluted. Measurement of the emission signal was performed by the peak area integral method so as to improve precision and to reduce the matrix effect and the noise peaks.

2.4 Decomposition Method
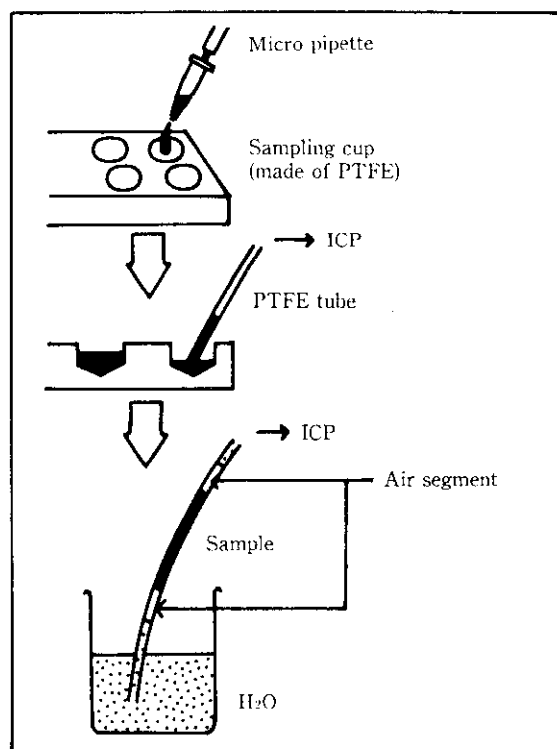
Several decomposition methods[2] for fine ceramics

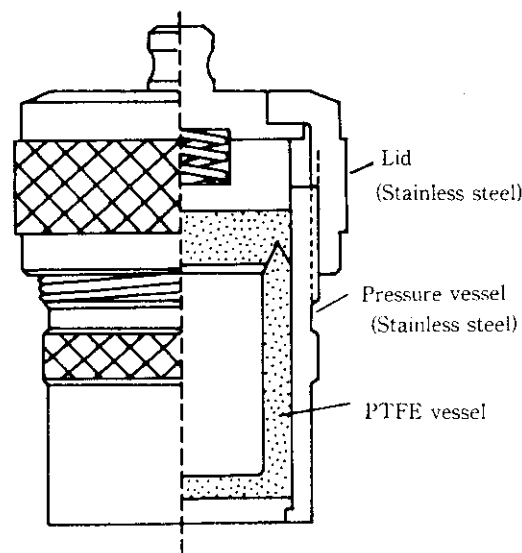Fig. 1 Introduction of sample solution with microinjection technique

Fig. 2 Sample decomposition vessel (Parr pressure bomb)

have been reported, and are broadly classified into acids and fusion methods. Since the determination of trace elements is required for fine ceramics, acid decomposition methods are preferred because of their low level of impurities. However, in general, ceramics are corrosion resistant and are often difficult to decompose in atmos-

pheric conditions, thus decomposition in PTFE bomb (Fig. 2) under pressure was employed. This method also has the merit of reducing contamination from the vessel and the atomosphere. The fusion method was adopted when decomposition could not be completely achieved by the acids method under pressure. Acid decomposition under pressure was carried out at 150°C for 11 h (over night). In order to automatically fuse many ZrO$_2$ samples simultaneously, a glassbead preparing machine for X-ray fluorescence spectrometer was used. After holding at 860°C for 10 min., the furnace temperature was raised to 900°C and the melting of the sample was confirmed by observation, and then the melt was shaken and swirled in the furnace at 1000°C to be fused completely.

3 Results and Discussion

3.1 Sample Decomposition Procedure

Since BN was decomposed by hot HF,[3] the decomposition of BN was investigated by H$_2$SO$_4$ + HF, HCl + HF, and HNO$_3$ + HF systems in a PTFE vessel under pressure. It was found that BN can be decomposed completely by HNO$_3$ + HF system. However, the alkali fusion method using Na$_2$O$_2$ + Na$_2$CO$_3$ was applied to the determination of Si and B, which are liable to vaporize with acid decomposition. The decomposition procedure for BN is shown in Fig. 3.

AlN has been decomposed by fusion using Na$_2$CO$_3$ + H$_3$BO$_3$ or H$_3$PO$_4$ + H$_2$SO$_4$. Recently, HCl or H$_2$SO$_4$ decomposition under pressure has been reported[4]. AlN is difficult to decompose except by alkali fusion at atomospheric pressure, and aluminium fluoride is precipitated when HF is used. Thus, decomposition by HCl + HNO$_3$ and H$_2$SO$_4$ + HNO$_3$ under pressure was investigated. However, the outer vessel of PTFE, which was made of stainless steel, was corroded when HCl + HNO$_3$ system was used, so that H$_2$SO$_4$ + HNO$_3$ system was adopted. When insoluble residues were recognized, they were fused with Na$_2$CO$_3$ + H$_3$BO$_3$. The decomposi-
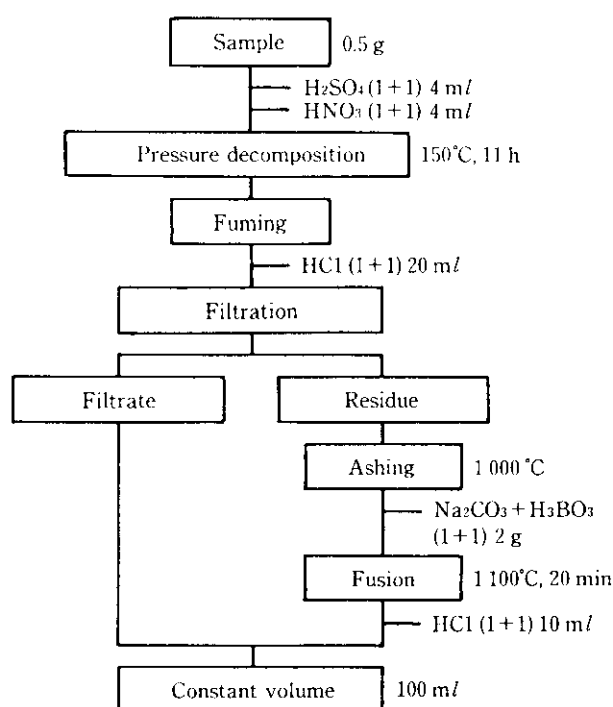

Fig. 4   Decomposition procedure for aluminum nitride

tion procedure for AlN is given in Fig. 4.

Concerning ZrO$_2$, a fusion method using Na$_2$CO$_3$ + H$_3$BO$_3$ has been also adopted for the decomposition of zircon sand according to the standard of JCRS (Japanese Ceramics Standard). Also, the HF and H$_2$SO$_4$ decomposition methods applied to ZrO$_2$[5] was also reported. However, complete decomposition of high purity ZrO$_2$ is difficult using the former method. Similarly, in the latter method acid decomposition of ZrO$_2$ is difficult under certain processes or composition of ZrO$_2$. Thus, the alkali fusion method[6] was investigated in order to decompose both ZrO$_2$ and raw materials (ZrO$_2$·SiO$_2$) completely. Na$_2$O$_2$ can decompose them completely, but results in a considerably high impurities,
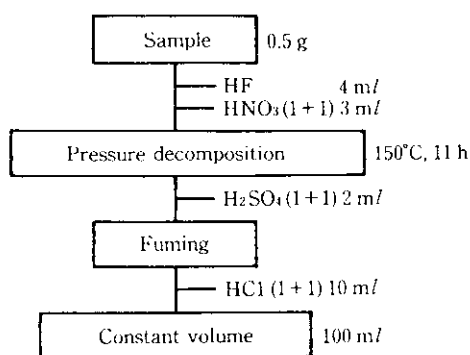
(1) Acid decomposition
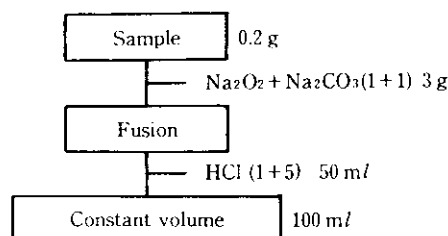
(2) Alkali fusion

Fig. 3   Decomposition procedure for boron nitride

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┌─────────────┐
│   Sample    │  0.5 g
└──────┬──────┘
       ├── Na₂CO₃ + Na₂B₄O₇  (3+2) 5 g
┌──────┴──────┐
│   Fusion    │  850~860°C  10 min
└──────┬──────┘      900°C    2 min
       │           1 000°C   15 min
       ├── HCl    (1+5) 45 ml
       ├── H₂SO₄(1+1) 10 ml
┌──────┴──────────┐
│ Constant volume │  100 ml
└─────────────────┘
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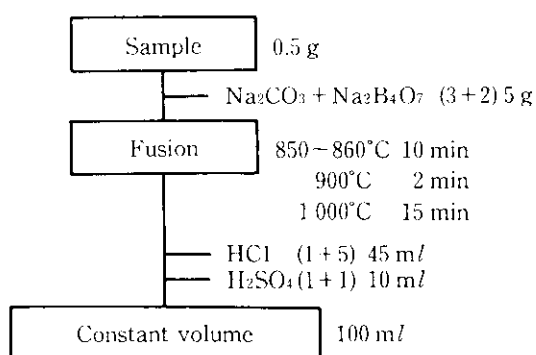
Fig. 5 Decomposition procedure for zirconium oxide

and it also gave high blank values, especially for Ca and Al. Thus, in order to lower the blank values, H_3BO_3/$Na_2B_4O_7$ was studied as a fusion agent with Na_2CO_3 added, which enables the easy dissolution of melt. In the case of $Na_2CO_3 + H_3BO_3$ the sample could not be decomposed completely, when the sum of the fusion agent was less than 5 g and the ratio of the agents were between (3 + 1) and (1 + 3). On the other hand, when more than 4 g of $Na_2B_4O_7$ or 5 g of $Na_2CO_3 + Na_2B_4O_7$

(1 + 4)~(3 + 2) were used, complete decomposition was achieved, and the melt was dissolved easily. However, dissolution of the melt was easier when less boric acid was used. In the case of $Na_2CO_3 + Na_2B_4O_7$ (3 + 2) 5 g, complete decomposition and dissolution of the melt was achieved. In consideration of the hydrolysis of Zr and the solubility of $Na_2B_4O_7$, the dissolution of melt was carried out by immersing and heating the platinum dish in H_2SO_4 (1 + 1) 10 ml and HCl (1 + 1) 45 ml. The decomposition procedure for ZrO_2 by alkali fusion is shown in Fig. 5. Acid decomposition in HF + H_2SO_4 under pressure can also decompose ZrO_2, although YF was precipitated in the case of partially stabilized ZrO_2 which contains a high concentration of Y, but cannot decompose zircon sand containing a high amount of SiO_2. A comparison of decomposition methods is summarized in Table 2.

3.2 Condition of Measurement

Table 3 shows the analytical lines used for the determination of each element studied. In the case of BN and AlN, the matrix components, B and Al, have no spectral interference for analytical lines usually employed in steel analysis. An increase in the background level was not found when B was matrix, but an

Table 2 Comparison of decomposition methods

Decomposition condition			Result		
Reagents	Ratio	Quantity	BN	AlN	ZrO₂
Na₂CO₃+H₃BO₃	3+1	2~5 g	—	—	×
	2+1	2~5 g	—	—	×
	1+1	2~5 g	△	○	×
	1+2	2~5 g	△	—	×
	1+3	2~5 g	△	—	×
Na₂B₄O₇		2~3 g	—	—	×
		4~5 g	—	—	△
Na₂CO₃+Na₂B₄O₇	1+4	5 g	△	—	△
	1+3	5 g	△	—	△
	1+2	5 g	△	—	△
	3+2	5 g	○	—	○
	2+1	5 g	○	—	×
Na₂O₂+Na₂CO₃	1+1	3 g	○	—	—
H₂SO₄(1+1)+HF	1+3	4 ml	△	—	○
H₂SO₄(1+4)+HF	2+3	5 ml	△	—	—
HCl(1+1)+HF	1+3	8 ml	×	—	—
HNO₃(1+1)+HF	3+4	7 ml	○	—	—
HCl+HNO₃	1+1	8 ml	—	○	—
HNO₃+H₂SO₄	1+1	8 ml	—	○	—

Note. ○: good, △: fair, ×: bad

Element	Wave length (nm)	Interference*[1]
Fe	259.94	Al, Zr (B. G. increase)
Si	251.61	Mo 251. 61 (0.011)
		Al, Zr (B. G. increase)
Mn	257.61	
Ni	231.60	
Cr	267.72	Nb 267.78 (<0.001)
Ca	393.37	
Mg	279.55	
Ti	334.94	Nb 334.91 (<0.001)
Al	396.15 (BN)	Zr 396.15
	308.21 (ZrO_2)	
V	311.07 (BN, AlN)	
	309.37 (ZrO_2)	
P	178.29 (ZrO_2)	
Cu	327.40 (AlN)	
Y	371.03 (ZrO_2)	
Hf	264.14 (ZrO_2)	

*[1]( ): correction factor

Fig. 7 Interference of zirconium on silicon line

3.3 Application of Micro-Injection Technique

increase in the background was noticed with Fe and Si when Al was matrix. Since for both BN and AlN, the nebulization efficiency varied with the quantity of the matrix, due to the change of viscosity and surface tension of the solution, the calibration curve obtained has a different slope. Thus, in order to suppress the matrix effect and match the matrix with calibration solution, H_3BO_3 was added to the calibration solution in the case of BN, and Al solution was added in the case of AlN.

Concerning ZrO_2, there is no spectral interference for Fe, Y, Ti, Mg and Ca, but a spectral line of Zr completely overlaps Al I 396.15 nm, which is used in steel analysis. Therefore, Al I 308.21 nm, which has high sensitivity and no obstruction line, was selected. For Si I 251.6 nm, there is a spectral line of Zr 251.67 nm in the vicinity which can be separated from Si peak, but background correction was necessary because of the increase in the background caused by the tailing of the Zr line (Fig. 6 and 7).
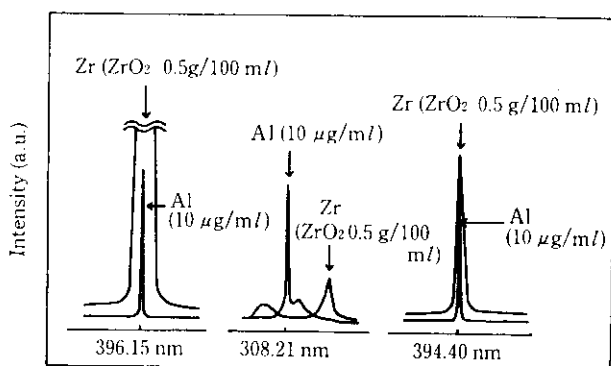
Since the BN and AlN sample solution contain only acid and a small quantity of fusion agent used for decomposition of the residue, these low salt containing solutions can be measured by the ordinary nebulizing method. However, in the case of ZrO_2, a sample solution containing a high concentration of salt, the conventional method causes clogging of the nebulizer and the tubing, and the baking at the tip of the torch. Therefore, the emission signal decreases extraordinarily in successive measurements. Dilution of the high salt concentration solution gave a lower relative sensitivity. Therefore, a micro-injection technique, which is useful when only small amounts of sample solution is obtained, was applied to the measurement of high salt concentration solution. The effect of sample injection volume on signal intensity and precisions are shown in Fig. 8. In the case of a sample injection with a volume
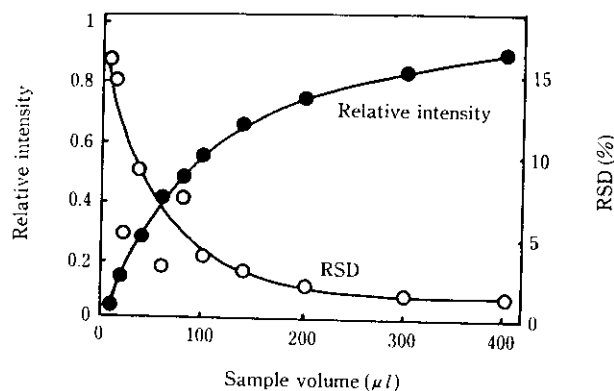

Fig. 6 Interference of zirconium on aluminum lines

Fig. 8 Effect of sample injection volume on signal intensity and relative standard deviation (RSD) for P 178.29 nm

of 300 μl, the intensity obtained was almost equal to that of continuous nebulization and the relative standard deviation was also less than 1%, nearly the same as those of the continuous method. With this injection volume, successive measurement was achieved without clogging at the introductory system and without baking at the torch tip even with a highly concentrated solution of 5~10%. As described in Sec. 3.2, in the ICP-AES analysis using continuous nebulization, the emission signal of analytical elements was affected by the types and the amounts of matrix. These were caused by changes in the aspiration rate and nebulization efficiency which depend on physical effects such as the viscosity of the sample solution, or on chemical, excitation, and spectral interferences of measuring elements. On the other hand, with the micro-injection technique, integration of the entire emission signal, namely, determination of the total amount of analysis elements injected, can suppress the effect of change in aspiration speed caused by the presence of salt. The effect on the nebulization efficiency of the micro-injection technique was smaller than that of the continuous method, and can be ignored if the quantity of fusion agent is constant. Spectral interference can be eliminated by the selection of an optimum analytical line free from an interference of matrix, and by background correction. Therefore, the same calibration solution which contains only a fusion agent and acid can be applied to ZrO_2 and $ZrO_2 \cdot SiO_2$, with background correction by subtracting the integral count of a solution which contains the same amount of high purity Zr as the ZrO_2 and $ZrO_2 \cdot SiO_2$. Figure 9 shows the calibration curve for Al obtained by the injection technique with background correction. It was found that the same calibration curve was obtained regardless the existence of Zr. ZrO_2 and $ZrO_2 \cdot SiO_2$ were measured by the same calibration curve, allowing
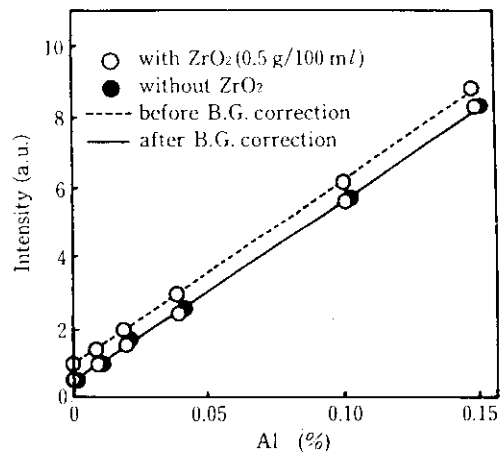

Fig. 9 Matrix effects on calibration curves for Al 308.29 nm

for a simple analytical procedure.

However, the injection method has the lower ratio of SB than that of the continuous method, because of higher background integral count to the signal, and is, in some cases, strongly affected by excitation interference, depending on the matrix or analytical line. Further study is necessary in order to broader its application.

3.4 Analytical Results

BN, AlN and ZrO_2 were decomposed and analyzed according to the procedure shown in Fig. 3~5. Table 4, 5 and 6 show the analytical results. In every case, a concentration level of 0.001% was obtained with good precision, and some elements were determined at a ppm level. On the analysis of ZrO_2, results of Hf which had a considerably high concentration level, are also shown. Because of the chemical similarity between Hf

Table 4 Analytical results for boron nitride samples (%)

Sample		Si	Mn	Al	Ti	Cr	Fe	Ca	Mg
A	$\bar{x}$	0.008	<0.0001	0.0018	0.0050	<0.0001	0.0051	0.0090	0.0016
	σ	0.0005	—	0.0001	0.0002	—	0.0004	0.0001	0.0001
B	$\bar{x}$	0.020	0.0003	0.0130	0.0001	0.0004	0.0065	0.0066	0.0004
	σ	0.0004	0.0000	0.0012	0.0000	0.0001	0.0012	0.0003	0.0001

Note (1) $N=5$

Table 5 Analytical results for aluminum nitride samples (%)

Sample		Si	Mn	Ni	Cr	Ti	Ca	Mg	Co	Fe	Nb
A	$\bar{x}$	0.0029	0.0005	0.0005	0.0006	0.0012	0.0038	0.0001	0.0020	0.0020	0.0001
	σ	0.0006	0.0001	0.0002	0.0003	0.0001	0.0002	—	0.0001	0.0004	—
B	$\bar{x}$	0.173	<0.0001	0.0017	0.0020	0.0035 ·	0.0049	0.0030	0.0002	0.127	0.0001
	σ	0.0042	—	0.0003	0.0015	0.0000	0.0003	0.0001	0.0001	0.0033	—

Note (1) $N=5$

Table 6 Analytical results for zirconium oxide samples (%)

Sample		Hf	Y	Si	Al	V	P	Ti	Ca	Mg	Fe
A	$\bar{x}$	1.673	0.0024	0.0051	0.0021	0.0005	0.0007	0.022	<0.0001	<0.0001	0.083
A	σ	0.001	0.0001	0.0005	0.0003	0.0001	0.0001	0.0007	—	—	0.002
B	$\bar{x}$	1.653	0.0007	0.011	0.0071	0.0006	<0.0001	0.015	0.0088	0.0023	0.0020
B	σ	0.014	0.0001	0.001	0.0009	0.0002	—	0.0004	0.0007	0.0004	0.0003

Note (1) $N=5$

and Zr, separation and analysis of them by chemical method took a long time, and were not precise. On the contrary, ICP-AES can determine Hf in Zr without requiring a complicated separation pretreatment. However, the conventional continuous nebulization method requires the same amount of Zr as the sample to be contained in the calibration solution. Furthermore, high purity Zr which does not contain Hf is hard to obtain. Thus, it is difficult to determine Hf in Zr accurately. By employing the micro-injection technique, Hf in Zr is determined easily at a ppm level by background correction, because, under this method the calibration solution does not need to contain Zr as matrix. Since the high purity ZrO_2 used for background correction might include Hf, background correction was carried out by substracting the signal measured in the vicinity of the analytical line with a sequential spectrometer, ICPS 100V.[7] The analytical results of commercial ZrO_2 (purity > 99.9%) by this method revealed that it contained more than 1.5% of Hf. The high purity ZrO_2 (impurity, max 10 ppm) used for background correction was found to include about 80 ppm of Hf.

In the determination of AlN and ZrO_2, analytical results for Fe varied greatly at first. After examination, it was found that this was caused by contamination of the platinum crucible and platinum dish used for fusion. The platinum crucible contains about 0.1% of impurities.[8] Futhermore, after the fusion of the high Fe content sample, the blank value obtained was considerably high, and was not reduced by cleaning with $K_2S_2O_7$-HCl. Therefore, crucibles employed exclusively for this analysis were used. On the other hand, since insufficient sintering caused Fe and Ni to alloy with platinum, giving low analytical values for Fe and Ni, it was important to select optimum temperature and time for fusion conditions.

4 Conclusions

A method for the simultaneous multi-element determination of impurities in fine ceramics by ICP-AES has been established.

(1) BN was decomposed in HNO_3 + HF in a PTFE vessel under pressure, and analyzed by using a calibration solution containing a certain amount of boric acid. Fusion with $Na_2O_2 + Na_2CO_3$ was employed for Si and B, which partially vaporize by the above method.

(2) AlN was decomposed in H_2SO_4 + HNO_3 under pressure. A calibration solution containing Al was used for background correction. The residue recognized in some cases was fused with $Na_2CO_3 + H_3BO_3$ and was dissolved completely.

(3) ZrO_2 was fused with $Na_2B_4O_7 + Na_2CO_3$, and was analyzed by a micro-injection technique, which enabled the successive measurement of highly concentrated solutions including a large amount of fusion agents, and the use of a single calibration curve. The determination of Hf in Zr, which is difficult under the conventional method, was achieved easily by this method.

(4) Establishment of a decomposition method, and the development and application of the micro-injection technique have made it possible to accurately determine the impurities in fine ceramics at a concentration level of 0.001% or ppm.

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