Direct Determination of Iron in Silicon Carbide and Silicon Nitride by Electrothermal Atomic Absorption Spectrometry with Slurry-Introduction

Yukitoki MORITA[†], Akinori TANAKA, Akinori ISOZAKI and Tadao OKUTANI

Department of Materials and Applied Chemistry, College of Science and Technology, Nihon University, Kanda-Surugadai, Tokyo 101-8308, Japan

Keywords Direct determination of iron, electrothermal atomic absorption spectrometry, slurry-introduction, silicon carbide, silicon nitride

Silicon carbide and silicon nitride possess chemical resistance, thermal resistance and abrasive resistance. Owing to their properties, silicon carbide and silicon nitride have been utilized in various fields, such as the energy and precision-machinery industries. These properties are subject to the material's chemical composition and constitution. Atomic spectrometry, such as ICP-AES and FAAS, has been applied to the analysis of trace impurities in ceramics.¹⁻⁵ The trace impurities from raw materials or those produced from the manufacturing process of ceramics have great influence on the properties and capacities of ceramics. Thus, it is essential to determine trace impurities to characterize the quality of ceramics.

Generally, solid and powdered samples are dissolved by a pretreatment, such as using a decomposition method with acid or fusion with alkali salts. However, the pretreatment is somewhat complicated and requires time-consuming procedures. To avoid these problems, the direct analysis of trace metals in solid and powdered samples by electrothermal AAS was proposed.⁶⁻⁸

In direct analysis, a solid-sampling technique and a slurry-sampling technique are used to introduce a sample into a furnace. The solid-sampling technique requires special tools, such as a microboat⁹, a miniature cup¹⁰, a cup in tube¹¹ and a ring chamber tube.¹² Moreover, a calibration graph using a reference material is required in the analysis. Also, the reproducibility of analytical values is not always good, due to segregation of the samples. Nakamura *et al.*¹³ determined copper and lead in silicon nitride and silicon carbide by a solid-sampling technique using a cup-type graphite furnace.

For the slurry-sampling technique, there are following important factors: choice of dispersing agents; several reports were described "stabilizing agent", such as glycerine¹⁴⁻¹⁶, Triton X-100¹⁷⁻¹⁹, Viscalex HV30^{20,21} and sodium hexametaphosphate²², the slurry concentration and the stability of a slurry with time.

Docekal and Krivan²³ proposed a method for the determination of impurities in silicon carbide by introducing a slurry prepared with water. The slurry was introduced into a graphite furnace by using an autosampler. Furthermore, the accuracy was checked by the comparing the analytical results with those obtained by ETAAS and ICP-AES involving the decomposition of a sample, and by INAA.

Oimatsu *et al.*^{24,25} reported a direct determination of impurities in titanium dioxide by graphite-furnace AAS using a slurry sampling. The slurry was prepared by 0.1% sodium hexametaphosphate.

On the other hand, the determination of copper in glass¹⁵ and rock samples¹⁶ has been investigated by using a slurry prepared by 10% glycerine and ammonium fluoride as a chemical modifier.

In this study, the slurry-sampling technique using 10% glycerine as a dispersing agent by GF-AAS under a deuterium background correction was investigated. The proposed method has been applied to the determination of trace iron in silicon carbide and silicon nitride.

Experimental

Apparatus

Atomic-absorption measurements were carried out on an AA-880 MARK-II (NIPPON Jarrell-Ash) atomic absorption spectrometer equipped with an L-233 iron hollow-cathode lamp (Hamamatsu Photonics), deuterium lamp for a background correction, and an FLA-1000 (NIPPON Jarrell-Ash) flameless atomizer. Graphite cuvettes (NIPPON Jarrell-Ash Part No. 230-0106) were used. The sample-injection volume into the furnace was 10 µl. The integrated absorbance (peak area) for iron was measured for all work.

A Hitachi Model U-3200 spectrophotometer was used for the experiments to stabilize the slurry.

The particle size distribution was measured with a

[†] To whom correspondence should be addressed.

Table 1 Instrumental operating conditions

Operating step	Temperature/°C	Time/s	
		Ramp	Hold
Dry	160	20	40
Pyrolysis	900	10	20
Atomization	2500		5
Wavelength: 248.3 nm			
Lamp current: 15 mA			
Argon gas flow rate: 2.5 l/min			

Shimadzu Model SALD-2000 laser diffraction particle size-distribution analyzer.

Reagents and materials

Iron standard solutions were prepared by diluting a 1000 mg l⁻¹ atomic-absorption standard (Wako Pure Chemical Industries, Ltd.) with 0.1 mol l⁻¹ nitric acid.

Glycerine (Wako Pure Chemical Industries, Ltd.) was prepared to the final concentration of 10v/v%.

Ultra-pure water was prepared by a Milli-Q Labo reagent Water System (Millipore Co.). All other reagents used were of analytical grade.

Silicon carbide (JCRM R021 and R023) and silicon nitride (JCRM R003 and R004) reference materials were obtained from the Ceramics Society of Japan. The median sizes were 1.2, 2.3, 0.27 and 0.32 µm for R003, R004, R021 and R023, respectively.

Analytical procedure

Silicon carbide and silicon nitride were weighed out in 1–15 mg batches containing less than 0.50 µg of iron by a micro balance, and were put into 15 ml polystyrene test tubes. Five milliliters of 10% glycerine solution as a dispersing agent was added to each test tube. The sample was then dispersed by an ultrasonic agitator for 1 min. After shaking the test tube for about 10 s by a hand, 10 µl aliquot of the slurry was taken out by using a micropipet equipped with a polypropylene tip and injected into a furnace. All measurements were performed under the furnace program given in Table 1. The calibration could be performed with iron standards.

Results and Discussion

Effect of the pyrolysis temperature

In order to achieve sufficient atomization of the analyte elements and to obtain accurate results, it is important to examine several experimental factors. The effect of the pyrolysis temperature on the peak areas of iron was investigated for both iron standards and the slurries of silicon nitride and silicon carbide. The obtained results were shown in Fig. 1.

Plots of the areas from standards and these from 10% glycerine of iron indicate a similar tendency. The areas

Fig. 1 Effect of the pyrolysis temperature on the peak area of iron. (○) Standard (Fe, 0.60 ng); (●) 10% glycerine (Fe, 0.60 ng); (□) R003 (6.412 mg) dispersed in 5.0 ml of 10% glycerine; (△) R023 (1.804 mg) dispersed in 5.0 ml of 10% glycerine.

Fig. 2 Effect of the concentration of glycerine on the dispersibility by spectrophotometry. Glycerine concentration: 0% (○), 10% (●) and 20% (□); wavelength, 660 nm; contrast solution, water; cell, 10 mm; slurry, about 2 mg of R023 dispersed in 5.0 ml of 10% glycerine. The relative absorbance was normalized to the absorbance with a standing time of 0 min.

decrease rapidly above 900°C because of the loss of iron due to its partial volatilization during the pyrolysis step. On the other hand, in the case of slurries, the areas decrease above 1100°C. This could be due to a difference in the existent states of irons in the slurry sample and the standard solution. Since the reproducible and constant areas were obtained at the range of 600°C to 900°C, the pyrolysis temperature was set at 900°C.

Choice of dispersing agent

In order to disperse a solid sample homogeneously and to maintain suspension state, the choice of a proper dispersing agent is quite important. We tested various agents in this study. When water was used as a dispersing agent, some of the particles adhered to the test tube and

Fig. 3 Atomic-absorption profiles of iron standard and slurry. A and a, iron standard (0.60 ng); B and b, R023 (1.985 mg) dispersed in 5.0 ml of 10% glycerine; C and c, R003 (7.243 mg) dispersed in 5.0 ml of 10% glycerine; background-corrected iron: A, B and C; background absorption: a, b and c.

settled rapidly after shaking. The slurry was unstable, and the reproducibility of analytical values was poor. When Triton X-100 was used, it formed bubbles after shaking, and some of the particles were concentrated in the bubbles, and a part of the slurry remained in a micropipet upon sampling. When phosphates, such as sodium-diphosphate and sodium-hexametaphosphate, were used, strong background absorption was observed. On the other hand, in the case of glycerine, these problems did not occur. The dispersion by an ultrasonic agitator for 1 min was effective to avoid agglutination of the sample and sample's adsorption on the surface of the test tube.

Stabilization of slurry

The effect of the glycerine concentration on the dispersibility of a powdered sample was studied by measuring the relative absorbance for the slurry *versus* time by spectrophotometry. The obtained results are shown in Fig. 2. The wavelength used was 660 nm, at which no absorption spectrum of glycerine existed. As the glycerine concentration was increased, the decrease in the relative absorbance was restrained. This could have been due to the improvement of stability for the slurry. However, as the glycerine concentration was increased above 20%, a part of the slurry remained in a micropipet upon sampling. Thus, a glycerine concentration of 10% was chosen.

Also, the stability of the slurry with time by atomic-absorption measurements resulted in a good reproducibility of the measurement values for less than 5 min.

Atomic-absorption profiles of iron

Figure 3 shows the atomic-absorption profiles of iron in silicon nitride and silicon carbide slurry and 0.60 ng of the standard under the conditions given in Table 1. The obtained signals from the slurry appeared later than that of the standard, and background absorption was also observed. In the case of an iron standard containing

silicate, the background absorption matched the shapes obtained from the slurry. Therefore, the background absorption was observed by the existence of the silicate in the sample. In order to restrain the background absorption, various matrix modifiers were tested. Morita *et al.*¹⁵ have reported an effective method to restrain the background absorption from the glass sample by utilizing ammonium fluoride as a matrix modifier. Ammonium fluoride could not restrain the background absorption for silicon carbide and silicon nitride. Other agents, such as hydrofluoric acid, carbon black, ascorbic acid and palladium, were also tested, but were not effective. These results were obtained due to the fact that the silicon carbide and silicon nitride possess both chemical resistance and thermal resistance. However, slurry prepared with less than about 15 mg of the sample is possible for an atomic-absorption measurement without any problem involving background absorption.

Calibration graph

The calibration graphs obtained with the standards and 10% glycerine solutions, and standard addition methods for the slurry are shown in Fig. 4. They were linear up to 1.0 ng of iron. The gradients of the calibration graphs from standards and 10% glycerine solutions were in agreement with the gradients of those obtained by the standard-addition method. Therefore, the standard solution could be used for determining the iron in a slurry. The detection limit was 0.03 ng (3σ), corresponding to $1.0 \mu\text{g g}^{-1}$ in the sample (15 mg sample in 5.0 ml of slurry).

Analytical results

The determination of iron in silicon carbide and silicon nitride was performed by GFAAS using the proposed method. The results are given in Table 2. The values obtained in this study were in good agreement with the reference values, and the RSDs were within

Fig. 4 Calibration graphs of iron and the standard addition method. (○) Standard; (●) 10% glycerine; (I) R023 (1.024 mg/5.0 ml of 10% glycerine); (II) R023 (1.771 mg/5.0 ml of 10% glycerine); (III) R003 (2.893 mg/5.0 ml of 10% glycerine); (IV): R003 (6.887 mg/5.0 ml of 10% glycerine).

Table 2 Analytical results of iron in silicon carbide and silicon nitride

Sample	Fe content/ $\mu\text{g g}^{-1}$		Reference value, wt%
	Proposed method	Another method	
JCRM R003	40 $\pm$ 3	43 $\pm$ 2 ^a	0.0042 $\pm$ 0.0004
JCRM R004	286 $\pm$ 13	287 $\pm$ 18 ^a	0.028 $\pm$ 0.001
JCRM R021	174 $\pm$ 9	153 $\pm$ 18 ^b	0.018
JCRM R023	145 $\pm$ 5	139 $\pm$ 31 ^b	0.015

a. The standard addition method after acid decomposition (HNO_3 -HF). b. The standard addition method after fusion with alkali salt (Na_2CO_3). R003 and R004, silicon nitride; R021 and R023, silicon carbide.

$\pm 7.0\%$. In this study, the proposed method was not complicated and the reagent was the minimum. Therefore, the proposed method can be applied to the direct determination of iron without contamination. This method is also suitable for routine analysis and possible for applications to other elements and/or samples.

References

1. T. Ishizuka, Y. Uwamino and A. Tsuge, *Bunseki Kagaku*, **33**, 576 (1984).
2. Y. Uwamino, H. Morikawa, A. Tsuge, N. Nakane, Y. Iida and T. Ishizuka, *Bunseki Kagaku*, **41**, T151 (1992).
3. T. Uchida, H. Kano, N. Ohnishi, C. Iida and I. Kojima, *Bunseki Kagaku*, **35**, 681 (1986).
4. M. Hayashi and H. Endo, *Bunseki Kagaku*, **37**, T202 (1988).
5. Y. Uwamino, H. Morikawa, A. Tsuge, Y. Iida and T. Ishizuka, *Bunseki Kagaku*, **40**, T183 (1991).
6. C. Bendicho and M. T. C. de Loos-Vollebregt, *J. Anal. At. Spectrom.*, **6**, 353 (1991).
7. I. Atsuya, *Bunseki Kagaku*, **43**, 661 (1994).
8. U. Kurfürst (ed.), "Solid Sample Analysis", Springer-Verlag, Berlin, Heidelberg, 1998.
9. J. Y. Hwang, G. P. Thomas, *Am. Lab.*, **6**, 42 (1974).
10. I. Atsuya and K. Itoh, *Bunseki Kagaku*, **31**, 708 (1982).
11. U. Voellkopf, Z. Grobowski and B. Welz, *Analyst* [London], **110**, 573 (1981).
12. K. P. Schmidt and H. Falk, *Spectrochim. Acta*, **42B**, 431 (1987).
13. T. Nakamura, Y. Noike, Y. Koizumi and J. Sato, *Analyst* [London], **120**, 89 (1995).
14. M. Hoenig and P. V. Hoeyweghen, *Anal. Chem.*, **58**, 2614 (1986).
15. Y. Morita, H. Tsukada and A. Isozaki, *Bunseki Kagaku*, **42**, 551 (1993).
16. Y. Morita and A. Isozaki, *Bunseki Kagaku*, **44**, 703 (1995).
17. N. J. Miller-Ihri, *J. Anal. At. Spectrom.*, **3**, 73 (1988).
18. N. J. Miller-Ihri, *J. Anal. At. Spectrom.*, **9**, 1129 (1994).
19. G. S. B. Januzzi, F. J. Krug and M. A. Z. Arruda, *J. Anal. At. Spectrom.*, **12**, 375 (1997).
20. S. C. Stephen, D. Littlejohn and J. M. Ottaway, *Analyst* [London], **110**, 1147 (1985).
21. Z. Yu, C. Vandecasteele, B. Desmet and R. Dams, *Mikrochim. Acta*, **1990**, I, 48.
22. I. L. Garcia, P. Viñas and M. H. Córdoba, *J. Anal. At. Spectrom.*, **7**, 529 (1992).
23. B. Docekal and V. Krivan, *J. Anal. At. Spectrom.*, **7**, 521 (1992).
24. T. Oimatsu, H. Manabe and T. Nakahara, *Bunseki Kagaku*, **42**, 599 (1993).
25. T. Oimatsu and T. Nakahara, *Bunseki Kagaku*, **45**, 959 (1996).

(Received June 10, 1999)

(Accepted August 4, 1999)