Determination of Trace Impurities in Graphite and Silicon Carbide by Total Reflection X-ray Fluorescence Spectrometry after Homogeneous Liquid–Liquid Extraction

Hitoshi YAMAGUCHI, Shinji ITOH, Shukuro IGARASHI,1) Kunishige NAITOH1) and Ryosuke HASEGAWA

National Research Institute for Metals, Sengen, Tsukuba, Ibaraki 305-0047 Japan. 1) Department of Materials Science, Faculty of Engineering, Ibaraki University, Nakanarusawa, Hitachi, Ibaraki 316-8511 Japan.

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Using homogeneous liquid–liquid extraction as a pre-concentration method, a determination procedure of trace impurities (Fe, Ni and Cu) by total reflection X-ray fluorescence (TXRF) analysis was developed and optimized for graphite and silicon carbide samples. The samples were decomposed by alkali fusion. The residue was dissolved in a mixture of pentadeca-fluorooctanoic acid (PFOA), acetone and water, and the analytes were homogeneously dispersed by the aid of phenanthroline (phen). After phase separation with pH-adjustment, a portion of the sedimented water-immiscible liquid was pipetted on the polyester film that covered a silicon wafer sample-carrier. Then, the droplet was dried in a vacuum and analyzed by TXRF. Analytical values in the sub-ppm or ppm level were well agreed with the certified values of the standard samples or the values observed by ICP-OES for a few samples.

KEY WORDS: homogeneous liquid–liquid extraction; total reflection X-ray fluorescence analysis; trace impurities; graphite; silicon carbide.

1. Introduction

Total reflection X-ray fluorescence (TXRF) analysis is capable of conducting simultaneous determination of trace impurities on solid surface. Consequently, the TXRF analysis has been mainly utilized in the area of semiconductor materials and recently in the studies of environmental water, biological materials and geological minerals.1–4) When the sample to be analyzed is a solution, it is changed to the solid film on a sample-carrier by the micro-drop method.5,6) Hence, the preparation of analytical samples and the calibration of observed data are very important in the TXRF analysis of solution samples. If the matrix of a sample solution remains in the solid film, the background and the detector counting-loss possibly increase. In advance of the X-ray measurement, matrix removal is therefore required. For example, the separation using organic complex was investigated for the analysis of environmental samples.7–9) On the other hand, it was reported that the relative sensitivity factors to the internal standard could compensate the errors due to the thickness and the area of the solid film.10)

In the present study, TXRF analysis has been studied for the determination of trace impurities (Fe, Ni and Cu) in graphite and silicon carbide. In order to enrich the analytes and separate them from the matrix sodium introduced by the alkali fusion of the samples, recently noticed homogeneous liquid–liquid extraction was examined. The extraction method offers the advantage that particular elements in a large volume of solution are concentrated into several milliliters of sedimented liquid.11–15) The presence of a chelating agent such as phenanthroline (phen)16) is indispensable to practice the extraction, and phen was utilized also in this study. Scandium was selected as the internal standard to evaluate the relative sensitivity factors of the analytes, because the quantities of the element in the samples are negligible.

2. Experimental

2.1. TXRF Apparatus

The TXRF apparatus used is a TREX 610 spectrometer (Technos, Osaka, Japan). The X-ray source was a rotating tungsten counter-cathode and operated at 30 kV–150 mA. The primary X-ray was W-Lγ, which was monochromatized in an analytical crystal (LiF200). The incident angle of primary X-ray was 0.15° for the samples tested. A Si (Li) solid-state detector having an 80 mm2 (f: 10 mm) detection area was used. The energy resolution was about 150 eV for the MnKα spectrum (5.895 keV). Measurement was carried out in a vacuum of about 1×10−2 Pa. The integration time was 200 s. Since the apparatus was a proper machine for the inspection of silicon wafers, a silicon wafer covered with a 100 μm thick polyester film was used as a sample-carrier.

2.2. Reagents

High-purity reagents of HCl, HNO3, HF and HClO4 were all of Tampapure 100 grade (Tama Chemicals, Kanagawa,
Sodium carbonate was of Suprapure grade (Merck, Darmstadt, Germany). Phenanthrolinone (phen) was from Dojin Chemicals (Kumamoto, Japan). A 0.1 M solution was prepared by dissolving 0.99 g of phen with 1 cm$^3$ of nitric acid (1+1) and diluting to 500 cm$^3$. Pentadecafluoroalkanoic acid (PFOA) was from Fluka (Buchs, Switzerland). A 0.1 M solution was prepared by dissolving 20.7 g of PFOA with 0.1 M lithium hydroxide solution and diluting to 500 cm$^3$ after adjusted the pH to 7.0. Other reagents were all of special reagent grade. Doubly distilled water was prepared in a non-boiling type distillation apparatus (Fujiwara, Tokyo, Japan) and used throughout. The standard solutions (1 000 ppm) were of Cica-Merck special reagent grade for AAS-use (Kanto Kagaku, Tokyo, Japan). Pretreatment of the samples was carried out in a clean bench of class 100.

Polyester films were cleaned with nitric acid (1+3) for 0.5 h and rinsed with distilled water before use.

2.3. Digestion of Graphite

Graphite samples (1.0 g) were weighed into platinum crucibles, which were heated at 800°C for 12 h in the electric furnace to gasify the matrix carbon. The heating residue was melted with 0.5 g of sodium carbonate at 1 000°C for 0.5 h. After had been cooled, the product was moved into a beaker and dissolved in nitric acid.

2.4. Digestion of Silicon Carbide

Silicon carbide samples (0.5 g) were weighed into platinum crucibles and melted with 2.5 g of sodium carbonate at 1 000°C for 0.5 h. After had been cooled, the residue was transferred to a polytetra-fluoroethylene beaker and dissolved in hydrochloric acid. Then, 5 cm$^3$ of hydrofluoric acid and 10 cm$^3$ of perchloric acid was added and the solution was heated up to generate white fume to remove silicon. Then, the residue was dissolved with distilled water and moved into a beaker.

2.5. Homogeneous Liquid–Liquid Extraction

The sample solutions thus prepared were diluted with distilled water to 100 cm$^3$ and then 2 cm$^3$ of 3 % ascorbic acid was added to reduce ferric ions to ferrous ones. After 2 cm$^3$ of 0.01 M phen solution was added, the solution was allowed to stand for 10 min. Then, 3 cm$^3$ of 0.1 M PFOA solution and 5 cm$^3$ of acetone were added, and finally the pH-value of the solution was adjusted to 0.5 with nitric acid (1 : 1) to sediment a water-immiscible liquid. Finally, a 50 μm$^3$ portion of the sedimented phase was taken out, to which 130 μm$^3$ of distilled water containing 4 μg of scandium and 20 μm$^3$ of acetone were added. A 10 μm$^3$ aliquot of this solution was pipetted on the polyester film covering a silicon wafer sample-carrier and the droplet was dried in a vacuum. Then, the dry product was analyzed by TXRF.

3. Results and Discussion

3.1. TXRF Analysis

In general, the optimum incident angle of the primary X-ray depends on the geometry of the sample on a sample carrier. It is usually about 0.05° for the dry product given by the micro-drop method. However, the dry products possibly became massive owing to the phen and PFOA remaining in the analytical solutions. Hence, the correlation between the incident angle and the X-ray intensity of analyte was examined. The X-ray intensity decreased with an decrease of the incident angle. Taking account into consideration the increase of the detector counting-loss at higher incident angles, 0.15° was selected.

Relative sensitivity factor $S_j$ of each analyte $j$ to the internal standard element $i$ was evaluated using the equation,

$$ S_j = \frac{N_j \times C_j}{N_i \times C_i} \quad \text{...............(1)} $$

where $N_i$ and $N_j$ are respectively the net X-ray intensity of the internal standard element (Sc) and that of the analyte, and $C_i$ and $C_j$ are respectively the mass of Sc and that of the analyte. In this experiment, $C_i$ and $C_j$ were respectively 4 μg and 1 μg. Table 1 shows the relative sensitivity values of the analytes.

Using the sample solutions containing 0.5, 1.0 and 5.0 μg of the analytes, the dependency of the X-ray intensity ratio $N_i/N_j$ to the values of $C_j$ was studied. Figure 1 shows the result, suggesting that the relative sensitivity factor is almost constant up to 5.0 μg for each analyte.

3.2. Homogeneous Liquid–Liquid Extraction

The addition amount of PFOA for homogeneous liquid–liquid extraction was examined; namely, it was varied in the range 1–6 cm$^3$ and its influence on the sediment of water-immiscible phase was clarified. Figure 2 shows the result. The amount of the sedimented precipitated organic phase increased linearly with the addition amount of the PFOA solution. The former of 30 μm$^3$ was corresponding to the latter of 1 cm$^3$. Namely, the concentration of the analyte in
the sedimented phase was found to be adjustable by changing the addition amount of PFOA. In this experiment, 3 cm$^3$ was selected because the quantity of the water-immiscible phase required at a time of X-ray measurement was 50 μdm$^3$.

Since the kinds of organic solvent influence the amount of the sedimented phase, the degree of extraction of the analytes and the extraction time, the selection of solvent is important. Moreover, the organic solvent having a low boiling point is desirable, because it is easily removed in a vacuum. Regarding with PFOA, the various solvents including dimethylsulfoxide, ethanol and acetone have been studied. In this experiment, acetone was selected, and the relation between the concentration of acetone solution and the amount of sedimented phase was studied. Below 1.5 %, needle-like crystals of PFOA were deposited. In the range of 2 to 30 %, the slight increase of the sedimented phase was found owing to the dissolution of acetone into the water-immiscible phase. Above 40 %, only the liquid phase consisting of a complete homogeneous solution was observed. Thus, a 4.5 % acetone solution was selected as the water-miscible organic solvent.

Recoveries of the analytes were examined by flame-AAS and phenantroline-absorptiometric method. Table 2 shows the result. Recoveries more than 97 % were obtained for every analyte.

Detection limit of each analyte was calculated from the equation,

$$DL = \frac{3 \times m}{I_p} \times \frac{I_B}{t}$$

where $m$ is the mass of the analyte in the measurement solution, $I_p$ is the net X-ray intensity (cps) of the analyte at peak, $I_B$ is the background intensity (cps) and $t$ is the measuring time (s). In this experiment, $m$ was 13.9 ng for the initial amount of 500 ng and $t$ was 200 s. Table 3 shows the calculated values of the detection limit of the analytes. When the weighed amount of the sample is 1 g, the detection limit of 1 ng is corresponding to the concentration of 36 ppb.

3.3. Analysis of Practical Samples

Table 4 shows the analytical results of practical samples: the standard graphite sample of JAERI, a commercially available silicon carbide and a commercially available silicon nitride–silicon carbide composite.

Table 3. Detection limits of the analytes.

| Analyte | Peak (cps) | Background (cps) | Detection Limit (ng) |
|---------|-----------|------------------|----------------------|
| Fe      | 21.88     | 1.24             | 0.15                 |
| Ni      | 28.40     | 3.27             | 0.19                 |
| Cu      | 36.83     | 5.77             | 0.20                 |

Table 4. Analytical results of practical samples: the standard graphite sample of JAERI, a commercially available silicon carbide and a commercially available silicon nitride–silicon carbide composite.

| Sample          | Analytical value (ppm) |
|-----------------|------------------------|
|                | Fe  | Ni  | Cu  |
| JAERI G5       |     |     |     |
| Certified TXRF | <0.5| <0.1| -   |
| TXRF           | 0.18| 0.06| 0.14|
| JAERI G6       |     |     |     |
| Certified TXRF | 11  | 0.3 | -   |
| TXRF           | 10.1| 0.28| 0.18|
| SiC            |     |     |     |
| ICP-OES        | 2.7 | <0.5| 1.7 |
| TXRF           | 2.8 | 0.21| 1.7 |
| SiC-Si$_3$N$_4$|     |     |     |
| ICP-OES        | 3.3 | <0.5| 1.1 |
| TXRF           | 3.0 | 0.10| 1.1 |

*(n=2)*

Fig. 2. Relationship between the volume of added PFOA and that of sedimented liquid phase.

Table 2. Recoveries of the analytes observed for homogeneous liquid–liquid extraction; the values were obtained by flame-AAS and phenantroline-absorptiometric method.

| Element | Added (μg) | Found (μg) | Recovery (%) |
|---------|-----------|------------|--------------|
| Fe$^{3+}$ | 50        | 48.7       | 97           |
| Ni$^{2+}$ | 20        | 19.6       | 98           |
| Cu$^{2+}$ | 20        | 19.4       | 97           |

*1: phenantroline-absorptiometric method.  
*2: flame-AAS.

The digestion of acid-insoluble materials such as graphite and ceramics is usually carried out by alkali fusion. Because of a large quantity of sodium carbonate, the concentration of the solution is difficult without ion exchange separation of sodium. On the other hand, by using homogeneous liquid–liquid extraction, it became possible to concentrate a given analyte into a volume of several 10 μdm$^3$ at one step. Namely, the measurement is carried out without the influence of fusing reagent. A combined use of TXRF-analysis and homogeneous liquid–liquid extraction is promising to determine trace elements in a small amount sample. The increase of the kinds of analytes can be expected by selecting suitable complex reagents.
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