Characteristic X-ray Spectrum Analysis of Micro-Sized SiC

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It has been investigated what kind of characteristic X-ray in electron probe micro-analyzer (EPMA) is effective for the determination of compounds of Si series materials. After comparing the characteristic X-rays among the primary and secondary lines in K_α and K_β obtained from the Si series standard samples, it was found that the secondary line of K_α exhibited the most informative spectrum although the intensity was considerably weak. As a result of analyzing the spectrum shapes of the Si series standard samples, the spectrum shape of the secondary line of K_α for SiC was different from those for other Si compounds. To grasp the characteristics of the shape, a line was perpendicularly drawn from the peak top to base line in order to divide a spectrum into two areas. The area ratio of right to left was defined to call as the asymmetry index here. As a result, the asymmetry index value of the SiC was greater than one, while those of other Si compounds were less than one. It was found from the EPMA analysis that identification of SiC became successful to distinguish from other Si compounds and this method was applicable for micro-sized compounds in a practical composite material.

Key Words: Electron probe micro-analyzer, Characteristic X-ray, Chemical state, Asymmetry index, Silicon carbide

INTRODUCTION

It is general to use plural analysis methods to elucidate the structure and the composition of micro-sized materials. However, the following problems will arise during the use of these analysis methods:

(1) It may be difficult to pinpoint the analysis area in some analysis methods, such as the X-ray diffraction (XRD) analysis.

(2) Since an electron beam and X-rays are irradiated many times onto the same area, the sample surface gets damage such as carbon contamination.

(3) It takes a long time to analyze.

Therefore, electron probe micro-analyzer (EPMA) that can be used to elucidate the compound state of the micro-sized material by only once measurement has been discussed here. Generally, the EPMA can not only obtain the information of simple substances or elements, but also know the variation of the spectrum as changing the bonding state (Kinouchi, 2001; The Surface Science Society of Japan, 1998). However, since the spectrum cannot change regularly for each element in different bonding states, data such as peak shift, peak intensity ratio and half-value width must be one by one analyzed. As it is very difficult to prove the change of the characteristic X-ray spectrum theoretically from the viewpoint of the instrumental analysis according to many previous studies, a number of the analysis techniques of the characteristic X-ray have been established based on the experimental data (Abe et al., 2001; Honma et al., 1974; Murakami et al., 1991; Nishimura, 2007; Ohtsuka, 1982; Soejima, 1987; Uchikawa & Numata, 1973; Watanabe et al., 1970).

In this study, EPMA that is suitable for micro area analysis was used and we tried to distinguish the kind of compound of the Si series material. At the same time, it was also discussed

Table 1. Analytical instrument, analyzed standard samples, and measurement condition of EPMA

Analytical instrument	FE-EPMA (JEOL JXA-8530F)
Test sample	Si series standard sample for EPMA
	Si, SiC, SiO$_2$, CaSiO$_3$, Mg$_2$SiO$_4$, FeSiO$_4$, Al$_2$SiO$_5$
Measurement condition	Accelerating voltage: 15 kV
	Prove current: 100 nA
	Dwell: 500 msec

EPMA, electron probe micro-analyzer; FE, field emission.

Table 2. Analytical crystal, characteristic X-ray spectrum, and corresponding energy

Analytical crystal		TAP	PET
Characteristic X-ray spectrum	K$_\alpha$(1)	K$_\alpha$(2)	K$_\alpha$(1)
Energy (keV)	1.74	0.87	1.74

TAP, thallium acid phthalate; PET, pentaerythritol.

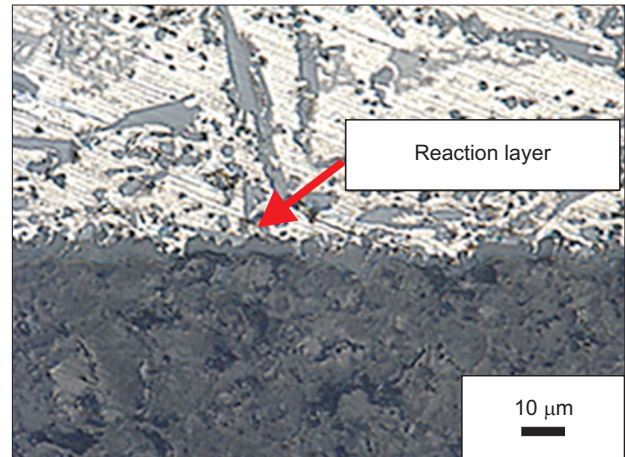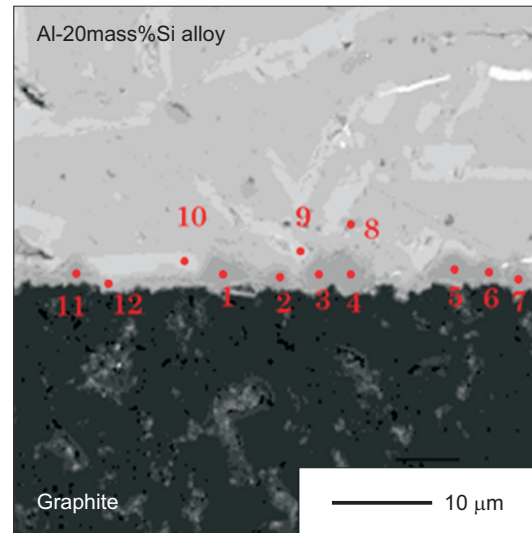whether this method is applicable for a practical composite material.

MATERIALS AND METHODS

Investigation of Characteristic X-ray Spectral Feature by Using Si Series Standard Samples

Firstly, 10 data of the characteristic X-ray spectrum for each of the Si series material were collected by using the EPMA. In order to ensure the conductivity on the sample surface, all the samples were carbon-coated. Table 1 shows a list of standard sample, equipment, and measurement condition in this study. The analytical crystal, characteristic X-ray spectrum and energy value are listed in Table 2. During the experiments, the measured characteristic X-ray was always referred from each of the standard sample investigated here and the analysis of the characteristic spectrum was performed.

Investigation of Characteristic X-ray Spectrum by Using Composites

High purity aluminum (99.99 mass%) and silicon (99.99 mass%) plates were employed in this study and they were placed on the graphite substrate (12×12×2 mm) in the order of Al/Si/graphite from top to bottom. The mass ratio of Al and Si was designed to be 80:20, and the total mass was approximately 0.4 g. The sample was heated to a temperature of 1,273 K under about 3 Pa to form the molten Al-20mass%Si alloy. After holding 1 hour at 1,273 K, the sample was immediately cooled to the room temperature. To observe the structure, the sample was embedded in resin, sectioned perpendicular to the Al-20mass%Si alloy interface and polished. Then, the polished sample was ultrasonically

Fig. 1. Photomicrograph of the cross section of Al-20mass%Si alloy/graphite system after reacting.

Fig. 2. Composition image of cross section of Al-20mass%Si alloy/graphite system after reacting and analyzed points.

cleaned in ethanol, dried in purified air, and carbon-coated for the EPMA analysis. The results of the EPMA mapping and XRD revealed that the reaction product SiC was formed at the interface between the Al-20mass%Si alloy and the graphite. Fig. 1 shows an optical micrograph of the cross section of Al-Si alloy/graphite. A new reaction layer was observed at the interface. Furthermore, according to the composition image (COMPO image) shown in Fig. 2, it was suggested that this reaction layer was not only formed at the interface, but also existed in the Al-20mass%Si alloy, which was recognized by the light-dark difference of the color. Therefore, the characteristic X-ray spectra of the light gray part and dark gray part were measured in this study.

RESULTS AND DISCUSSION

Characteristic X-ray Spectral Feature of Si Series Standard Samples

Fig. 3 shows an example of the characteristic X-ray spectra of various lines acquired from the pure Si standard sample. Intensity of the characteristic X-ray was large for the K_α line (primary line) that was generally utilized for qualitative, quantitative, line and mapping analyses. However, difference of the characteristic spectrum shape and peak shift for each of the standard sample was difficult to be observed. For the K_β line (primary line), since the intensity of the characteristic X-ray was low and the spectrum was broad, it was considered that the comparison among the spectra was also difficult. On the other hand, for the K_α line (secondary line) that had not been considered to be suitable for the analysis because of the low intensity in itself, it was found; however, that the feature of the spectral shape was informative. Fig. 4 shows the K_α line (secondary line) shape for each of the Si series standard sample. The peak top of the SiC standard sample existed on the low energy side (the left of center) while that of the other Si series standard samples was located on the high energy side (the right of center). In order to elucidate of difference in the shape, the spectrum was divided into left and right by drawing a line perpendicularly from the peak top. Generally, the length ratio of the left line and right line at the half-value intensity has been utilized and defined as the asymmetric index, that is, the spectrum profile was divided into two lines: the low energy side (left) and the high energy side (right). However, in the case of distorted spectrum, an exact asymmetry index

might be not obtained due to an error of the half-value. Therefore, we considered a new method that could eliminate the influence of the error of the half-value and analyzed by comparing the area of the right to left. Here we define the area ratio as the asymmetry index. Table 3 shows results of the asymmetry index calculated by the area ratio of right to left. Clearly, the value of SiC was greater than one, and the values of other Si series materials were less than one. The results indicated that it was possible to distinguish SiC by using the asymmetry index. Since it took several days to collect all the data, the peak shift caused by mechanical reasons of the equipment might occur. However, it had no effect on the asymmetry index due to the shift of the spectrum itself.

Distinction of SiC by Using Composites

As shown in Fig. 2, the main component in the gray part was detected to be α-Al while that in the light gray part was Si. In the dark gray part, the main component was suggested to be SiC.

As with the treatment of the standard samples, the area ratio of right to left for the spectrum was calculated and the results are shown in Table 4. For the points 1 to 8 and 11 existing in the gray black part, the values of the asymmetry index were larger than one, and those values for the points 9, 10, and 12 existing in the light gray part were less than one. Based on the asymmetry index values of the standard samples, the dark gray part could be identified as SiC, which corresponded to the above judgement from the COMPO image. Since the size of the reaction product in the vicinity of the interface (points 1 to 8 and 11) was as large as 1 μm, and the irradiated
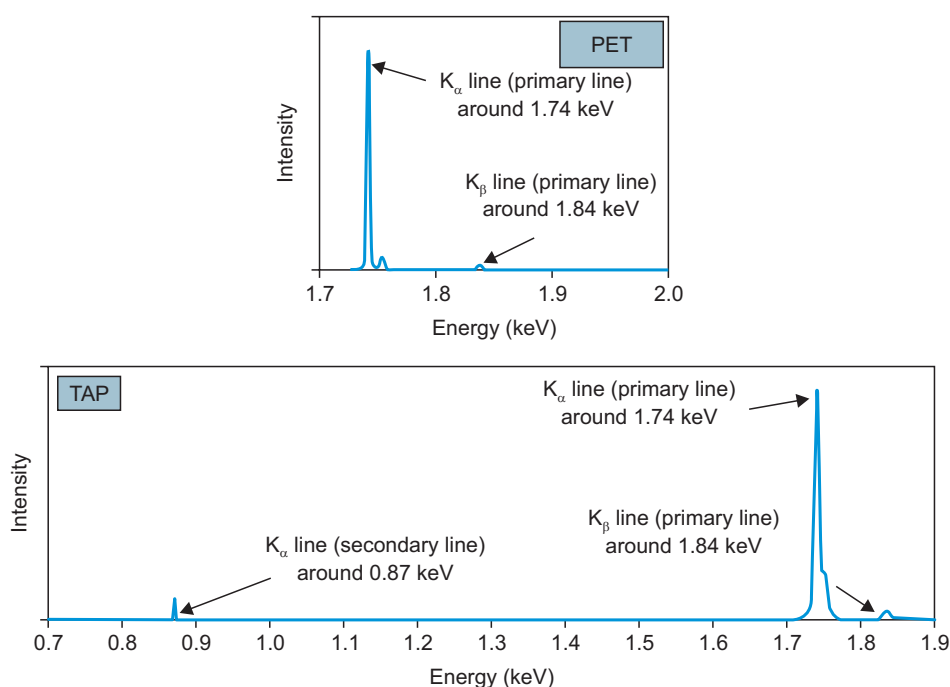

Fig. 3. Characteristic X-ray spectrum of pure Si: analytical crystals are PET (top) and TAP (bottom). PET, pentaerythritol; TAP, thallium acid phthalate.
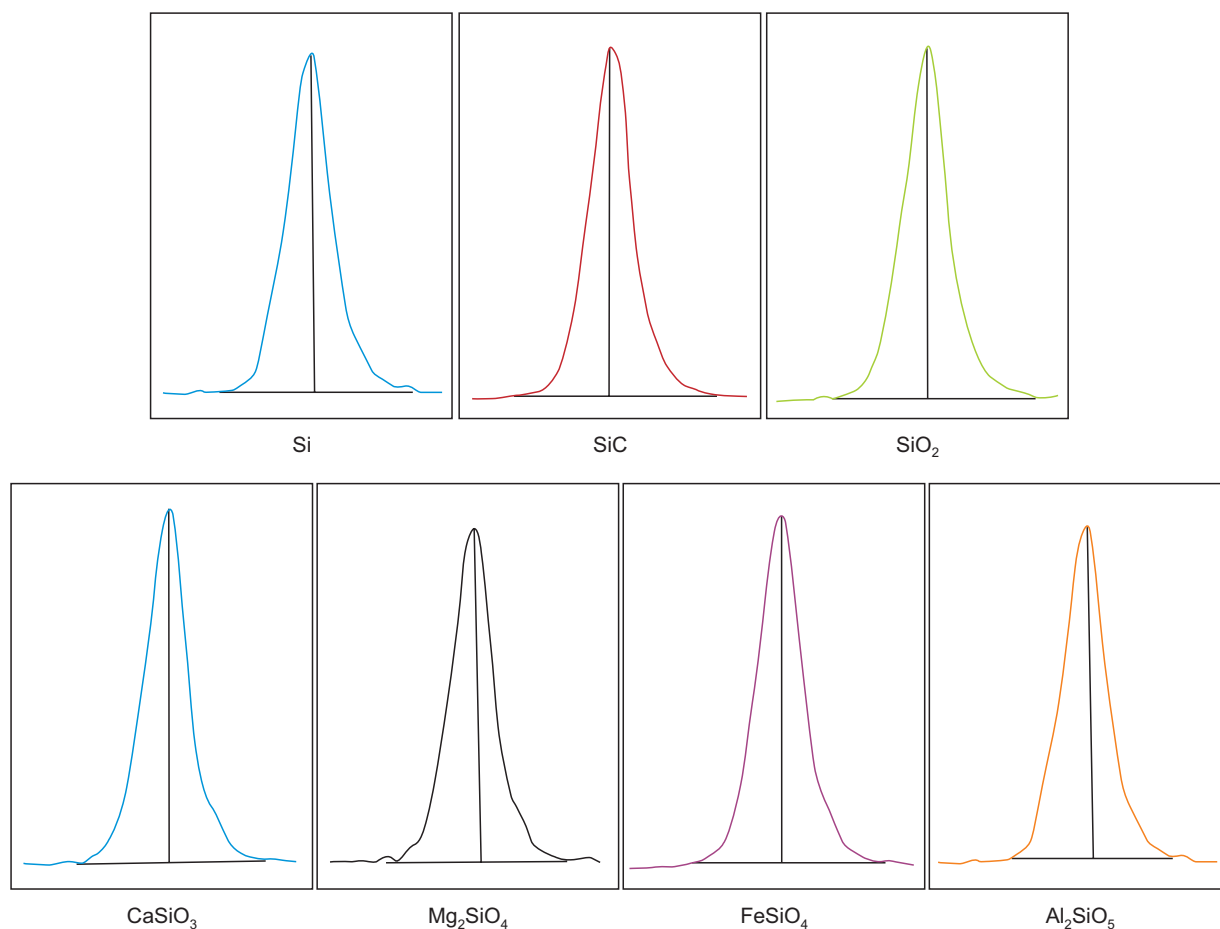
Fig. 4. Secondary K_α line shape for each of the Si series standard sample.

Table 3. Asymmetry index values for Si series standard samples

Standard sample	Asymmetry index
Si	0.76~0.84
SiC	1.10~1.18
SiO$_2$	0.89~0.93
CaSiO$_3$	0.85~0.87
Mg$_2$SiO$_4$	0.80~0.83
Fe$_2$SiO$_4$	0.78~0.80
Al$_2$SiO$_5$	0.84~0.87

Table 4. Area fraction of right and left side and asymmetry index values of points 1 to 12 at interface of Al-20mass%Si alloy/graphite system

Point	Right (%)	Left (%)	Asymmetry index
1	54.00	46.00	1.17
2	54.03	45.97	1.18
3	55.14	44.86	1.23
4	54.38	45.62	1.19
5	55.40	44.60	1.24
6	54.99	45.01	1.22
7	54.65	45.35	1.21
8	54.66	45.34	1.21
9	48.62	51.38	0.95
10	48.86	51.14	0.96
11	55.32	44.68	1.24
12	40.63	59.37	0.68

electron beam would spread into the sample, it was thought that the information around the reaction product could be also reflected. However, the asymmetry index value was approximate to the standard samples. Therefore, the asymmetry index of SiC was not affected by the surrounding region where the characteristic X-ray also generates. For the reaction product in the Al-20mass%Si alloy side (point 8), its diameter was less than 1 μm and the asymmetry index was not affected, resulting in a successful distinguishment of SiC. Since the size of the reaction product formed in the Al-

20mass%Si alloy side was smaller than that formed at the vicinity of the interface, the information of the region around the reaction product could be more reflected. As a result, the intensity of the K_α line (secondary line) for SiC decreased.

When the dwell time was prolonged, the intensity increased and the shape of the spectrum became clear. Therefore, even if SiC would be in or under microsize, it could still be distinguished by adjusting the analysis condition such as the dwell time.

On the other hand, it was judged that the light gray part (points 9, 10, and 12) was not SiC.

CONCLUSIONS

In this study, the shape of the characteristic X-ray spectrum for the Si series samples was investigated by using the EPMA, and the following conclusions have been drawn:

(1) The shape of the secondary K_a line for SiC was different from those for the other Si materials. The spectrum area ratio of right to left, namely, the asymmetry index defined here, was 1.1 to 1.2 for SiC and was less than 0.9 for other Si materials.

(2) The asymmetry index was applicable for a micro-sized SiC.

(3) The asymmetry index was not changed even when the peak shift occurred by mechanical reasons.

(4) Carbon deposition had no effect on the asymmetry index, suggesting that the method in this study is effective in eliminating the disturbance of carbon contamination.

CONFLICT OF INTEREST

No potential conflict of interest relevant to this article was reported.

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