The Effect of Adding TiO\textsubscript{2} on Synthesis of Al\textsubscript{4}SiC\textsubscript{4} powders

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Abstract. Three powders of aluminum, silicon and graphite were mixed with the molar ratio corresponding to the chemical composition of Al\textsubscript{4}SiC\textsubscript{4}, and then a small amount of titanium oxide was added into the mixture. The mixtures were heated at 1973 K in argon, and the Al\textsubscript{4}SiC\textsubscript{4} phase was obtained. Conversely, the two phases, Al\textsubscript{4}O\textsubscript{4}C and TiC, were detected when the increasing of additive amount of TiO\textsubscript{2} was made, and the grain sizes of Al\textsubscript{4}SiC\textsubscript{4} were refined from 10~20 \( \mu \text{m} \) to 1~5 \( \mu \text{m} \) at the same time. Further, the morphology of Al\textsubscript{4}SiC\textsubscript{4} without addition of TiO\textsubscript{2} is irregular shape, but changes into tabular structure after adding TiO\textsubscript{2}.

1. Introduction
Aluminum silicon carbide (Al\textsubscript{4}SiC\textsubscript{4}) is a potential material for refractory and high temperature structural material, and it has received considerable attention because of its low density (3.03 g/cm\textsuperscript{3}), high melting point (~2353 K) and excellent oxidation resistance [1-3]. Recently, some researches have been performed about the Al\textsubscript{4}SiC\textsubscript{4} powder synthesis from the raw mineral materials [4,5], and it was believed the impurities in the raw materials will be an inevitable influence on the synthesis of Al\textsubscript{4}SiC\textsubscript{4}, several investigations have shown the effects of various doping elements on synthesis and characteristics of Al\textsubscript{4}SiC\textsubscript{4} and Al\textsubscript{4}O\textsubscript{4}C [6-8]. However, the effects of titanium oxide on synthesis of Al\textsubscript{4}SiC\textsubscript{4} have not been reported. In this study, the effect of adding titanium oxide on synthesis of Al\textsubscript{4}SiC\textsubscript{4} was investigated by X-ray diffraction and scanning electron microscopy. Therefore, the study on the effect of titanium oxide on that composite refractory is very important for explosion of natural mineral resources.

2. Experimental
Aluminum (5 \( \mu \text{m} \), purity 99.9 %), silicon (5 \( \mu \text{m} \), purity 99 %), graphite (5 \( \mu \text{m} \), purity 99 %) and titanium oxide (analytically pure, anatase) were used as starting materials. The molar ratios of the starting materials were varied as shown in Table 1, and mixed with alcohol and dried at 373 K for 12 h in a vacuum dryer. Samples were heated to 1973 K at a rate of 10 K/min and maintained for 3 h in flowing Ar (purity 99.999%) before being naturally cooled in the power off furnace.

In order to examine the structure of the products, X-ray diffraction measurement (XRD: X’Pert Pro MPD) using Cu K\( \alpha \) radiation was carried out. Powder XRD samples with the particle size of less than 50 \( \mu \text{m} \) were made by milling the calcined samples. The microstructure was characterized by scanning electron microscope (SEM: FEI Nova 400 Nano).

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Table 1. The molar ratio of starting materials in mixture powders

| Sample | Al+Si+C (g) | TiO$_2$ (g) | Molar ratio of TiO$_2$ |
|--------|-------------|-------------|------------------------|
| T0     | 20          | 0           | 0                      |
| T3     | 20          | 0.6         | 3%                     |
| T6     | 20          | 1.2         | 6%                     |
| T9     | 20          | 1.8         | 9%                     |

3. Results and Discussion

Fig. 1 shows XRD patterns of the mixture of aluminum, silicon and graphite after heating at 1973 K for 6 h. In both cases, the main phases are Al$_4$SiC$_4$. Without addition of TiO$_2$ (Fig. 1a), the diffraction peaks gives the diffraction peaks corresponding to Al$_4$SiC$_4$ and C. This result is almost the same as that reported by Yamaguchi et al [9]. However, the mixture with the addition of TiO$_2$ gives the diffraction peaks are identified as belonging to three phases, namely Al$_4$SiC$_4$, TiC and C (Fig. 1b), and with the increasing of TiO$_2$, Al$_4$O$_4$C formed (Fig. 1c and d).

The main reactions that occurred during the formation of Al$_4$SiC$_4$ were supposed as follows [10]:

$$4\text{Al}_6\text{Si} + 4\text{C} = \text{Al}_4\text{SiC}_4 + 4\text{C}$$
(1)

$$\text{Al}_4\text{C}_3 + \text{SiC} = \text{Al}_4\text{SiC}_4$$
(2)

TiC apparently formed by the reaction of TiO$_2$, Al and graphite, as indicated in Eq. (3):
3TiO_2(s) + 4Al(s) + 3C(s) = 3TiC(s) + 2Al_2O_3(s). \hspace{1cm} (3)

Al_4O_4C formed with the increase of additive amount of TiO_2, which promoted the formation of Al_2O_3, the formation equation of Al_4O_4C using this method was as follows:

2Al_2O_3(s) + 3C(s) = Al_4O_4C(s) + 3CO(g) \hspace{1cm} (4)

The relative ratios of diffraction peak intensities of the (101) and (0010) planes for samples are listed in Table 2. The obvious distinction from the value reported in previous studies indicates the orientation of the powders along the c-axis \[11\]. The ratios of \(I_{(101)}/I_{(0010)}\) were close to the theory value when no addition or a little addition of TiO_2 was made (T0 and T3), while decrease with the increase of TiO_2 (T6 and T9). The growth of (0010) plane relative to (101) plane determines the shape and size of Al_4SiC_4 crystal \[12\].

**Table 2.** The ratios of diffraction peak intensities of samples

| Sample | \(I_{(101)}/I_{(0010)}\) |
|--------|--------------------------|
| PDF35-1072 | 1.43 |
| T0           | 1.48 |
| T3           | 1.45 |
| T6           | 1.30 |
| T9           | 1.31 |

Fig. 2 shows SEM images of samples synthesized at 1973 K for 3h in flowing Ar. Al_4SiC_4 particles exists as irregular shape without TiO_2 (Fig. 2(a)). With the addition of TiO_2, mass of tabular structure of Al_4SiC_4 grains are found in Fig. 2(b)–(d), and the grain sizes of Al_4SiC_4 were refined from 10–20 μm to 1–5 μm with TiO_2 addition increasing. The morphology of TiC in samples is small granule structure. In the case of powder synthesized with the highest TiO_2 content (Fig. 2(d)), Al_4SiC_4 particles are observed together with TiC. The refined mechanisms are considered to the presence of number of TiC particles acting as the nucleate sites, which promoted the nucleation rate.
Fig. 2 SEM images of samples synthesized at 1973 K for 3h in flowing Ar: (a)T0, (b)T3, (c)T6 and (d)T9.

4. Conclusions
The effect of adding titanium oxide on synthesis of Al$_4$SiC$_4$ was investigated. The increase of TiO$_2$ addition promoted the formation of TiC and Al$_4$O$_4$C. Al$_4$SiC$_4$ particles exist as irregular shape without TiO$_2$. With the addition of TiO$_2$, the synthesized Al$_4$SiC$_4$ grains have plate-like morphology. The grain sizes of Al$_4$SiC$_4$ were refined from 10–20 μm to 1–5 μm with TiO$_2$ addition increasing. The refined mechanisms are considered to the presence of number of TiC particles acting as the nucleate sites, which promoted the nucleation rate.

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