Synthesis and Characterization Al_2OC–SiC Composites by Carbothermal Reduction

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ABSTRACT: Al_2OC-SiC composites were synthesized using a mixture of α-Alumina, silica, carbon black and magnesium oxide as the starting materials. The effects of MgO addition on synthesis of Al_2OC-SiC composites were investigated. The results showed that $Al_4Si_2C_5$ formed at elevated temperature without MgO addition, and MgO addition accelerated the synthesis reaction for Al_2OC-SiC composites. The synthesized powders consisted of particle-like Al_2OC and whisker-like SiC. The oxidation characteristics of Al_2OC-SiC composites was measured by TG method.

KEYWORDS:

- Al_2OC
- SiC
- Synthesis
- Microstructure

INTRODUCTION

Silicon carbide (SiC) is a promising material for high-temperature ceramics due to its high thermal conductivity, low density, excellent mechanical, corrosion resistance and low thermal expansion coefficient[1]. It is worth noting that SiC whiskers also have their excellent properties, such as high hardness, good flexibility, high thermal conductivity, high thermal stability and large band gap[2,3]. Due to the desirable properties of SiC whiskers, numerous studies have been performed to investigate its synthesis, including direct chemical reactions[4], carbon nanotube-confined reaction[5], chemical vapor deposition[6], sol-gel synthesis[7], carbothermal reduction[8] and etc. Al_2OC is also a promising high-temperature ceramic because of its high melting point, oxidation resistance and hydration resistance[9]. To combine SiC with Al_2OC into a composite is in line with the trend of development of oxides-nonoxide materials[1,10].

Al_2OC-SiC composites has been prepared using mechanically mixed powders[1]. Although this mixing technique is very simple and easy to control the composition of the powder, the chemical compositions in the resulting ceramics tend to be inhomogeneous locally, due to the difficulty in “thorough” mixing. The inherent problems could be solved since the different composite are synthesized by chemical reactions during the composite fabrication.

In this work, Al_2OC-SiC composites were synthesized using α-Alumina, carbon black, silica and magnesium oxide powders. The effect of MgO on the phase composition and microstructure of Al_2OC-SiC composites were investigated by XRD and SEM method, and the oxidation characteristics of Al_2OC-SiC composites was measured by TG method.

EXPERIMENTAL

α–Alumina (99%, 20 μm), carbon black (99.9%, <800 mesh size), silica (99.5%, 20 μm) and magnesium oxide (99.5%, 20 μm) powder were used as starting materials. The composition of Al_2OC-SiC composites are shown in Tab. 1. The powder mixtures according to Tab. 1 were ball milled for 5 h and dried at 100 °C for 12 h in a vacuum dryer. The samples were then placed in a graphite crucible and sintered in flowing argon atmosphere (purity 99.995%) in electric furnace with a graphite heater at 1800 °C and holding for 3 h.

Tab. 1 Composition of starting powders (wt%).

Samples	Al_2O_3	SiO_2	C	MgO
S1	40.5	23.8	35.7	0
S2	40.5	23.8	35.7	3

Crystalline phases in the fired samples were examined by powder X-ray diffractometer (XRD, Philips, X’pert Pro MPD) with a monochromatic

Cu-K_α (λ=1.5406 Å) radiation. And the scanning electron microscopy (SEM, FEI, Nova 400 Nano) with an energy-dispersive spectroscopy detector (EDX, Penta FETx3, Oxford) was used to observe microstructure and phase morphology of samples.

Thermogravimetry differential scanning calorimetry (TG-DSC, STA449, NETZSCH, Germany) was employed to analyze the oxidation resistance of graphite and Al_2OC-SiC composites in oxidizing atmosphere (oxygen partial pressure = 0.21 atm, heating rate = 10 °C·min^{-1}). The aim of this test was to determine the oxidation behavior of Al_2OC-SiC composites.

RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of sample S1 and S2 synthesized at 1800 °C for 3 h in argon atmosphere. As indicated in the figure, Al_2OC and SiC are the main phase composition in sample S1 and S2. The relative intensities of Al_2OC in the powder sample synthesized using α–Alumina, carbon black, silica and magnesium oxide powders as raw materials are much higher than using α–Alumina, carbon black and silica powders as raw materials. Besides, $Al_4Si_2C_5$ formed at elevated temperature without MgO addition in sample S1.

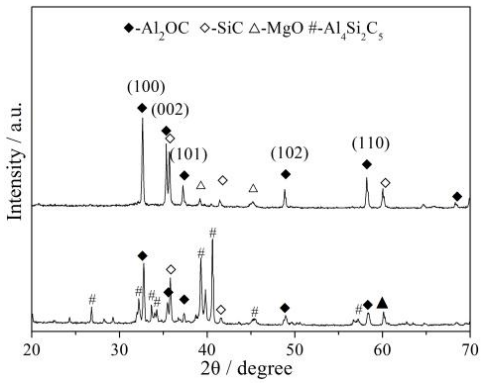

Fig. 1 XRD patterns of samples S1 and S2 synthesized at 1800 °C for 3 h in argon atmosphere.

In order to clarify the effect of MgO on Al_2OC, the shift of angle of Al_2OC diffraction peaks were further investigated. The (100), (002), (101), (102) and (110) peaks are the characteristic peaks of Al_2OC phase, the changes of the peak positions are shown in Tab. 2. It can be seen that with the addition of MgO, Al_2OC (100), (002), (101), (102) and (110) peaks shift to lower degree, which means the lattice distance increases. This is because Mg^{2+} (0.66Å) enters the lattice and replaces Al^{3+} (0.50Å) in Al_2OC crystal forming the finite substitution solid solution, and Mg^{2+} is lower than that of Al^{3+}. Therefore, in order to preserve the balance of electricity before and after substitution, 3 mol Mg^{2+} instead of 2 mol Al^{3+} to maintain the price balance, causing structural expansion, resulting in larger interplanar spacing. This is because Mg^{2+} enters the lattice and replaces Al^{3+} in Al_2OC crystal forming the finite substitution solid solution, but solid solubility is generally lower than l%.

From the results obtained above, the following information about the reaction can be used to describe. Initially, SiO_2 reacted with C to form SiC via the reaction (1).

$$SiO_{2(s)} + 3C_{(s)} = SiC_{(s)} + 2CO_{(g)} \quad (1)$$

At the same time, Al_2O_3 reacted with C to form Al_4O_4C via the reaction (2).

$$2Al_2O_{3(s)} + 3C_{(s)} = Al_4O_4C_{(s)} + 2CO_{(g)} \quad (2)$$

Once Al_4O_4C formed, Al_2OC can be generated by Eq. (3).

$$Al_4O_4C_{(s)} + 3C_{(s)} = 2Al_2OC_{(s)} + 2CO_{(g)} \quad (3)$$

Tab. 2 The angles of Al_2OC diffraction peaks.

degree	(100)	(002)	(101)	(102)	(110)
S1	32.673	35.379	37.260	48.843	58.314
S2	32.624	35.330	37.211	48.822	58.166

The SEM micrographs of samples S1 and S2 synthesized at 1800 °C for 3h are shown in Fig. 2. The S1 sample is composed of various crystals with different shape and size: SiC (whisker-like), $Al_4Si_2C_5$

(plate-like) and Al_2OC (particle-like), as shown in Fig. 2a. Many SiC were randomly distributed on the surface of the Al_2OC in the S2 sample, and the beaded structures of Al_2OC–SiC composites were observed (Fig. 2b), suggesting that MgO addition is benefit for promoting synthesis of Al_2OC-SiC composite. Combined with XRD analysis, it can be seen that the SEM micrographs of samples S1 and S2 are in agreement with those experimentally observed in this work.

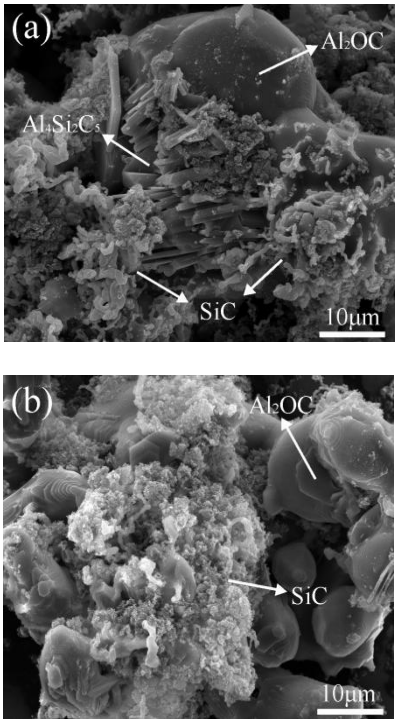

Fig. 2 SEM images of samples S1 and S2 synthesized at 1800 °C for 3 h in argon atmosphere: (a) S1 and (b) S2.

In order to simulate a reducing atmosphere, TG tests of the graphite and the Al_2OC–SiC composites (the S2 samples synthesized at 1800 °C for 3h) were carried out and the results are shown in Fig. 3, where the oxygen comprising the synthetic air reacted with C to form CO gas and CO_2 gas during the experiment, exposing the antioxidant to these gases. Regarding the reactivity of the used carbon sources, graphite started oxidizing at approximately 560 °C (Fig. 3a). Conversely, the Al_2OC-SiC composite oxidizes above 690 °C in the presence of air giving rise to Al_2O_3 and SiO_2 (Reaction (4) and (5)), which results in an expressive mass gain up to 1500 °C. A small weight loss at temperatures approximately 560 °C in TG curve (Fig. 3b) may be attributable to the unreacted carbon (Reaction (6)).

$$SiC_{(s)} + O_{2(g)} = SiO_{2(s)} + CO_{(g)} \quad (4)$$

$$Al_2OC_{(s)} + O_{2(g)} = Al_2O_{3(s)} + CO_{(g)} \quad (5)$$

$$C_{(s)} + O_{2(g)} = CO_{2(g)} \quad (6)$$

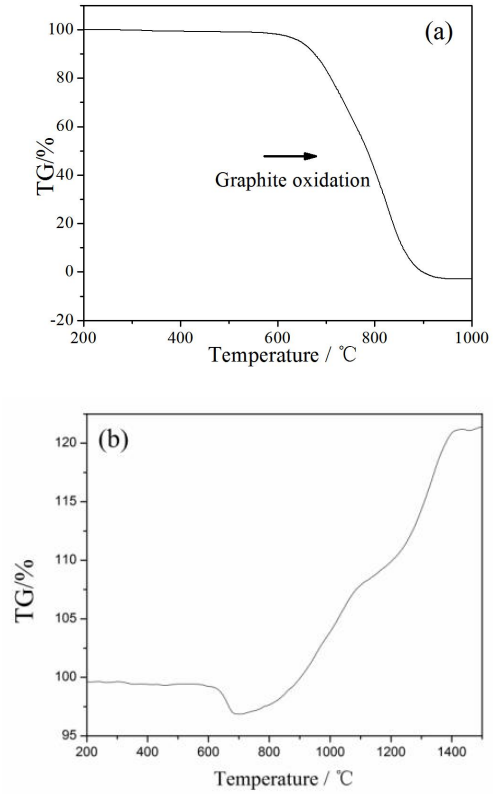

Fig. 3 Oxidation behavior of of samples in oxidizing atmosphere: (a) graphite and (b) Al_2OC-SiC composites.

CONCLUSIONS

Al_2OC-SiC composites has been successfully synthesized by heating a mixture of α-Alumina, silica, carbon black and magnesium oxide at 1800 °C for 3 h in flowing Ar. The addition of MgO promoted the synthesis of Al_2O_3 and SiC, the beaded structures of

Al_2OC–SiC composite were obtained. In addition, Al_2OC-SiC composite started to oxidize from about 690 °C when heated in air.

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