



Rare-earth nitrate additives for the sintering of silicon carbide

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Abstract

Fourteen rare earth elements in their nitrate form were evaluated as sintering additives for β -SiC. All rare earth nitrates transformed to oxides by a reaction with the surface-adsorbed thin SiO₂ during heat treatment, which enhanced the density of the SiC monolith without decomposing SiC. In particular, Sc, Yb, Tm, Er and Ho were quite effective sintering additives; $a > 99\%$ relative density was observed by the addition of 5 wt.% rare earth oxide, whereas the other rare earth additives (Lu, Dy, Tb, Gd, Eu, Sm, Nd, Ce and La) revealed 77–92% density. Moreover, a fine 156 nm-sized SiC grain could be acquired by Sc addition, whereas the other additives showed a SiC grain size of approximately 1 μm . The mean hardness and K_{Ic} of the dense SiC containing rare earth elements were 24–27 GPa and 3.3–5.0 MPa m^{1/2}, respectively.

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1. Introduction

Silicon carbide (SiC) is a very important high temperature structural material with excellent mechanical, thermal and chemical properties. Dense SiC-based ceramics are used widely in aerospace- and energy-related areas and are being considered as structural materials for future fusion reactors owing to their low activation under neutron irradiation conditions.^{1–5} On the other hand, the high covalence and low self-diffusivity of SiC make it difficult to consolidate. For example, pure SiC can be only densified to near the theoretical density by hot pressing at 2500 °C and 50 MPa.⁶ Therefore, sintering additives are generally used to decrease the temperature by both solid-state reactions and liquid phase sintering. Compared to solid-state sintering using B₄C and C which requires >2000 °C, the sintering temperature can be decreased to 1750–2000 °C by liquid phase sintering due to the presence of a liquid that provides both a capillary force and high diffusivity path. The additives reported thus far for liquid phase sintering include the following: Al, Mg, Al₂O₃, MgO, Al₂O₃–Y₂O₃, Al₂O₃–Y₂O₃–MgO,

Al₂O₃–Y₂O₃–CaO, Al₂O₃–Y₂O₃–SiO₂, Y–Mg–Si–Al–O–N glass system and some rare earth oxides.^{7–25}

Rare earth elements refer to 15 lanthanide elements from the 57th to 71st atomic number in the periodic table, as well as scandium (Sc) and yttrium (Y). The chemical properties of lanthanide elements were reported to be similar to each other with partially filled 4f orbit electrons, which induce f–f electron transitions easily. Because rare earth elements have strong chemical activity, they tend to form oxides, halides and sulphides at low temperatures.²⁶ Table 1 lists the physical properties of the 17 rare earth elements assessed in this study. Although each rare earth element may have many different ionic states due to the electron transition, only the most probable ionic state, radius and coordination number, according to Shannon,²⁷ are presented. Sc has the smallest ionic radius, and the 15 lanthanides show a decrease in ionic radius by an increase in the atomic number at the same +3 charge status. Typical rare earth oxide forms are also shown in the table because these might be formed at high temperatures by a reaction with oxygen existing on the surface of SiC as an impurity. Moreover, the eutectic temperature between each rare earth oxide and SiO₂ are also shown using the available data, whereby the eutectic temperatures are <1700 °C.

Some rare earth oxides enhance the density, high temperature properties and oxidation resistance of SiC by changing the

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Table 1
17 rare earth elements and their physical properties.

| Element | Atomic number | Coordination number ^a | Charge ^a | Ionic radius ^a (pm) | Rare earth oxide | | |
|---------|---------------|----------------------------------|---------------------|-----------------------------------|--------------------------------|--|-------------------------|
| | | | | | Form | T_{EU} with SiO ₂ ^b (°C) | ΔG_f^c (kJ/mol) |
| Sc | 21 | 6 | +3 | 74.5 | Sc ₂ O ₃ | 1660 | −498.0 |
| Y | 39 | 6 | +3 | 90.0 | Y ₂ O ₃ | 1660 | −505.3 |
| La | 57 | 6 | +3 | 103.2 | La ₂ O ₃ | 1625 | −401.2 |
| Ce | 58 | 6 | +3 | 101.0 | Ce ₂ O ₃ | N.A. | −429.4 |
| | | 6 | +4 | 87.0 | CeO ₂ | N.A. | −125.2 ^d |
| Pr | 59 | 6 | +3 | 99.0 | Pr ₂ O ₃ | N.A. | −417.5 |
| Nd | 60 | 6 | +3 | 98.3 | Nd ₂ O ₃ | 1600 | −416.8 |
| Pm | 61 | 6 | +3 | 97.0 | Pm ₂ O ₃ | N.A. | −413.1 |
| Sm | 62 | 6 | +3 | 95.8 | Sm ₂ O ₃ | 1650 | −406.1 |
| Eu | 63 | 6 | +3 | 94.7 | Eu ₂ O ₃ | N.A. | −218.0 |
| Gd | 64 | 6 | +3 | 93.8 | Gd ₂ O ₃ | 1630 | −448.0 |
| Tb | 65 | 6 | +3 | 92.3 | Tb ₂ O ₃ | N.A. | −482.5 |
| Dy | 66 | 6 | +3 | 91.2 | Dy ₂ O ₃ | 1640 | −458.4 |
| Ho | 67 | 6 | +3 | 90.1 | Ho ₂ O ₃ | N.A. | −487.0 |
| Er | 68 | 6 | +3 | 89.0 | Er ₂ O ₃ | 1680 | −496.7 |
| Tm | 69 | 6 | +3 | 88.0 | Tm ₂ O ₃ | N.A. | −469.1 |
| Yb | 70 | 6 | +3 | 86.8 | Yb ₂ O ₃ | 1650 | −420.4 |
| Lu | 71 | 6 | +3 | 86.1 | Lu ₂ O ₃ | N.A. | −478.8 |

^a Presented for the most reliable status based on Shannon.²⁷^b From Phase Diagrams for Ceramists by Levin et al.²⁸^c ΔG_f for the reaction of $2RE + 3/2SiO_2 \rightarrow RE_2O_3 + 3/2Si$ at 1750 °C.^{29,30}^d ΔG_f for the reaction of $Ce + SiO_2 \rightarrow CeO_2 + Si$ at 1750 °C.

crystalline structure of the grain boundary phases. On the other hand, most rare earth oxides are added as oxide form along with Al₂O₃ or AlN,^{15,22,23,25} which makes difficult to determine the effects of rare earth oxides themselves as sintering additives. Therefore, the present study examined the effects of 14 rare earth elements on the sintering of SiC by hot pressing at 1750 °C. Each rare earth element was added in nitrate form after dissolving in ethyl alcohol, and the transformation of nitrate to oxide during high temperature treatment was confirmed. The addition of the sintering additive by the wet chemical method are expected to provide many advantages, such as uniform distribution of additives, enhanced densification by uniformly distributed liquid phase and a decreased amount of additive required, compared to the direct addition of oxide. The density of SiC, microstructural evolution, the phase generated during heat treatment and mechanical properties after adding each rare earth element were studied.

2. Experimental procedure

Commercial β -SiC (>97.5% purity, 4620KE, NanoAmor Inc., USA) with a mean particle size of 52 nm and a specific surface area of 80 m²/g was used as the starting material. The impurities in the powder were <1.25% of O, <0.75% of free C, <0.15% of Cl and <0.15% of free Si, according to the supplier. Fourteen rare earth nitrates (RE(NO₃)₃·xH₂O, where RE = Sc, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, all from Alfa Aesar or Sigma Aldrich) with purities >99.9%, were used as the sintering additives after dissolving each in ethyl alcohol. As all nitrates were confirmed to have transformed to rare earth oxides during the high temperature treatment

according to a preliminary test, the amount of addition was fixed to 5 wt.% based on each rare earth oxide form. The amount of Ce addition was calculated for CeO₂ instead of Ce₂O₃ because the formation of CeO₂ was confirmed, whereas the others were calculated based on the RE₂O₃ forms.

In order to find an optimum condition for uniform adsorption of rare earth ions on the SiC surface, the zeta potential of the 10 wt.% β -SiC suspension in ethyl alcohol with 2 wt.% dispersant (Disperbyk-103, BYK Chemie, Germany) with respect to the powder was characterized using an electroacoustic-type zeta potential analyzer (ZetaProbe using non-aqueous option, Colloidal Dynamics, USA). The pH of the suspension was adjusted using NH₄OH and HCl to the range of pH 2.9–10.0, whereas the ionic strength was not considered based on a preliminary test. Ten grams of β -SiC powder was dispersed in 100 g of ethyl alcohol containing each of the rare earth nitrates and 2 wt.% of dispersant, after adjusting the pH to 9.2 based on the zeta potential results. The resulting slurry was ball-milled for 24 h using 3 mm SiC balls followed by drying in a rotary evaporator at 70 °C.

Calcination was performed at 600 °C for 2 h in a N₂ atmosphere and 2 cm diameter pellets were hot-pressed at 1750 °C for 1 h at 20 MPa in an Ar atmosphere using each rare earth ion-coated SiC powder.

The morphology of the particles and sintered bodies were observed by scanning electron microscopy (SEM: S-4800, Hitachi at 15 kV and 10 μ A) and high-resolution transmission electron microscopy (HR-TEM: Tecni G2F20 S-twin, FEI operated at 200 keV). Energy dispersive X-ray spectrometry (EDS: Horiba EX-250) combined with SEM was used to analyze the distribution of each rare earth element. The mean grain size was

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