



Rare-earth oxide additives for the sintering of silicon carbide

Alfian Noviyanto, Dang-Hyok Yoon*

School of Materials Science and Engineering, Yeungnam University, Gyeongsan, 712-749, Korea

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ABSTRACT

The feasibility of a single component rare-earth oxide (Sc_2O_3 , CeO_2 , Nd_2O_3 , Sm_2O_3 , Gd_2O_3 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , La_2O_3 , Tm_2O_3 , Yb_2O_3 and Lu_2O_3) as a sintering additive for β -SiC was examined. The Gibbs formation free energies were first considered to identify the rare-earth oxides that would not decompose SiC at the typical hot pressing temperatures (1973–2123 K). The results from the thermodynamic calculations were then tested experimentally. All rare-earth oxides examined in this study increased the density of the samples without decomposing SiC, which is in contrast to that observed with most main-group oxides reported previously. Rare-earth oxide appeared to form a eutectic composition with SiO_2 existed on the SiC surface at temperatures lower than 1700 °C and acted as a liquid-phase sintering additive. The decrease in particle size of the sintering additive resulted in an increase in SiC density, indicating the importance of a uniform additive distribution to achieve a dense SiC.

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1. Introduction

Silicon carbide (SiC) and its composites are high-performance ceramics that can be used under extreme conditions on account of their excellent mechanical, chemical and thermal properties. SiC is generally consolidated by liquid-phase sintering after adding metal oxide additives because of its high covalent nature and low self-diffusivity. The known metal oxide sintering additives include Al_2O_3 , MgO , Y_2O_3 , Al_2O_3 - Y_2O_3 , Al_2O_3 - Y_2O_3 - MgO , Al_2O_3 - Y_2O_3 - CaO , Al_2O_3 - Y_2O_3 - SiO_2 and Y-Mg-Si-Al-O-N glass system [1–8]. Some rare-earth oxide additives have also been reported to exhibit favorable high-temperature properties and oxidation resistance of SiC by changing the crystalline nature of the grain boundary phases [9–13]. On the other hand, most rare-earth oxides were added with Al_2O_3 or AlN [9–12], which makes difficult to distinguish the effectiveness of rare-earth oxide itself as a sintering additive. Rare-earth elements are defined as the fifteen lanthanides plus scandium (Sc) and yttrium (Y); promethium (Pm) is a radioactive element.

Since Negita [14] suggested a theoretical approach for identifying an effective sintering additive for SiC by considering the standard Gibbs free energy and vapor pressure, Noviyanto and Yoon [15,16] evaluated the feasibility of this approach using a range of main-group single component metal and metal oxide systems based on thermodynamic calculations and experimental observations. To be an effective sintering additive in this approach, the additive should not decompose SiC at high sintering temperatures. In addition, other factors, such as the volume fraction, liquid formation and wettability on SiC of the sintering additive, might also be important. Their experimental results were in good

agreement with those predicted from thermodynamic calculations for both main-group metal and metal oxide systems, indicating the effectiveness of this approach [15,16].

The present study examined the feasibility of the thermodynamic approach to find an effective sintering additive for β -SiC by expanding it to various types of single component rare-earth oxides. In this regard, this study focused on the following three aspects. The first is a comparison of the Gibbs formation free energy of rare-earth oxide and SiC to predict whether the sintering additive would decompose SiC at high temperatures by forming the corresponding rare-earth metal carbide and/or silicide. The second is an experimental verification of the thermodynamic prediction by measuring the sintered density of SiC containing each rare-earth oxide. The third is a processing attempt to increase the SiC density by reducing the particle size of the additive for a more uniform distribution. The thermodynamic calculations were performed at typical hot pressing temperatures of 1700–1850 °C, while to evaluate the future applications of this result to the fabrication of SiC_f/SiC composite, the sintering was fixed at 1750 °C because temperatures > 1850 °C might cause damage to SiC fibers [8,17–19].

2. Materials and method

Thermodynamic calculation was performed first to estimate the stability and vapor pressure of each rare-earth oxide at the temperature range of 1700–1850 °C because rare-earth oxide should not decompose SiC and evaporate during sintering to be an effective sintering additive. For this calculation, thermochemical software (HSC Chemistry 5.1, Chemistry Software Ltd., USA) was used, while thermodynamic data from Barin [20] and Chase [21] was also considered.

For experiment, the starting powder used was a commercial β -SiC (4620KE, NanoAmor Inc., USA) with a mean particle size, specific

* Corresponding author. Tel.: +82 538102561; fax: +82 538104628.
E-mail address: dhyoon@ynu.ac.kr (D.-H. Yoon).

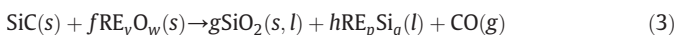
surface area and purity of 52 nm, 80 m²/g and >97.5%, respectively. The main impurities in this powder were <1.25% of O, <0.75% of free C, <0.15% of Cl and <0.15% of free Si, according to the supplier's data sheet. Twelve rare-earth oxides (Sc₂O₃, CeO₂, Nd₂O₃, Sm₂O₃, Gd₂O₃, Dy₂O₃, Ho₂O₃, Er₂O₃, La₂O₃, Tm₂O₃, Yb₂O₃ and Lu₂O₃; Alfa Aesar, USA) were used as the sintering additives by adding 5 wt.% of the oxide to β-SiC. All as-received rare-earth oxides had a purity >99.9% and a mean particle size >2 μm. Ten grams of formulated powder was dispersed in 100 g of ethanol containing 2 wt.% of dispersant (Disperbyk-103, BYK Chemie, Germany) with respect to the powder. The resulting slurry was ball-milled for 24 h using 3 mm SiC balls followed by drying in a rotary evaporator at 70 °C. Hot pressing of 2 cm diameter pellets was carried out at 1750 °C for 1 h at 20 MPa in an Ar atmosphere using a graphite mold which was sprayed with a boron nitride powder to minimize the reaction between the sample and mold. Heating rates of 15 and 10 °C/min were used for the ramping from room temperature to 1500 °C and from 1500 °C to 1750 °C, respectively, while the samples were furnace-cooled to room temperature.

Because the particle size of the rare-earth oxides was much coarser than that of β-SiC (*D_m* = 52 nm), some of the additives, such as Sc₂O₃, Gd₂O₃, Ho₂O₃ and Yb₂O₃, were exposed to 3 h of high-energy milling (MiniCer, Netzsch, Germany) at 3,000 rpm using 0.45 mm ZrO₂ beads. The initial micrometer-sized Sc₂O₃, Gd₂O₃, Ho₂O₃ and Yb₂O₃ decreased to a mean particle size of 118, 143, 112 and 193 nm, respectively. The same experimental procedures were performed after adding 5 wt.% of the milled additives to β-SiC. This reduction in additive size was believed to enhance the homogeneous distribution as well as the final sintered density of SiC.

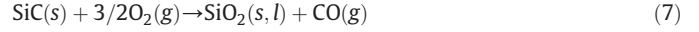
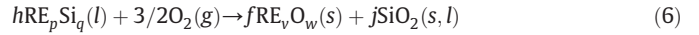
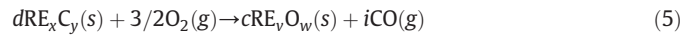
The morphology of the particles and sintered bodies were observed by scanning electron microscopy (SEM: S-4800, Hitachi at 15 kV and 10 μA) and high-resolution transmission electron microscopy (HR-TEM: Tecnai G2F20 S-twin, FEI operated at 200 keV). To observe the grain morphology, thermal etching was performed at 1400 °C for 30 min for the sintered body. The mean particle and grain sizes were estimated from the SEM/TEM images by measuring the maximum and minimum diameters of 100 particles/grains using image analysis software (SigmaScan, Systat Software, USA). Energy-dispersive X-ray spectrometry (EDS: Horiba EX-250) combined with SEM was used to analyze the sample composition. The density was measured using the Archimedes method, and the phase generated during hot pressing was calculated by a Rietveld simulation using X-ray diffraction (XRD: X'Pert-PRO MPD, Pananalytical using CuKα line, 40 kV and 30 mA) patterns.

3. Results and discussion

The detailed theoretical approach for thermodynamic calculation is reported elsewhere [14–16]. Briefly, to be an effective sintering additive under the sintering condition, the rare-earth metal oxide (RE_vO_w) additive should be stable enough not to decompose SiC. If the additive (RE_vO_w) is unstable, it might transform to one of the 3 possible phases of pure rare-earth metal (RE), metal carbide (RE_xC_y) and silicide (RE_pSi_q) during sintering, along with the oxidation of SiC, as shown in Eqs. (1)–(3), respectively.



Eqs. (1)–(3) can be derived by subtracting reactions (4)–(6) from the most probable SiC oxidation reaction Eq. (7) at 1973–2123 K, respectively.



As the standard Gibbs free energy (ΔG_f°) for the reactions (1), (2) and (3) are given by $\Delta G_4^\circ - \Delta G_7^\circ$, $\Delta G_5^\circ - \Delta G_7^\circ$ and $\Delta G_6^\circ - \Delta G_7^\circ$, respectively, the decomposition of SiC can be predicted by comparing ΔG_4° , ΔG_5° and ΔG_6° with ΔG_7° . The condition that RE_vO_w does not decompose SiC is given by $\Delta G_7^\circ > \Delta G_4^\circ$, ΔG_5° and ΔG_6° because a negative ΔG_f° indicates a spontaneous reaction.

Fig. 1 shows the stability diagram of rare-earth oxides at (a) 1973 K and (b) 2123 K using the available thermodynamic data, where the rare-earth oxides (RE_vO_w) located in the hatched area are stable and

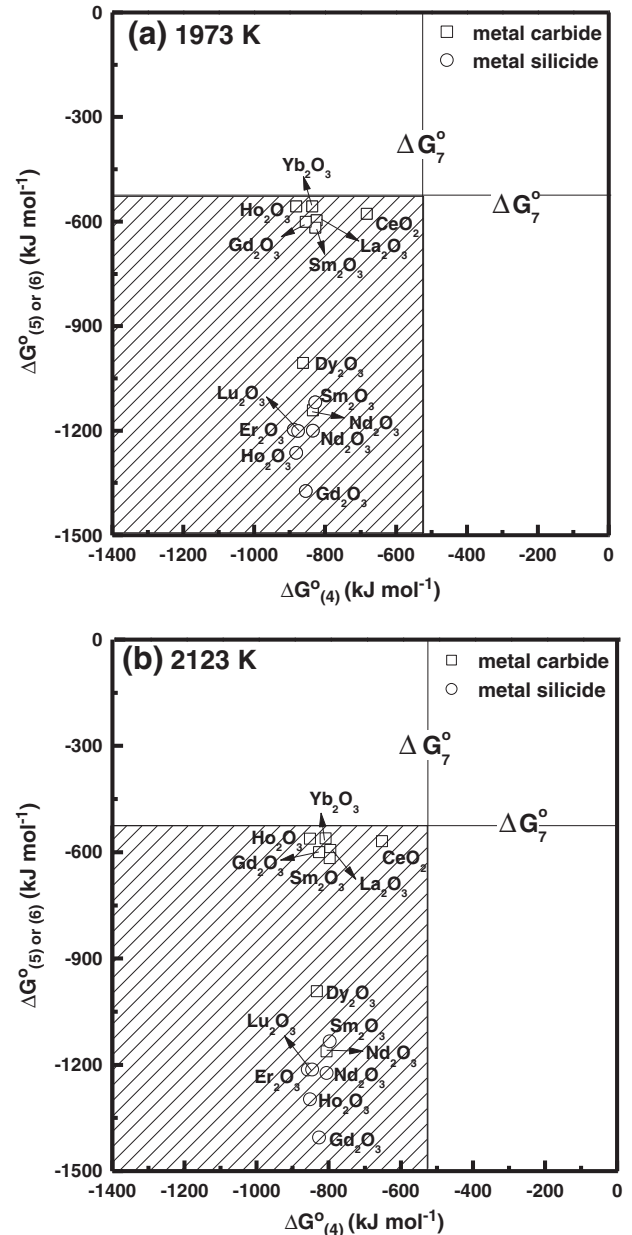


Fig. 1. Thermodynamic stability diagram based on a comparison of the Gibbs formation free energy for various rare-earth oxide additives at (a) 1973 K and (b) 2123 K. The horizontal and vertical lines represent ΔG_7° , and the hatched area satisfies $\Delta G_7^\circ > \Delta G_4^\circ$, ΔG_5° and ΔG_6° .

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