NOTE

Rapid reaction sintering of silicon carbide using Nd:YAG laser

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Reaction sintering of silicon carbide (SiC) using a continuous-wave Nd:YAG laser as a heating source was investigated. The laser was used to irradiate pellets of a stoichiometric powder mixture of Si and C under Ar gas flow. At an appropriate laser power, a dense SiC layer was formed consisting of grains with a size of 100–500 nm; this layer was several micrometers thick. At lower laser power, fine grains of SiC were formed and dispersed in the unreacted Si–C matrix. On the other hand, at higher power, larger faceted SiC grains (1–3 μm) were formed.

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Silicon carbide (SiC) is a promising structural material due to its low weight and excellent mechanical properties. SiC has been extensively investigated for various applications, such as components in gas turbines and in semiconductor manufacturing apparatus.^{1)–4)} However, the direct sintering of SiC is difficult because this material has no melting point under atmospheric pressure and sublimates around 2500°C. Therefore, reaction sintering (RS) techniques have been widely used to obtain SiC parts, where molten Si is infiltrated into porous SiC–C precursor bodies. RS is an advantageous industrial process, because the reaction temperature is relatively low (around 1400°C), and close to the melting point of Si. Reaction-sintered SiC (RS-SiC) usually contains 5–10 vol.% Si, because the molten Si infiltrates through open pores into the bulk of the sintered body and unreacted Si solidifies in the pores. It is known that the mechanical properties of RS-SiC at high temperature are strongly affected by this residual Si.⁵⁾⁶⁾ Hence, in order to improve the mechanical properties of SiC at high temperature, minimizing the residual Si content is necessary. Recently, ceramics manufacturing processes using a high-intensity laser as a heating source were proposed^{7)–10)} for the manufacture of Al₂O₃/SiO₂ composites,¹¹⁾ Al₂O₃/Y₃Al₅O₁₂ eutectic composites,¹²⁾ Ti–Si–C MAX-phase ceramics,¹³⁾ and WC–Co cemented carbides.¹⁴⁾ In particular, Mayers et al. reported that porous Si-bonded SiC (Si–SiC) was formed using direct laser sintering; after laser sintering, the sample was impregnated with phenolic resin in the furnace.¹⁵⁾ However, in this study, we investigated the formation of SiC from C and Si using laser sintering, and analyzed the microstructures and crystalline phases of the RS-SiC.

Reagent-grade Si (purity: 99%; average particle size: 5 μm ; Kojundo Chemical Laboratory) and C (particle size: <100 nm; Sigma-Aldrich) powders were used as starting materials. They were weighed at a 1:1 molar ratio and ball-milled in ethanol media for 24 h. After drying at 120°C in air, the powder mixture was uniaxially pressed at 10 MPa into pellets (10 mm in diameter, 1 mm in thickness), followed by cold isotactic pressing at 245 MPa. The experimental setup for this study is shown in **Fig. 1(a)**. The pellet was placed in a vacuum chamber and irradiated from above by a continuous-wave Nd:YAG laser [$\lambda = 1064$ nm; laser power density (P_L) = 5, 10, 12 kW/cm²] through a quartz window under a flow of Ar. The pressure was maintained at 10⁴ Pa during heating. The laser scanned the entire surface of the pellet using a Galvano-mirror, as shown in **Fig. 1(b)**. Microstructures were observed by field-emission scanning electron microscopy (FE-SEM; SU-8000, HITACHI), and crystalline phases were analyzed by X-ray diffraction (XRD; RINT-2000, Rigaku).

Figures 2(a)–2(d) shows the surface SEM images of the samples before and after single laser scanning (the total irradiation time was about 10 s). At $P_L = 5$ kW/cm² [**Fig. 2(b)**], faceted grains 100–500 nm in diameter were dispersed in a porous matrix. At $P_L = 10$ kW/cm² [**Fig. 2(c)**], the grain size increased to 1 μm . At $P_L = 12$ kW/cm² [**Fig. 2(d)**], larger faceted grains 1–3 μm in diameter were clearly observed. The relative fraction of the matrix material observed in these SEM images clearly decreases with increasing P_L .

Figure 3 shows XRD patterns of the (a) precursor powder; and RS-SiC samples sintered at (b) 5 kW/cm², (c) 10 kW/cm², and (d) 12 kW/cm². Patterns of the samples. SiC was formed in the irradiated samples ($P_L = 5$ –12 kW/cm²), and diffraction peaks from the unreacted Si

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Fig. 1. Schematic illustrations of the (a) direct laser heating apparatus and (b) laser scanning conditions.

Fig. 2. SEM images of the surfaces of the (a) precursor powder; and RS-SiC samples sintered at (b) 5 kW/cm², (c) 10 kW/cm², and (d) 12 kW/cm².

and C decreased with increasing P_L . The SEM and XRD results indicate that the faceted grains and the matrix in Figs. 2(b)–2(d) were crystalline SiC grains and a mixture of Si and C, respectively. Thus, a single laser scan is insufficient to completely form SiC. Crystalline phases of SiC were the β phase at $P_L = 5, 10$ kW/cm², and α -SiC at $P_L = 12$ kW/cm². The α phase is a high-temperature phase of SiC formed above 2000°C. In addition, the crystal phase composition of SiC was further evaluated by laser Raman spectroscopy. **Figure 4** shows laser Raman spectra (NRS-7100, JASCO) recorded using an excitation wavelength of 532 nm in the Si–C vibration range of 750–850 cm^{−1} for SiC samples prepared using the various P_L values. For the sample prepared at $P_L = 5$ kW/cm², no peak attributable to Si–C vibration was detected. In the case of $P_L = 10$ kW/cm², a strong peak corresponding to the TO mode of 3C-SiC (β phase) was observed at 796

cm^{−1}.^{16,17} Finally, shoulder peaks at 796 and 785 cm^{−1} observed for $P_L = 12$ kW/cm² corresponded to the TO mode of 3C-SiC (β phase) and the TO mode of 15R-SiC (α phase), respectively.

In order to complete the reaction to form SiC, laser scanning was repeated five times (the total irradiation time was about 1 min). Surface and cross-sectional SEM images of the resulting sample are shown in **Figs. 5(a)** and **5(b)**, respectively. The matrix phase was not present at the surface, suggesting that the reaction was complete, and a dense 3-μm-thick SiC layer was formed. Under the SiC layer, no changes were observed in the powder mixture, suggesting that the laser penetrated only several micrometers from the surface. Considering that the absorption coefficient of C is much higher than that of Si, the C powder would be preferentially heated during Nd:YAG laser irradiation. Si would be melted by heat transfer from

Fig. 3. XRD patterns of the (a) precursor powder; and RS-SiC samples sintered at (b) 5 kW/cm², (c) 10 kW/cm², and (d) 12 kW/cm².

Fig. 4. Raman spectra of RS-SiC prepared at P_L = (a) 5 kW/cm², (b) 10 kW/cm², and (c) 12 kW/cm².

Fig. 5. (a) Surface and (b) cross-sectional SEM images of the RS-SiC sample produced at a laser power of 12 kW/cm² using five laser scans.

the C powder, where SiC subsequently forms via a liquid–solid reaction between molten Si and solid C.

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