FULL PAPER

Preparation of crystalline SiC coating from Si and C powder mixture using laser sublimation technique

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A crystalline SiC coating was prepared by laser sublimation deposition from a powder mixture of Si and C as source materials under an Ar atmosphere at slightly reduced pressure (1×10^{-4} Pa). A continuous-wave fiber laser ($\lambda = 1070$ nm) was used to irradiate the Si + C source pellets through a 4H-SiC wafer substrate in order to heat and react the powder mixture of Si and C, and to then sublimate the formed SiC. A (111) oriented dense columnar 3C-SiC coating layer, free from unreacted Si and C, was formed at a deposition rate of $30 \mu\text{m}/\text{min}$.

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1. Introduction

Silicon carbide (SiC) is an archetypal structural ceramic material with high mechanical strength and excellent resistance to heat and oxidation, which is widely used as a high-temperature structural material for aircraft engines and gas turbines.^{1)–4)} SiC coating has been applied as an abrasion-resistant coating on sliding members and to coat fuel-cladding tubes used in nuclear power plants.^{5)–7)}

Application of a SiC coating typically involves vapor deposition techniques such as chemical vapor deposition^{8)–10)} and pulsed laser deposition.^{11)–13)} High-quality semiconductor-grade SiC films have been obtained using these techniques, although the deposition rate is very low (only a few nanometers per minute). Moreover, preparation of single-crystal SiC from the sublimation and recrystallization of SiC—which does not melt under atmospheric pressure and sublimates at high-temperature^{14),15)}—has also been explored. However, it is difficult to apply this technique to SiC coatings because the sublimation temperature is over 2300°C . For wide industrial application, a new SiC deposition process that combines low cost with high deposition rate must be developed.

Recently, direct manufacturing using high-intensity lasers has received much research attention as a next-generation manufacturing technology.^{16)–18)} For example, Ma et al. prepared an $\text{Al}_2\text{O}_3\text{--Y}_3\text{Al}_5\text{O}_{12}$ eutectic composite from Al_2O_3 and Y_2O_3 mixed powder pellets using a CO_2 laser.^{19),20)} Meyers et al. prepared Si-bonded SiC parts using a 100 W continuous-wave (CW) fiber laser.²¹⁾ Furthermore, highly crystalline SiC was previously formed from Si and C sample pellets using brief Nd:YAG laser irradiation.²²⁾

In this study, a crystalline SiC coating process was investigated, in which a SiC pellet was formed from a powder mixture of Si and C using a laser. The formed SiC pellet was then sublimated and recrystallized on a 4H-SiC substrate under laser irradiation.

2. Experimental

2.1 Deposition of SiC coatings by laser sublimation

A schematic of the SiC coating apparatus is shown in Fig. 1(a). Reagent-grade Si (99 % purity, $5 \mu\text{m}$ average particle size, Kojundo Chemical Laboratory) and C (<100 nm particle size, Sigma-Aldrich) powders were used as the starting materials. They were weighed in a 1:1 molar ratio and mixed by ball-milling in ethanol for 24 h. After drying at 120°C in air, the powder mixture was uniaxially pressed at 10 MPa into pellets (10 mm diameter, 1 mm thick). A CW fiber laser (red power-SP-400C, $\lambda = 1070$ nm, SPI

Fig. 1. Schematic illustration of the deposition apparatus.

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Laser Ltd.) was used to irradiate the surface of each sample (spot size: $\phi 6$ mm), and the sublimated vapor was deposited on a 4H-SiC wafer (Cree, {0001} orientation on axis) placed on a sample holder under a flow of Ar at 1×10^4 or 1×10^{-1} Pa.

2.2 Materials characterization

Crystalline phases and morphologies of the coatings were studied using a field-emission scanning electron microscope (SU-8000, HITACHI and JSM-7900 F-PRIME, JEOL), equipped with an electron backscatter diffraction (EBSD) probe. Elemental analysis was performed using energy dispersive X-ray spectroscopy. The surface temperature of the source pellet under laser irradiation (without substrate and sample holder) was measured using a two-color pyrometer (ThermEra-Phantom edition, Nobby Tech. Ltd.) and analyzed with ThermEra HSS software (Mitsui Photonics, Ltd.).

3. Results and discussion

The surface temperature distribution of the source powder pellet during laser irradiation was measured at a laser power (PL) of 1.2 kW/cm^2 under slightly reduced Ar flow

conditions ($P_{\text{Ar}}, 1 \times 10^4 \text{ Pa}$). Optical and temperature distribution images are shown in Fig. 2(a), with temperature profiles at the center and the edge shown in Fig. 2(b). The surface temperature was the highest at the central position due to the Gaussian distribution of the laser intensity. At the center of the pellet, the temperature reached 1500°C approximately 4 s after laser irradiation, remained at 1500°C for $\sim 0.2 \text{ s}$, and then rapidly increased to $\sim 2600^\circ\text{C}$. The rapid temperature increase from 1500 to 2600°C is caused by formation of SiC ($\text{Si}_{(s)} + \text{C}_{(s)} = \text{SiC}_{(s)} + 65.3 \text{ kJ}$), with SiC vapor formed when the surface temperature reaches 2600°C . SiC is reported to sublime at $2300\text{--}2350^\circ\text{C}$;¹⁵⁾ unfortunately, measurement of the sublimation temperature during deposition was not possible due to strong thermal radiation from the surface of the source pellets. Considering the change in the surface temperature distribution over time, sublimation first occurred at the center of the pellet surface, and then spread out over the entire surface.

SEM images of the surface of the source pellets obtained after irradiation at $PL = 1.2 \text{ kW/cm}^2$ for 0–120 s are shown in Figs. 3(a)–3(e). Before laser irradiation [Fig. 3(a)], dark and light gray particles identified as

Fig. 2. (a) Optical (left) and temperature distribution (right) images. (b) Temperature profiles of the surface of powder pellets as a function of laser irradiation time.

Fig. 3. SEM images of the surface of the source pellets after different laser irradiation times ($PL = 1.2 \text{ kW/cm}^2$): (a) 0 s, (b) 2 s, (c) 4 s, (d) 8 s, and (e) 120 s.

carbon and silicon particles, respectively, were observed. After laser irradiation for 2 s, agglomerates of 3–10 μm in diameter appeared [Fig. 3(b)]. After 4 s [Fig. 3(c)], particles 3–10 μm in diameter, consisting of faceted particles with diameters of 0.5–3 μm were observed. After 8 s [Fig. 3(d)], the particle surface contained many voids, several tens of nanometers in size, and after 120 s [Fig. 3(e)], a coarse microstructure was observed. After laser irradiation, the Si/C ratio in the remaining pellets was 0.95 ($N = 5$), which suggests that the sublimated vapor was nearly stoichiometric. During irradiation of the Si and C mixed pellet, C was heated and melted with Si to form SiC,²²⁾ which was then sublimated upon further laser irradiation. The weight loss profile of the source pellet under laser irradiation ($PL = 1.2 \text{ kW/cm}^2$) is shown in Fig. 4. The weight of the source pellet decreased with increasing irradiation time, and the rate of weight loss was estimated to be $2 \times 10^{-6} \text{ g/s}$.

Fig. 4. Weight loss of source pellets during laser irradiation ($PL = 1.2 \text{ kW/cm}^2$).

Surface SEM images of the layers deposited on the substrate for 120 s at $P_{\text{Ar}} = 10^4 \text{ Pa}$ are shown in Figs. 5(a)–5(c). At $PL = 0.8 \text{ kW/cm}^2$ [Fig. 5(a)], particles 50 nm in diameter were observed. At $PL = 1.0 \text{ kW/cm}^2$ [Fig. 5(b)], needle-like particles 1 μm in length were formed, and at $PL = 1.2 \text{ kW/cm}^2$ [Fig. 5(c)], plate-like crystals 1–5 μm in diameter were observed. There are two likely explanations for such a change in microstructure. Firstly, an increased amount of SiC is deposited due to the increase in laser power. The change in microstructure from particles to needles and plates is a common change seen in crystal growth. Secondly, the substrate temperature increases from increasing the laser power. In this study, laser irradiation of the source pellets occurs through the substrate; thus, the coated substrate could absorb more laser energy as the deposition progresses, resulting in an increase in the temperature of the substrate due to changes in the microstructure.

Cross-sectional SEM images of the deposited layer obtained at a lower pressure of $P_{\text{Ar}} = 10^{-1} \text{ Pa}$ after irradiation for 120 s were also observed, as shown in Figs. 6(a) and 6(b). At $PL = 1.0 \text{ kW/cm}^2$ [Fig. 6(a)], the deposition layer had a columnar structure wider than that obtained at $PL = 1.2 \text{ kW/cm}^2$ [Fig. 6(b)]. However, at this lower pressure, the deposited layer was Si-rich (average Si/C = 1.42, $N = 5$). Because the vaporizing temperature of Si is 1650°C at $1 \times 10^{-1} \text{ Pa}$,²³⁾ Si in the source pellet is directly vaporized in conjunction with SiC sublimation.

Surface and cross-sectional SEM images were recorded after deposition for 30 and 120 s, as shown in Fig. 7 ($PL = 1.2 \text{ kW/cm}^2$, $P_{\text{Ar}} = 10^4 \text{ Pa}$). The film thicknesses of these samples were 10 μm [Fig. 7(b)] and 50–60 μm [Fig. 7(d)], respectively, and the deposition rate was estimated to be 30 $\mu\text{m/min}$.

Fig. 5. SEM images from the center of each substrate showing the surface morphology of coating layers deposited at various laser powers (PL): (a) 0.8 kW/cm^2 , (b) 1.0 kW/cm^2 , and (c) 1.2 kW/cm^2 , under $P_{\text{Ar}} = 1 \times 10^4 \text{ Pa}$ for 120 s.

Fig. 6. Cross-sectional SEM image of the SiC coating at (a) $PL = 0.8 \text{ kW/cm}^2$ and (b) $PL = 1.0 \text{ kW/cm}^2$, under $P_{\text{Ar}} = 1 \times 10^{-1} \text{ Pa}$ for 120 s.

Fig. 7. (a–d) Surface and cross-sectional SEM images of SiC coated samples obtained with different laser irradiation times. Laser irradiation times of (a, b) 30 s and (c, d) 120 s, at $PL = 1.2 \text{ kW/cm}^2$ under $P_{Ar} = 1 \times 10^4 \text{ Pa}$ for 120 s.

Fig. 8. Cross-sectional SEM-EBSD analysis of a sample at $PL = 1.2 \text{ kW/cm}^2$ under $P_{Ar} = 1 \times 10^4 \text{ Pa}$. Mapping of the SiC phase showing (a) the crystal orientation of the 3C-SiC film, (b) the film perpendicular to substrate, and (c) the film in the in-plane direction. Inverse pole figures of the 3C-SiC films (d) perpendicular to the substrate and (e) in the in-plane direction. (f) Illustration of arrangement of Si and C atoms of 3C-SiC on 4H SiC{0001}.

Cross-sectional SEM-EBSD images of the coating layer deposited at $PL = 1.2 \text{ kW/cm}^2$ under $P_{Ar} = 10^4 \text{ Pa}$ are presented in **Figs. 8(a)–8(e)**. A columnar structure grew perpendicular to the substrate, which is often observed when a

coating is deposited from a supersaturated gas phase. The deposited layer predominantly consisted of the 3C-SiC phase [Fig. 8(a)], with a small amount of the 4H-SiC phase was observed at the grain boundaries. Generally,

polycrystals have lower optical transmittance than single crystals owing to absorption at the grain boundaries. The formation of 4H-SiC at the grain boundaries was caused by laser absorption and increased heating at these sites. After SiC deposition, transmittance of the samples decreased by $\sim 10\%$, indicating that the source pellets could be heated by the laser through the 4H-SiC substrate—even after the substrate was coated with SiC—because the deposited layer was 3C-SiC, which is the low-temperature phase (stable under 1300°C). Therefore, the substrate temperature remained under 1300°C . The deposited 3C-SiC had a (111) orientation on the 4H-SiC{0001} surface [Fig. 8(b)] because the 3C-SiC(111) and 4H-SiC{0001} surfaces have a similar atomic arrangement, whereby alternating Si and C planes are stacked, as shown Fig. 8(f).²⁴⁾

4. Conclusions

In this study, laser sublimation deposition was used to prepare a crystalline SiC coating from Si and C. SiC began to sublime at an estimated rate of 2×10^{-6} g/s from the center of a raw material pellet after about 4 s when a mixture of Si and C powders was laser-irradiated. The substrate surface morphology transformed into fine particles, needles, and then plate-like crystals with increasing laser power. A Si-rich SiC coating was formed at $P_{\text{Ar}} = 10^{-1}$ Pa due the simultaneous formation of Si vapor along with SiC sublimation under these conditions. On the other hand, (111) oriented stoichiometric 3C-SiC was deposited at an estimated rate of $\sim 30 \mu\text{m}/\text{min}$ at $PL = 1.2 \text{ kW}/\text{cm}^2$ and $P_{\text{Ar}} = 10^4$ Pa.

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