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SiC nanowire-induced fabrication of fine-grained and highly-density SiC coating by pressure-less reactive sintering

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ABSTRACT

Fine-grained and high-density SiC coating was fabricated on carbon materials by incorporating SiC nanowires during the pressure-less reactive sintering for the first time. The grain size, relative density, and fracture toughness of the as-fabricated coating are 1.5 ± 0.6 μm, 95%, and 5.03 ± 0.73 MPa $m^{1/2}$, respectively, resulting in a good oxidation protective ability, which can efficiently protect carbon materials from oxidation at 900 °C for more than 70 h or at 1500 °C for more than 90 h. The formation of such microstructure may be associated to the increasing nucleation rate resulting from the microstructure evolution and phase transformation of SiC nanowires during the sintering process.

1. Introduction

Silicon carbide (SiC) ceramic arouses considerable attentions owning to its remarkable physical, chemical and mechanical properties, including low density, high melting point, high hardness, high Young's modulus, and good corrosion resistance [1]. The combination of these properties makes SiC a fascinating candidate for applications, such as advanced engineering ceramics, aerospace materials, nuclear energy processing materials, and ballistic protection materials [2]. Owning to the properties of anti-oxidation and good compatibility with carbon materials, SiC ceramic has been typically used as the coating on carbon materials to prohibit their oxidations at elevated temperatures [3].

Up to now, various approaches, such as pressure-less reactive sintering [4], hot-pressing reactive sintering [5], and chemical vapor deposition (CVD) [6], were previously used to fabricate SiC coating on carbon materials. Among these approaches, the pressure-less reaction sintering has gained considerable attention, since it is convenience and easy to handle, possesses good interface bonding between the coatings and the substrates, and can be applied for various shape-and size-substrates [4]. However, this method requires high sintering temperature and long sintering and cooling periods, it makes the as-prepared coating exhibit a low-density microstructure with a large grain size (>10 μm) [4]. This largely reduces the mechanical and oxidation protective properties of the coating, which prohibits its further applications as an effective coating on carbon materials.

In the present work, we fabricated a fine-grained and high-density SiC coating on carbon materials by incorporating SiC nanowires during the pressure-less reactive sintering. The microstructure, fracture toughness, and oxidation protective ability of the coatings were investigated, as well as the formation mechanism of such microstructure in the coating.

2. Experimental procedure

Small samples (10 mm × 10 mm × 10 mm) cut from graphite with a density of 2.13 g/cm^3 were first hand-abraded using 300 grit SiC paper and then cleaned ultrasonically with ethanol and finally dried at 100 °C for 2 h to be used as substrates. First, the porous SiC nanowire skeleton was synthesized on the graphite substrates by CVD. The CVD precursor powders were mixed as follows: 55–75 wt % SiO_2 (300 mesh, 99.7%), 15–25 wt% Si (300 mesh, 99.7%) and 5–15 wt% graphite (500 mesh, 99.7%). Details of the preparation of the porous SiC nanowire skeleton on the graphite samples were reported elsewhere [4]. Afterwards, the samples with porous SiC

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nanowire skeleton were subjected to pressure-less reactive sintering using the following powder compositions: 55–75 wt% Si (300 mesh, 99.7%), 20–35 wt% graphite (300 mesh, 99.7%) and 5–10 wt% Al_2O_3 (300 mesh, 99.7%). These powders were first mixed by a blender for 2 h, and then the samples with porous SiC nanowire skeleton were immersed in the powder mixture in a graphite crucible followed by heat-treatment in argon at 2150 °C for 2 h to form the desired coating. Samples were also prepared by similar pressure-less reactive sintering method on the graphite samples but without SiC nanowires for comparison.

The indentation technique has been widely used to measure the fracture toughness of the small scale materials, especially the coatings, due to its convenience and easy-to-handle [4,5,7]. The fracture toughness (K_c) of the as-obtained coatings was measured on the well-polished cross-section of the coatings by the indentation technique using a micro-indentation tester with a Vickers indenter. The loads with 5 N were used to generate the cracks in the coatings for the calculation of the fracture toughness using the following equation [8].

$$K_c = 0.203 H_v a^{1/2} (c/a)^{-3/2} \quad (1)$$

where H_V is the hardness, a is the half diagonal of the indents, and c is the radial crack length. A total of 10 indentations were performed on each sample.

The isothermal oxidation tests of the coated samples were carried out at 900 °C and 1500 °C in air in a corundum tube furnace. These two choices could well reflect the oxidation protection ability of the coatings at both low temperature and high temperature because the microcracks in the coating remained open at 900 °C but would be closed at 1500 °C. After the furnace was heated up to 900 °C or 1500 °C, the coated samples were directly put into the furnace, whereafter they were taken out at the designated time and cooled at room temperature in air to measure their weights, and then they were put directly into the furnace again for the next oxidation period. An electronic balance with a sensitivity of ±0.1 mg was used to calculate mass change percentages ($W\%$) of the coated samples by the following equation.

$$W\% = \frac{m_0 - m_1}{m_0} \times 100\% \quad (2)$$

where m_0 and m_1 are the weight of the coated samples before oxidation and after oxidation, respectively.

Microstructure characterization of the as-obtained samples was performed using a scanning electron microscopy (SEM; supra-55, Zeiss, Oberkochen, Germany) with energy dispersive X-ray spectroscopy (EDS). The crystalline structure of the as-obtained samples was analyzed by using X-ray diffraction (XRD; X'Pert PRO, PANalytical, Almelo, Netherlands). The density of the coating was measured by Archimedes method. The measured coating was cut from the substrate using the high-speed wire electrical discharge machining. The grain size of the coating was measured from representative SEM micrographs using Image J. Length.

3. Results and discussion

Fig. 1(a) shows an representative SEM image of the as-obtained porous nanowire skeleton on the graphite substrates. It clearly demonstrates that the as-obtained skeleton is uniformly distributed on the substrates. A high-magnification SEM image (Fig. 1(b)) shows that it consists of a large amount of random-oriented nanowires with a length ranging from several tens to over one hundred microns and the diameter of 100–200 nm. XRD pattern shows that the nanowires possess a single-crystal 3C-SiC phase (Fig. 1(e), C peak comes from the graphite substrates). Fig. 1(c) shows that SEM fracture surface image of the coating after incorporating SiC nanowires, which indicates a dense fracture surface morphology without any observable holes or microcracks. As further shown by SEM image at high magnification (Fig. 1(d)), a large number of individual grains with regular facet-shaped are clearly seen. These grains remain intact and no cleavage plans are observed. These observations suggest that the fracture mode of the coating after incorporating SiC nanowires is a representative intergranular fracture. XRD pattern shown by Fig. 1(e) further demonstrates that the coating is mainly composed of a large proportion of 6H-SiC phase together with a small fraction of Si, without any other impurity phase being detected. It is also worth noticing that no pullout or debonding nanowires are found on the fracture surface of the coating (Fig. 1(d)). Combining with XRD (Fig. 1(e)) analysis, it can be concluded that most of 3C-SiC nanowires may have transformed into 6H-SiC particles during the pressure-less reactive sintering. Fig. 1(f) presents that SEM fracture surface image of the pure coating (without incorporating SiC nanowires). The fracture surface is smooth and with steps, on which no distinct intact grains with regular facet-shaped but distinct cleavage planes are observed. This indicates that the fracture mode of the pure coating is a representative transgranular fracture.

Table 1 shows the thickness, grain size, and relative density of the as-obtained samples, as well as fracture toughness. After incorporating SiC nanowires, the coating exhibited large thickness (125 ± 3.2 μm), but it is in agreement to the thickness of the as-obtained skeleton (120 ± 4.6 μm). Furthermore, the coating presented not only small grain size (1.5 ± 0.6 μm) but also high relative density (95%). What's more, the coating exhibited high fracture toughness (5.03 ± 0.73 MPa $m^{1/2}$), which largely exceeds the one for the pure coating (3.02 ± 0.69 MPa $m^{1/2}$).

Fig. 2 shows SEM images of the generated radial cracks in the coatings after the indentation testing. After incorporating SiC nanowires, the radial crack exhibits obvious zigzag propagation path in the coating (Fig. 2(a)). It does not pass through the grains, but propagates along the grain boundaries, which matches the features of the intergranular fracture well. This demonstrates that the fracture of the coating after incorporating SiC nanowires is the intergranular fracture. A striking example of intergranular fracture in the coating after incorporating SiC nanowires is shown in Fig. 2(b). It is clear that both the individual grains with regular facet-shaped and the cracks propagating along the grain boundaries can be clearly seen in SEM image. However, the radial crack exhibits straight propagation path in the pure coating (Fig. 2(c)). Combined with SEM observation (Fig. 1(f)), it can be suggested that the radial crack does not propagate along the grain boundaries, but passes through the grains [9]. This is the characteristic feature of the transgranular fracture. Therefore, compared to the transgranular fracture, the intergranular fracture increases the propagation path and dissipates the energy more during its propagation, improving the fracture toughness.

Fig. 3 shows the isothermal oxidation curves of the coated samples in air at 900 °C and 1500 °C, respectively. It can be seen that the weight loss of the pure coated samples rose quickly with the increase of the oxidation time, and reached 8.72% after oxidation at 900 °C in air for only 40 h (Fig. 3(a)) or 4.47% after oxidation at 1500 °C in air for only 20 h (Fig. 3(b)). After incorporating SiC nanowires into the coating, the coating presented good oxidation protective ability at 900 °C and 1500 °C. The weight loss of the coated samples was only 0.28% after oxidation at 900 °C for 70 h (Fig. 3(a)) or 0.59% after oxidation at 1500 °C for 90 h, (Fig. 3(b)), which is better than that of the previous reported SiC nanowire-toughened SiC coating [4]. Thus the as-fabricated fine-grained and high-density SiC coating possesses the good oxidation