Processing and measurement of basic properties of SiC and cordierite coatings of carbon/carbon composite

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Abstract

SiC and four cordierite materials, which are compounds of $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ mixed with B_2O_3 and GeO_2 , were selected in this work as coatings on a three-dimensional carbon/carbon composite (3D C/C). A CVD carbon film, which was treated as a bond coat, was first applied to homogenize the surface of the C/C, then an SiC coating was deposited. The SiC was prepared by reaction-sintering an Si powder layer with the precoated CVD carbon film. The sintering of cordierite materials and the reactions between the cordierite and SiC coatings were investigated. The processing parameters of CVD carbon, SiC and cordierite coatings were optimized for the formation of SiC and the densification and crystallization of cordierites. The dual coating, SiC/225 cordierite, was selected to coat on the C/C and exhibited good protection against oxidation. The combination of coating layers successfully prevented oxygen from reaction with the C/C substrate.

Keywords: Carbon-carbon composite; oxidation; silicon carbide; cordierite; activation energy

1. Introduction

Carbon/carbon composite (C/C) is an important engineering material for aerospace applications owing to its excellent performance at high temperature. The development of C/C is divided into two main areas: the manufacture of dense C/C monolith and improvement of its resistance to oxidation in an oxidizing environment.

There have been many investigations of the protection of C/C against oxidation for practical applications. The methods of oxidation protection can be summarized in three categories: surface coating with ceramic materials [1,2], addition of oxidation inhibitors to diminish the active surface area of carbon [3,4], and the infiltration of refractory metals into C/C [5]. Among the published literature [1–6] we find that surface coating is the most effective process for improving the resistance to oxidation of C/C. The coating separates the oxygen from contact with the C/C substrate; hence oxidation is avoided.

SiC was selected as a good coating material from the

standpoint of its capability to resist oxidation and its physical compatibility with C/C, i.e. its small coefficient of thermal expansion (CTE), about $2 \times 10^{-6} \text{ K}^{-1}$. Previous results [7] revealed that the induced thermal stress was still too large, and resulted in microcracks on the SiC coating. As a consequence, the SiC coating did not prevent oxygen from reacting with the carbon substrate [8].

Cordierite is another oxide material that displays a small CTE and easy flowing at high temperature exceeding 1300 °C. In this work, dual coatings of cordierite/SiC were applied on the surface of C/C. We evaluated the formation of the coatings by means of reaction-sintering methods and the reactions and bonding conditions between coatings, to understand the influence of the processing parameters. The CTE values of these materials (four cordierites, SiC, and C/C) with respect to their processing history and calculation of the thermal stresses will be presented in a second paper.

2. Experimental procedure

Bulky 3D C/C was supplied by the Chung-Shan Institute of Science and Technology (CSIST), Taiwan.

¹ Part of the research was performed while Dr. Wu was associated with the Institute of Materials Science and Engineering, National Taiwan University.

The C/C, of density 1.85 gm ml^{-1} , was cut into a cube or plate with respective dimensions $10 \times 10 \times 10$ or $25 \times 10 \times 5 \text{ mm}^3$. Sample surfaces were polished with SiC paper and $1 \mu\text{m}$ alumina suspension. Before the ensuing coating procedure, all samples were cleaned in an ultrasonicating bath to give the same conditions at the surfaces of all C/C samples.

Chemical vapor deposition (CVD) of carbon film was conducted in a tube furnace equipped with a horizontal alumina tube of diameter either 41 or 50 mm. The flowing gases including methane and argon were controlled accurately in the ratio either 1:4 or 1:7. The gases were mixed before entering the reaction tube. The C/C sample was placed on a graphite platform and tilted 15° with respect to the flow direction of the reactant gases. The coating procedure lasted for 1–3 h, followed by cooling to room temperature in an argon atmosphere.

The SiC coating was made by the reaction sintering of high purity Si powder (Silcomill 4E, KemaNord Co., USA, average size $4.7 \mu\text{m}$ and purity 99.8%) with pre-coated CVD carbon film. The coating procedure for Si powder was described previously [9]. In summary, the SiC powder in volume fraction (30%) was added to dry ethanol with polyethyleneimine (PEI, 2.5 wt.%) dispersant, followed by mixing in a high-shear turbo-shaker. The CVD-coated C/C sample was then immersed in the Si suspension and drawn slowly from the suspension at a constant rate of 0.5 cm s^{-1} to ensure homogeneity of the thickness of silicon powder. After being dried in a hot chamber (about 100°C), the reaction sintering of C/C as coated was performed at 1600°C for 2 h in an argon atmosphere. Using a similar dipping procedure, we prepared a cordierite suspension and made a top coat of cordierite on the SiC layer.

Four cordierites of various compositions were prepared in this work. The nomenclature of each compound with respect to their constitution is listed in Table 1. Ge225 has nearly zero CTE [10] near room temperature and the constitution of 7310 is close to the eutectic composition of the $\text{MgO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ ternary system. The oxide powders were first mixed in dry ethanol. Part of the dried mixtures was calcined at 1340°C for 2 h before being milled to -325 mesh. The rest was dis-

persed directly in water for preparation of the coating suspension. The SiC-coated sample was then dipped in the cordierite suspension, and followed by liquid-phase sintering. The sintering of the upper layer of cordierite was conducted from 1000°C to a temperature 30°C above its melting point and lasted for 2 h.

A diffractometer (Philips PW1729) was used to identify the crystalline phase(s) of the coating materials. A scanning electron microscope (SEM, Philips 515) equipped with electron dispersive X-ray spectroscopy (EDS), operating at 20 kV was used for morphological observation and composition analysis. A dilatometer (Setaram DHT 2400KN) was employed to measure the CTE of the coatings and C/C materials.

The oxidation behavior of the coated C/C was measured using a thermal gravimetric analyzer (TGA, Ulvac TGD 7000). The sample was held in a high-purity argon atmosphere until reaching the testing temperature. Air from a compressor was then flowed into the testing tube at a constant rate of 100 ml min^{-1} . The rate of oxidation was measured when the loss of mass attained a constant rate. The oxidation rate was obtained from the slope of the curve in units of $\text{mg h}^{-1} \text{ cm}^{-2}$ for comparison among the tests.

3. Results and discussion

3.1. CVD carbon film

The thickness of the CVD carbon film on the C/C sample shows a good linear relationship with respect to processing duration, but the curves of thickness vs. time fail to pass through the origin (Fig. 1). Hence the growth of the carbon layer does not occur at the beginning of CVD processing. There is about 0.5 h delay before the carbon starts to grow. This incubation period is expected to be due to the pyrolysis or nucleation of carbon from the gas phase [11] before deposition, and depends on the concentration of reactant gases.

Fig. 1 reveals that the growth rate was influenced by the diameter of the alumina tube (one is 41 mm, the other is 50 mm), and also by residual carbon on the surface of the reaction tube. The rate of growth of CVD carbon in a clean tube is smaller than that in the carbon-precoated tube as shown in Fig. 1. A growth rate of $17.2 \mu\text{m h}^{-1}$ was measured in a 41 mm diameter tube with carbon precoated on the inner surface, when the reactant methane-argon gas was in the ratio 1:4. However, the coating rate was only $6.5 \mu\text{m h}^{-1}$ when the reactor tube was previously unused. The rate of deposition decreased to $10.2 \mu\text{m h}^{-1}$ and the incubation period prolonged to about 1 h when the tube was replaced by a 50 mm diameter alumina tube precoated with carbon film. Thus, the growth rate of CVD carbon coating is a function of the rate of gas flow, temperature,

Table 1
Chemical composition (wt.%) of various cordierite materials

Cordierites	MgO ^a	Al ₂ O ₃ ^b	SiO ₂ ^c	GeO ₂	B ₂ O ₃ ^d
225	13.8	34.9	51.3	—	—
7310	23	27	50	—	—
225B	13.1	33.2	48.9	—	4.8
Ge225	13.2	33.3	43.2	10.3	—

^a MgO, Gredmann Taiwan MgO, 99.6% pure.

^b Al₂O₃, Alcoa A16SG, 99.2% pure.

^c SiO₂, Harrison Walker Refractories, fused silica, 99.9% pure.

^d B₂O₃, Ching-Liang Co., 99% pure.

Fig. 1. Growth thickness of CVD carbon film plotted against coating duration for various coating conditions.

state of the reactor and arrangement of the sample. The rate of growth of CVD carbon film is difficult to predict, but the rate data show good reproducibility in our experiment.

The carbon films delaminated when the coating thickness exceeded 50 μm . Interruption during the coating procedure also caused the deposited layers to delaminate, as observed in Fig. 2. Generally, a low quality carbon film exhibits a laminar structure and typically delaminates on cooling to room temperature. The delamination

Fig. 2. SEM images of carbon coatings in (a) one layer or (b) two layers. The carbon layers are marked "1" or "2". "R" is a cold-mould resin for the fixation of carbon layers. "C" is the C/C matrix.

is due to the anisotropic CTE of the coating and to the difference with the C/C substrate.

3.2. Reaction sintering of SiC

The ease of formation of SiC was first tested by a direct reaction of well mixed silicon-carbon black powders, and holding for 3 h at 1350 $^{\circ}\text{C}$ was enough to complete the reaction. In this work, the CVD-coated carbon film is in an amorphous state, according to X-ray diffraction, similar to carbon black. Consequently, the carbon film is expected to react easily with the top-coated silicon powder to form SiC at 1350 $^{\circ}\text{C}$ or above. The formation of SiC in the reaction processing of the silicon powder with the layered CVD carbon film has a greater rate at the beginning but is limited by mass diffusion through the newly formed SiC layer. The mass transport of silicon and carbon through the SiC layer becomes a rate-controlling factor in the middle and later period of the reaction when the SiC grows increasingly thick.

In previous work, the processing temperature of SiC was set at 1600 $^{\circ}\text{C}$ [9] and the reaction proceeded rapidly enough to form a SiC layer. However, control of the reaction was difficult owing to the evaporation of Si. Thus the lower processing temperature of 1430 $^{\circ}\text{C}$ was selected to form an SiC layer on C/C. Fig. 3 shows SiC protective films of two types on the C/C after processing in either a carbon-poor or carbon-rich atmosphere. In addition to the carbon atmosphere, the residual silicon in the sintering zone may influence the state of SiC. Thin SiC may crack owing to large shrinkage from embedded silicon which has 9% linear shrinkage when it solidifies from the liquid phase. Fig. 3(a) depicts a thin layer of SiC that was formed between a dense (melted) Si layer and carbon substrate. Fig. 3(b) shows

Fig. 3. Optical micrographs of an Si/SiC coated C/C which was heat treated at 1430 $^{\circ}\text{C}$ for 3 h and processed in a (a) carbon-poor or (b) carbon-rich atmosphere. The Si layer has a strong metallic refraction that appears the brightest contrast in (a). The contrast difference of Si to SiC is small in (b); Si shows a gray contrast.

a sample processed in a carbon-rich atmosphere, resulting in an additional outer SiC layer (with a dark gray contrast) and polygonal SiC grains (one is indicated in Fig. 3(b)) embedded inside the Si layer (the central gray area). A similar SiC/Si composite was reported by Sawyer and Page [12] which was thought to be due to carbon dissolution and diffusion through melting silicon (the processing temperature 1430 °C exceeds the melting point of Si).

3.3. Sintering of cordierite

The densities and open porosities of cordierite mixtures sintered between 1000 and 1400 °C were investigated and are shown in Figs. 4 and 5. Stoichiometric cordierite is a material in which it is difficult to achieve complete densification. The apparent densities of the cordierites 225, 225B and 7310 are near 2.7 g ml⁻¹ which is greater than the theoretical density (2.51 g ml⁻¹) of a stoichiometric cordierite [13]. (The sintered cordierite was partially reacted. The matrices showed glassy and crystalline phases.) Before full reaction of the oxides, the average density of three oxides MgO, SiO₂ and Al₂O₃ in the 225 cordierite composition is close to 2.95 g cm⁻³, and reduces to 2.57 g cm⁻³ if the oxides react to form a uniform glassy state [14]. The cordierite Ge225 has the greatest density (about 3.0 g cm⁻³) because the mass of Ge is greater than that of Si which is replaced in Ge225.

The cordierites show great variability in their porosity. 225B (with 4.8 wt.% B₂O₃) and 7310 (eutectic composition) cordierites have a low melting point that results in early densification of their surface, so that their open porosity decreases near 1350 °C, from 30% to less than 5%. The decrease in open porosity is more pronounced for 7310 cordierite pre-treated at 1340 °C. In comparison, the 225 composition needs a higher sintering temperature to melt and to close its open pores. The purpose of the pre-treatment at 1340 °C is to let the three components MgO, SiO₂ and Al₂O₃ of the cordierites react and become more uniform. Therefore, more liquid phase is formed at an early stage of the sintering, resulting in decreased open porosity and apparent density, especially for 7310 that favors the formation of an eutectic liquid at 1370 °C, shown in Figs. 4(b) and 5(b). The 225 and Ge225 samples without pre-treatment at 1340 °C show no apparent change in density and open porosity. The 225 composition, however, is relatively difficult to sinter because of its lack of liquid phase below 1400 °C.

3.4. Formation of crystalline cordierite

Two X-ray diffractograms of 225 with various treatments are shown in Fig. 6. One 225 sample was sintered at 1340 °C for 1 h, the other was sintered on the C/C matrix for 3 h at 1480 °C, 30 °C above the melting point of pure 225 cordierite. The 225 cordierite with sintering

Fig. 4. Density of (a) 225, (b) 7310, (c) 225B, or (d) Ge225 cordierites with or without pre-heat-treatment at 1340 °C sintered for 1 h.

Fig. 5. Open porosity (%) of (a) 225, (b) 7310, (c) 225B, and (d) Ge225 cordierites with or without pre-heat-treatment at 1340 °C sintered for 1 h.

Fig. 6. X-ray diffractograms of (a) a 225 cordierite sintered at 1340 °C for 1 h, (b) a 225 cordierite on C/C substrate sintered at 1480 °C for 3 h.

at 1340 °C showed some degree of solid-state reaction. There is one intermediate phase, spinel, and a high-cordierite phase found in the X-ray diffractogram (Fig. 6(a)), but the phases disappeared and transformed

to low-cordierite and mullite phases when sintered at 1480 °C for 3 h.

Results from the heat treatment of the cordierites are illustrated in Table 2. A high-cordierite phase is readily formed in calcined products. The spinel phase in the calcined 225 is an intermediate phase that is finally converted to cordierite at higher temperature. There is no spinel phase formed for 225B, 7310 and Ge225 compositions, possibly owing to the melting process and lower melting temperature than for 225. The existence of a liquid phase may help the transport of oxide species and enhance the reaction of precursor oxides to form cordierite and mullite phases. In addition, the melting process of 225B and Ge225 was found favoring the phase transformation of high-cordierite to μ cordierite. Qualitatively, the melting process favors the production of μ cordierite or low-cordierite phases which easily nucleate and grow in the ternary-oxide matrix.

3.5. Coating of cordierite on SiC substrate

The coating process on SiC includes wetting and spreading of melted cordierite. In this work we define the dihedral angles of cordierite on SiC to achieve wetting and spreading to be less than 90° and 20° respectively. The temperatures T_1 and T_2 corresponding to wetting and spreading for each cordierite on SiC, are

Table 2
Formation of crystalline phases of various cordierites

Sample phase	High-cordierite	Low-cordierite	μ -cordierite	Mg–Al spinel	Mullite
Calcined ^a 225	Major	—	—	Minor	—
Melted ^b 225 °	—	Major	—	—	Minor
Calcined 7310	Major	—	—	—	—
Melted 7310	Major	—	—	—	—
Calcined 225B	Major	—	—	—	—
Melted 225B	—	—	Major	—	Very few
Original Ge225	—	Major	—	—	—
Melted Ge225	—	—	Major	—	Very few

^a Calcination of cordierites was treated at 1340 °C for 2 h.

^b Melting process of cordierites was conducted at 5 °C above the cordierite melting temperature for 2 h.

^c 225 cordierite was melted at 1480 °C for 6 h.

shown in Table 3. One set of photographs revealed the melting condition of one reacted 225 at 1460 °C and 1500 °C are shown in Fig. 7. The cordierite spreads on the SiC substrate homogeneously when the processing temperature was kept 30 °C above the pertinent T_2 .

All cordierites in our experiments displayed good wetting on the SiC substrate when they were melted. Among the specimens, Ge225 exhibited the best wetting on an SiC substrate, but a dark gray layer was found at the interface. This layer could be a result of chemical reaction between the cordierite and substrate SiC. [15]. There was an amorphous interlayer formed when cordierite reacted with silicon carbide at 1000 °C or above. In addition to the interlayer, we occasionally often found that the Ge225-coated sample was in pieces. The Ge225 coating may undergo enormous thermal stress after cooling. For this reason we hesitate to undertake further examination of the feasibility of Ge225 as a coating to inhibit oxidation.

Two representative interfaces, 225–SiC and Ge225–SiC, are shown in Fig. 8. Interesting features,

Fig. 7. Photographs of reacted 225 cordierite wetting on a SiC substrate while heated at (a) 1460 °C, (b) 1500 °C.

Table 3
Temperatures T_1 and T_2 (for definition see text), for various cordierite wetting or spreading on an SiC substrate

Material	T_1 (°C)	T_2 (°C)
Reacted 225	1460	1500
Reacted 225B	1440	1490
Reacted 7310	1370	1490
Reacted Ge225	1420	1470

rectangular and leaf-shaped crystals, are found in regions of the 225 cordierite. The SEM images (Fig. 8) are not able to confirm the above features as crystalline mullite or cordierites, but previous X-ray diffraction results show that only cordierite and mullite are possible phases. Large pores (of diameter 10 μ m) at the interface of Ge225–SiC, shown in Fig. 8(b), are absent in other samples, such as 225/SiC (Fig. 8(a)), 225B or 7310. The formation of pores may be due to gaseous emission from the reaction between Ge225 and silicon carbide at the interface. The accumulation of carbon monoxide gas

Fig. 8. SEM and Si-element line scanning images of the cross-section, revealing regions near the interface of (a) 225/SiC, (b) Ge225/SiC.

results in a porous interface. According to the previous discussion on the wetting temperature, the low melting point of Ge225 cordierite is expected to be responsible for the ease of glass formation, good wetting and spreading, and the formation of interfacial pores.

3.6. Oxidation properties of coated C/C

One C/C with SiC/225 cordierite dual coating was tested for oxidation as follows: (1) bond-coat CVD carbon layer, processed at 1250 °C for 2.5 h; (2) SiC layer, reaction-sintered at 1450 °C for 1 h; (3) top-coat 225 layer, sintered at 1480 °C for 3 h, followed by slow cooling (cooling rate 3 °C min⁻¹) to 1000 °C, then held for 3 h at 1000 °C for crystallization of cordierite grains.

A SEM image of a cross-section of the sample is shown in Fig. 9 which shows a layer structure, from left to right of the C/C substrate, of partially reacted CVD carbon, SiC and cordierite layers. The CVD carbon layer shows a characteristic nodular feature, and has a

Fig. 9. Cross-section of a cordierite/SiC coated C/C. One large crystal is marked "a" next to the SiC layer.

thickness of about 10 μm. The reaction-sintered SiC is polycrystalline and covers the bond-coated carbon layer well. The cordierite outer layer exhibits a glassy texture, and has grown some large crystals, e.g. the crystal "a" in Fig. 9. The crystalline phase of the "a" crystal was not determined, but could only be either cordierite or mullite.

The coated C/C was tested in flowing air at temperatures from 700 to 1000 °C (limited by the maximum temperature of the TGA). The maximum rate of oxidation was measured to be 1.5×10^{-2} mg h⁻¹ cm⁻² at 1000 °C. The high-temperature oxidation of the sample was limited by protection of the SiC/225 cordierite coatings. The activation energy of the oxidation calculated is 39.4 kJ mol⁻¹ which is different from the oxidation energies of carbon materials reported by Luthra [16] and Walker [17]. The activation energy of oxidation of the coated C/C implies the oxidation mechanism is diffusion of oxygen through the protective coatings. In addition to the TGA test, the coated sample was tested in air in a furnace. The sample showed a small loss of mass when it was oxidized at 1420 °C for 2 h.

4. Conclusions

Four cordierite materials and reaction-sintered SiC were prepared either in bulk or as a thin coating on the surface of 3D C/C. The processing parameters of reaction-sintering and the physical properties of the coatings were investigated. The observations are summarized as follows.

(1) The formation of CVD carbon film underwent an incubation period, following growth at a rate depending on the concentration of the reactants, the ratio of the gases CH₄ and argon, and reduction conditions of the reaction tube. This bond-coated CVD carbon was useful for enhancing the homogeneity of the surface of C/C, and activated the reaction of silicon to form a continuous SiC coating.

(2) SiC prepared by reaction sintering of an Si powder layer with the CVD carbon layer was processed at temperatures near the melting point of Si. The morphology of SiC depended mainly on the carbon-reduction atmosphere in the reaction tube and the reaction temperature.

(3) 225B and 7310 cordierites were densified to no open porosity at temperatures above 1400 °C. Pre-treatment of cordierite mixtures at 1340 °C influenced not only sintering, but also the wetting and spreading of cordierites on SiC.

(4) All cordierites in this work wetted and spread on an SiC substrate and, apart from Ge225, they had good bonding with the SiC substrate. There was no detectable reaction interlayer between SiC and the cordierites,

but Ge225 showed reaction features consisting of micro-meter-sized pores and an interdiffusion layer.

(5) The formations of various crystalline cordierites, high, low and μ cordierite crystals, and mullite phases in association with the appearance of intermediate Mg–Al spinel, were detected.

(6) One selected 225 cordierite/SiC coated C/C exhibited good oxidation resistance in the tests from 700 to 1000 °C and also at 1420 °C. An activation energy of oxidation was measured, which indicated oxidation of the coated C/C way controlled by diffusion of oxygen through the solid layer.

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