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Thermal shock resistance of SiC compositionally graded C/C composites

Kimio Fujii, Reiji Yamada *

Department of Materials Science and Engineering, Materials Processing and Qualification Laboratory, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki-ken 319-11, Japan

Abstract

Thermal shock resistance of SiC compositionally graded carbon fiber reinforced carbon composite (CFC) materials that are composed of a CVD SiC layer, a SiC/C graded layer and a CFC substrate was studied by thermal shock tests in air. Two types of CFCs were used: 1-D continuous fiber reinforced and 2-D felt reinforced composites. It was found that the SiC/C graded layer was to some extent effective to increase the resistance and that its effectiveness was larger when a difference in thermal expansion coefficient (CTE) between a substrate and β-SiC was smaller. The degree of an improvement of the thermal shock resistance for CFC substrates was lower than that for isotropic graphite substrate. The difference was attributed to the original cracks in CVD SiC layers on CFC substrates.

1. Introduction

Carbon fiber reinforced carbon composites (CFCs) are considered divertor materials because of high strength, high toughness, and good thermal conductivity at high temperatures [1–3]. These materials, however, have a drawback that they are subjected to erosion by active species like hydrogen or oxygen atoms at high temperatures. One of the ways to prevent these materials from eroding through formation of hydrocarbon or carbon oxide is to cover the surfaces with a protective layer. As the protective layer, SiC has shown the best performance for non-fusion applications [4,5], and it will be also excellent for fusion applications due to low induced radioactivity as well as good resistance to attack by hydrogen. During heat loading and unloading, the protective layer suffers thermal stresses that arise from the different thermal expansion coefficients (CTEs) between the substrate and the coated layer. A concept of compositionally graded material is useful for reducing such a mismatch of the CTEs, and for moderating the thermal stress distribution, which will result in strengthening thermal shock resistance. From the above viewpoint, we developed SiC compositionally graded graphite materials that consisted of a CVD SiC layer, a SiC/C graded layer and a graphite substrate for nuclear applications [4–6].

Employing the same method, we have fabricated SiC compositionally graded CFC materials. In this paper we report the results of the thermal shock resistance of these CFC materials and compare them with the results of SiC compositionally graded graphite materials.

2. Experimental

2.1. Substrate materials

Materials used as substrates were two kinds of CFCs: one was named MFC and delivered by Mitsubishi Chemical, and the other was CX2002U from Toyo Tanso. MFC contained uni-directional continuous carbon fibers that gave anisotropy in mechanical and thermal properties of the composite. CX2002U consisted of a stack of mats in which felt-type carbon fibers were dispersed and impregnated with pyrolytic carbon. CX2002U has been used for the divertor of JT-60 and is also considered one of candidate materials of plasma

* Corresponding author. Tel.: +81-29-282-5403; fax: +81-29-282-6556; e-mail: reiji@popsvr.tokai.jaeri.go.jp.

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Table 1
Thermal and mechanical properties of CFRCs, monolithic SiC and isotropic graphite

Brand	Type of fiber	Thermal expansion coefficient ($\times 10^{-6}$/K)	Thermal conductivity at 293 K (W/mK)	Bending strength (MPa)	Thickness of CVD SiC (μm)
MFC	1D continuous carbon fiber				
(*X*-*X*)		0.9 (0.19) [a]	640	480	210
(*Y*-*Y*)		12.0 (2.55) [a]	–	5	210
CX2002U	2D dispersed carbon felt				
(*X*-*X*)		1.7 (0.36) [a]	360	47	67,210
(*Y*-*Y*)		2.3 (0.49) [a]	290	43	67,210
(*Z*-*Z*)		5.3 (1.13) [a]	200	17	67,210
β-SiC		4.7 (1.00) [a]	80	165	–
IG-110		4.0 (0.85) [a]	136	36	100

[a] Ratio of CTEs (Substrate/SiC).

facing components for a fusion reactor due to good thermal characteristics [1]. Typical properties of MFC and CX2002U are listed in Table 1. For comparison, those of β-SiC and isotropic graphite named IG-110 from Toyo Tanso are also included. The notations of (*X*-*X*), (*Y*-*Y*), and (*Z*-*Z*) in the table were as follows: for MFC, (*X*-*X*) was parallel to, and (*Y*-*Y*) normal to the fiber direction; for CX2002U, (*X*-*X*) and (*Y*-*Y*) were parallel to, and (*Z*-*Z*) vertical to the mat surface. These directions and how to cut CFCs for specimens are depicted in Fig. 1.

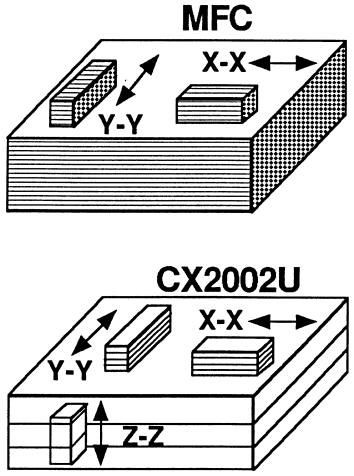

Fig. 1. Two types of CFC substrates: MFC contains uni-directional continuous fibers, and CX2002U consists of mats containing two dimensionally dispersed felts. How to cut specimens of *X*-*X*, *Y*-*Y*, and *Z*-*Z* are illustrated.

2.2. Fabrication of SiC compositionally graded CFC materials

The specimens of CFCs were cut in a form of cylinder, 15 mm in length and 8 mm in diameter for MFC, and 20 mm in length and 10 mm in diameter for CX2002U. All edges of a cylinder were rounded to reduce the stresses occurring at formation of SiC/C graded layer and/or CVD SiC coating. The SiC/C graded layer was formed by the following reaction, 2C (solid) + SiO (gas) → SiC (solid) + CO (gas), at a temperature of 1380°C in the carrier gas of high purity helium with SiO molecules that were gasified at a temperature of 1300°C. After the reaction a mass gain of the specimen was observed owing to formation of SiC. SiC concentrations in the layer were controlled by reaction time since the increase of mass gain was nearly proportional to the reaction time. Each specimen was fabricated so as to have one of mass gains, 0.5, 1 or 2 mass%. X-ray analysis identified that SiC in the layer had a structure of β-SiC although the surface of the graded layer may be covered with free Si(not reacted to SiC). The details of processing the SiC/C layer have been described in previous papers [6,7].

Similar to SiC compositionally graded graphite materials [6–8], CFCs with a SiC graded layer were coated with CVD SiC for increasing the resistance to chemical reactions; from here on, we note these materials as

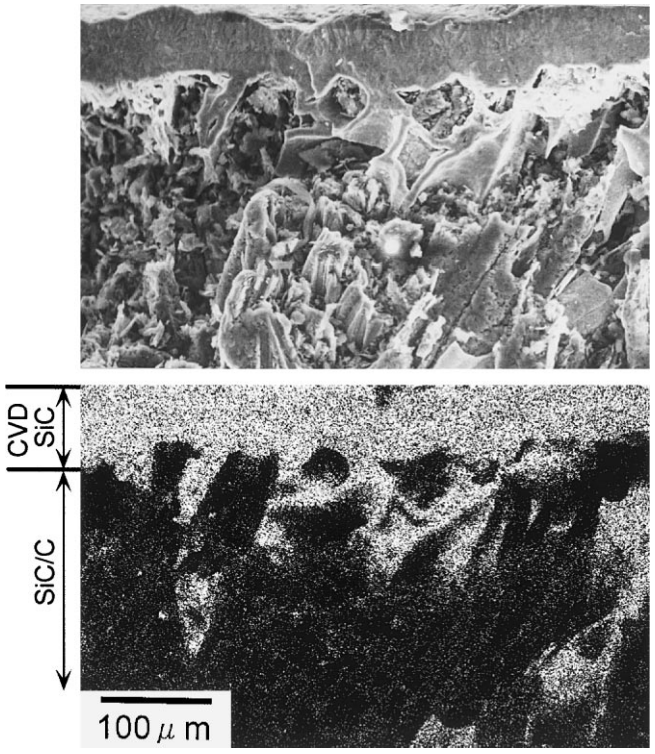

Fig. 2. SEM micrograph of a cross-sectional view of SiC-SiC/CX2002U that has a surface CVD SiC layer and a SiC/C graded layer beneath it, and the corresponding X-ray map for Si.

SiC–SiC/CFCs. The CVD SiC thickness was 210 μm. For comparison, CFCs directly coated with CVD SiC were also prepared (noted as SiC-CFCs). The CVD coating was performed at a temperature lower than 1380°C to maintain the structure of SiC/C graded layer. A typical example of cross-sectional view and corresponding X-ray map for Si of SiC–SiC/CX2002U is shown in Fig. 2.

2.3. Thermal shock tests

Cyclic thermal shock tests were conducted in air environment as follows: A specimen was heated in an infrared furnace from room temperature to a maximum temperature of 1020°C at a heating rate of 20°C/s; after holding the temperature for 5min, the specimen was quenched into water of 20°C. After each thermal shock test, the specimen was isothermally heated at 800°C in air for 1 h, and then was weighed at room temperature. The above procedure was repeated to obtain a mass loss exceeding a value more than 20%. The reason why oxidation tests were employed after thermal shock tests is that cracking in CVD SiC layer was easily detected by observing the mass loss during oxidation, since a large mass loss took place at oxidation tests after cracks occurred in the CVD layer.

The temperature history in this study does not necessarily simulate the thermal shock behavior under fusion relevant conditions. The present quenching condition, however, gives strong tensile stresses in the CVD SiC layer since the CTEs of carbon fiber directions are smaller than that of β-SiC(see Table 1). This study can, therefore, evaluate adhesion of CVD SiC layer to a substrate under a condition severer than the fusion relevant condition, i.e., a thermal shock with positive thermal gradient in vacuum.

3. Results and discussion

Fig. 3 shows the results of mass loss from original mass of specimens, as a function of number of thermal cycles for SiC–SiC/CX2002U(*Z-Z*) and SiC-CX2002U(*Z-Z*). There were somewhat scatters of the curves, where several specimens with a different SiC content in a SiC/C layer were used. Since any particular dependence was not found in these curves, we did not specify the values of SiC contents in the figure. The number of thermal cycles to cause the 20% of mass loss, where many cracks and a partial exfoliation of CVD SiC layer were observed, was chosen to compare thermal shock resistance for all kinds of specimens. The average

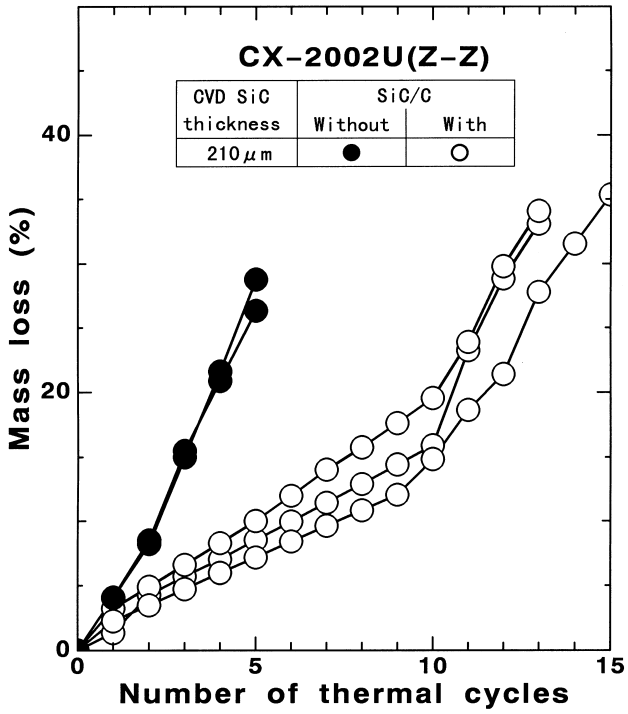

Fig. 3. Mass losses for 2-D composite specimens with both a surface CVD SiC layer and a SiC/C graded layer, SiC–SiC/CX2002U(*Z-Z*), and those with a surface CVD SiC layer alone, SiC-CX2002U(*Z-Z*), as a function of number of thermal cycles.

number was obtained for specimens with a different SiC content in each kind, and bar-graphed in Fig. 4. It is evident that the SiC/C graded layer plays a role in increasing the number, namely improving the thermal shock resistance for all specimens except MFC(*Y-Y*) substrate. We took the ratios of these numbers for specimens with a SiC/C graded layer to those without the layer, and plotted them as a function of the ratio of CTE of a substrate to that of β-SiC in Fig. 5. It is seen that an improvement of thermal shock resistance was affected by a difference in CTE between a substrate and CVD SiC, and the improvement ratio had the maximum around the unity of the ratio of CTEs. The reasons why the case of MFC(*Y-Y*) substrate was unable to improve the resistance may be that the CTE of the carbon fibers was too small compared to that of CVD SiC, and that the SiC/C graded layer was not sufficient to relax the thermal stresses.

For comparison, mass loss curves of SiC–SiC/IG-110 graphite are given in Fig. 6, which show no significant mass losses at the initial stage. Concerning SiC content, similar to the results of CFC substrates, the above curves had no specific tendency even if the mass gain due to SiC formation ranged from 0.1 to 2 mass%. As discussed in the previous paper [7], Fig. 6 also shows two stages: the first was extended from the first thermal cycle to the cycles for which mass losses were less than 1%, where strong oxidation resistance was kept because of no cracks in the CVD SiC layer; the second was from initiating a crack to successive crack production prior to a partial exfoliation of CVD layer (approximately 5% in this case). Comparing specimens with and without SiC/C graded layer, the onset of the second stage was retarded, and the span of the second stage was widened for those with SiC/C graded layer (SiC–SiC/IG-110).

From the above discussion, as long as the surface CVD SiC coating layer has no cracks, the mass loss curves keep very low values. Since there was no region where mass loss was quite small for CX2002U substrate in Fig. 3, it can be said that from the beginning of the thermal shock test the case of CX2002U was in a similar condition to the second stage of the graphite case. As a matter of fact, cracks were observed in as-received SiC CVD layer of SiC–SiC/CX2002U specimens, as shown in Fig. 7(a). It is thus considered that cracks, which were initiated in the SiC coating layer during CVD processing due to larger mismatch of CTEs than the case of graphite substrate, permit oxygen to penetrate through them and to erode the CFC substrates during the isothermal heating at 800°C. Similar cracks were also observed in specimens of MFC composites. Fig. 7(b) shows an example of surface morphology change, i.e., the surface cracks and partial exfoliation of CVD SiC layer, after thermal shock tests that caused 15.8% mass loss for SiC–SiC/CX2002U.

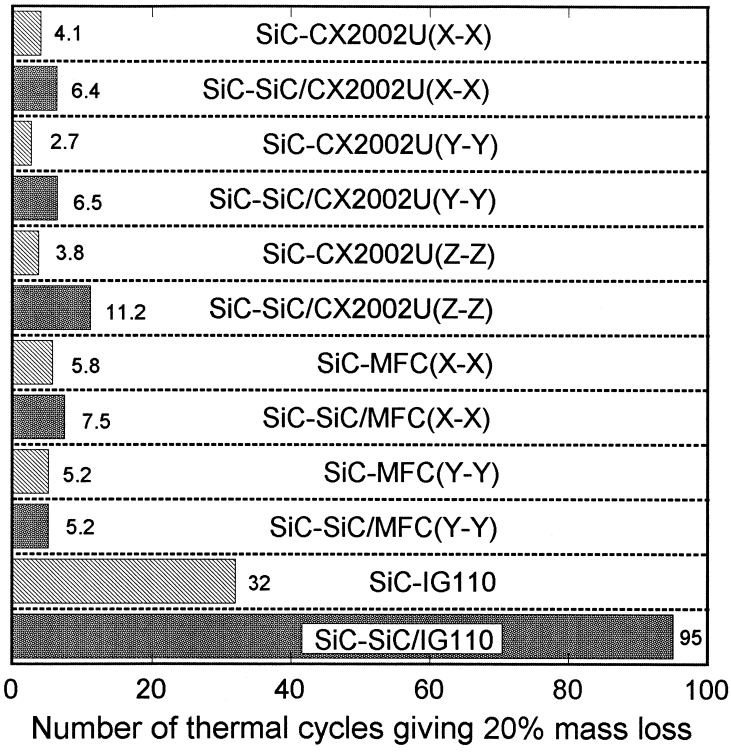

Fig. 4. Number of thermal cycles to cause 20% of mass loss for specimens with and without a SiC/C graded layer, noted as SiC–SiC/substrate and SiC-substrate, respectively. All substrates of CX2002U(CFC), MFC(CFC), and IG-110 (isotropic graphite) were coated with a surface CVD layer.

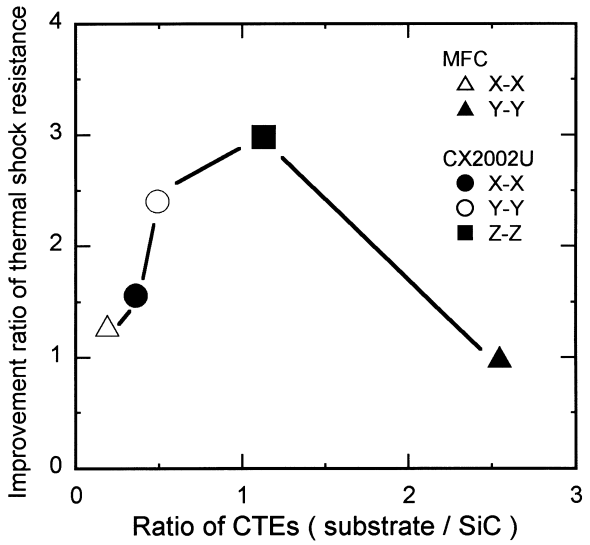

Fig. 5. Ratio of number of thermal cycles causing 20% of mass loss for a specimen with a SiC/C graded layer to that without the layer vs. ratio of CTEs between a substrate and SiC.

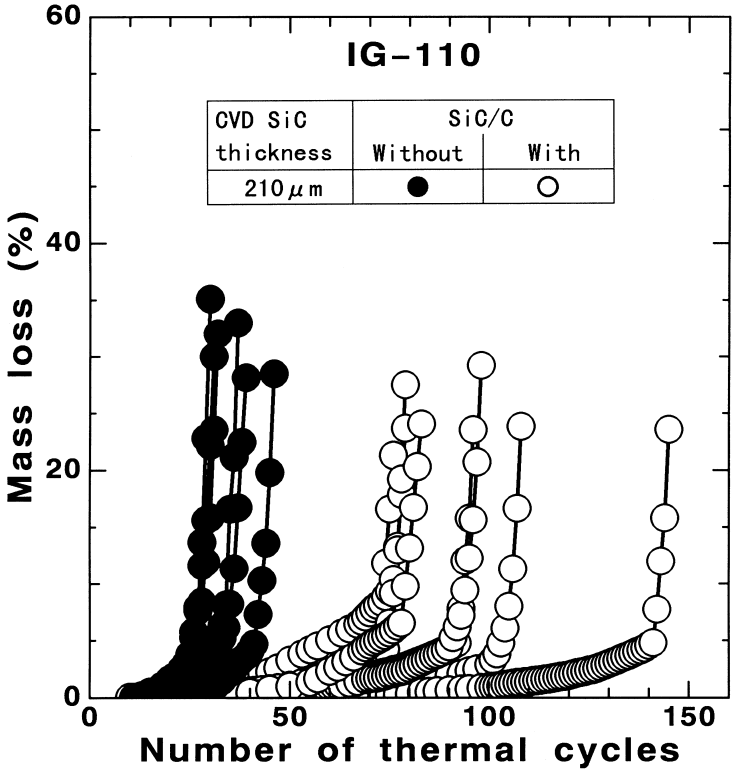

Fig. 6. Mass losses for isotropic graphite specimens with both a surface CVD SiC layer and a SiC/C graded layer, SiC–SiC/IG-110, and those with a surface CVD SiC layer alone, SiC-IG-110, as a function of number of thermal cycles.

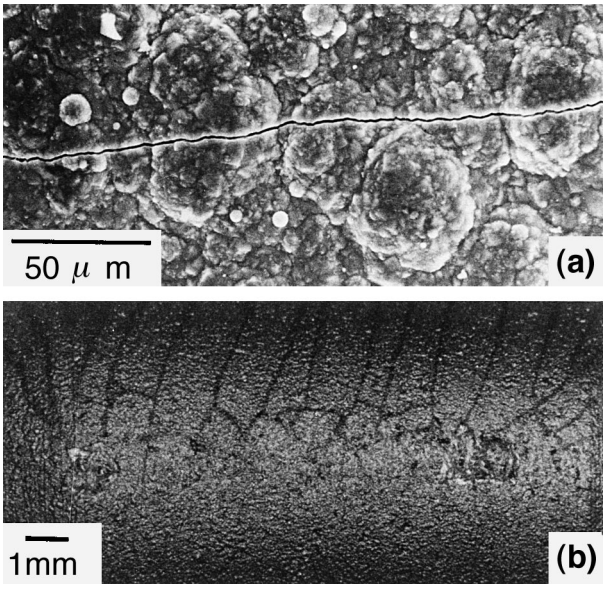

Fig. 7. (a) SEM micrograph of surface morphology of as-received SiC CVD layer of SiC–SiC/CX2002U. (b) Photograph of SiC CVD layer of SiC–SiC/CX2002U after thermal shock tests that caused 15.8% mass loss.

It should be here pointed out that the SiC grading to carbon fibers or felts is much more difficult than to graphite due to low reactivity between SiO and fibers or felts. This difficulty would lead to imperfection of SiC/C layer, which results in less relaxation of interfacial thermal stresses. To increase the thermal shock resistance of CFC materials we need to increase the thickness of the graded layer as well as its perfection by additional measures.

4. Conclusions

Thermal shock tests at a temperature difference of 1000°C in an air were performed to SiC compositionally graded CFC materials, which are composed of a surface CVD SiC layer, a SiC/C graded layer and a substrate of CFC. Both CX2002U and MFC composites showed the increase of thermal shock resistance by forming a SiC/C graded layer, and the layer's effectiveness was larger when a difference in CTE between substrate and SiC was smaller. The thermal shock resistance of the SiC compositionally graded CFC materials was not so good as that of SiC compositionally graded isotropic graphite. The difference is attributable to the fact that the CFC materials originally had surface cracks that occurred at CVD coating prior to thermal shock tests, which would act as paths for species to reach and erode the CFC substrates.

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