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A SiC–Si–ZrB_2 multiphase oxidation protective ceramic coating for SiC-coated carbon/carbon composites

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Abstract

In order to improve the oxidation protective ability of SiC-coated carbon/carbon (C/C) composites, a SiC–Si–ZrB_2 multiphase ceramic coating was prepared on the surface of SiC-coated C/C composite by the process of pack cementation. The microstructures of the coating were characterized using X-ray diffraction and scanning electron microscopy. The coating was found to be composed of SiC, Si and ZrB_2. The oxidation resistance of the coated specimens was investigated at 1773 K. The results show that the SiC–Si–ZrB_2 can protect C/C against oxidation at 1773 K for more than 386 h. The excellent oxidation protective performance is attributed to the integrity and stability of SiO_2 glass improved by the formation of $ZrSiO_4$ phase during oxidation. The coated specimens were given thermal shocks between 1773 K and room temperature for 20 times. After thermal shocks, the residual flexural strength of the coated C/C composites was decreased by 16.3%.

Keywords: C. Thermal shock resistance; C. Mechanical properties; D. SiC; Oxidation protective coating; ZrB_2

1. Introduction

The oxidation problem is an urgent barrier to the application of carbon/carbon (C/C) composites as high-temperature structure materials [1,2]. Applying multiphase ceramic coating is considered as an efficient method to address the oxidation problem of C/C composites [2–5].

SiC is usually applied as a bonding layer between C/C composites and outer layer of coating because of its good physical and chemical compatibility with C/C composites and ceramic coating [5–7]. The oxidation of silicon-based ceramics generates uniform and dense SiO_2 glassy film with low oxygen permeability at high temperature, which provides good oxidation protection for C/C composites [3,7–9]. However, with the increase of oxidation time or oxidation temperature, the holes and bubbles may be formed in the SiO_2 glassy film, which provide channels for oxygen to diffuse into C/C substrate. Moreover, the unitary SiO_2 glass has been found to volatilize slowly and the coating materials also consume gradually [10–12].

ZrB_2 based materials have been indicated as promising candidates for use in aerospace application owing to its several excellent properties, such as high melting point, high strength and good oxidation resistance at high temperature [13–15]. The ZrO_2 from the oxidation of ZrB_2 can reacts with SiO_2 to form $ZrSiO_4$, which has excellent high temperature oxidation resistance ability at 1973 K for a long time [16,17]. The high-thermally stable $ZrSiO_4$ phase exists in the SiO_2 film can be expected to minimize the consumption of SiO_2 and improve the oxidation protective ability of SiC coating at high temperature.

In the present work, a SiC–Si–ZrB_2 coating was prepared by pack cementation on SiC-coated C/C composites. The microstructures of the prepared coating were studied. The anti-oxidation performance at 1773 K and thermal shock properties between 1773 K and room temperature (RT) were investigated.

2. Experimental

Two dimensional C/C composites with a density of 1.70 g/cm^3 were used as a substrate for coating. For measuring the anti-oxidation performance, the sample dimension was kept 10 mm × 10 mm × 10 mm; while for investigating the flexural strength after thermal shock, the sample dimension was kept

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50 mm × 8 mm × 4 mm. Before coating, the samples surface were mechanically abraded using 320 and 800 grit SiC papers. The samples were then ultrasonically cleaned and dried at 373 K. The SiC bonding layer was formed on the surface of C/C composites by the process of pack cementation with Si (300 mesh), C (325 mesh) and Al_2O_3 (300 mesh) powders at 1973–2273 K for 2 h in argon protective atmosphere. The preparation details have been reported elsewhere [7]. The SiC–Si–ZrB_2 exterior coating was prepared on the surface of SiC-coated C/C composites at 2173–2473 K for 2 h in argon protective atmosphere, using analytical grade Si (300 mesh), B_2O_3 (300 mesh), graphite (325 mesh) and ZrB_2 (800 mesh) with a weight proportion of 40–65%, 10–15%, 15–25% and 20–30% respectively.

The isothermal oxidation tests of the coated specimens were carried out in air at 1773 K in an electrical furnace. For thermal shock tests, the coated specimens were kept for 10 min in furnace in air at 1773 K and for 10 min in RT alternatively for 20 times. The specimens were weighted by an electronic balance with a sensitivity of ±0.1 mg. Flexural strengths of the coated specimens before and after thermal shocks were measured by three-point bending test on the CMT-5304 universal machine with the span of 40 mm and the strain rate of 0.5 mm/min. The crystalline structures of the virgin and oxidized coating were structurally analyzed by X-ray diffraction (XRD, X' Pert PRO) and scanning electron microscopy (SEM, JSM-6460) with energy dispersion spectroscopy (EDS).

3. Results and discussion

3.1. Microstructure of the coating

Fig. 1(a–c) illustrates the SEM morphology and XRD patterns of SiC–Si–ZrB_2 outer coating. Fig. 1(a) reveals the coating surface is dense with a great deal of continuous phases. In addition, a microcrack can be seen at the lower-left corner, which may have formed due to the rapid cooling from high temperature to RT during pack cementation process. XRD analysis (Fig. 1(b)) shows that the as-prepared coating is composed of SiC, ZrB_2 and Si. Fig. 1(c) exhibits the cross-section of the as-received multiphase coating. The coating is about 120 μm in thickness without any penetrable cracks or holes. Moreover, there is no obvious crack or gap between the inner SiC coating and the outer SiC–Si–ZrB_2 coating, which indicates a good bonding. These observations indicate the formation a dense multiphase SiC–Si–ZrB_2 coating for SiC-coated C/C composites, which is expected to have much better oxidation resistance than SiC layer in air at 1773 K.

Fig. 2 displays the backscattered electron image of the coating surface. The coating consists of three kinds of crystalline particles characterized by EDS as black SiC (A), white ZrB_2 (B) and gray Si (C). The free Si combines the SiC particles to form a whole which ensures the integrity of the coating. The distribution of ZrB_2 is on the edge of the liquid Si and SiC phase which is expected to improve the oxidation resistance for C/C composites at high temperature.

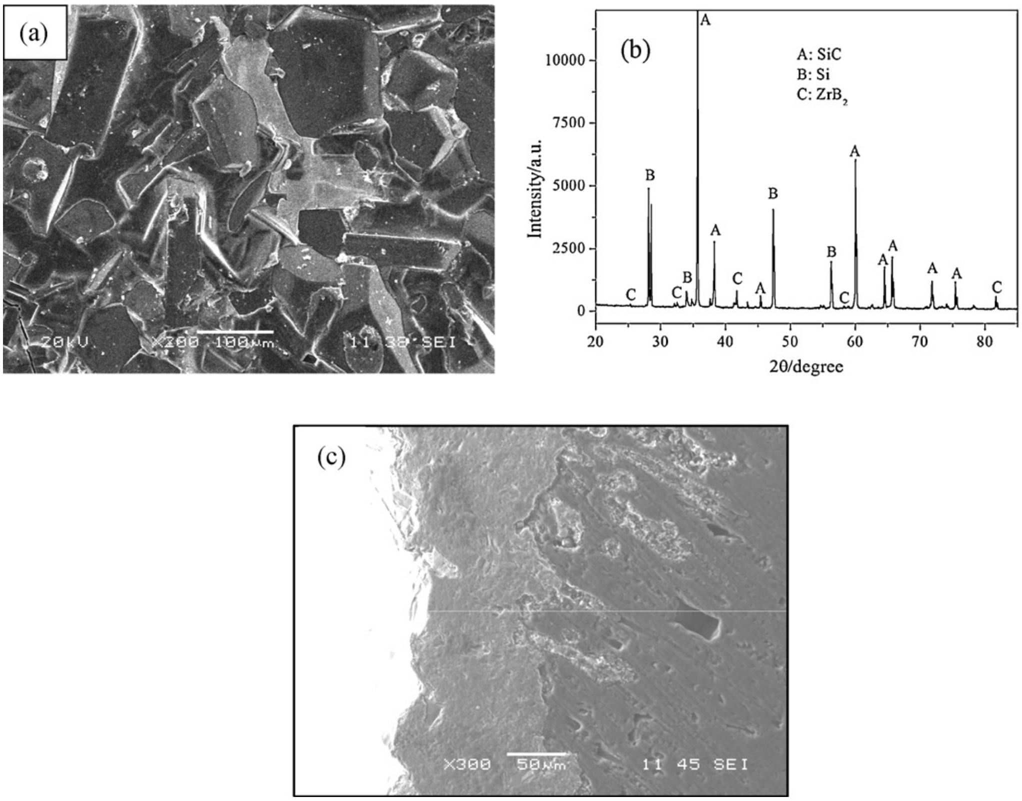

Fig. 1. SEM images and XRD pattern of the SiC–Si–ZrB_2 coating for SiC-coated C/C composites. (a) Surface SEM image, (b) XRD pattern, (c) cross-section SEM image.

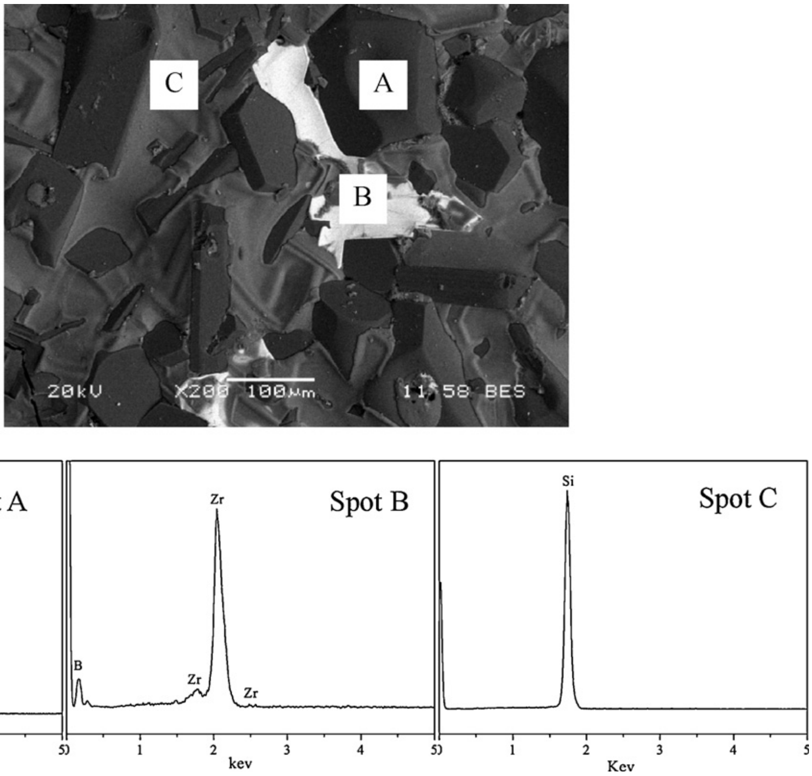

Fig. 2. Backscattered electron image and spot EDS analyses of the surface of the coating on C/C composites.

3.2. Oxidation protective property of the coating

Fig. 3 illustrates the isothermal oxidation curves of the specimens at 1773 K in air. Compared with the double SiC-coated C/C composites, the SiC/SiC–Si–ZrB_2 coated specimen exhibits better oxidation protective ability. The weight loss of SiC-coated C/C composites increases quickly and reaches to 2.5% after oxidation only after 42 h. However, the SiC–Si–ZrB_2 coating can efficiently protect C/C composites from oxidation for more than 386 h with a slight weight gain.

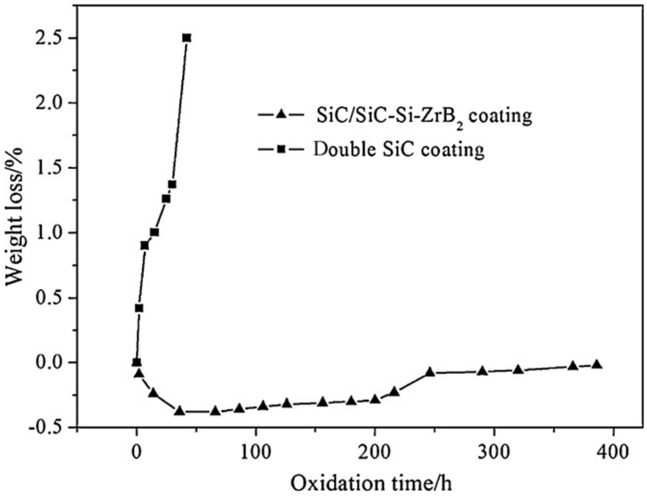

Fig. 3. Isothermal oxidation curves of coated C/C composites in air at 1773 K.

During the oxidation test, the coated specimens react with oxygen as follows:

$$SiC(s) + 2O_2(g) \rightarrow SiO_2(s) + CO_2(g) \quad (1)$$

$$2SiC(s) + 3O_2(g) \rightarrow 2SiO_2(s) + 2CO(g) \quad (2)$$

$$Si(s) + O_2(g) \rightarrow SiO_2(s) \quad (3)$$

$$2ZrB_2(s) + 5O_2(g) \rightarrow 2ZrO_2(s) + 2B_2O_3(g) \quad (4)$$

$$ZrO_2(s) + SiO_2(s) \rightarrow ZrSiO_4(s) \quad (5)$$

According to the oxidation curves as shown in Fig. 3, in the initial stages of oxidation, the coating is exposed to the atmosphere and reacts with oxygen directly according to Eqs. (1)–(4). As a result, the oxides are generated on the surface of the coatings, which results in the increase in the total weight. After 36 h of oxidation, the weight gain reaches to 0.38%. Beyond 36 h, the weight starts decreasing. Because the oxidation of the coating is an increasing process, the slight weight change beyond 36 h oxidation might be attributed to the consumption of glass or the oxidation of C/C composites during oxidation test.

Fig. 4(a) shows the SEM micrograph of the surface of coating after oxidation at 1773 K in air for 386 h, A smooth glassy film with dispersed particles and some microcracks caused by the quick cooling from 1773 K to RT can be seen on the surface which are supposed to be self-sealed by SiO_2 glass when the coating is heated to 1773 K again [18]. The coating is chemically composed of $ZrSiO_4$, SiO_2 and SiC, as reveal by the XRD pattern of oxidized surface of coating as shown in Fig. 4(b). Fig. 5

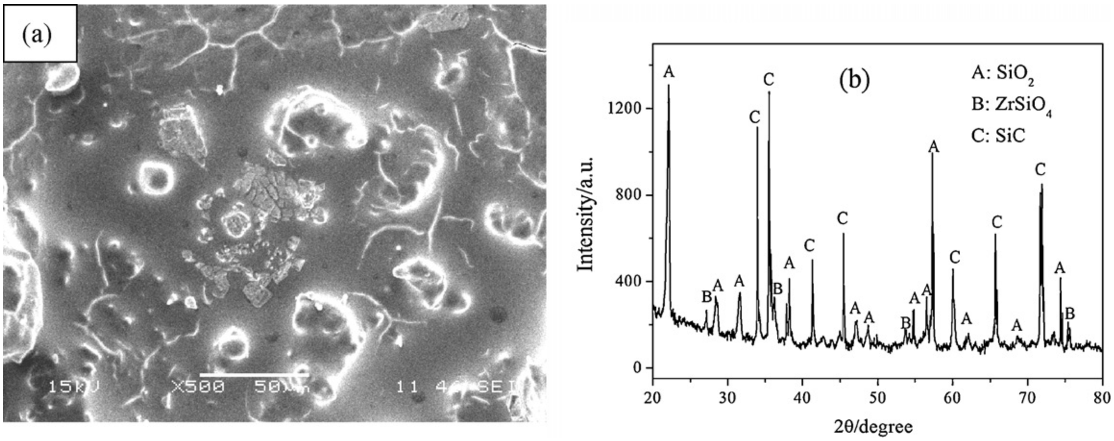

Fig. 4. SEM micrograph and XRD pattern of the coated C/C composites after oxidation for 386 h. (a) Surface SEM image, (b) XRD pattern.

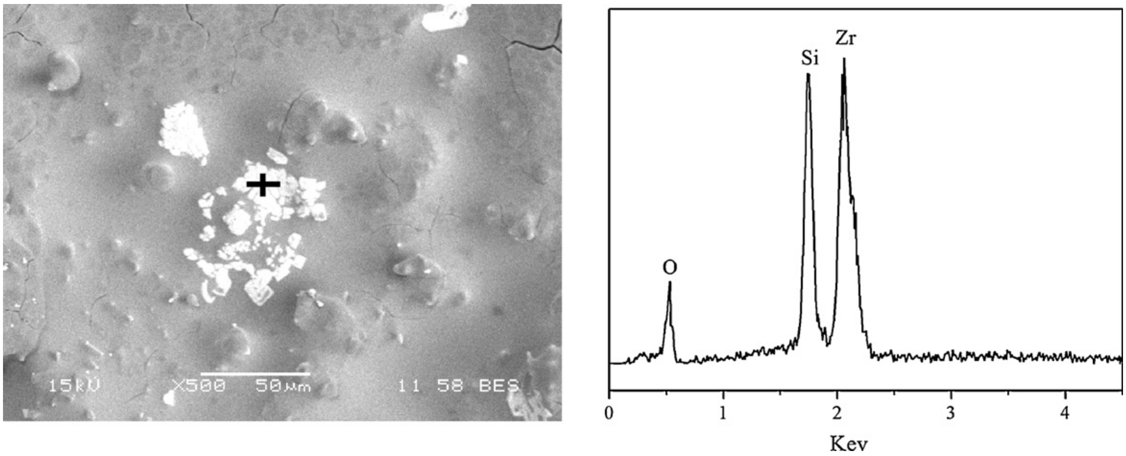

Fig. 5. Backscattered electron image and spot EDS analyses of the coated C/C composites after oxidation for 386 h.

displays the backscattered electron image of the oxidized coating surface. The white particles characterized by EDS are $ZrSiO_4$ which exist in the SiO_2 glassy film. $ZrSiO_4$ has formed when ZrO_2 from the oxidation of ZrB_2 reacts with SiO_2 though Eq. (5). $ZrSiO_4$ has excellent high temperature oxidation resistance ability at high temperature for a long time in air. $ZrSiO_4$ dispersed in the SiO_2 film in the form of granules, which can highly improve the oxidation resistance of C/C composites as compared to double-layer SiC coating. The SiO_2 glassy film exhibits very low oxygen permeability and the $ZrSiO_4$ can further improve the stability of SiO_2 film, which ensures the coating to provide effective oxidation protection for C/C composites at high temperature. As shown in Fig. 4(a), there are no holes and bubbles in the coating surface, which infers that the complex glassy film also improves the integrity of SiO_2 film.

Fig. 6 shows the cross-section micrograph of the multi-layer coated C/C composites after oxidation for 386 h. The multi-layer coating is looking as dense as before oxidation, i.e. no holes or penetrating cracks are found in the coating. The multilayer coating is about 100 μm in thickness after oxidation as compared to the original 120 μm which indicates that the consumption rate of coating is very slow. The ceramic particles are seemed to consume gradually by prolonging oxidation time to form SiO_2 glassy film. It is concluded that oxygen can diffuse through the glass film and react with SiC and ZrB_2 gradually, resulting the formation of thermally stable SiO_2–$ZrSiO_4$ glass.

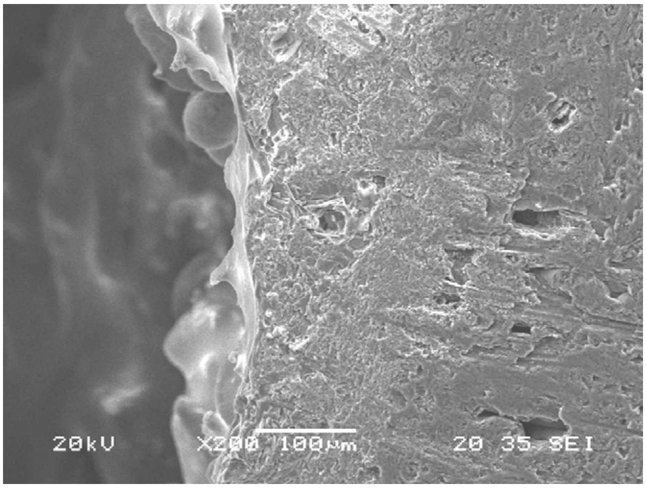

Fig. 6. Cross-section SEM micrograph of the coated C/C composites after oxidation for 386 h.

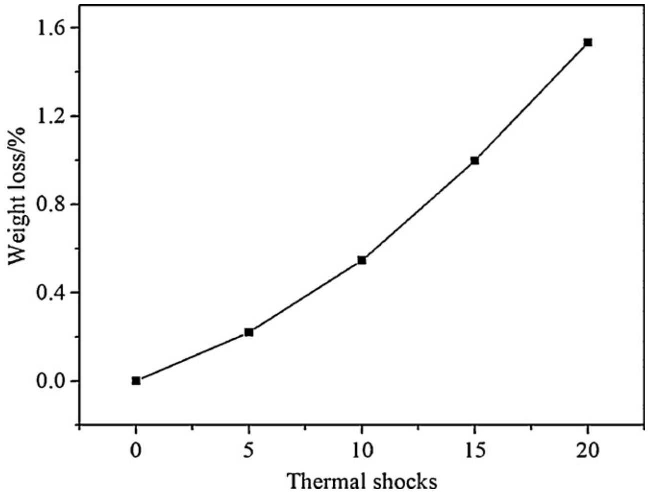

Fig. 7. The weight loss curve of the coated specimen during thermal shock between 1773 K and RT.

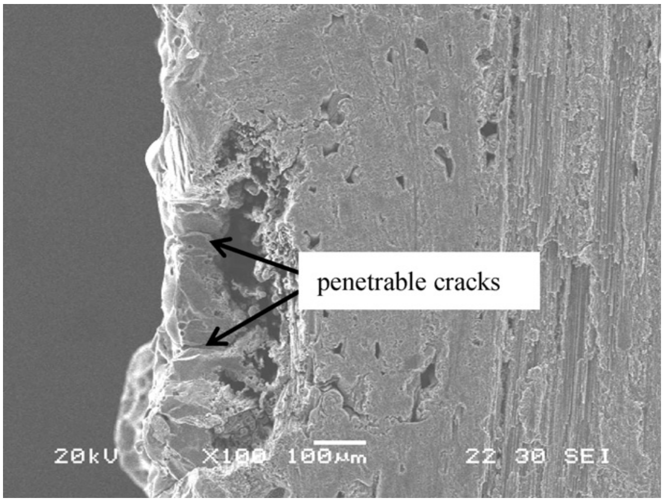

Fig. 8. Cross-section micrograph of coated specimen after 20 thermal shocks between 1773 K and RT.

3.3. *The thermal shock resistance of the coating*

The thermal shock resistance of the multilayer coating was investigated between 1773 K and RT. After 20 thermal shocks, the total weight loss of coated specimens is observed to be 1.53%. The weight loss of the sample increases linearly with the increase in thermal shocks as shown in Fig. 7. The SEM of the cross-section of the coating shows the formation of penetrable cracks after subjected the samples to thermal shocks, as shown in Fig. 8. It can be attributed to the difference in thermal expansion coefficient between coating and substrate. The micrograph also shows the existence of the holes at the end of the penetrable cracks which have formed due to the oxidation of C/C composites.

There are a total of 16 thermal cycles during the 386 h of oxidation from RT to 1773 K. The weight loss of the coated sample during each thermal cycle of oxidation was comparatively smaller than that during thermal shocks in the same temperature range. It can be attributed to the fact that oxidation thermal cycles give sufficient time for the formation of SiO_2 film to heal the cracks, while during thermal shocks the time duration is too short to form the sufficient amount of SiO_2 to heal the pre-existing cracks formed during the preparation and the cracks caused by thermal shocks.

The bending strengths of coated specimens before and after thermal shocks are 55.3 MPa and 46.3 MPa, respectively. The results show a small strength loss (16.3%) after 20 thermal shocks. The decrease on mechanical property of the specimens is attributed to the weight loss caused by the penetrable cracks and the decrease in interfacial bonding.

4. Conclusion

A dense SiC–Si–ZrB_2 coating has been obtained on the surface of SiC-coated C/C composites for the oxidation protection at elevated temperature by pack cementation process. The as-received coating was found to protect efficiently SiC-coated C/C composites from oxidation at 1773 K for more than 386 h. The excellent anti-oxidation property of the coating can be attributed to the formation of integrity layer of the SiO_2–$ZrSiO_4$ glass. Moreover, the weight loss is only 1.53% and the flexural strength retention is 83.7% after 20 thermal shocks between 1773 K and RT.

Acknowledgements

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