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Anti-oxidation and Infrared Characteristics of ZrSiO4 Coating

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Abstract. In this paper, preparation and properties of ZrSiO4 coating prepared by pressureless sintering coated carbon/carbon (C/C) composites and the effect of different temperature on coating in 3-5μm and 8-12μm infrared emissivity were studied. The composition and structure of the ZrSiO4 coatings were examined by XRD and SEM that showed the main phase was ZrSiO4. With the addition of mineralizer, ZrSiO4 synthesis rate increased from 68.58% to 83.47%. The anti-oxidant performance of the prepared SiC layer and SiC-ZrSiO4 coating at 1500℃ in air for 24h with a mass loss was 1.5% and 0.4%, respectively. In addition, the experimental results indicated that the emissivity of ZrSiO4 coating declined with the decrease of ZrO2, and the infrared emissivity of ZrSiO4 coating in the 3-5μm and 8-14μm wavebands was 0.55 and 0.64 at 50℃, 0.18 and 0.43 at 300℃, 0.35 and 0.74 at 500℃, respectively.

1 Introduction

In recent years, the rapid development of aerospace technology and modern needs of war, has led to the continuous improvement of Mach number of flights. Aircraft parts that undergo aerodynamic heating need to withstand more high temperature and thermal shock during flight. Hence, high temperature resistant and low emissivity materials play an important role in modern weapon system [1]. Infrared stealth includes near-infrared (1-2.7 μ m), mid-infrared (3-5 μ m), and far infrared (8-14 μ m) three atmospheric windows. Among these, 3-5 μ m and 8-14 μ m wavebands are the most important infrared detected wavebands [2]. ZrSiO4 is a tetragonal structure with the islands of silicate minerals. Due to its high melting point, low thermal conductivity, low thermal expansion coefficient, excellent chemical and phase stability and other characteristics, ZrSiO4 is widely used in the high-temperature environment. Moreover, sintered ZrSiO4 has excellent thermal shock resistance. It is therefore an important candidate for high temperature structural ceramic materials [3, 4].

ZrSiO4 has rarely been reported as a high-temperature ceramic coating, especially considering the infrared stealthy characteristic and the traditional technologies, such as chemical vapor deposition, plasma or thermal spraying, sol-gel andelectrophoretic deposition. The preparation of ZrSiO4 coatings is complex, and the production cycles are long, making it not suitable for large complex shape components. Hence, pressureless sintering ZrSiO4 coating is a good choice. This paper describes a pressureless sintering method for synthesizing ZrSiO4 ceramic coatings and a preliminary investigation was undertaken to measure the performance of the coating.

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2 Experimental details

Small specimens (100×100×5mm3) as substrates were cut from bulk 2D-C/C composites (prepared in Changsha China) with a density of 1.70 g/cm2. Before the coating process, the specimens were cleaned using ultrasonic cleaner for 5 min,and dried at 100℃ for 2 h. SiC bonding coating was prepared by a method of CVD (Chemical Vapor Deposition) for 10 h. An SiC coating structure was achieved with a thickness of about 20μm.

After the preparation of the SiC buffer layer, an in-situ formation process was conducted. ZrSiO4 coating was prepared using the optimal sintering additive MgO. The commercially available powders of MgO, ZrO2 and SiO2 are of analytical grade with a particle size from 1 to 4 μm. Raw materials formula are shown in Table 1, which LiF and CaCl2 are used as mineralizer.

Table 1. Raw materials formula.

Formula	ZrO_2	SiO2	MgO	LiF	$CaCl_2$
ZS-1	123	72	5.85	/	/
ZS-2	123	72	5.85	1.95	3.9

The starting powders were mixed for 12 h by ball milling in water-free ethanol with an agate media, and then dried at 70℃ for 12 h. First, a slurry of powders was applied to the SiC coating surface. It was made by mixing the powders, distilled water and a little PVB (polyvinylbutyral) (0.5~1wt.%) binder.

After applying the slurry to the surface of the SiC bonding layer, the samples were dried in air for sufficient time. Finally, the pressureless sintering of bar samples was conducted in a high-temperature furnace with with 1 atm argon gas, by heating at a ramp rate of 5℃•min-1 from room temperature to 500℃ and then heating at a ramp rate of 10℃•min-1 to 1500℃, holding for 1.5h at this temperature to transfer into ZrSiO4.

After sintering, the preparation of ZrSiO4 coating was applied directly to the surface of SiC coating. Product phases were characterised by X-ray diffraction (XRD) using a D/MAX-RB diffractometer and CuKα1 radiation for the range 15° ~80° in 2θ with a step-width of 0.02°. The morphologies of the as-prepared multi-layer coatings were analyzed using JEOL-6360LV scanning electron microscope (SEM). The anti-oxidation property of the ZrSiO4 coating was studied at 1500℃ using tubular oxidation furnace (Type SK-1600℃, Tianjin, China). Using emissivity measuring instrument, the average infrared emissivity of samples was measured at different temperatures in the 3-5μm and 8-14μm (Test in Xi'an Institute of Applied Optics).

3 Results and discussion

3.1 Composition and Structure Analysis

Fig. 1 shows the XRD spectrum of ZS-1 and ZS-2 formulas. It was found that both of the main phases were ZrSiO4, though a small amount of ZrO2 and SiO2 were detected. But compared to the ZS-1 formula, ZS-2 formula relative intensity of ZrO2 and SiO2 is significantly lower than ZS-1 formula with higher relative intensity of ZrSiO4. This is because on the basis of ZS-1 formula, ZS-2 formula accordingly added a little mineralizer which are LiF and CaCl2, improving the conversion rate of ZrSiO4 obviously. From the chemical reaction dynamics analysis, the role of mineralizer is mainly due to the formation of active reactive groups in the synthesis process, thereby reducing the activation energy. So the synthesis rate of ZrSiO4 increase at a certain temperature [5]. R. A. Epplerm [6] first quoted famous symbol method to study the ion diffusion problems, and thus explained the mechanism of how the mineralizer to improve zirconium silicate synthesis rate. By using the following formula to calculate a relative content of ZrSiO4 phase:

$$W=Ai/\sum Aij*100\% \quad (1)$$

Where Ai is the relative integral area of ZrSiO4 strongest peak and Aij the sum of the relative integral area of all phases strongest peak.

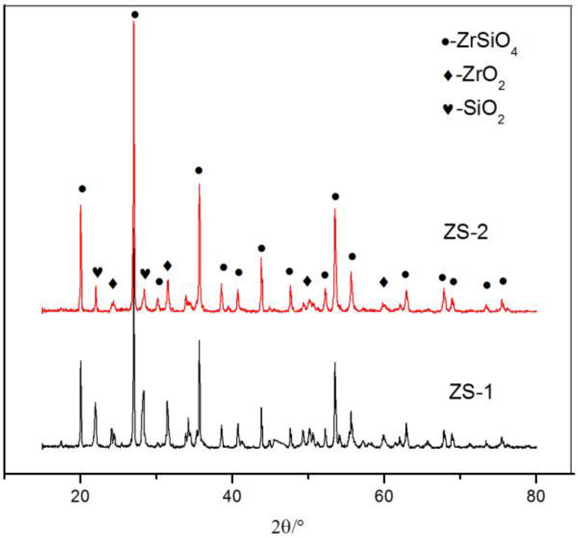

Figure 1. XRD spectrum of the ZrSiO4 coating.

From XRD analysis calculations, the peak integral area and relative content of ZrSiO4 prepared from ZS-1 formula and ZS-2 formula are about 68.58% and 83.47,respectively. So with the addition of mineralizer, ZrSiO4 synthesis rate increased obviously.

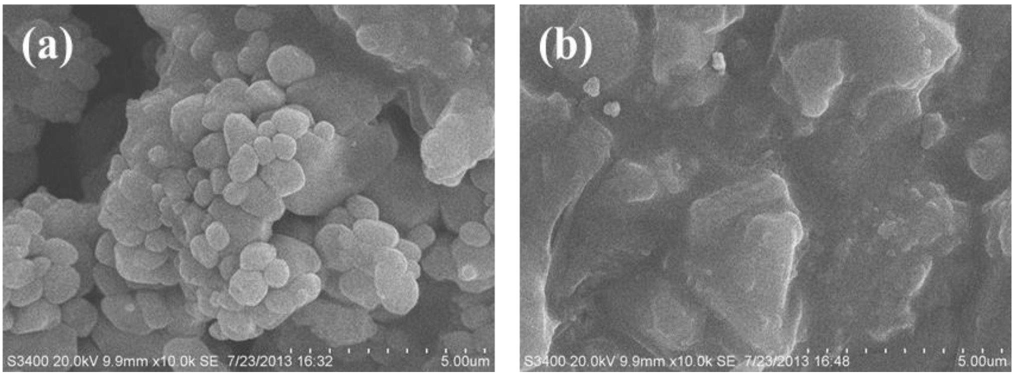

Figure 2. Surface SEM microstructures of coating: (a) ZS-1; (b) ZS-2.

Fig. 2 shows the coating surface SEM microstructures pictures of ZS-1 and ZS-2. It can be seen from the Fig. 2(a) that a lot of tiny particles covered on a large grain which is ZrSiO4 grain, and the tiny particles can be regarded as ZrO2 particles. However, in Fig. 2(b), these tiny particles covered on ZrSiO4 grains were rare. This is because as the mineralizer was added, most of the ZrO2 transform to ZrSiO4 completely. And the images displayed that the ZrSiO4 grains embedded in the glass state, which might be SiO2 melting. From Fig. 2(b), SiO2 melting wrapped ZrSiO4 grains, well filled in the gaps between the grains, which indicated SiO2 can effectively fill the cracks between the grain boundaries, prevent grain boundary diffusion of oxygen. This improves the oxidation resistance of coating.

3.2 Oxidation Resistance

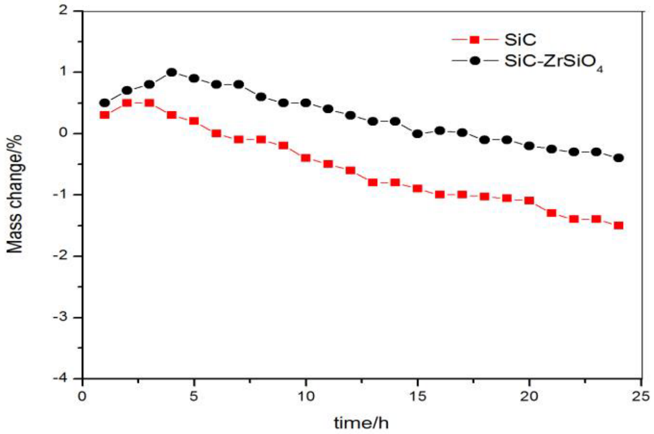

Figure 3. Isothermal oxidation curves for samples of the ZS-2 coating at 1500℃

Due to the higher synthetic rate of ZrSiO4, we chose ZS-2 for oxidation resistance test. Fig. 3 shows the isothermal oxidation curves for samples of the coating at 1500℃. The mass rate of both curves at the beginning of the oxidation was increased first, and then decreased slightly. Mass loss of SiC-coated C/C was 1.5% during 24h oxidation, which indicated that the as-prepared SiC coating could effectively protect C/C during the oxidation process. This is because in high temperature air, SiC coating surface generates a dense thin layer of SiO2, which can effectively block the diffusion of oxygen [7,8]. The formation of the SiO2 was attributed to the reactions displayed in Eqs. (2)

$$SiC+2O2 \rightarrow SiO2+ CO2 \qquad (2)$$

This explains why the weight had some increase at the start of oxidation experiments. Even though SiC caoting can effectively protect C/C, it is not employed in practial application. Because at the temperature above 1400 ℃ stage, SiO2 melted into liquid, can effectively fill the cracks, which can exhibit excellent oxidation resistance, but in the medium temperature stage, the viscosity of SiO2 is very big, which can not fill the micro-cracks in the coating, and in the environment of high temperature scouring, SiO2 is easily torn away, so it is necessary to prepare a coating of high temperature oxidation resistant coating on the surface of SiC layer. From Fig. 3, ZrSiO4/SiC coating has a better oxidation resistance than SiC coating and there is almost no mass loss in the progress of oxidation. The mass loss of ZrSiO4/SiC-coated C/C was only 0.4% during 24h oxidation. As a result of the preparation of dense ZrSiO4 ceramic coating, O2- did not easily diffuse into the coating surface, to combine with the SiO2 liquid glass phase formed at high temperature. This can effectively make up for the microcracks to prevent the diffusion of oxygen. As shown in the Fig. 2(b), ZrSiO4 grains embeded in SiO2 glass state, and the coating has no microcracks, so the oxidation rate of the coating depends on the diffusion rate of oxygen in the ZrSiO4 and SiO2. At the same time, SiC used as a buffer layer, also forming a dense SiO2 layer on the surface in high temperature, can prevent oxygen diffusing, which further improves the property of oxidation resistance.

3.3 Infrared Characteristics

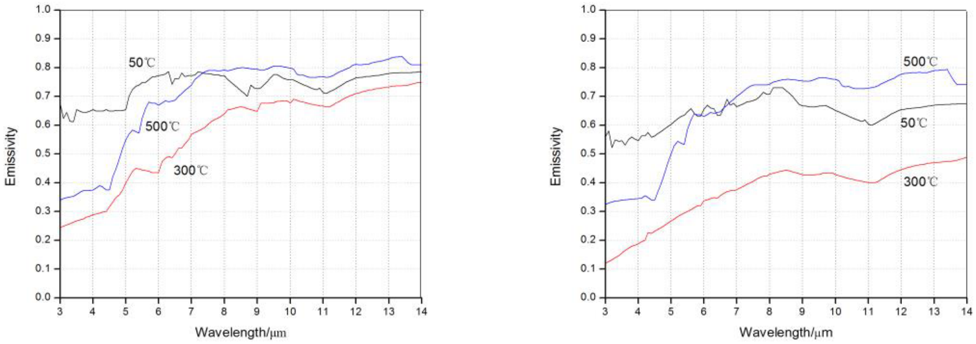

Figure 4. Spectral emissivity curves for ZrSiO4 coating at different temperature: (a) ZS-1; (b) ZS-2

Figure 4 shows the emissivity curves for ZrSiO4 coating at 50℃, 300℃ and 500℃. It can be seen from the picture that the emissivity of ZrSiO4 coating was the lowest when the temperature is at 300 ℃ and the measured value of infrared emissivity is increasing with the wavelength increase. When the temperature is above 300℃, the emissivity increases. When the wavelenght is above 7 μm， the emissivity at 50℃ is lower than that at 500℃. Compared with Fig. 4(a) and (b), the emissivity of ZS-2 is lower than ZS-1, overall. From Fig. 4(b), the emissivity of 3-14 μ m band of ZrSiO4 coating is less than 0.8 at different temperature which expresses an excellent infrared characteristic. Kruse et al. [9] according to the experimental results thought that the emissivity decreases with temperature for non-metallic materials. However, in this study, the emissivity of ZrSiO4 coating presents a different rule. This may be because the residual ZrO2 changes the trend that the emissivity decreases with temperature increase. When the temperature is above 300℃, residual ZrO2 on the emissivity have a significant impact, the residual ZrO2 more, the temperature higher, the emissivity higher.

Table 2. Average emissivity

	The average emissivity			
	ZS-1		**ZS-2**	
	3-5μm	8-14μm	3-5μm	8-14μm
50℃	0.65	0.71	0.55	0.64
300℃	0.28	0.68	0.18	0.43
500℃	0.38	0.79	0.35	0.74

Table 2 lists average emissivity of ZS-1 and ZS-2 in the 3-5 μ m and 8-14 μ m wavebands at different temperatures. The emissivity on 8-14 μ m waveband is higher than the emissivity in 3-5 μ m waveband at any temperature. From ZS-1 formula, the emissivity of both bands are the lowest with value of 0.28 and 0.68 when the temperature is at 300℃, while the lowest value of the emissivity of ZS-2 is 0.18 and 0.43 when the temperature is at 300 ℃. Compared with ZS-1, the data of ZS-2 emissivity is lower, which indicated that the emissivity of ZrSiO4 coating declined with the decrease of ZrO2. This may be because, in ZS-1 formula, many of the remaining ZrO2 will cause vibration strongly and affect absorption of infrared radiation, thereby increasing the infrared emissivity of the coating. And the effect of ZrO2 on the emissivity is more evident in the high temperature. Before 300℃, the emissivity of ZrSiO4 is mainly determined by the temperature, so the emissivity declease with the temperature increase. Due to the fact that higher the temperature of an object, the better the crystallinity and periodicity of crystal, so emissivity declined; After 300℃, ZrO2 content on the emissivity plays a main role, so at 500℃, the emissivity has increased significantly.

4 Conclusions

ZrSiO4 ceramic coatings were prepared by pressureless sintering in a argon atmosphere at 1500℃. With the addition of mineralizer, ZrSiO4 synthesis rate increased from 68.58% to 83.47%. The anti-oxidant performance of the prepared SiC layer and SiC-ZrSiO4 coating at 1500℃ in air for 24h with a mass loss was 1.5% and 0.4%, respectively. The average infrared emissivity of ZrSiO4 coating in the 3-5 μ m and 8-14 μ m wavebands decreased with increase temperature. The emissivity of ZrSiO4 coating declined with the decrease of ZrO2, and the infrared emissivity of ZrSiO4 coating in the 3-5 μ m and 8-14 μ m wavebands was 0.55 and 0.64 at 50℃, 0.18 and 0.43 at 300℃, 0.35 and 0.74 at 500℃, respectively.

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References

1. J. Zueco, F. Alhama., J. Quant. Spectrosc. Radiat. Transfer, **14**, 7 (2006)
2. Y. T. Jiang, Y. Wang. Infrared Technology, **25**, 5 (2003)
3. Y. Shi, X.X. Huang, D.S. Yan, J. Eur. Ceram. Soc., **13**, 2 (1994)
4. Y. Kubeta, S. Yamamoo, T. Mori, J. Ceram. Soc. Jpn., **102**, 1 (1994)
5. J. Wen，S. Z. Sun, Bulletin of The Chinese Ceramic Socity, **18**, 6 (1999)
6. R. A. Eppler, J. Am. Ceram. Soc, **53**, 8 (1970)
7. J. D Buekley, D. D Edie, Noyes Publications,USA (1993)
8. O. V. Mazurin, Handbook of glass data-Part A, Silica glass and binary silicat glasses, **15**, (1985).
9. W. P. Kruse, D. Laurence, McGlauchlin, Elements of Infrared Technology. New York: Wiley, (1962)