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Comparative study of $MoSi_2$-borosilicate glass coatings on fibrous ceramics prepared by in-situ reaction method and two-step method

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ABSTRACT

Two infrared radiating coatings with borosilicate glass as binder and $MoSi_2$ as emittance agent were prepared on mullite fibrous ceramics by an in-situ reaction method and a two-step method, respectively. The in-situ reaction coating was prepared from Si, B_2O_3 and $MoSi_2$, in which borosilicate glass was obtained through the in-situ reaction of Si, B_2O_3 and O_2. By contrast, the two-step method included the preparation of borosilicate glass powders by a melt-quench technique and then coating preparation with $MoSi_2$ and the glass powders. The structure, phase composition, thermal endurance, infrared radiation property and impact resistance of the two coatings were compared. The results showed that the in-situ reaction coating was denser, and much less $MoSi_2$ therein was oxidized during sintering (11.3%) than that in the two-step coating (67.0%), resulted from the oxygen diffusion barrier formed by molten B_2O_3 at approximately 450 °C. The in-situ reaction coating possessed better thermal endurance due to its higher $MoSi_2$ content and denser structure. In addition, the in-situ reaction coating had higher emissivity (0.787) and better impact resistance (0.051 J) than the two-step coating (0.706, 0.038 J).

1. Introduction

Fibrous ceramics are promising insulation materials with inorganic fibers as matrix and glass as high-temperature binders [1]. They are widely used in aerospace and industrial fields for energy conservation and thermal insulation [2,3] because of their good thermal endurance, excellent thermal shock resistance, ultra-low thermal conductivity and density [4,5]. The insulating effect of them will be greatly improved when coated with an infrared radiating coating, which can re-radiate heat away and reduce surface temperature [6–8]. For example, a spacecraft, at a pressure of 0.24 atm and a speed of Mach 10, with surface emissivity of 0.5 and 1.0 has a surface temperature of 2400 °C and 2100 °C, respectively [9].

Infrared radiating coatings comprise an emittance agent which can improve radiation property, and a binder which can be coupled with the emittance agent and the substrate [10,11]. Glasses are regarded as versatile binders of coatings for their chemical stability, tailorable thermal and mechanical properties, and self-sealing property [12,13]. In this study, borosilicate glass was chosen as the binder for its good wetting on fibrous ceramics and relatively low thermal expansion coefficient [14,15]. Meanwhile, molybdenum disilicide ($MoSi_2$) with a high melting point (2020 °C), relatively low density (6.24 g/cm^3) and excellent high-temperature oxidation resistance [16,17] was chosen as the emittance agent.

As for the coating preparation method, most glass coatings were prepared by a two-step method, in which glass powders with specific compositions were firstly prepared by a melt-quench method [12,18,19], and then the as-prepared glass powders were used as raw materials for coating preparation by diverse technologies, such as plasma spraying [20], sol-gel method [21], and electrophoretic deposition [22]. The method had also been used to prepare $MoSi_2$-glass coatings on fibrous ceramics, and the coatings had a common problem, that is, the oxidation of $MoSi_2$ during preparation. Wang et al. [23] prepared a gradient $MoSi_2$–BaO–Al_2O_3–SiO_2 glass coating on mullite fibrous ceramics with high bonding strength and excellent thermal shock resistance; nevertheless, most of the $MoSi_2$ was oxidized during coating preparation,

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and plentiful oxidation products including Mo and Mo_5Si_3 existed in the prepared coating. Shao et al. [24] prepared a $MoSi_2$-borosilicate glass coating on ZrO_2 fibrous ceramics and increased the $MoSi_2$ content in raw materials to 80%; however, the results showed that most $MoSi_2$ was oxidized in the prepared coating and the coating surface was infested with pores and cracks. These $MoSi_2$-glass coatings prepared by the two-step method were commonly faced with the oxidation of $MoSi_2$ during coating preparation, which would harm the infrared radiation property and thermal endurance of the coatings.

Novel in-situ reaction method was put forward to prepare $MoSi_2$-borosilicate glass coating and solve the above problem. Silicon (Si) and boron oxide (B_2O_3) were employed as raw materials instead of glass powders, and borosilicate glass was obtained through the in-situ reaction of Si, B_2O_3 and O_2 during the sintering process of the coating. In this study, two $MoSi_2$-borosilicate glass coatings with the same initial composition were prepared on mullite fibrous ceramics by an in-situ reaction method and a two-step method, respectively. Their microstructures and phase compositions were compared, and the oxidation of $MoSi_2$ was investigated. In addition, thermal endurance, infrared radiation property and impact resistance of them were measured and the results showed that the coating prepared by an in-situ reaction method outperformed the two-step coating in all aspects.

2. Experimental

Polycrystalline mullite fibrous ceramic blocks (70 mm × 70 mm × 10 mm) with a density of 0.40 g/cm^3 and compressive strength of 0.85 MPa were chosen as the substrates. The substrates were firstly polished with 2000 grit SiC abrasive paper and then cleaned with a vacuum sweeper before coating preparation.

Two $MoSi_2$-borosilicate glass coatings were prepared on fibrous ceramics by an in-situ reaction method and a two-step method, respectively, in which the molar ratio of SiO_2, B_2O_3 and $MoSi_2$ was 6:1:1.7. We assumed that Si would be fully oxidized to form borosilicate glass in the in-situ reaction coating, and therefore, the two coatings will have the same composition.

Coating preparation mainly included slurry preparation, coating depositing and sintering. In the in-situ reaction coating, Si (1 μm, Jinan Tianqin Silicon Industry, China) and B_2O_3 (200 mesh, Tianjin Guangfu Chemical Co., China) were mixed with $MoSi_2$ (2 μm, Qinghuangdao Eno Material, China) and deionized water by ball milling to form a homogeneous slurry with solid content of 50%. In the two-step coating, borosilicate glass powders were firstly prepared from fused silica (300 mesh, Xuzhou Sainuo Quartz Co. Ltd., China), B_2O_3 and alumina (0.5 wt%, 3000 mesh, Zhengzhou Yiyang Aluminum Co. Ltd., China) by a melt-quench technique. The XRD pattern of the prepared borosilicate glass powders was shown in Fig. 1, which suggested the amorphous nature of the glass powders. Then the glass powders and $MoSi_2$ were mixed with deionized water, ball milled to form the coating slurry. After slurry preparation, the slurries were deposited on fibrous ceramics by brushing, and finally the fully dried specimens were sintered in a tabular oven at 1500 °C for 1 h, under air atmosphere.

Field Emission Scanning Electron Microscope (S-4800, Hitachi, Japan) was employed to characterize coating structure. The crystalline phases in the coatings and the molecular structure of the glasses were identified by XRD (Cu Kα radiation D/Max-2500, Rigaku, Japan) and FTIR (WQF-510, Mitech Instrument, China), respectively. Besides, the oxidation degrees of $MoSi_2$ in the two coatings were compared by DSC analysis (STA 449C, Netzsch, Germany), obtained at a heating speed of 10 °C/min from 50 °C to 1500 °C in static air. Dried specimens were calcined at 600 °C for 15 min before sintering to investigate the oxidation of $MoSi_2$. Isothermal oxidation test at 1500 °C for 40 h was carried out to compare the thermal endurance of the coatings. The infrared emissivity was measured by IR Spectroradiometer (SR-5000N, CI Systems, Israel) with a speed of 0.5 μm/min; the specialized samples were 40 mm in diameter and 1 mm in height, with coatings deposited on the upper surface. Electronic Charpy Impact Testing Machine (XJJD-5, Chende Jinjian, China) was employed to evaluate the impact resistance of the coatings; the coatings were deposited on substrates with dimensions of 60 mm × 10 mm × 5 mm, and the tests were conducted on the entirety.

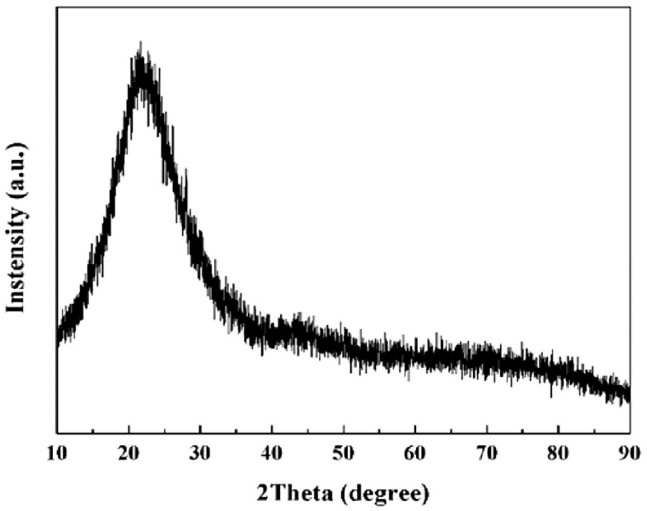

Fig. 1. XRD pattern of borosilicate glass powders.

3. Results and discussion

3.1. Microstructural characterization of the $MoSi_2$-borosilicate glass coatings

The morphology of the $MoSi_2$-borosilicate glass coatings were shown in Fig. 2. The cross-sectional micrographs (Fig. 2a,b) show that the thicknesses of the coatings were approximately 250 μm; the in-situ reaction coating was dense and uniform with favorable interface bonding, while the two-step coating was uneven and coarse. The surface micrograph evidenced the flat and smooth characteristics of the in-situ reaction coating (Fig. 2c); by contrast, big and non-uniform pores were observed in the two-step coating (Fig. 2d), demonstrating that the coating was not fully densified during sintering.

In the sintering process, glass coatings experienced glass redistribution, grain rearrangement and viscous flow to realize densification and planarization, and therefore, the densification degree of the glass coatings mainly depended on the glass liquid viscosity at the sintering temperature [25,26]. A log-mean approximation for viscosity (η) calculation was used to estimate the viscosity of borosilicate glass in the two-step coating at 1500 °C [13]:

$$\mathrm{Log}_{10}\,\eta = 11 - 9X \quad (1)$$

where X stands for the molar ratio of B_2O_3, and the calculated viscosity was 5.17 GPa s. While in the sintering process of the in-situ reaction coating, Si melted at about 1400 °C and material migration within the coating was thereby promoted; then the molten Si was oxidized into SiO_2; finally, homogeneous borosilicate melt