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Effect of glass phase content on structure and properties of gradient $MoSi_2$–BaO–Al_2O_3–SiO_2 coating for porous fibrous insulations

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ABSTRACT

The gradient $MoSi_2$–BaO–Al_2O_3–SiO_2 ($MoSi_2$-BAS) coating with $MoSi_2$ as high emissive agent, BAS glass as binder and B_2O_3 as annexing agent has been prepared on porous fibrous insulation, and the influence of B_2O_3 content on their structure and properties has been investigated. The addition amount of B_2O_3 affects the formation of liquid glass phase during the sintering. As the B_2O_3 content increases, the $MoSi_2$-BAS coatings gradually change from a porous structure into a dense structure with obviously decreasing porosity. A desired gradient coating consisting of a porous bonding-layer and a dense surface-layer has been obtained by adding 2 wt% or 4 wt% B_2O_3, while the porous coating has been obtained without B_2O_3 and the dense coating with 6 wt% or 8 wt% of the B_2O_3. Then the interface bonding strength and thermal shock resistance of the $MoSi_2$-BAS coatings were measured. The results show that the gradient coatings have much better interface bonding strength (1.4 ± 0.1 MPa) and thermal shock resistance (75 cycles without cracking) than the porous coating (0.9 ± 0.1 MPa, 60 cycles with cracking) and the dense coating (0.7 ± 0.1 MPa, 30 cycles with cracking).

1. Introduction

High temperature resistance coatings have been widely used on the surface of the first to the third generation ceramic insulation tiles on the space shuttle such as RSI (Reusable Surface Insulation), FRCI (Fibrous Refractory Composite Insulation) and AETB (Alumina Enhanced Thermal Barrier) [1]. These coatings provide enhanced radiant heat transfers from refractory surfaces [2–5], which is an important path to avoid thermal failure of ceramic insulation tiles on the surface of vehicles [6–9]. Therefore, high temperature resistance coatings are important for the thermal control of high temperature conditions [10–12], especially for thermal protection [13–17], radiative cooling applications [18] and electrical insulation [19]. These harsh application environments have raised a higher requirement for the coating, and then the coating with good thermostructural and functional properties has attracted tremendous attention recently [20].

National Aeronautics and Space Administration (NASA) has developed a series of high temperature resistance coatings ranging from dense coating to gradient porous coating. Fletcher et al. [21] prepared a unilaminar dense Reaction Cured Glass (RCG) coating consisting of SiB_4, SiB_6 powders and borosilicate glass, and this coating could be used at temperatures up to 1260 °C. Beggs et al. [22] prepared a dense two-layer coating consisting of a surface-layer with high scattering coefficient and a bonding-layer with high infrared emissivity, and this coating could withstand the temperature up to 1700 °C. Mahadik et al. [23] prepared a double layer Al_2O_3/SiO_2 coating which could retain its properties when it was exposed at 1000 °C in air. These dense coatings exhibited excellent high temperature stability, oxidation resistance and water proof properties. However, the thermal shock resistance of these dense coatings needed further enhancement, especially for porous fibrous insulations, because they were prone to crack and peel off from the matrix under the dramatic changes in temperature resulting from the structural mismatching and thermal stress concentration.

Kourtides et al. [24] prepared a protective porous coating that showing good combination with the matrix from SiO_2 powder, colloidal SiO_2 and emissive agents (for instance SiC, SiB_4, SiB_6 powders). Leiser et al. [25] declared a Toughened Uni-piece Fibrous Insulation (TUFI) coating owning gradient porous structure. The gradient porous structure could increase the toughness of coating

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by preventing the crack propagation, therefore, the impact resistance of the TUFI coating was greatly improved comparing with dense RCG coating though they have the same components. Furthermore, compared with dense coating, gradient porous coating had higher interface bonding strength and thermal shock resistance due to the similar structure between the coating and matrix provided more gradual transition which could decrease the concentration of stress at the interface.

Owning to the gradient porous structure, TUFI [25] coating became a promising candidate with good properties which has received much attention currently. The gradient porous structure of the TUFI coating was implemented by ball milling raw material to a certain size to control slurry infiltration. In this work, we got the gradient porous structure by controlling the amount of liquid glass phase formed during sintering. A high temperature resistant porous gradient $MoSi_2$-BAS coating was prepared on the porous fibrous insulations using $BaO–Al_2O_3–SiO_2$ (BAS) glass as binder, $MoSi_2$ as high emissive agent and B_2O_3 as annexing agent. B_2O_3 with contents of 0 wt% to 8 wt% was added into the coating to study the effect of glass phase on structure and properties of the $MoSi_2$-BAS coating. The microstructure, element distribution and phase composition of the coating were studied, and the interface bonding strength, thermal shock resistance and emissivity were measured. It was observed from the study that the gradient porous coating could achieve the expected performance.

2. Experimental

The gradient $MoSi_2$-BAS coating was prepared on the surface of porous fibrous material from the slurry consisted of homemade $BaO–Al_2O_3–SiO_2$ (BAS) glass as binder, $MoSi_2$ (99.9%, Beijing Meng Tai Metal Material Research Institute, China) as high emissive agent, and B_2O_3 (99.5%, Sinopharm Chemical Reagent Co., Ltd, China) as annexing agent followed by spraying and sintering. BAS glass was prepared from $BaCO_3$ (99.0%, Sinopharm Chemical Reagent Co., Ltd, China), SiO_2 (99.0%, Sinosi Group Corporation, China) and Al_2O_3 (99.0%, Zhengzhou Tianma micro powder Co., Ltd, China) by high temperature fusion technique.

The $MoSi_2$-BAS coating consisting of a bonding-layer and a surface-layer was obtained by changing the component of slurries. The surface-layer slurry contained BAS, $MoSi_2$ and B_2O_3, while the bonding-layer slurry just contained BAS and $MoSi_2$ without B_2O_3. Aqueous coating slurry was prepared by mixing BAS, $MoSi_2$, B_2O_3 and distilled water by ball milling with the 50 wt% solid content. The bonding layer slurry was sprayed to the porous substrate followed by drying at room temperature for 12 h, and then the surface layer slurry was sprayed to it and dried at the similar condition. Finally the coatings were sintered at 1500 °C for 20 min. Five coatings with different surface-layers were obtained by changing the content of B_2O_3 (0 wt%, 2 wt%, 4 wt%, 6 wt% and 8 wt%) namely $MoSi_2$-BAS-0, $MoSi_2$-BAS-2, $MoSi_2$-BAS-4, $MoSi_2$-BAS-6 and $MoSi_2$-BAS-8, respectively.

The micro-morphology, crystal phase structure of $MoSi_2$-BAS coating were analyzed by scanning electron microscopy (SEM, s4800, Hitachi, Japan), X-ray diffraction (XRD, Rigaka D/Max 2500, Tokyo, Japan) using a Bruker D8 Advanced diffractometer with CuKα radiation ($\lambda = 1.5418$ Å), respectively.

The interface bonding strength was performed on specimens (8 mm × 25 mm × 25 mm) by a conventional method of pull-off test [26–28]. The thermal shock resistance was performed on the specimens (8 mm × 25 mm × 25 mm) in air furnace (SX-5-12, Yixing Qianjin furnace equipment Co. Ltd., Yixing, China) at 1500 °C for about 20 min, then took out the specimens from the furnace into the air (10 °C). Repeat this step until the coating stripped from matrix. At least, three specimens were tested for each testing. The emissivity of coating was measured by total hemispherical emittance measurement (Harbin Institute of Technology, China).

3. Results and discussion

3.1. Microstructural characterization

The formation mechanism of the gradient structure of $MoSi_2$-BAS coating is shown in Fig. 1. The structure of coating is controlled by the addition amount of B_2O_3 which can promote the formation of liquid phase during the sintering. The gradient coating consists of a bonding-layer and a surface-layer. The surface-layer contains BAS, $MoSi_2$ and B_2O_3, while bonding-layer just contains BAS and $MoSi_2$, therefore, less liquid phase is generated in bonding-layer during sintering resulting in the porous structure. Yet, in the surface-layer, B_2O_3 distributes around the BAS and $MoSi_2$ particles, thus a dense structure is obtained through the reaction of B_2O_3 and partial BAS particles which can form liquid borosilicate glass phase with low melting point. The liquid phase formed in the surface-layer also gradually infiltrates into the bonding-layer to form the gradient porous structure with the decreasing porosity from matrix to surface.

The $MoSi_2$-BAS coating surface is smooth without cracking, and it is like shiny glass (as shown in Fig. 2 (a)–(e)). In the XRD spectrum of the unpolished coating surface with 2wt% B_2O_3, the X-ray amorphous phase is found in the range of 15 °C–25 °C suggesting a glassy structure is formed (as shown in Fig. 2 (f)). The $MoSi_2$-BAS-0 coating has some pores on its surface (as shown in Fig. 2 (a)) and the coating becomes dense without holes and microcracks on its surface when B_2O_3 content is more than 2 wt%, indicates that the addition of B_2O_3 can form dense surface-layer.

Fig. 3 shows the micromorphology and chemical components of $MoSi_2$-BAS-2 coating surface after hydrofluoric acid corrosion. After the coated glass phase is etched, the crystalline grains are exposed (Fig. 3 (a)) indicating the glass phase is filled in the void between the refractory particles after the sintering. The energy spectrums and the element content of crystalline and glass phase areas are shown in Fig. 3 (b) and (c) and Table 1 respectively. The crystalline phase mainly consists of Si and Mo with the atom ratio of 1.74 which is very close to $MoSi_2$, while the glass phase mainly consists of Ba, Al and Si corresponding to BAS glass. The high oxygen content of the coating mainly results from the corrosion of hydrofluoric acid which causing a certain degree of oxidation of $MoSi_2$ in the process of corrosion [29].

Micrographs of cross-sections of $MoSi_2$-BAS coatings with different B_2O_3 content are shown in Fig. 4. All of the $MoSi_2$-BAS coatings are about 300 μm in thickness as observed from SEM images, yet they show different morphologies. The coatings change from porous structure (Fig. 4 (a)) to gradient porous structure (Fig. 4 (b) and (c)) and finally to dense structure (Fig. 4 (d) and (e)) indicating the decrease of the porosity of coating as the increase of B_2O_3. $MoSi_2$-BAS-0 coating is porous with the estimated porosity of ~50% (Fig. 4 (a)), while the $MoSi_2$-BAS-6 and $MoSi_2$-BAS-8 coatings are dense without pore (Fig. 4 (d) and (e)). Both of the $MoSi_2$-BAS-2 (with ~30% estimated porosity) and $MoSi_2$-BAS-4 (with ~10% estimated porosity) coatings show gradient structures with decreasing porosity from the matrix to the surface. Their two layers containing a porous bonding-layer and a dense surface-layer are clearly observed from cross-sections (Fig. 4 (b) and (c)). Careful observing shows there is no obvious interface between the bonding-layer and the matrix indicating their close combination (Fig. 4 (f)), which can be further proved by bonding strength testing.

The different structures observed above are achieved by adding different amount of B_2O_3 which can control the formation of liquid phase during sintering. An increase in the B_2O_3 content will