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Effect of $TaSi_2$ content on the structure and properties of $TaSi_2$-$MoSi_2$-borosilicate glass coating on fibrous insulations for enhanced surficial thermal radiation

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ABSTRACT

$TaSi_2$-$MoSi_2$-borosilicate glass coatings with high emissivity were prepared on mullite fibrous ceramics via a slurry technique to enhance surficial thermal radiation and serve in the thermal protection systems for aircrafts. The effect of $TaSi_2$ dosages on the coatings' structure, phase composition, emissivity, thermal shock resistance and thermal endurance were investigated. The results show that all the coatings were flat and uniform, while the surface roughness and porosity increased with $TaSi_2$ dosages. Part of $TaSi_2$ was oxidized into Ta_2O_5 during the coating preparation, and finally, the coating with $TaSi_2$ dosage of 45 wt% (C-45Ta) had the highest $TaSi_2$ content. Emissivity of the coatings increased with $TaSi_2$ contents. The total emissivity of C-45Ta was 0.855 in the range of 3–14.5 μm at 150 °C, while that of the coating without $TaSi_2$ (C-0Ta) was 0.809. However, compared with C-0Ta, C-45Ta showed worse thermal shock resistance because of its higher CTE mismatch with the substrate and higher porosity. The thermal endurance of C-45Ta was worse due to the limited oxidation resistance of $TaSi_2$ and the lower borosilicate glass content.

1. Introduction

Hypersonic aircrafts enter across the atmosphere with high flight speed above Mach 7 and over a long period of time, resulting in an intense aerodynamic heating load during the launch and re-entry flight. Thermal protection system is necessary to protect the internal structures inside the aircrafts from the large heat fluxes on the external surfaces [1–3]. Ceramic tiles with glass-based coatings have been the mainstay of reusable thermal protection system for over three decades [4]. The ceramic tiles consist of ceramic fibers and possess high porosity, low density, low thermal conductivity and relatively high strength [5–7]. At such a high temperature as it on the surface of an aircraft, the effective thermal conductivity of the tiles increased leading to worse thermal insulation effect, but thermal radiation elevated dramatically. Therefore, a high emissivity coating is desirable to be deposited on the ceramic tiles to reduce the heat flux to the substrate by radiation and keep the maximum temperature below a certain critical value in high-temperature environment [8,9].

The high emissivity coating on ceramic tiles is composed of emittance agent, which can improve the property of radiation, and a binder, which can be coupled with the emittance agent and the substrate. Borosilicate glass was widely used as the binder because of its low thermal expansion coefficients, good thermal stability and good wetting on fibrous ceramics [10–12]. By contrast, there were various emittance agents, which had a major effect on the coating property. Oxides such as iron, chromium, hafnium, and cobalt are common emittance agents, but they were either contaminants to the ceramic tiles or unstable in the convective heating environment [13]. Carbides such as silicon carbide had high emissivity, but they generally formed carbon dioxide when exposed to high temperatures, which finally foamed the glass coating [14]. Silicon borides were the first generation of emittance agent fit for the high emissivity coating and was applied in Reaction Cured Glass layer (RCG); however, they would be oxidized at high temperatures to form borosilicate glass and thereby undermine the thermal stability of the coating [12,15]. $MoSi_2$ with excellent high-temperature oxidation resistance was subsequently developed as a superior emittance agent, and was successfully applied in Toughed Uni-piece Fibrous Insulation (TUFI) [16]. In recent years, high emissivity coating with better temperature capability was urgently needed, and $TaSi_2$ was developed as a new emittance agent used in Toughened Uni-piece Fibrous Reinforced Oxidation-resistant Composite (TUFROC) and the temperature capability of the coating was increased to 1950 K, highlighting the great potential of $TaSi_2$ as emittance agent [17,18]. However, most of

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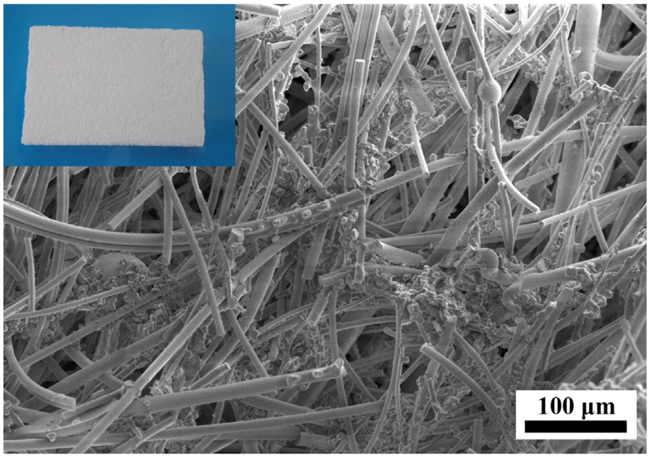

Fig. 1. SEM image of mullite fibrous ceramics (inset shows the photograph).

the investigations on silicides as emittance agents have focused on $MoSi_2$, $TaSi_2$ has received relatively limited attention [19,20].

As the emittance agent in high emissivity coatings for ceramic tiles, the effect of $TaSi_2$ was not clear. Compared with $MoSi_2$, $TaSi_2$ has similar melting point ($TaSi_2$: 2025 °C; $MoSi_2$: 2030 °C), higher density ($TaSi_2$: 9.25 g/cm^3, $MoSi_2$: 6.25 g/cm^3) and higher coefficient of thermal expansion (CTE, $TaSi_2$: 8.8×10^{-6}/K; $MoSi_2$: 7.8×10^{-6}/K) [21,22]; the higher density does not favor the light weight requirement of aircrafts, and the larger CTE makes $TaSi_2$ coatings suffer a bigger thermal mismatch with the substrates (CTE: 3–4 $\times 10^{-6}$/K). Shao et al. reported a $MoSi_2$-$TaSi_2$-borosilicate glass porous coating and the emissivity in the range of 2.5–15 μm was increased to 0.87 compared with their previous $MoSi_2$-borosilicate glass coating (emissivity: around 0.75); however, the XRD analysis of their $MoSi_2$-$TaSi_2$-borosilicate glass coating suggested that $TaSi_2$ was totally oxidized and thereby could not contribute to the high emissivity [23,24]. NASA Ames Research Center developed TUFROC, a $TaSi_2$-$MoSi_2$-borosilicate glass coating, and the temperature capability was increased above 1650 °C compared with their previous $MoSi_2$-borosilicate glass coating (TUFI: below 1400 °C) [16,25]; however, the thermal stability of $TaSi_2$ was reported to be worse than that of $MoSi_2$, because $TaSi_2$ exposed in air at high temperatures may be oxidized into Ta_2O_5 and SiO_2, while $MoSi_2$ was oxidation resistant [26,27]. To solve these contradictions, it is necessary to further investigate the effect of $TaSi_2$ addition on the thermal shock resistance, emissivity and thermal endurance of the coatings.

In this work, high emissivity coatings with $MoSi_2$ and $TaSi_2$ as emittance agents and borosilicate glass as a binder were prepared on mullite ceramic tiles by a slurry technique. The effect of $TaSi_2$ content on the thermal shock resistance, emissivity and thermal resistance of the $TaSi_2$-$MoSi_2$-borosilicate glass coatings were investigated. The $TaSi_2$ dosages were chosen within the preferable scopes proposed by reference [10,25].

2. Material and methods

The substrates used in this study were commercially available mullite fibrous ceramics, and their basic properties and pre-treatment method before coating deposition were reported in reference [28]. Fig. 1 shows the SEM image of the mullite fibrous ceramics and the photograph was inserted. It can be observed that the fibers therein can build a "birds nest" structure to obtain its high porosity, low thermal conductivity and relatively high strength. The pore size distribution curve presented a single peak in the range of 20–100 μm and the peak had a relatively narrow width, suggesting the uniform pore size distribution of mullite fibrous ceramics [29].

Fig. 2 shows the composition diagram of $TaSi_2$-$MoSi_2$-borosilicate glass coatings, excluding processing aid (B_4C) and solvent (silica sol),

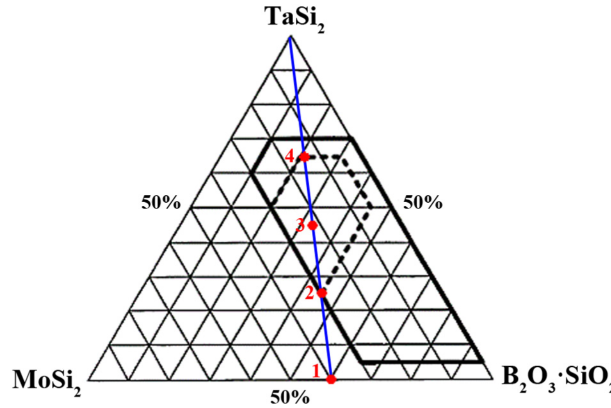

Fig. 2. Composition diagram of the coatings excluding processing aid and solvent (wt%): C-0Ta (1), C-25Ta (2), C-45Ta (3) and C-65Ta (4).

and the boxed area by dashed illustrated the preferable composition [10,25]. In order to investigate the influence of $TaSi_2$ content on the coating property, four coatings with $TaSi_2$ dosages of 0%, 25%, 45% and 65%, were prepared and donated as C-0Ta, C-25Ta, C-45Ta and C-65Ta. Their compositions were marked in red in the diagram, and the mass ratio of $MoSi_2$ and borosilicate glass was 2:3. The total composition of the four coatings including processing aid and solvent was listed in Table 1.

The coatings were fabricated by a slurry technique, which mainly included slurry preparation, spraying and sintering (Fig. 3). Firstly, fused silica (SiO_2, 500 mesh, Sinoteng Silica Materials Technology, Jiangsu, China), boron oxide (B_2O_3, 200 mesh, Guangfu chemical company, Tianjin, China) and boron carbide (B_4C, 1500 mesh, Mudanjiang Chenxi Boron Carbide Company, Heilongjiang, China) were mixed and dry-milled for 4 h (ball percentage: 70 wt%). The as-received powders were then mixed with molybdenum disilicide ($MoSi_2$, 3 μm, Eno Material, Hebei, China), tantalum disilicide ($TaSi_2$, 500 mesh, Ketai Advanced Material, Jiangxi, China) and silica sol (solid content: 20%) by milling for 0.5 h (ball percentage: 20 wt%) to form a homogeneous slurry. Secondly, the slurry was deposited on the substrates by spraying. Then, the coated specimens were dried at 50 °C for 10 h in a drying oven. Finally, the fully dried specimens were inserted into a furnace at 1350 °C, held for 2 h and later taken out of the furnace for rapid cooling to room temperature. The rapid cooling after sintering is required to minimize the as-processed residual tensile stress on the coating and inhabit quartz crystallization.

3. Characterization

Phase composition of the coatings was analyzed via X-ray Diffraction (XRD, D/Max-2500 Rigaku, Japan) with filtered Cu-Kα radiation. Scanning Electron Microscope (SEM, S-4800, Hitachi, Tokyo, Japan) equipped with an Energy Dispersive Spectrometer (EDS) was used for microstructural and elemental analysis. Thermogravimetric analysis of $TaSi_2$ was performed using a combined TGA/DSC instrument (STA-449C, Netzsch, Bavaria, Germany) with a heating speed of 10 °C/min in static air.

Table 1
Composition of the coatings including processing aid and solvent (wt%).

Samples	$TaSi_2$	$MoSi_2$	Borosilicate glass		B_4C	Silica sol
			SiO_2	B_2O_3		
C-0Ta	0	24	30	6	1	39
C-25Ta	15	18	22.5	4.5	1	39
C-45Ta	27	13.2	16.5	3.3	1	39
C-65Ta	39	8.4	10.5	2.1	1	39