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The Oxidation of Polymethylsiloxane/$MoSi_2$/SiC/Si-Derived Ceramic Composite Coatings

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Abstract

By utilization of preceramic polymer of polymethylsiloxane (PMS), a $MoSi_2$/SiOC/SiC ceramic composite was fabricated. The prepared composite displayed superior high temperature oxidation resistance by forming SiO_2 on the surface. The thin SiO_2 layer had some surface cracks, but they had not adversely deteriorated the oxidation resistance. The composite fabrication method employed in this study can be applied to protect any possible substrate material from aggressive oxidative attack, if the composite were coated on the substrate material.

Keywords : *Polymethylsiloxane (PMS), $MoSi_2$, SiC, Si, SiO_2, Oxidation*

1. INTRODUCTION

Ceramics such as SiC and $MoSi_2$ are widely used as heating elements. SiC has superior high-temperature oxidation and thermal shock resistance, and can be heated to 1650℃[1]. $MoSi_2$ has a high melting point (2020℃), excellent oxidation resistance, and good mechanical properties[2]. On the other hand, organosilicon polymers like polymethylsiloxane (PMS ; $CH_3SiO_{3/2}$) can be pyrolyzed to Si-containing ceramics by heating at 1400℃. Hence, much efforts have been paid to the conversion of PMS to ceramics. The utilization of preceramic polymers like PMS has advantages such as good formability and workability[3-6]. In this study, PMS, together with $MoSi_2$, SiC and Si were pyrolyzed to manufacture the $MoSi_2$/SiOC/SiC ceramic composites, which can be used as heat-resisting coating materials. The oxidation properties of the prepared ceramic composites were described.

2. EXPERIMENTAL PROCEDURE

Fig. 1. shows the experimental procedure. Powders of 60vol% PMS (Hules NH2100, Germany), 20vol% $MoSi_2$ (10(μmφ), 10vol% SiC (0.8(μmφ), and 10vol%Si (<8(μmφ) were mixed in acetone, evacuated using a rotary vacuum pump to remove acetone, pressed at 230℃ for 45min under 30MPa in accordance with the general plastic molding process, and heated at 1400℃ for 4hr in argon atmosphere to fabricate the $MoSi_2$/SiOC/SiC composite coating material. During heating, the pyrolysis

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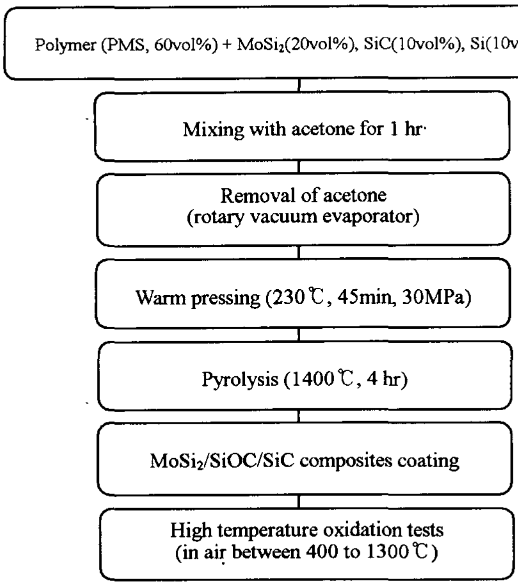

Fig. 1. Flow chart of expserimental procedure

of PMS and the subsequent reaction of powders of $MoSi_2$ SiC and Si with the decomposed PMS occurred. The volume fraction of starting materials in this study was chosen appropriately to compensate the shrinkage that occurred during decomposition of the PMS by the expansion that occurred when $MoSi_2$, SiC and Si which acted as filler materials were reacted with the decomposed PMS. The oxidation properties of the prepared material were investigated at 1000, 1100, 1200, and 1300℃ in air for long time utilizing SEM/EDS, EPMA and XRD.

3. RESULTS AND DISCUSSION

Fig. 2 shows a typical cross-sectional image, (a), the corresponding elemental maps, (b)-(e), and the XRD pattern of the oxide scale, (f). The oxide layer consisted primarily of thin SiO_2. The matrix consisted of randomly scattered, coarse $MoSi_2$ particles, very fine, scattered SiC particles, and an interconnected, amorphous SiOC phase which was not detectable in the XRD pattern. $MoSi_2$ and SiC powders initially added during sample preparation appeared not to be completely decomposed. They remained as white spots in Fig. 2(a). The PMS ini-

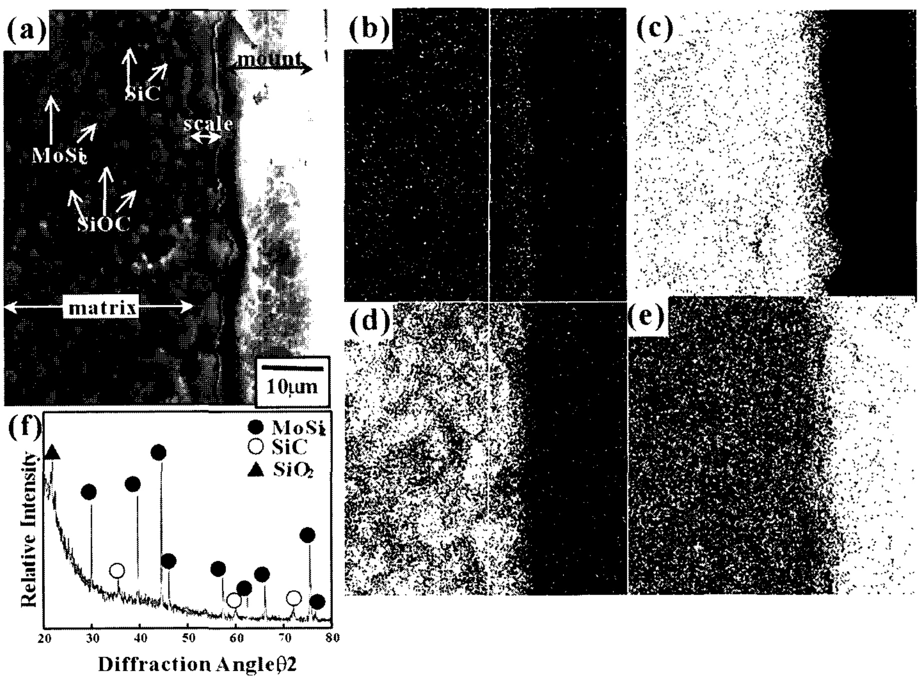

Fig. 2. Oxide scale formed after oxidation at 1100℃ for 1700 hr. (a) EPMA image, (b) oxyge map, (c) Si map, (d) Mo map, (e) carbon map, (f) XRD pattern.

tially added was decomposed and reacted into SiOC. During oxidation, $MoSi_2$ oxidized to SiO_2, probably accompanying the evaporation of highly volatile Mo-oxides such as MoO_2 and MoO_3. Similarly, SiC and SiOC in the matrix oxidized to SiO_2, possibly accompanying the evolution of CO vapor formed[3-6]. In Fig. 1(a), it is seen that the silica layer formed protected the matrix effectively under the given serious oxidizing condition.

Fig. 3 shows the SEM top view of the SiO_2 oxide layer formed after oxidation at 1200℃ for 1530hr. A glassy surface is seen, strongly indicating that SiO_2 formed is not only crystalline, as displayed in Fig. 2(f), but also amorphous, as shown in Fig. 3. The gradual transformation of SiO_2 from amorphous to crystalline at high temperatures is well known. Though cracks that possibly formed by the vaporization of volatile species such as Mo-oxide or CO during oxidation and shrinkage occurred during the subsequent cooling were seen, the matrix shown in Fig. 3 was still oxidation resistant due mainly to the SiO_2 formation.

Fig. 4 shows the SEM images of oxide scales formed at 1300℃ for long time. The SiO_2 layer formed after oxidation for 1900 hr was still thin, with a thickness of 6 (m, as shown in Fig. 4(a). When the specimen was oxidized at 1300℃ for long

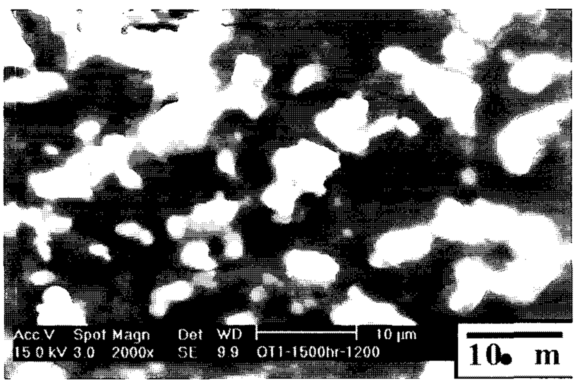

Fig. 3. SEM top view of theoxide scale formed after oxidation at 1200℃ for 1530 hr.

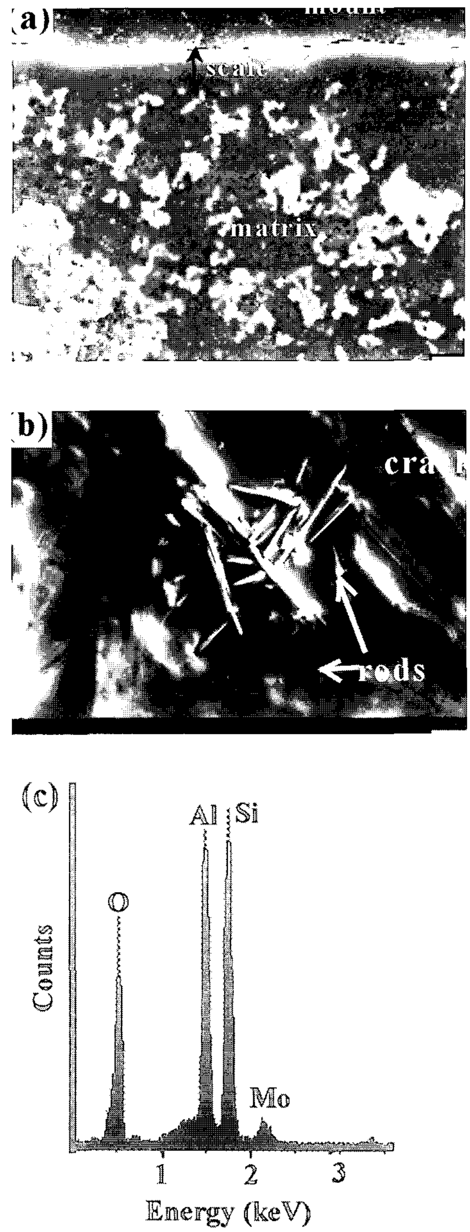

Fig. 4. SEM results of the prepared specimen after oxidation. (a) cross-sectional image, 1300℃, 1900 hr, (b) top view, 1300℃, 2036 hr, (c) spectrum of rods shown in (b).

time, some rods were existed on the glassy SiO_2 surface, as shown in Fig. 4(b). The EDS analysis shown in Fig. 4(c) indicated that rods were probably Al_2O_3, which could came from the Al_2O_3-containing heating furnace wall or Al_2O_3-crucible. The Si and Mo peaks shown in Fig. 4(c) may be originated from the SiO_2 layer.

4. CONCLUSION

The ceramic composite that consisted of $MoSi_2$, SiOC and SiC oxidized to SiO_2 during oxidation between 1000 and 1300℃ for long time. Silica formed was not only crystalline but also amorphous. The initially formed amorphous silica appeared to gradually transform to crystalline. Despite of the surface crack, the thin SiO_2 layer effectively provided the oxidation resistance to the fabricated ceramic composite.

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