Oxidation of MoSi₂-Coated and Uncoated TZM (Mo–0.5Ti–0.1Zr–0.02C) Alloys under High Temperature Plasma Flame

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Oxidation of coated and uncoated TZM alloys has been investigated under high temperature plasma flames with varying exposure time. TZM alloy specimens were pack-cemented in a powder mixture of Si, NaF and Al₂O₃ (25, 5 and 70 mass%) in an Ar atmosphere at 1173 K, resulting in the formation of MoSi₂ and Mo₅Si₃ layers on the TZM alloy. When the uncoated alloy was exposed to the flame for up to 4 min, the TZM alloy specimen showed a significant weight loss. However, the MoSi₂-coated TZM alloy specimen did not exhibit a measureable weight loss during the same exposure time due to the presence of the MoSi₂ layer. The effect of coating layers on the oxidation of TZM alloy under the dynamic flame is discussed based on the surface morphology and the microstructural observations, together with the weight changes during the test. [doi:10.2320/matertrans.M2013065]

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1. Introduction

TZM (Mo–0.5Ti–0.1Zr–0.02C) alloy is a Mo based alloy that has been used for high temperature applications. The alloy exhibits high melting point, good resistance to molten metal and alloys, and high creep strength at elevated temperatures. The alloy properties have been reported in many previous reports.^{1–8)} However, since the alloy is mainly composed of Mo, the alloy usually exhibits poor oxidation resistance. When the alloy is exposed to ambient atmospheres at temperatures of ~873 K, a volatile and non-protective MoO₃ forms, and the alloy is damaged due to significant weight loss.⁹⁾ Thus, in order to use the alloy in practical applications, the alloy needs some surface protection to combat the oxidation at high temperatures. Among the reported various coating processes, pack cementation coating process appears to be one candidate to protect the alloy. Desired coating layers can be generated via gas diffusion of coating elements towards embedded substrates. Detailed coating procedures and basic principles are given elsewhere.^{10–13)} An advantage of the process is the high bond-strength between the coating layers and the substrate through interdiffusion of respective metal elements. Furthermore, the coating process is generally economic and is considered to be suitable to mass production. In addition, components of complicated shape can be uniformly coated if the gas diffusion is well controlled.

Systematic investigations of the coating layers via pack cementation on TZM alloys have been reported together with their oxidation resistance. When Si pack cementation coating is applied to the TZM alloy, MoSi₂ layer forms as a result of Si diffusion into the Mo matrix. Majumdar *et al.* studied the Si coating processes to generate the MoSi₂ coating layer on TZM alloy with various activator species. They reported that the Mo (Si, Al)₂ layer with both Si and Al in it provides a

better protection than MoSi₂.^{14,15)} Chakraborty *et al.* reported a detailed coating process involving reactions of Si chlorides with the TZM alloys.¹²⁾

When MoSi₂ is exposed to air at high temperatures, an amorphous SiO₂ layer is formed on the surface of the MoSi₂ layer.^{12,14)} This SiO₂ layer provides an excellent oxidation resistance when exposed to isothermal air at high temperatures.^{16,17)} However, MoSi₂ becomes non-protective (i.e., pesting phenomenon) at low temperatures.^{18,19)} When MoSi₂ is exposed to low temperature air (~773 K), mixed oxides of MoO₃ and SiO₂ are produced, and the volume expansion of MoO₃ at the surface of MoSi₂ provides a channel for continuous oxidation routes. Also, it has been reported that the pesting process of MoSi₂ depends on fabrication conditions of MoSi₂, implying that the presence of grain boundary can affect the oxidation response of the alloy.¹⁸⁾ In this regard, it appears that the diffusion rate of Mo and/or Si with oxygen in MoSi₂ is one important factor that affects the oxidation of MoSi₂.¹⁹⁾ During oxidation, if the diffusion rate of Si in MoSi₂ is high enough to produce a continuous SiO₂ layer (usually at high temperatures), the formation of uniform SiO₂ layer can protect the surface. Otherwise, formation of oxide mixture including MoO₃ does not protect MoSi₂, resulting in the occurrence of the pest phenomenon. While studies are ongoing to examine the oxidation of MoSi₂, oxidation of the MoSi₂-coated TZM alloys needs further investigation as well. The alloy is considered for use in a defense system such as projectile engine components that are exposed to dynamic high temperature oxidation environments for relatively short period of time (<5 min). However, the oxidation resistance of TZM alloys to high temperature flame has not been investigated so far. For example, there are several un-identified but significant features of the TZM alloy; (i) how high will the temperature of the TZM alloys raise upon exposure to continuous flame impingement? (ii) is the oxidation of TZM alloy under static oxidation condition similar to the flame impingement conditions? (iii) if the

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uncoated TZM exhibits non-protective oxidation response, how much weight loss is expected under flame conditions? (iv) if SiO_2 scale is produced on the MoSi_2 -coated TZM alloys, can the surface SiO_2 layer survive during the exposure to the dynamic flame? (v) are the MoSi_2 coatings on the TZM alloy effective under the flame environments? and (vi) does the peeling phenomenon occur for the MoSi_2 coated TZM alloys under the flame conditions?

In this study, oxidation of TZM alloy was investigated under plasma flame impingement conditions that would provide a large amount of heat in oxidation environments. The plasma flame tests were selected to provide constant and reproducible oxidation environments for the TZM alloy. The MoSi_2 -coated and the uncoated TZM alloys were exposed to the flame with various exposure times. Structural changes of the Si coated and the uncoated TZM alloys under the flame impingement conditions were investigated by weight change measurements together with microstructural observations.

2. Experimental

A bar shape of TZM alloy with a diameter of 12 mm has been purchased from Hansh[®] in Korea, and cut perpendicular to the longitudinal direction with a wall thickness of 5 mm. The TZM discs were polished with fine Al_2O_3 powders and ultrasonically cleaned. For Si pack cementation coatings, a powder mixture of Si, NaF and Al_2O_3 (25 : 5 : 70 mass%) was prepared by a milling machine. The TZM discs with the powder mixture were put into an Al_2O_3 crucible and annealed at 1173 K for 12 h in an Ar atmosphere. In order to examine the oxidation resistance of the coated TZM alloys, more than twenty specimens of the same coating conditions were prepared for oxidation tests. The MoSi_2 -coated and the uncoated TZM alloys were exposed to high temperature dynamic flame. In order to provide a constant and reproducible large heat amount, plasma flame impingement tests were provided on the TZM alloy. Ar and H_2 gas mixture was used for the present experiments. While the gas mixture may not completely prevent oxidation environments, oxygen may be involved during the turbulence of the flame in air atmosphere. A polished TZM alloy specimen was placed in front of the plasma gun with a distance of 8 cm, so that the specimen is exposed to the flame in air at high temperature. A plasma gun (Model 9MB, SULZER METCO[®]) was used to produce a high temperature flame. The schematic figure of the equipment is shown in Fig. 1. The mixture gas of Ar and H_2 was used with a gas flow rate of 45 liters/min and 5 liters/min, respectively. The electric input powers of 220 kV and 40 amperes were selected for producing reproducible and constant flames. The estimated velocity of the flame was identified as ~ 400 m/sec. The temperature of the specimen was measured with R-type thermocouple and temperature indicator (MV1000[®], YOKOGAWA), which was spot welded behind the specimen. When the temperature exhibited a plateau, the plasma flame was turned off. The temperature of the specimen was continuously measured until the temperature reached to the plateau. Temperature of TZM alloy increased from room temperature to about 1823 K as shown in Fig. 2. The specimen temperature did not exceed the maximum plateau possibly due to heat dissipation from

Fig. 1 Schematic illustration of the equipment and set up.

Fig. 2 Temperature variation of TZM alloy with respect to the exposure time.

Fig. 3 The outlook of the plasma flame and TZM alloy during the flame test.

the TZM alloy specimens. The longest flame exposure time was selected as 4 min for both the coated and the uncoated TZM alloys. After the flame test was finished, a new specimen was placed for the flame tests with an exposure time interval of 30 s and up to 4 min. The outlook of the system and location of the TZM alloy is shown in Fig. 3. Before and after the flame tests, weight changes of the uncoated and the coated TZM alloys were measured. Oxide

Fig. 4 (a) outlook of the as-received TZM alloy, (b) optical microstructure of the as-received TZM alloy and (c) surface shape of the as-coated TZM alloy.

Fig. 5 (a) SEM BSE image of the cross section of the coated TZM alloy after pack cementation coatings, (b) EDS measurements of 'A' marked in (a) and (c) EDS measurements of 'B' marked in (a).

scale and coating structure were identified by XRD (D/Max 2500H, Rigaku®), and Cu K α radiation with an operating voltage of 40 V was employed. The cross sections were examined with SEM (Scanning Electron Microscope) (JEOL-6300) with EDS (Energy Dispersive Spectrum).

3. Results and Discussion

The appearance of the specimen shape of (a) the as-received, (b) optical micrograph and (c) the coated TZM alloy is shown in Fig. 4. The as-received TZM alloy showed a mirror-like shiny surface, and the grain morphology of the TZM alloy showed a typical microstructure, in which the

grain was elongated in one direction (Fig. 4(b)). The coated TZM alloy exhibited a grayish surface as shown in Fig. 4(c). Cross section of the coated TZM alloy indicated formation of MoSi₂ layer of ~55 μm thickness on the specimen surface (Fig. 5(a)). A thin Mo₅Si₃ layer (~5 μm) was also observed between the MoSi₂ and the TZM substrate as shown in Fig. 5(a). The EDS measurements of the two layers showed that the coated layers were MoSi₂ (marked 'A' in Fig. 5(a)) and Mo₅Si₃ (marked 'B' in Fig. 5(a)). The Mo₃Si phase between the TZM alloy and the Mo₅Si₃ layer was not obvious at the present observations, possibly due to nucleation difficulty of Mo₃Si.^{11,20} The outlook of the uncoated and the coated TZM alloys exposed to the high temperature

Fig. 6 Surface outlook after the flame tests of (a) the uncoated TZM for (a) 2 min and (b) 4 min of exposure, and the MoSi₂ coated TZM alloys after flame tests for (c) 2 min and (b) 4 min of the flame exposure.

plasma flame is shown in Fig. 6. The surface of the uncoated TZM alloy turned into a dark gray color and some oxide pieces were detected from the substrate. At the same time, the surface shape became irregular when the exposure time extended to 4 min. It was also clearly noted that the TZM alloy lost its original shape, and the alloy was seriously damaged by the flame. However, when the coated TZM alloy was exposed to the flame, the situation was totally different. The TZM alloy maintained its original shape under the exposure of flame. When the exposure time reached to 4 min, the surface color did not critically change, and the surface remained shiny due to the formation of an well known amorphous SiO₂ phase. XRD test results of the coated and the uncoated specimen are shown in Fig. 7. The as-received TZM alloy exhibited a major Mo peaks (Fig. 7(c)). When the TZM alloy was MoSi₂-coated, the surface layer changed to MoSi₂ (Fig. 7(a)). However, the Mo₅Si₃ phase beneath the surface MoSi₂ phase was not identified by XRD (please see Fig. 5), since XRD does not detect the inside phase. The present results are consistent to the previous results that the XRD can detect the only surface phase (MoSi₂), and the formation of both MoSi₂ and Mo₅Si₃ after the pack cementation coating process.¹¹⁾ However, as shown in Fig. 5, two distinct layers of MoSi₂ and Mo₅Si₃ were formed after coatings as confirmed by the BSE image and EDS measurements.

When the as-received alloy was exposed to the high temperature plasma flame, the Mo oxide, MoO₃, became predominant as shown in Fig. 7(d). However, when the MoSi₂ layer was exposed to the flame, the coating layer maintained its structure without phase changes (Fig. 7(b)). While all of the major peaks were analyzed, some minor peaks in Fig. 7(a) were not identified. Further XRD analysis will be reported in other papers. Amorphous SiO₂ phase is suggested to have been produced as a result of the dynamic oxidation. Typical cross section of the coated TZM alloy after

Fig. 7 XRD patterns of (a) coated TZM, (b) coated TZM after oxidation, (c) as-received TZM and (d) uncoated TZM after oxidation.

exposure to the high temperature flame is shown in Fig. 8. The EDS measurements of the surface scale show that the surface scale was identified as SiO₂. The formation of SiO₂ is a well known phase that is normally formed after oxidation of MoSi₂.^{12,14)} Also, any of the SiO₂ peaks from XRD was not detected (Fig. 7(b)), indicating that SiO₂ is an amorphous phase. Some area of the SiO₂ scale was detached from the surface possibly during polishing process, since SiO₂ scale can be brittle at room temperature. At the same time, it is noted that there are some vertical cracks developed in the MoSi₂ layer. The coefficients of thermal expansion (CTE) of SiO₂ (273–1273 K),²¹⁾ MoSi₂ (298–773 K),²²⁾ Mo₅Si₃ (298–773 K)²²⁾ and TZM²³⁾ (298–373 K) have been reported as 0.5, 8.8, 8.4 and 5.3 ($\times 10^{-6}/\text{K}$), respectively. While the CTE data of the phases do not provide the appropriate temperature range of the present experiments, it appears that the vertical cracks inside the MoSi₂ coating layer resulted due to the CTE difference. At the same time, since the coated specimen did not change significantly its shape (Fig. 6), it appears that the cracks did not affect the oxidation of the alloy. Surface morphology of the uncoated and the coated TZM alloy after the exposure to the flame for 4 min is shown in Fig. 9. Irregular platelet-shape oxides generated upon oxidation was identified as MoO₃ phase, which is a typical oxide phase produced at isothermal oxidation tests.¹⁸⁾ On the other hand, the coated TZM alloy oxidized in the flame resulted in the formation SiO₂ layer, which is a well known phase that is formed during the oxidation of MoSi₂.

In order to examine the oxidation kinetics of these alloys, ratios of the remaining mass to the original mass of the uncoated and the coated TZM were plotted with respect to the oxidation time as shown in Fig. 10. Upon exposure to the high temperature plasma flame, the weight of the coated TZM did not change, but the uncoated TZM alloy specimen underwent a serious weight loss, which agrees well with the surface damage as shown in Fig. 6. When the uncoated TZM alloy specimen was exposed to the flame for 4 min, weight loss of about 70 mass% resulted. Smolik *et al.* reported detailed oxidation behavior of TZM alloy.⁹⁾ In this study, only one side of the specimen was oxidized with plasma flame. Therefore, a direct comparison between this study and the literature is not possible. For the MoSi₂-coated TZM alloy, thickness of the surface MoSi₂ scale and the underneath

Fig. 8 (a) Cross section of the MoSi₂ coated TZM alloy after exposure to the high temperature flame for 4 min (b) EDS measurement results of the SiO₂ layer.

Fig. 9 Surface morphology of (a) uncoated and (b) coated TZM alloy after exposure to the high temperature flame for 4 min.

Fig. 10 Weight changes of uncoated and coated TZM alloy after exposure to the flame.

Fig. 11 Changes in the thickness of the MoSi₂ and Mo₅Si₃ coating layers upon exposure to the flame.

Mo₅Si₃ layer were measured with respect to the exposure time to the flame as shown in Fig. 11. When severe oxidation occurs, the thickness of coating layers is usually changed. However, in the current situation, thicknesses of the MoSi₂ and Mo₅Si₃ layers did not significantly change, demonstrat-

ing good resistance at the high temperature oxidizing environment. The flame did not critically affect the degradation of the coated TZM alloy due to the presence of the MoSi₂ layer within the oxidation time.

While the current study was done under dynamic oxidation conditions, it is useful to review the oxidation behavior of MoSi₂ for comparison. It has been documented that when the

MoSi₂-coated TZM alloy was exposed to isothermal high temperature at 1273 K, the weight of the coated alloy increased at the very beginning tests of exposure due to the passivation of the surface SiO₂.¹¹⁾ However, in the current tests, weight of the coated alloy remained the same regardless of the exposure time. The unchanged weight of the coated TZM alloy specimen indicates that there may be some weight loss at the specimen surface. In this regard, there are three possibilities; (i) spallation of the SiO₂ layer during the flame tests, (ii) extremely small increment of the specimen weight during the exposure time (maximum 4 min) and (iii) evaporation of MoO₃ at the surface of SiO₂. If the surface SiO₂ was physically detached from the surface, there should be some irregularity in the surface roughness. While there are areas observed in the cross section where SiO₂ scale was not found (Fig. 8), the surface shape did change for the MoSi₂-coated specimen. Instead, the surface coating layer was tightly bonded and the specimen dimension was not significantly changed at all after the flame tests (Figs. 6(c) and 6(d)). Thus, the SiO₂ scale was considered to remain on the coating layer during the test.

Regarding to the oxidation of MoSi₂, thermodynamically possible reactions have been reported as follows.^{11,19)}

When MoSi₂ is exposed to air, MoO₃ is produced and evaporated at the surface especially during the initial period of heating. When the oxidation temperature is not high enough to allow Si diffusion, reaction (1) dominates and the surface is not protected from the gas atmosphere. However, when the oxidation temperature is high enough to allow Si diffusion towards the surface, the SiO₂ scale is formed and the SiO₂ layer covers the entire surface with the formation of Mo₅Si₃ underneath the surface (reaction (2)). Due to uniform formation of the SiO₂ layer on the surface, in fact, the oxygen partial pressure in the MoSi₂ reduces allowing formation of Mo₅Si₃. In this regard, ternary phase diagram in the Mo–Si–O system shows that it is possible that molybdenum silicides can be generated together with SiO₂ at the temperatures of 773 and 1873 K,¹⁹⁾ and Kurokawa reported that Mo–Si phases can be formed with oxides depending on oxygen partial pressure and activity ratio of Si to Mo at 1773 K.²⁴⁾ Liu *et al.* concluded that kinetics rather than thermodynamics would govern in the oxidation process, because stable phases such as MoO₂ or Mo₃Si phase are not often found in the oxidation tests.¹⁹⁾ Regarding to the oxidation of MoSi₂, Liu *et al.* pointed that the effective diffusion length, L_d , relates to the oxide unit layer thickness of silica (α). They suggested that when $L_d \gg \alpha$, a continuous silica layer is possible to produce, and the SiO₂ layer protects the surface of MoSi₂. When the MoSi₂ phase is oxidized at high temperature (>1273 K), effective bulk diffusion length (L_d) is evidently larger than α , resulting that a continuous and protective silica layer is formed and protects the surface from further oxidation.¹⁹⁾

For the current observation, the temperature increment during initial period of time was fast, i.e., the specimen

temperature reached to 1273 K for almost 20 s, and exhibited a plateau at ~1823 K. When MoSi₂ is exposed to air at high temperatures (>1573 K), a continuous formation of SiO₂ scale due to the high diffusion rate of Si in MoSi₂ is attained ($L_d \gg \alpha$). However, the growth rate of SiO₂ scale is sluggish at high temperatures due to the nature of network diffusion of the amorphous SiO₂ phase.²⁵⁾ In the current observations, the surface scale of SiO₂ was identified, and it appears that the amorphous SiO₂ layer protects the MoSi₂ surface. Since the flame increases the temperature of the specimen fast, it appears that the reaction (2) governs the oxidation of TZM. When SiO₂ is formed by the reaction MoSi₂ and oxygen, Si should diffuse out from MoSi₂ in order to maintain the mass balance. Otherwise, there is no Si source for producing SiO₂. If Si diffuses out from MoSi₂ in order to form SiO₂, the Mo₅Si₃ phase should be formed following the above reaction (2). However, Mo₅Si₃ was not found in the current observations. While the matrix alloy is different from TZM, it is useful to address the oxidation of MoSi₂-coated Mo alloy (Mo + Mo₃Si + Mo₅SiB₂ alloy).²⁶⁾ The oxidation of MoSi₂-coated Mo alloy (Mo + Mo₃Si + Mo₅SiB₂ alloy) has been previously reported, and the Mo₅Si₃ phase was found inside the surface MoSi₂ layer by forming SiO₂ on top of MoSi₂, when the MoSi₂-coated Mo alloys are exposed in air above 1473 K for 100 h.²⁶⁾ Thus, it appears that the relatively short time exposure of TZM lead to the formation of SiO₂ (not Mo₅Si₃). At the same time, the invariant weight change of the MoSi₂-coated TZM after exposure of the flame is also due to the relatively short exposure of the flame. Further study on the phase evolution during longer time experiments are underway. While further study on simulation efforts responding to the dynamic flame exposure is needed, the current observations clearly show that the MoSi₂ coatings on TZM are effective in terms of protection surface of TZM alloy during the examined time range.

4. Summary

Oxidation of MoSi₂-coated and the uncoated TZM alloys has been investigated under high temperature plasma flame with respect to exposure of various time frames. The TZM alloys were coated by pack cementation method with a powder mixture of Si, NaF and Al₂O₃ in an Ar atmosphere, resulting that MoSi₂ (~55 μm) and Mo₅Si₃ layers (~5 μm) were synthesized on the TZM alloy. When the alloy was exposed to the high temperature flame, the uncoated TZM alloys started to lose their weights. When the exposure time reaches up to 4 min, the weight loss of ~70 mass% was observed. The MoO₃ phase was identified at the surface of the uncoated TZM after oxidation. However, the MoSi₂-coated TZM alloys did not exhibit any weight loss during the exposure of the same time due to the presence of the synthesized MoSi₂ layer. A SiO₂ layer was observed on top of the MoSi₂ layer after the exposure of the flame. Also, the thicknesses of MoSi₂ and Mo₅Si₃ layers were not changed within the examined time. The MoSi₂ coatings on the TZM alloy appear to be one of the most promising coating routes for the application of the high temperature components under dynamic flame environments.

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