Oxidation of MoSi$_2$-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 Al$_2$O$_3$ (25, 5 and 70 mass%) in an Ar atmosphere at 1173 K, resulting in the formation of MoSi$_2$ and Mo$_5$Si$_3$ 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 MoSi$_2$-coated TZM alloy specimen did not exhibit a measurable weight loss during the same exposure time due to the presence of the MoSi$_2$ 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]

(Received February 15, 2013; Accepted May 27, 2013; Published July 25, 2013)

Keywords: molybdenum-titanium-zirconium, oxidation, diffusion coatings

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 $\sim$873 K, a volatile and non-protective MoO$_3$ 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 for 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, MoSi$_2$ layer forms as a result of Si diffusion into the Mo matrix. Majumdar et al. studied the Si coating processes to generate the MoSi$_2$ 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 MoSi$_2$. Chakraborty et al. reported a detailed coating process involving reactions of Si chlorides with the TZM alloys.$^{12}$

When MoSi$_2$ is exposed to air at high temperatures, an amorphous SiO$_2$ layer is formed on the surface of the MoSi$_2$ layer.$^{12,14}$ This SiO$_2$ layer provides an excellent oxidation resistance when exposed to isothermal air at high temperatures.$^{16,17}$ However, MoSi$_2$ becomes non-protective (i.e., pesting phenomenon) at low temperatures.$^{18,19}$ When MoSi$_2$ is exposed to low temperature air ($\sim$773 K), mixed oxides of MoO$_3$ and SiO$_2$ are produced, and the volume expansion of MoO$_3$ at the surface of MoSi$_2$ provides a channel for continuous oxidation routes. Also, it has been reported that the pesting process of MoSi$_2$ depends on fabrication conditions of MoSi$_2$, 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 MoSi$_2$ is one important factor that affects the oxidation of MoSi$_2$. During oxidation, if the diffusion rate of Si in MoSi$_2$ is high enough to produce a continuous SiO$_2$ layer (usually at high temperatures), the formation of uniform SiO$_2$ layer can protect the surface. Otherwise, formation of oxide mixture including MoO$_3$ does not protect MoSi$_2$, resulting in the occurrence of the pest phenomenon. While studies are ongoing to examine the oxidation of MoSi$_2$, oxidation of the MoSi$_2$-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\textsubscript{2} scale is produced on the MoSi\textsubscript{2}-coated TZM alloys, can the surface SiO\textsubscript{2} layer survive during the exposure to the dynamic flame? (v) are the MoSi\textsubscript{2} coatings on the TZM alloy effective under the flame environments? and (vi) does the pesting phenomenon occur for the MoSi\textsubscript{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\textsubscript{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 Hanshin\textsuperscript{6} in Korea, and cut perpendicular to the longitudinal direction with a wall thickness of 5 mm. The TZM discs were polished with fine Al\textsubscript{2}O\textsubscript{3} powders and ultrasonically cleaned. For Si pack cementation coatings, a powder mixture of Si, NaF and Al\textsubscript{2}O\textsubscript{3} (25 : 5 : 70 mass\%) was prepared by a milling machine. The TZM discs with the powder mixture were put into an Al\textsubscript{2}O\textsubscript{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\textsubscript{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\textsubscript{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\textsuperscript{6}) 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\textsubscript{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\textsuperscript{6}, 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 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
scale and coating structure were identified by XRD (D/Max 2500H, Rigaku), and Cu Kα 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 MoSi$_2$ layer of ~55 µm thickness on the specimen surface (Fig. 5(a)). A thin Mo$_5$Si$_3$ layer (~5 µm) was also observed between the MoSi$_2$ and the TZM substrate as shown in Fig. 5(a). The EDS measurements of the two layers showed that the coated layers were MoSi$_2$ (marked ‘A’ in Fig. 5(a)) and Mo$_5$Si$_3$ (marked ‘B’ in Fig. 5(a)). The Mo$_5$Si$_3$ phase between the TZM alloy and the Mo$_5$Si$_3$ layer was not obvious at the present observations, possibly due to nucleation difficulty of Mo$_3$Si.$^{11,20}$ The outlook of the uncoated and the coated TZM alloys exposed to the high temperature...
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 uncoated specimens 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 XRD 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 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 (×10−6/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
Mo$_5$Si$_3$ 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 MoSi$_2$ and Mo$_5$Si$_3$ layers did not significantly change, demonstrating 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 MoSi$_2$ layer within the oxidation time.

While the current study was done under dynamic oxidation conditions, it is useful to review the oxidation behavior of MoSi$_2$ for comparison. It has been documented that when

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic%</th>
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<tr>
<td>O K</td>
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</tr>
<tr>
<td>Si K</td>
<td>32.12</td>
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<tr>
<td>Totals</td>
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Fig. 8 (a) Cross section of the MoSi$_2$ coated TZM alloy after exposure to the high temperature flame for 4 min (b) EDS measurement results of the SiO$_2$ 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 MoSi$_2$ and Mo$_5$Si$_3$ coating layers upon exposure to the flame.
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. 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)

\[
\begin{align*}
2/7 \text{MoSi}_2 (s) + O_2 (g) & = 2/7 \text{MoO}_3 (g) + 4/7 \text{SiO}_2 (s) & (1) \\
5/7 \text{MoSi}_2 (s) + O_2 (g) & = 1/7 \text{Mo}_5\text{Si}_3 (s) + \text{SiO}_2 (s) & (2)
\end{align*}
\]

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 Mo5Si3 phase was found inside the surface MoSi2 layer by forming SiO2 on top of MoSi2, when the MoSi2-coated Mo alloys were 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.
REFERENCES