Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 26(2016) 2603−2608
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Oxidation resistance of Si-coated TZM alloy prepared through combined process of plasma spray and laser surface melting

Jeong-Min KIM[1], Tae-Hyung HA[1], Joon-Sik PARK[1], Hyun-Gil KIM[2]

1. Department of Advanced Materials Engineering, Hanbat National University, Daejeon 34158, Korea;
2. Korea Atomic Energy Research Institute, Daejeon 34057, Korea

Received 11 October 2015; accepted 18 January 2016

Abstract: Plasma thermal spraying of Si coating layer on titanium−zirconium−molybdenum (Ti−Zr−Mo), TZM alloy, was conducted for the surface protection of the Mo substrate that is unstable in air at high temperatures. Although the plasma thermal spraying alone could protect the Mo alloy from oxidation at a high temperature for a short time, the post laser surface melting process further improved the oxidation resistance of Si-coated alloy. In the case of the post laser treated specimen, MoSi compounds, mainly $MoSi_2$ phases, were formed during the additional annealing process, and the oxidation resistance could be even further enhanced. The corrosion behaviors of Si-coated specimens in 3.5% NaCl solution were also investigated; however, no significant variations with respect to the post treatment procedure were found.

Key words: Ti−Zr−Mo alloy; Si; oxidation; plasma spray; laser melting

1 Introduction

Mo alloys such as TZM (Ti−Zr−Mo) have gained much attention for high temperature applications in the areas of aerospace and nuclear industries because of their excellent mechanical properties at elevated temperatures [1]. However, the Mo alloys usually exhibit poor oxidation resistance since a volatile MoO_3 forms almost instantly when the alloys are exposed to oxidizing environment at a high temperature like 873 °C [2]. Therefore, in order to utilize the Mo alloys in practical applications, various protective coating processes such as pack cementation and plasma thermal spray are applied to the surface of the alloys [3−9]. Silicon has been widely used as the coating material since resultant SiO_2 layer provides an excellent oxidation resistance [3,8]. The plasma thermal spray coated alloys generally show improved oxidation resistance as compared to the substrate alloy [8,9], but some pores are inherent to the thermal spray coating and undoubtedly harmful to the oxidation resistance.

Post thermal spray treatments like laser surface melting can be desirable to obtain higher oxidation resistance. Some research results showed that post laser treatments contributed to the removal of porosity and the strengthened coating adhesion in various coating/substrate systems [10−13]. However, there has been no literature on the clarified effects of the post laser surface melting on the oxidation behaviors of Si-coated Mo alloys. Furthermore, the mixing of the Si coating layer and the substrate may occur during the laser surface treatment. And this mixing can cause not only the increased interface stability between the coating and the substrate but also the formation of MoSi compounds. Microstructural changes in the Si/TZM system owing to the laser surface melting have not been fully elucidated. Additional annealing treatment of Si-coated Mo alloys at high temperatures should cause the interface reactions, resulting in better interfacial bonding and intermetallic compounds formation. Because the general corrosion of the Si-coated Mo alloys can be also industrially important, the influence of post treatments on the corrosion resistance of the alloys also needs to be investigated.

2 Experimental

TZM Mo alloy (Mo−0.5Ti−0.1Zr−0.02C) sheet was used as the substrate in this research. Silicon was deposited on the sand blasted and ultrasonic cleaned TZM substrate via air plasma thermal spray process.

Corresponding author: Jeong-Min KIM; E-mail: jmk7475@hanbat.ac.kr
DOI: 10.1016/S1003-6326(16)64386-8

A mixture of Ar and H_2 was used as the plasma gas and Ar was used as the powder carrier gas. The plasma spraying process parameters employed in this research are as follows: 400 A, Ar gas pressure of 100 MPa, H_2 gas pressure of 6 MPa, and spray distance of 100 mm.

The as-sprayed Si coatings on the specimens were then surface-treated by using a continuous wave (CW) diode laser with a maximum power of 300 W (PF−1500F model; HBL Co.,) and a power supplier (Pwp14Y04K model; Yesystem Co.,). The laser process parameters such as laser power, specimen velocity, powder injection, and gas flow were set-up based on a preliminary study. The applied power for the laser treatment ranged up to 300 W, and the scanning speed was 14 mm/s. To prevent any oxidation during the process, an inert gas (Ar) was continuously blowed into the melting zone. An isothermal heating of the Si-coated specimens under Ar atmosphere at 1100 °C was carried out to observe the interface reactions between the Si coating layer and the Mo substrate.

Oxidation test was conducted in air at 1100 °C to measure the mass change of Si-coated specimens of about 12 mm × 12 mm × 10 mm in size that were prepared by different procedures. The test was carried out only up to 120 min because severe spalling of the Si coating layer occurred and even some parts of surface of the substrate became detached after that. Electrochemical experiments to evaluate the corrosion behavior in an aqueous solution at room temperature were also carried out using a potentiostat (ZIVE SP1). The reference electrode used for the tests was a saturated calomel electrode (SCE) and platinum plate was used as a counter electrode. 3.5% NaCl solution was used as the electrolyte and potential scan rate for polarization tests was 1 mV/s. Microstructural analyses were performed using a SEM, equipped with energy dispersive X-ray spectrometer (EDS), and an X-ray diffractometer (XRD).

3 Results and discussion

Figure 1 shows a typical granular microstructure of TZM alloy, whose feature is similar with that of standard TZM alloy, used as the substrate [8]. The grain size varied between 10 and 50 μm and some carbides were observed. SEM images with EDS profiles in Fig. 2 represent the cross sectional images of the coating layers that were prepared through various processes. Formation of a thick and a little porous Si coating layer is observed in the as-plasma thermal sprayed specimen. The microhardness of the surface Si coating layer for the as-sprayed specimen was found to be significantly higher (HV ~474) than that of the substrate (HV ~334). The porous Si coating layer was remelted and then solidified rapidly through the post laser surface treatment,

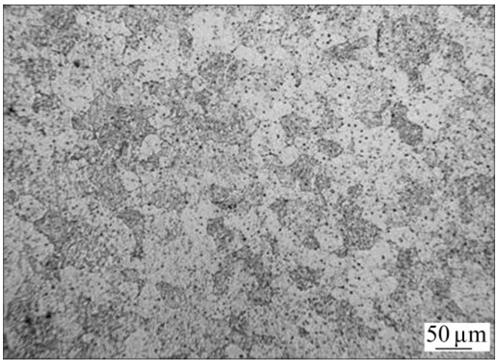
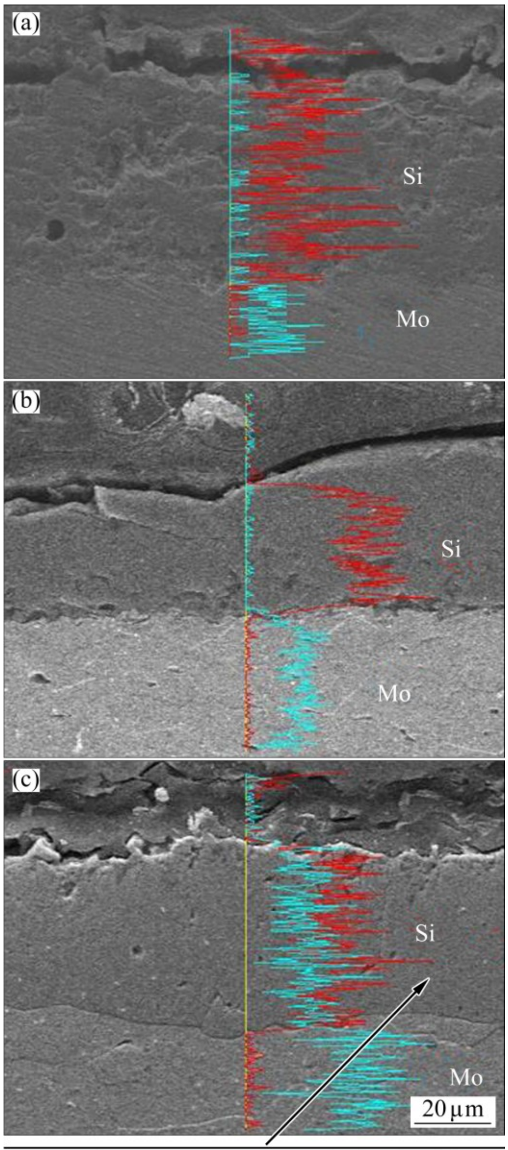


Fig. 1 Typical optical micrograph of TZM alloy used as substrate



Element	Mole fraction/%
Si	63.90
Mo	36.10
Total	100.00

Fig. 2 SEM images with EDS profiles showing effect of processing on coating layer: (a) As-sprayed; (b) Post laser-treated; (c) Isothermally heated

therefore, the majority of porosity in the coating could be eliminated [10]. A more compact coating structure is shown in the post laser surface remelted specimen as compared to the as-plasma sprayed specimen (Fig. 2(b)). But no MoSi compounds were observed at the laser treated Si coating/substrate interface.

As shown in Fig. 2(c), some interfacial reactions apparently occurred during the isothermal heating at 1100 °C so that the original Si coating layer was converted into MoSi compounds. The main compound was indentified as $MoSi_2$ phase by EDS analysis. XRD analyses in Fig. 3 revealed that two kinds of MoSi compounds, namely $MoSi_2$ and Mo_5Si_3, were formed in the isothermally heated specimen [8]. It is postulated that the interface bonding between the plasma sparyed Si coating and the substrate became stronger by the post laser surface melting. As aforementioned, many previous research results showed that laser surface treatments reduced the porosity and strengthened coating adhesion in a variety of thermal spray coated specimens [10−13].

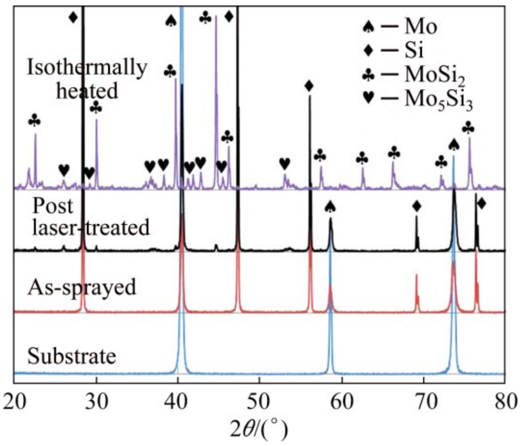


Fig. 3 XRD analyses of phases formed on surfaces of Si-coated specimens prepared through different processes

Any interface reactions were not observed when the identical isothermal heating at 1100 °C was directly applied to the as-plasma thermal sprayed specimen without the laser surface melting process. As demonstrated in Fig. 4, no MoSi compounds were found at the interface and the orginal Si coating layer remained unchanged possibly due to the relatively loose mechanical bonding at the interface.

Oxidation resistance of coated specimens evaluated as mass change is compared in Fig. 5. Although the mass of specimens should be increased due to formation of oxides such as SiO_2, rather mass loss was observed in this study [4]. Unlike the case of compact coating process such as pack cementation, the as-sprayed or the post laser treated specimens are likely to have some porous areas in the coating layers. In the case of porous coating, oxygen reactions may diffuse through the coating layer and some oxidation reactions may take place at the coating/substrate interface. The mass of the as-plasma thermal sprayed specimen remained almost unchanged up to 30 min, but a significant mass loss owing to spalling occurred after that. The post laser surface treatment could apparently improve the oxidation resistance of the as-sprayed specimen. In the case of combined process of the plasma thermal spray and post laser surface treatment, the coated specimen could endure up to 60 min. This enhanced resistance should be related to the reduced porosity in the coating layer. Apparently, the oxygen diffusion through defected coating layer should be easier than it through the denser layer. Another reason might be related to the bonding characteristics of the interface. The interface between the as-sprayed coating and the substrate is mechanically bonded, while the interface bonding appears to become stronger (metallurgical bonding) after the laser treatment [10]. This factor can be important if there are some macro-defects in the coating layer.

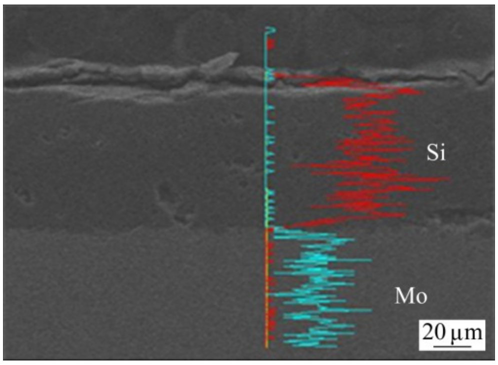


Fig. 4 SEM image with EDS profile of plasma sprayed Si coating layer after isothermal heating at 1100 °C

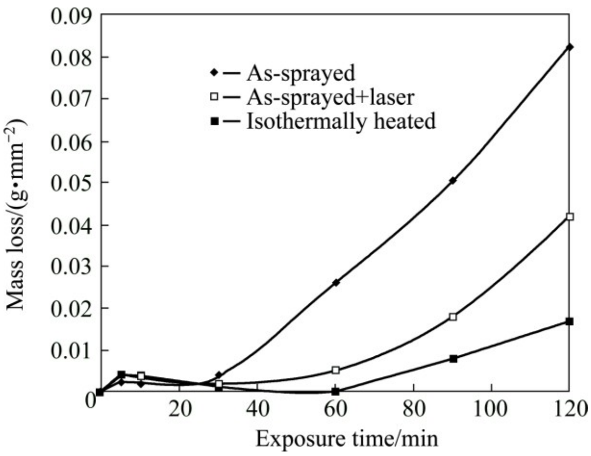


Fig. 5 Oxidation behaviors of as-sprayed and post treated specimens at 1100 °C

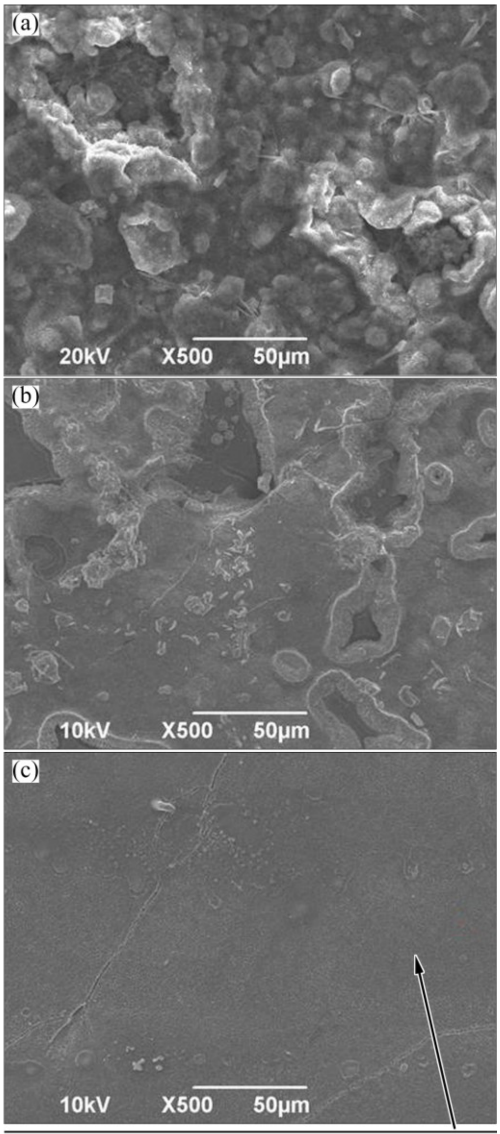
It is worthwhile to emphasize the fact that the oxidation resistance of TZM alloy could be effectively increased by the plasma thermal spraying of silicon on it, even though the as-sprayed specimen endured under oxidation environment only up to 30 min. It is well known that the bare TZM alloy is easily oxidized within a short period time at high temperatures [2]. Considering that air plasma spraying is an economical and convenient process, this enhancement method can be utilized in various industries.

The most oxidation resistant specimen is the one that was prepared via the combination of plasma spraying, post laser surface melting, and final isothermal heating under an inert atmosphere. The diffusion and reaction took place between the Si layer and the Mo substrate. So, the coating layer could be more compact and the interfacial bonding could be strengthened. Furthermore, $MoSi_2$ is known to be an excellent material against oxidation at very high temperatures [4]. Figure 6 shows surface morphologies of the specimens after the oxidation test. The as-sprayed specimen indicates a relatively rough suface, which is a typical feature of plasma sprayed coating. The post laser surface melting process appears to make the surface smooth; however, the laser treated specimen and the as-sprayed specimen apparently show some pits on the surface layers in Figs. 6(a) and (b). Meanwhile, comparatively perfect and smooth surface is found in the case of isothermally heated specimen. SEM-EDS analysis results reveal that the main phase formed on the suface is SiO_2 and a little amount of molybdenum oxide, typically MO_3 phase, is present. Similar EDS analysis results were obtained for the as-sprayed and the post laser surface treated specimens, but a little higher content of Mo (~2.67%, mole fraction) was detected. This is possibly attributed to partly exposed Mo substrate because of the surface pits. Thermodynamically possible reactions for the oxidation of $MoSi_2$ have been reported as follows [3,8].

$$2MoSi_2+7O_2=2MoO_3+4SiO_2 \quad (1)$$

$$5MoSi_2+7O_2=Mo_5Si_3+7SiO_2 \quad (2)$$

When $MoSi_2$ phase is exposed to air at a low temperature (<800 °C), the oxidation is governed by Eq. (1). However, when the exposure temperatue is higher (>800 °C), there is enough time for Si to diffuse toward the surface so that SiO_2 layer covers the surface with the formation of Mo_5Si_3 between inner layer of $MoSi_2$ and outer layer of SiO_2 (Reaction (2)). Although the specimens were oxidized at a high temperature of 1100 °C in the present experiment, MoO_3 phase was also found. It is postulated that the reason why MoO_3 phase formed is not because Reaction (1) dominantly occurred but some parts of surface coating layers were detached during the oxidation test. The plasma spray coating layer often possesses some porous spots even after the post treatment such as laser surface melting and isothermal heating although it becomes more compact after the treatment. Therefore, oxygen may penetrate rapidly through the imperfect region, resulting in some pits in the coating and the formation of MoO_3 phase.



Element	Mole fraction/%
Si	32.92
O	66.39
Mo	0.687

Fig. 6 SEM images of surface morphologies for different specimens: (a) As-sprayed; (b) Post laser-treated; (c) Isothermally heated

The electrochemical test was also conducted to compare the general corrosion resistance of the coated specimens at room temperature. Figure 7 shows the polarization curves for the Si-coated specimens prepared through different processes in 3.5% NaCl solution. It is presented that the corrosion potential (φ_{corr}) tends to become nobler when the post laser process is employed after the plasma spray. Additional isothermal heating process further moves upward the corrosion potential.

Meanwhile, as shown in Table 1, the corrosion current density (J_{corr}) was rather slightly increased by conducting the post processes after the spray, but the degree of increase was not significant. The corrosion resistance of the Si-coated specimens in 3.5% NaCl solution appears to be generally high regardless of the coating preparation method. The post laser treated or isothermally heated coating is denser than the as-sprayed coating. Since the smoother and denser surface of the coating layer is more effective for preventing infiltration of solution through the coating, better corrosion resistance is expected to be obtained in the post processed specimens. However, it has been known that the substrate, Mo alloy, possesses higher corrosion resistance in aqueous solution [14], therefore, no significant variations of the corrosion resistance in terms of the coating procedure seem to be observed in this study.

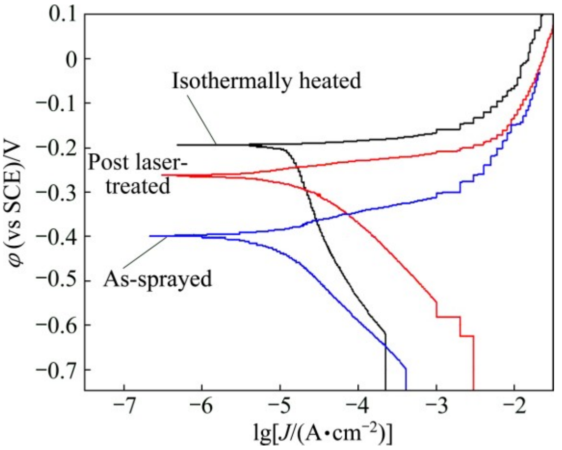


Fig. 7 Polarization curves for Si-coated specimens prepared by different processes in 3.5% NaCl solution

Table 1 Electrochemical parameters of Si-coated specimens obtained from polarization test in 3.5%NaCl solution

Specimen	Corrosion potential, φ_{corr}(vs SCE)/V	Corrosion current density, J_{corr}/(μA·cm^{-2})
As-sprayed	−0.340	17.67
Post laser-treated	−0.266	28.39
Isothermally heated	−0.251	25.49

4 Conclusions

Some pores and cracks were found in the as-sprayed Si coating layer, while comparatively compact coating could be obtained after the laser surface melting. The oxidation tests conducted at 1100 °C under atmosphere indicated that the post laser process enhanced the oxidation resistance of TZM alloy. The additional isothermal heating process under Ar caused the formation of intermetallic compound between the silicon coating and the substrate, and resulted in the further enhancement of the oxidation resistance. It is suggested that the increased oxidation resistance is mainly due to the improved soundness of the coating layer and the strengthened bonding at the interface. Although the corrosion potential for the Si-coated specimens in 3.5% NaCl solution was slightly increased by the post laser treatment and the annealing process, the general corrosion resistance of specimens appears to be similar regardless of whether the post treatment was carried out or not.

References

[1] ALUR A P, CHOLLACOOP N, KUMAR K S. High-temperature compression behavior of Mo−Si−B alloys [J]. Acta Mater, 2004, 52: 5571−5587.

[2] SMOLIK G R, PETTI D A, SCHUETZ S T. Oxidation and volatilization of TZM alloy in air [J]. J Nucl Mater, 2000, 283−287: 1458−1462.

[3] PARK J S, KIM J M, CHO S H, SON Y I, KIM D. Oxidation of $MoSi_2$-coated and uncoated TZM alloys under high temperature plasma flame [J]. Mater Trans, 2013, 54: 1517−1523.

[4] MAJUMDAR S. Formation of $MoSi_2$ and Al doped $MoSi_2$ coatings on molybdenum base TZM alloy [J]. Surf Coat Tech, 2012, 206: 3393−3398.

[5] MAJUMDAR S, SHARMA I G, RAVEENDRA S, SAMAJDAR I, BHARGAVA P. In situ chemical vapour co-deposition of Al and Si to form diffusion coatings on TZM [J]. Mater Sci Eng A, 2008, 492: 211−217.

[6] CHAKRABORTY S P, BANERJEE S, SINGH K, SHARMA I G, GROVER A K, SURI A K. Studies on the development of protective coating on TZM alloy and its subsequent characterization [J]. J Mater Process Tech, 2008, 207: 240−247.

[7] TIAN X, GUO X, SUN Z, YIN Z, WANG L. Formation of B-modified $MoSi_2$ coating on pure Mo prepared through HAPC process [J]. Int J Refract Met Hard Mater, 2014, 45: 8−14.

[8] CHAKRABORTY S P. Studies on the development of TZM alloy by aluminothermic coreduction process and formation of protective coating over the alloy by plasma spray technique [J]. Int J Refract Met Hard Mater, 2011, 29: 623−630.

[9] WANG Y, WANG D, YAN J, SUN A. Preparation and characterization of molybdenum disilicide coating on molybdenum substrate by air plasma spraying [J]. Appl Sur Sci, 2013, 284: 881−888.

[10] LI C, WANG Y, WANG S, GUO L. Laser surface remelting of plasma-sprayed nanostructured Al_2O_3−13wt%TiO_2 coatings on magnesium alloy [J]. J Alloys Comp, 2010, 503: 127−132.

[11] QIAN M, LI D, LIU S B, GONG S L. Corrosion performance of laser-remelted Al−Si coating on magnesium alloy AZ91D [J]. Corr Sci, 2010, 52: 3554−3560.

[12] SOVA A, GRIGORIEV S, OKUNKOVA A, SMUROV I. Cold spray deposition of 316L stainless steel coatings on aluminium surface with following laser post-treatment [J]. Sur Coat Tech, 2013, 235: 283−289.

[13] MARROCCO T, HUSSAIN T, McCARTNEY D G, SHIPWAY P H. Corrosion performance of laser posttreated cold sprayed titanium coatings [J]. J Therm Spray Tech, 2011, 20: 909−917.

[14] GONZALRZ-RIDRIGUEZ J G, ROSALES I, CASALES M, MARTINEZ L. Corrosion resistance of molybdenum silicides in aqueous solutions [J]. J Solid State Electrochem, 2005, 9: 691−697.

等离子喷涂和激光表面熔化制备 Si 喷涂 Ti−Zr−Mo 合金的抗氧化性能

Jeong-Min KIM[1], Tae-Hyung HA[1], Joon-Sik PARK[1], Hyun-Gil KIM[2]

1. Department of Advanced Materials Engineering, Hanbat National University, Daejeon 34158, Korea;
2. Korea Atomic Energy Research Institute, Daejeon 34057, Korea

摘　要：由于 Mo 基体在热空气中不稳定，采用等离子热喷涂工艺将 Si 涂覆于 Ti−Zr−Mo 合金表面以保护 Mo 基体。虽然单独使用等离子热喷涂工艺能使 Mo 合金表面在高温下及较短时间内不被氧化，但是后续的激光表面熔化工艺能提高 Si 喷涂合金的抗氧化性能。对于后续激光处理样品，在随后的退火工艺中形成了钼硅化合物(主要成分为 $MoSi_2$)，且其抗氧化性能得到进一步改善。另外，研究了 Si 喷涂样品在 3.5% NaCl 溶液中的腐蚀行为，然而经激光表面熔化工艺处理样品的耐腐蚀性能与未经激光表面熔化处理样品的耐腐蚀性能无明显差异。

关键词：Ti−Zr−Mo 合金；Si；氧化；等离子喷涂；激光熔化

(Edited by Wei-ping CHEN)