STRUCTURAL CHARACTERIZATION OF MOLYBDENUM SILICIDES
DEPOSITED ON MOLYBDENUM BY PACK METHOD

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Abstract

In this study, molybdenum was siliconized by pack method which is realized by diffusion of silicon on the molybdenum substrate at high temperature. Coating treatment was realized at 1100°C for 1-4 h. Coated samples were examined by optical and scanning electron microscopy (SEM), Energy dispersive spectroscopy (SEM-EDS) and X-ray diffraction analysis (XRD). Siliconized layer of the coated molybdenum is compact, smooth and porosity free. X-ray diffraction analysis showed that siliconized molybdenum includes MoSi₂ and Mo₅Si₃ phases. The depth of siliconized the layer depending on treatment time is changing between 24.2±1.03 µm and 70.6±1.52 µm. While the hardness of the molybdenum silicide layer is changing between 1262.5 and 1791.48 HV₀.₀₁, the hardness of the matrix is 260 HV₀.₀₁.

Keywords: Molybdenum silicide, Pack Siliconizing, Hardness

1. INTRODUCTION

Recently, transition metal disilicides, in particular those formed with refractory metals such as molybdenum, tantalum, niobium and tungsten have drawn considerable attention for structural applications at high temperatures because of their high melting temperature, intrinsic oxidation resistance, relatively low density and high thermal conductivity. Of these disilicides, MoSi₂, exhibits the highest oxidation resistance and the lowest density. On top of that, MoSi₂, is thermodynamically compatible with many ceramic reinforcements. Thus, considerable efforts have been devoted to develop MoSi₂-based composites of engineering utility at high temperatures [1-3].

The mechanical properties of MoSi₂-based composites are now adequate for a wide range of industrial and military applications. The corrosion of MoSi₂ materials in molten glass was observed to be similar to that of the ceramic refractory material alumina-zirconia-silica (AZS), which is currently widely used in the glass industry. MoSi₂ has advantages over AZS in that it is electrically conductive (AZS is an insulator), it is significantly stronger than AZS, and it does not contain environmentally undesirable chromium, which is a constituent of AZS. Maximum corrosion rates for MoSi₂ occur at the glass–air interface (glass line) [4]. MoSi₂, is one of the most promising candidate materials for structural applications at temperatures above 1500°C and considerable effort has been devoted to develop MoSi₂-based alloys of engineering utility [5]. MoSi₂ show excellent high temperature properties, oxidation and thermal shock resistant and very good creep and wear properties and low density (6.3 g.cm⁻³) comparison to silicon-based ceramics. Engineering studies for developing MoSi₂-based alloys have focused on improving their mechanical properties, in particular the poor fracture toughness at ambient temperatures [1,4,6].

Owing to its unique combination of a high melting point, superior high-temperature stability and strength, and excellent oxidation resistance at high temperatures, molybdenum disilicide (MoSi₂) has received much attention as a promising coating material for structural application in extremely harsh environments [7-9]. Current potential applications of MoSi₂-based materials include turbine airfoils, combustion chamber components in oxidizing environments, missile nozzles, molten metal lances, industrial gas burners, diesel engine glow plugs, and materials for glass processing. In microelectronic devices, thin silicide layers are used as contacts and interconnections because they have low electrical resistance, high thermal stability, high electron-migration resistance, and excellent diffusion-barrier characteristics [10-12].

The main objective of this study was to investigate some structural, morphological and mechanical properties of molybdenum silicide layers formed on the pure molybdenum produced by pack method.

2. EXPERIMENTAL PROCEDURE

In this study, pure molybdenum 99.8 wt.% was used as substrates. The samples to be coated were machined as coupons to the dimensions of 15x12x10 mm and prepared metallographically by grinding with
1200 grid emery paper in the final stage. Siliconizing was performed by pack method in the powder mixture consisting of pure silicon, ammonium chloride and alumina in an alumina crucible sealed with an alumina led and alumina based cement. The coating was performed at 1100 °C for 1-4 h in an electrical resistance furnace, followed by quenching in the air. Siliconized samples were sectioned from one side and prepared metallographically up to 1200 grid emery paper and then polished using 1µm alumina paste. The thickness of coatings and their morphology were examined using NICKON ECLIPSE L150 optical microscopy and JEOL 6060 LV scanning electron microscopy (SEM) on the cross-sections of the siliconized layer of the coated molybdenum samples. The chemical analysis of the coating layers were determined by x-ray diffraction analysis using by RIGAKU XRD D/MAX/2200/PC x-ray diffractometer with Cu Kα radiation. The hardness of the coated molybdenum materials was also measured using a FUTURE TECH FM 700 micro-hardness tester fitted with a Vickers indenter under the loads of 10 gf.

3. RESULTS AND DISCUSSION

Fig. 1(a-c) show optical and SEM micrographs and EDS analysis of the siliconized layer of the coated molybdenum at 1100°C for 4h. Coating layers formed on the molybdenum were compact homogeneous, porosity free, with significant regularities in their thickness and presenting a smooth interface with the substrate (Fig. 1a,b). These micrographs are in studies of Riyosuke et al. [6]. EDS analysis showed that, the coating layer includes higher molybdenum and silicon as seen in Fig. 1(c).
XRD pattern (Fig. 2) of the coated molybdenum sample at 1100 °C for 2 h showed that, the phases formed on the siliconized molybdenum sample are MoSi$_2$ and Mo$_5$Si$_3$. This result agrees with earlier studies of Jiang et al. [7] and Riyosuke et al. [6]. The thickness of siliconized layer at 1100 °C for 1 h, 2 h and 4 h was measured as 24.2±1.03 µm, 66.0±4.37 µm and 70.6±1.52 µm, respectively. For thermo chemical coating processes, the longer the process time and the higher the treatment temperature, the thicker the coating layer become. The higher the treatment time, the thicker the molybdenum silicide layer became. Fig. 3 shows the molybdenum silicide layer thickness depending on process time. While the hardness of the molybdenum silicide layer is changing between 1262.5 and 1791.4 8 HV$_{0.01}$, the hardness of the matrix is 260 HV$_{0.01}$. Bath composition, substrate, treatment time and temperature affect the coating layer thickness in the TRD processes [13]. These are due to the presence of hard silicides (MoSi$_2$ and Mo$_5$Si$_3$) in the coating layer as verified by XRD analysis (Fig. 2).

Fig. 2. XRD pattern of the siliconized layer of the coated molybdenum at 1000°C for 2h.

4. CONCLUSIONS

Pure molybdenum was the substrate used for the deposition of molybdenum silicide coating by thermo-reactive deposition technique and the treatment was proved to be efficient in the production of silicide base coatings. The results obtained from present study can be summarized as follows:

- Coating layers formed on the pure molybdenum were compact, porosity free homogenous, with significant regularities in their thickness and presenting a smooth interface with the substrate.

- EDS analysis showed that, the coating layer includes higher molybdenum and silicon.

- XRD analysis showed that the coating layer includes MoSi$_2$ and Mo$_5$Si$_3$ phases.

- The thickness of siliconized layer at 1100 °C for 1 h, 2 h and 4 h was measured as 24.2±1.03 µm, 66.0±4.37 µm and 70.6±1.52 µm, respectively.
The hardness of the molybdenum silicide layer formed on the molybdenum samples was changing between 1262.5 and 1791.4 ± 0.01 HV which was much harder than pure molybdenum (260 HV ± 0.01).

REFERENCES


