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In-situ synthesis of $MoSi_2$ coating on Mo substrate under carbon protection and its short-term oxidation behavior

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ABSTRACT

$MoSi_2$ coating was in-situ synthesized on pure Mo substrate by a simple and improved packing method, in which carbon powder was used for providing a protective atmosphere. The microstructure and phase composition of the coated samples were characterized by SEM, EDS and XRD techniques. The mechanism of coating preparation was discussed. Results showed that the addition of carbon could effectively protect Mo from oxidizing during the coating preparation. A compact $MoSi_2$ coating with a loose surface layer was obtained. It was suggested that the trace oxygen availed the formation of the compact internal structure and the loose surface layer. And this particular coating structure was expected to contribute to a better oxidation resistance in high temperature. Additionally, the short-term oxidation behavior of the as-prepared $MoSi_2$ coating was investigated. The as-prepared $MoSi_2$ coating provided an unexceptionable protection for the Mo substrate from oxidation at 1600 °C for 1 h. The presence of a glassy silica layer that formed on the $MoSi_2$ coating during the oxidation exposure was proposed to explain the behavior. It shows the simple and improved packing method with carbon powder as protective medium is promising potential for the preparation of various anti-oxidation coatings.

1. Introduction

Since the shock melting data of molybdenum (Mo) are extraordinary similar in a wider pressure range, molybdenum is commonly used as an important standard material in the initial preheating impact experiment [1–5]. However, poor oxidation resistance at elevated temperature in oxidizing environments severely hinders its practical application [6,7]. Therefore, fabricating an antioxidation coating on Mo substrate is very necessary and important, which can provide a short-term of oxidation protection during the impact experiment. $MoSi_2$ coating has a high melting point (2030 °C) and can form an amorphous network structure during oxidation process which helps relieve the thermal stress and heal the surface cracks [8–10]. Thus, $MoSi_2$ coating possesses the excellent antioxidant properties at high temperature (up to 1700 °C), and then attracts extensive attention of researchers in recent years [11–13].

Various coating techniques such as packing method, magnetron sputtering, slurry process, plasma spraying or chemical vapor deposition (CVD) were applied to fabricate an silicide-based coatings [7,14–17]. Among them, the pack cementation method is often chosen due to the advantages of a facile preparation process and a good mechanical bond of the prepared coating. Usually, it was used to in-situ synthesizing $MoSi_2$ coating on pure Mo by siliconizing. Previous reports showed a controlled atmosphere, such as vacuum [18] or inert gas of Ar [19], was necessary to protect Si and Mo from oxidation during the siliconizing, which will greatly increase the difficulty and the cost of the coating preparation.

In this work, a simple and improved packing method is proposed to prepare $MoSi_2$ coating on pure Mo substrate in air. An appropriate amount of carbon powders was added into the filling powders (Al_2O_3), and thus the majority of oxygen was consumed by carbon to provide a protective atmosphere of preventing Mo oxidation during the coating preparation. The mechanism of the coating preparation was studied via morphology and structural analyses. And the antioxidant property of the as-prepared $MoSi_2$ coating was examined at 1600 °C for a short-term application. The microstructural degradation of the coated samples and the evolution of the coating morphology after oxidation were investigated.

2. Experimental

2.1. Fabrication of $MoSi_2$ coating

A molybdenum rod was cutted into pieces of 10 × 10 × 2 mm by

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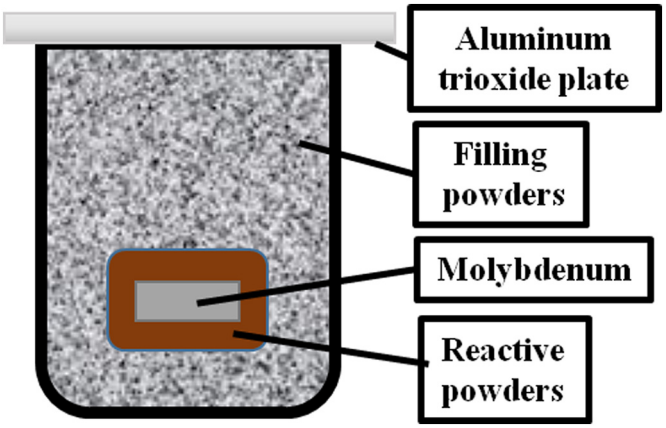

Fig. 1. Schematic diagram of the reaction model.

wire-electrode cutting, and then was abraded using a grit waterproof abrasive paper. Then, the Mo specimens were cleaned with ethanol and dried at 50 °C for 2 h. The well-proportioned reactive powders composed of Si powders and NaF (activator) were mixed by ball mill. A given mass of carbon powders and alumina powders were mixed as the filling powders. The alumina crucible was used as the container and covered by an aluminum plate. The schematic of the experimental setup is illustrated in Fig. 1. Finally, the whole unit was put into the furnace to carry out the siliconizing at 1200 °C for 2 h in air.

2.2. Tests and characterization

To simulate the working environment of Mo in impact experiment, the isothermal oxidation tests of the coated samples were performed in a ceramic fibre furnace at 1600 °C for 1 h in air. The weight change of the coating sample after oxidation test was recorded by an analytical balance with resolution of 0.1 mg. The phase composition of the coating was determined by X-ray diffractometer (XRD, DMAX1400, Rigaku Inc., Japan). The microstructure and chemical composition of the coated samples before and after oxidation were characterization by field emission scanning electron microscopy (FE-SEM, UItra55 Carl zeissNTS GmbH. Germany) equipped with energy dispersive spectroscopy (EDS, UItra55 Carl zeissNTS GmbH. Germany).

3. Results and discussion

3.1. The phase and morphology of the coating

Fig. 2(a) shows the XRD pattern of the coated sample prepared by the packing cementation under carbon protection. A major phase of $MoSi_2$ is detected, indicating that $MoSi_2$ coating was successfully prepared on Mo substrate. Although the coating preparation was carried out in air, no molybdenum oxide is detected. It was indicated that the carbon powders could effectively protect Mo from oxidizing. By comparison with the standard PDF file (JCPDS No. 41-0612), the crystal structure of $MoSi_2$ is tetragonal. This is consistent with the reported result [20]. Moreover, a minor SiO_2 phase also is found, suggesting trace oxygen may still exist in the present experimental condition. The residual oxygen will react with $MoSi_2$ coating on the surface to yield SiO_2 and Mo_5Si_3 [21], as described by reaction (1). Simultaneously the Mo_5Si_3 quickly converts to $MoSi_2$ through the reaction (2) due to high Si concentration in the reactive powders [22,23]:

$$5MoSi_2(s) + 7O_2(g) \rightarrow Mo_5Si_3(s) + 7SiO_2(s) \quad (1)$$

$$Mo_5Si_3(s) + 7Si(s) \rightarrow 5MoSi_2(s) \quad (2)$$

According to the above reactions, the growth of $MoSi_2$ grains on the coating surface was blocked. And it formed a loose surface layer, as shown in Fig. 2(b). It was expected that the special surface structure would be beneficial to the release of the thermal stress during the oxidation. Besides, the surface layer may provide a protective barrier to retard the oxidation of $MoSi_2$.

Fig. 3(a) shows the cross-sectional morphology (SEM) image of the coated sample. Obviously, there exists a coating of about 55 μm in thickness on Mo substrate. From the enlarged SEM image (Fig. 3(b)), it can be seen that the coating is composed of the rhomboid grains and the grain is tightly bound to each other to form a more compaction coating. Furthermore, the transgranular fracture is obviously found, indicating that the coating had excellent mechanical properties and a good bonding with the Mo substrate. And, there is a flat interface zone between the coating and the substrate. The EDS concentration profiles of Mo, Si and O elements in the coating are shown in Fig. 3(c). Obviously, the sudden reduction of Mo concentration is observed at the interface region of substrate and coating, while Si concentration shows a sharp increase. The phenomena corresponded to the formation of $MoSi_2$ phase in the coating. Besides, it was supposed Mo rich silicides such as Mo_5Si_3 and $MoSi_3$ were probably formed in the inter-diffusion zone, as reported in previous studies on siliconizing of Mo [17]. Trace of oxygen is also found in the coating surface, which may originate from the existence of a little SiO_2 phase.

Besides, several gaps are observed in the corner of the coating, as shown in Fig. 4(a). It was suggested that the gaps easily appeared in the edges and corners of coating due to the mismatch of coefficient thermal expansion (CTE) between $MoSi_2$ and Mo. However, it was noteworthy that the through-thickness cracks in coating which reported in the previous papers did not be detected in our work. This could be explained by that the remaining oxygen would permeate through these cracks and then react with $MoSi_2$ to form granular SiO_2. Thus, SiO_2 particles and re-forming $MoSi_2$ would fill and repair these cracks, which was verified from Fig. 4(b). As a result, a more compact coating structure was achieved at a trace oxygen environment by the addition of carbon powder, which would contribute to a better antioxidant

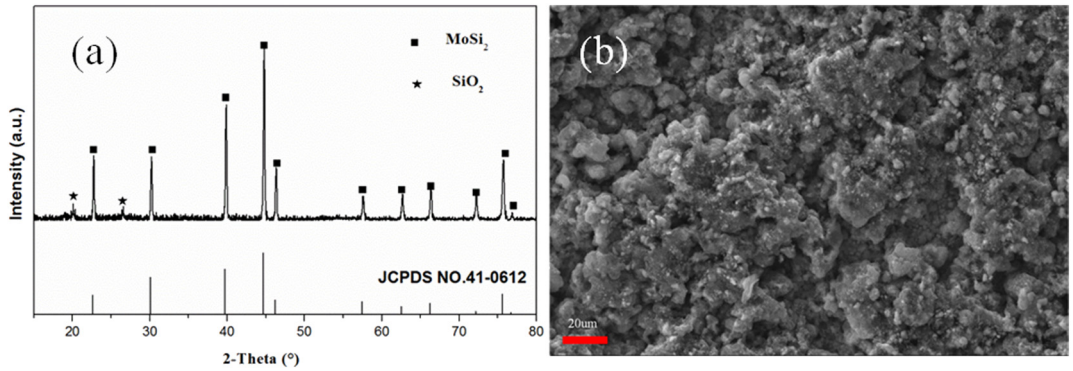

Fig. 2. XRD pattern (a) and surface morphology (b) of the $MoSi_2$ coating with pack siliconizing at 1200 °C for 2 h.