Study on Diffusive Reaction Between C-Si System and Mo Metal

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Abstract. Diffusive reaction layer on Mo metal covered by C powder (Si powder or SiC powder, i.e. C-Si system) and heat treated in vacuum ranging from 600°C to 1600°C for 2 h was investigated. Microstructure of interfacial reaction layer between C-Si system/Mo metal were characterized by XRD, SEM, and mechanical properties were compared between reaction layer based on Mo and Mo. The results show: after Si diffusing into Mo, Mo3Si phase appears after heat treatment higher than 1000°C, Mo5Si3 phase forms at 1400°C, even MoSi2 phase appears; after C diffusing into Mo, Mo2C phase appears firstly, then MoC forms at 1400°C; after SiC diffusing into Mo, Mo2C appears first, Mo3Si then forms at 1200°C, Mo5Si3(Mo2C and Mo5Si3C) multiphase coexist on Mo surface after heat treatment high than 1400°C. Tensile and specific elongation of C-Si system/Mo vary little, but Vickers hardness of Mo diffused by C or Si comparing with Mo enhance distinctly.

1. Introduction

Tensile strength of Molybdenum is relatively low at room temperature, while strength and ductile-brittle transition temperature of Mo are higher at relative higher temperature, and Mo is prone to internal cracking, too [1]. In order to improve mechanical property of Mo, a ceramic layer is formed on the surface of Mo in order to change surface properties mainly by micro-structure and interface of the reaction system. For example, Casimir [2] reported that C diffuses into Mo and forms Mo2C phase on the surface of Mo and diffusion coefficient of C in Mo2C phase was calculated. Xian Luo [3] reported modification effect of C/Mo double coating on SiC fiber reinforces γ-TiAl matrix. William B. Hillig [4] analyzed MoSi2 phase is synthesized firstly on the surface of Mo by diffusing Si into Mo and much thinner Mo3Si phase exists between Mo and Mo5Si3 phases. Zhenyang Cai [5] analyzed feasibility of Mo-Si coating deposits on the surface of Mo alloy.

Shiro Hara [6] reported there exists clear multilayer structures between SiC/Mo systems by solid-state reaction. A. E. Martinelli [7] hot-pressed a SiC/Mo diffusion couple, the phases formed on the surface of Mo are analyzed, and Vickers hardness of each phase is characterized. Solid-state reaction of SiC film with Mo matrix at temperature between 1100 °C and 1600 °C was investigated by J Rome Roger [8].

Comparison reaction between Si-C system and Mo has rarely been reported. Therefore, Solid-state reaction between Si-C system and Mo in vacuum was investigated, and formation phase of Mo surface and its effect on mechanical properties of Mo were analyzed.
2. Experimental

In present experiment, 1 mm thick brand Mo-1 molybdenum plate was prepared and standard plate type tensile specimens were processed by Wire-cut Electrical Discharge Machining along rolling direction. C(99.95%, D_{50}=0.5 \mu m), Si(99.95%, D_{50}=0.2 \mu m) and SiC(99.95%, D_{50}=0.2 \mu m) powders were selected as diffusion materials.

When Mo is heated in air, oxidation occurs at temperature higher than 300°C. while heating temperature exceeds 600°C, its oxidation rate increases [9]. Therefore, diffusion reaction between Mo plate and C-Si system must be done in vacuum. Mo plate sample were covered with C powder, Si powder and SiC respectively. the samples were heated by vacuum tube furnace at 800, 1000, 1200, 1400 and 1600°C, respectively.

Synthesized phases on surface of Mo plate after vacuum heat treatment were used to characterized by Rigaku D/max-rA X-ray diffractometer with Cu Kα radiation. The morphology of synthesized phases on surface of Mo plate was characterized by Cam Scan MX-2600 scanning electron microscope (SEM).

Mo plate after heat treated was characterized by Instron 5569 tensile tester at room temperature, its stretching velocity was 0.05 mm/min. In order to determine the hardness of diffusion layer on Mo plate surface, hardness test was carried out with model MHV2000 digital micro-Vickers hardness testing machine (testing load 0.49N, dwell time 20s).

3. Results and discussion

Interfacial reaction between C-Si system/Mo belongs to reactive type ceramic/metal system.

As shown in Figure1 (a), XRD diffraction patterns of Si/Mo are obtained at different temperatures in vacuum. At 800°C, Mo and Si do not react with each other, and the diffraction peaks of Mo plate (200) is strong. In the view of diffraction peaks, it can be seen that Mo plate still maintains texture characteristics produced by rolling process, with mainly dominant {100} < 100 > texture [9]. It can be seen that Mo3Si phase appears when Si/Mo reach 1000°C, Mo5Si3 phase appears when they are higher than 1400°C, and MoSi2 phase appears when the temperature is much higher.

As shown in Figure1 (b), XRD diffraction patterns of C/Mo are obtained at different temperatures in vacuum. It can be seen that C first reacts with Mo to form Mo2C, and MoC phase appears when heat treatment reaches 1400°C.

As shown in Figure 1(c), XRD diffraction patterns of SiC/Mo are obtained at different temperatures in vacuum. Mo2C appears at 800°C. After heat treatment at 1200°C, the phase on the surface of Mo plate mainly is Mo2C, which is similar to that at 800°C, but its diffraction intensity is enhanced. Mo3Si phase appears after heat treatment at 1200°C and Mo5Si3C coexist on the surface of Mo plate when the heat treatment temperature is as high as 1400°C.

Figure 2 shows SEM morphologies of surface for Si/Mo at 1200°C and 1400°C. Figure 2(a) shows the surface morphology of Si/Mo after heat treatment at 1200°C that rolling fibrous dendrite still retains on the surface of Mo plate after heat treatment, and it is obvious there is micron- sized grains to form reaction layer structure on the surface of Mo plate. Figure 2(b) shows SEM morphology of Si/Mo after heat treatment at 1400°C. The reaction layer structure of micron-sized grains is more remarkable. Because the theoretical melting point of Si powder is 1410°C, the Si ingredient may evaporate on the surface of Mo plate, or molten Si may infiltrate into Mo surface. Additionally, thermal expansion coefficient of MoSi2 and Mo5Si3 phase formed on the surface deviates greatly, and similarly elastic modulus of Mo5Si3 deviates from that of Mo, so surface reaction layer on Mo may crack during the cooling process.

Figure 3 shows SEM morphologies of reaction layer for C/Mo after heat treatment at 1200°C and 1400°C. An obvious reaction layer can be observed from figure 3(a). From figure 3(b), it can be observed that the reaction layer can be uniformly distributed on the surface of Mo plate. Thermal expansion coefficient of the Mo2C phase generated on the surface is similar to that of Mo matrix, so there is few surface cracks and reaction layer is uniformly distributed.
Figure 1. XRD patterns of surface for C-Si system/Mo reaction layer on Mo after heat treatment.
Figure 2. SEM morphologies of reaction layer for Si/Mo: (a, left) 1200°C; (b, right) 1400°C

Figure 3. SEM morphologies of reaction layer for C/Mo: (a, left) 1200°C; (b, right) 1400°C

Figure 4. SEM morphologies of reaction layer for SiC/Mo: (a, left) 1200°C; (b, right) 1400°C

Figure 4 shows SEM morphologies of reaction layer for SiC/Mo after heat treatment at 1200 °C and 1400 °C. The reaction layer formed by granular adhesion can be observed from figure 4(a). From figure 4(b), it can be observed that the reaction layer is uniformly distributed on the surface of Mo plate, and the cracks formed in rolling process are also filled by reaction layer.

Figure 5(a), 5(b), 5(c) are the stress-strain curves of Mo diffused by C-Si system under different temperatures tested at room temperature. It can be seen that basic trend is that tensile strength of specimens decreases gradually with increasing heat treatment temperature, while the elongation reaches theirs maximum at 1200 °C, and then decreases rapidly.
Figure 5. Relationship between stress and strain for Mo diffused by C-Si system at room temperature.
With heat treatment temperature increasing, fibrous dendrites transform into equiaxed grain, and elongation of the specimens decrease gradually with grain growing larger. Especially for specimens Si diffusing into Mo at 1600 °C, tensile strength fluctuates greatly due to partly melting of specimens for remarkable reaction between Si and Mo.

![Graph](#)

**Figure 6.** Mechanical properties of Mo diffused by C-Si system at different heat treatment temperatures: (a) Relationship between stress and heat treatment temperature for Mo diffused by C-Si system; (b) Relationship between elongation and heat treatment temperature for Mo diffused by C-Si system.

It can be seen from figure1 to figure 3 that new phases are formed at different heat treatment temperatures after SiC, C and Si diffusing into Mo. Figure1 For Si /Mo, Si atom diffuses into matrix Mo to form cubic Mo$_5$Si$_3$ phase. When temperature increases higher, Si atoms continue diffusing into interior Mo plate, prompting Si to continue to react with Mo$_5$Si$_3$ to form tetragonal Mo$_5$Si$_3$ phase, while Mo$_5$Si$_3$ on the surface layer reacts with Si to form tetragonal MoSi$_2$ phase. Figure 2 For C and Mo
systems, C atoms enter the Mo matrix, and Mo$_2$C phase is formed first, then more stable MoC phase is formed. A. E. Martinelli [10] also believes that MoC is formed at higher temperatures. Figure 3 For SiC and Mo systems, free-state atoms C and Mo generate Mo$_2$C due to SiC decomposition. For the diffusion of SiC into Mo, Si atom in SiC and Mo atom in the matrix form a cubic Mo$_5$Si. When the heat treatment temperature reaches a higher temperature, Si continues to react with Mo$_3$Si to form a tetragonal Mo$_5$Si$_3$ phase. Decomposed atom C from SiC enters into Mo$_5$Si$_3$ phase as center of the octahedron formed by Mo atom, and Mo$_5$Si$_3$C phase forms [11]. In theory, Mo$_5$Si$_3$ could continue to react with Si to synthesize MoSi$_2$. Shiro [6] suggested that diffusion of C atom into SiC is faster than that of Si atom. Therefore, in SiC and Mo systems, the diffusion layer of C is deeper than that of Si, so that surface diffusion layer is formed by Mo-Mo$_3$C-Mo$_5$Si$_3$-Mo$_5$Si$_3$C phases.

It can be seen from figure 6 that tensile strength and elongation of Mo specimens diffused by C, Si and SiC at different temperatures are higher than those of Mo specimens under the same conditions. Elastic moduli of Mo$_2$C, Mo$_5$Si$_3$ and MoSi$_2$ phases on surface of Mo plate is lower than that of Mo [7], while Vickers hardness of these formed phases is higher than that of Mo. Perhaps, as shown in Figure 6, these formed inhomogeneous layered structures or diffusion layers, which have the effect of similar dispersion strengthening, can improve their tensile strength slightly, that is to say, contribution of diffusion layer to their tensile strength and elongation is not significant.

![Figure 7. Relationship between surface hardness and heat treatment temperature for Mo diffused by C-Si system.](image)

As shown in figure 7, for Mo matrix, surface hardness decreases with increase of heat treatment temperature. The Vickers hardness of Mo specimens treated with diffusion C, Si and SiC at different temperatures is different. Surface hardness of Mo plate decreases more distinct than that of Mo after diffused by C-Si system because of formed phases on Mo surface. Hardness of Mo$_2$C, MoSi$_2$ and Mo$_5$Si$_3$ phases are higher than that of Mo matrix, especially when C diffuses into Mo, Mo$_2$C phase is main phase in the reaction layer, while Vickers hardness of Mo$_2$C is about 5 times of that of Mo matrix, Mo$_2$C has a strong bonding force with Mo matrix, and hardness of MoSi$_2$ phase formed by Si diffusing into Mo is near 4.5 times of that of Mo [7]. For SiC diffusing into Mo, hardness variation is not significant, perhaps complex phases of Mo-Mo$_2$C-Mo$_5$Si$_3$-Mo$_5$Si$_3$C layer formed on the surface of Mo matrix do not enhance its surface hardness.

4. Conclusions
After Si diffusing into Mo at 1000 °C in vacuum, Mo$_2$Si phase appears firstly, Mo$_2$Si$_3$ phase appears after heat treatment at 1400 °C, MoSi$_2$ phase appears after heat treatment high than 1400 °C.
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After C diffusing into Mo at 800 °C in vacuum, Mo2C forms firstly when C reacts with Mo, MoC phase appears when temperature is higher than 1400 °C.

After SiC diffusing into Mo at 800 °C in vacuum, Mo2C first appears on Mo surface, Mo2Si phase forms after heat treatment at 1200 °C, Mo2C, Mo5Si3 and Mo5Si3C coexist on the surface of Mo when temperature is higher than 1400 °C.

After diffusing by C-Si system, tensile strength and elongation of Mo enhance slightly while surface hardness increases significantly.

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