Corrosion Behavior of Mo₅Si₃-Based Metal Silicide Alloy

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The Mo₅Si₃-based alloy consisting of small particles Mo₃Si uniformly distributed in a Mo₅Si₃ matrix was fabricated by hot press sintering method. Corrosion properties of the alloy were investigated using anodic polarization and immersion tests in 1 mol/L HCl, 1 mol/L H₂SO₄ and 1 mol/L NaOH solutions, respectively. Results showed that the alloy had very low corrosion rate in three tests solutions due to the formation of a stable and compact passive film (SiO_x, MoO₃ and MoO₂) as well as the chemical stability and strong bonds with large covalent component inherent to Mo₅Si₃-based alloy. Only a slight pitting could be observed on the sample surface as a result of selective corrosion of the Mo₃Si phases with respect to the Mo₅Si₃ matrix in NaOH solution. Meanwhile, the alloy exhibited excellent electrochemical corrosion resistance in acidic environments excluding NaOH solution. The alloy was less corrosion resistance because of the formation and dissolution of Na₂SiO₃ and damaging the integrity of SiO₂ preservative in NaOH solution.

Keywords: Metal silicide; Corrosion; Mo₅Si₃; Passive film; Intermetallics

1. INTRODUCTION

In recent days, there is a need for materials with good properties to support extreme conditions such as high-temperature, high stresses and corrosive environments [1]. Wear and corrosion are two of the three most frequently encountered failure modes for mechanical components working under aggressive service conditions [2,3]. Many industries components are more severely degraded by the interaction of wear and corrosion. However, traditional materials are not always able to meet both the corrosion and wear resistance simultaneously [4,5]. Therefore, development of new materials working in corrosion and wear environments has important significance [6].

Mo-Si refractory metal silicides have many attractive properties such as high melting point, high hardness and excellent chemical stability due to their strong atomic bonds [7-11]. D8m-structured Mo₅Si₃ is the most refractory compound in the Mo-Si binary system with a melting point of 2180 °C [12,13]. And it has a great potential for structural application in harsh environment. It is well known that their high-temperature oxidation stability is due to the formation of a highly protective SiO₂ layer [14-16]. Meanwhile, due to its high hardness, unique chemical composition and strong bonds with large covalent component, Mo₅Si₃ is anticipated to be a novel wear and corrosion resistant candidate material [17]. While many studies for the strengthening and toughening of Mo₅Si₃ have been reported, corrosion behaviors of Mo₅Si₃ have hardly attempted [11,18].

Microstructural characteristics and compactness are considered to be beneficial to increase the corrosion resistance [11]. However, due to their high melting point and high vapour pressure, the complete densification of pure Mo and Si powder mixtures needs extremely high sintering temperatures. Mo_5Si_3 alloys have been synthesized by various methods such as arc-melting and casting, mechanical alloying, solid-state displacement reaction and self-propagating high-temperature synthesis [19-21]. However, the limitation of all these methods lies in that they are time consuming, microstructure stress and defects or the products are porous. Compared with those techniques mentioned above, medium frequency induction hot-pressing method has a high-energy heat source for sintering simultaneously with a uniaxial pressure to primarily sinter powders. This method ensures a very rapid heating rate and mass transfer speed, and allows the sample to be fabricated in a short period time at a relatively lower temperature. Some silicides and ceramics prepared by hot-pressing sintering have a high density and fine microstructure.

In this study, corrosion behaviors of a hot pressing sintered Mo_5Si_3 were investigated in 1 mol/L HCl, 1 mol/L H₂SO₄ and 1 mol/L NaOH solutions. Anodic potentiodynamic polarization and immersion tests were performed to evaluate the corrosion resistance of the Mo_5Si_3 -based alloy. The corrosion properties of Mo_5Si_3 -based alloy and corresponding corrosion mechanisms were studied in details.

2. EXPERIMENTAL

Commercial pure molybdenum and silicon elemental powders in purity of 99.5% and an average particle size ranging from 3 to 5 μ m were selected as the raw materials. The powders were blended and milled in a planetary ball mill at room temperature. Ball-to-powder weight ratio was 10:1 and rotation speed 300 rpm. The milled powder was loaded into a cylindrical carbon die with an inner diameter of 25 mm. The sintering temperature was set to 1450 °C (the melting point of silicon is 1415 °C and liquid phase sintering is promising for higher density) and the sample was heated at a rate of 75 K/min and kept at 1450 °C for 30 min. Meanwhile, a uniaxial pressure of 50 MPa was applied during the sintering cycle. The hot pressed product was a plate of 25 mm diameter and approximately 8mm thickness. Microstructure of Mo_5Si_3 alloy was characterized by JSM-6700F scanning electron microscopy (SEM). Phases of the alloy were determined by X-ray diffraction using the Rigaku D/max-2400 pc automatic X-ray diffractometer with Cu target K α radiation (λ =0.15418 nm). Chemical

compositions of the phase constituents were analyzed by energy dispersive X-ray analysis (EDS). The relative density of the alloy was measured by the Archimedes method.

Corrosion testing specimens were electrical discharge machined into 8 mm×8 mm×6 mm. Prior to the electrochemical tests, the specimens were grounds up to 2000 grit SiC emery paper. Then, they were ultrasonically cleaned in acetone and kept in desiccators for 10 h. Corrosion resistance of alloy was investigated by immersion and anodic potentiodynamic polarization measurements at ambient temperature (\sim 25 °C) in 1 mol/L HCl, 1 mol/L H₂SO₄ and 1 mol/L NaOH solutions, respectively. The corrosion solutions were prepared from reagent grade chemical and distilled water. Electrochemical measurements (CH1604C instrument) were conducted in a three-electrode cell, using a platinum counter electrode and a saturated calomel reference electrode. Experiments were performed by sweeping potential from -1000 to 2000 mV at a scan rate of 2 mV/s. All the tests were repeated at least three times for accuracy.

Austenitic stainless steel 0Cr18Ni9 was selected as the reference materials for both immersion and anodic polarization tests. The surface of samples after experiments was investigated using scanning electron microscopy. Meanwhile, in order to obtain a stable passive film for X-ray photoelectron spectrometer analysis using the AXIS Ultra X-ray photoelectron spectrometer with Al K α (1486.71 eV) monochromatic radiation, the electrochemical constant-potential passivation treatment at applied potential of 0.1 V for 10 min was conducted for the Mo₅Si₃ alloy in 1 mol/L HCl solution. Peak identification was performed by reference to a XPS database.

Immersion corrosion tests were conducted by immersing the Mo_5Si_3 alloy in 1mol/L HCl, 1 mol/L H₂SO₄ and 1 mol/L NaOH water solutions at ambient temperature for 100 h. The immersion corrosion resistance of the Mo_5Si_3 alloy and 0Cr18Ni9 was characterized by measuring the corrosion induced mass loss using a precision electronic balance with an accuracy of 0.1 mg. Corrosion rates were estimated from mass loss after immersion in these solutions.

3. RESULTS





Figure 1. X-ray diffraction pattern of the Mo₅Si₃ alloy

As shown in Fig. 1, the XRD pattern of the sample shows the main phase constituents of the alloy are Mo_5Si_3 and a small amount of Mo_3Si . As shown in Fig. 2, the Mo_5Si_3 alloy has a uniform microstructure free from pores and micro-cracks.



Figure 2. OM (a) and SEM (b) micrographs showing microstructure of the Mo₅Si₃ metal silicide alloy

3.2 Electrochemical test



Figure 3. Anodic potentiodynamic polarization curves of the Mo_5Si_3 alloy in comparison to the stainless steel 0Cr18Ni9 in 1 mol/L HCl (a), 1 mol/L H₂SO₄ (b) and 1 mol/L NaOH (c) solutions

17%, respectively.

Fig. 3(a) shows the polarization curves of the Mo_5Si_3 alloy and austenitic stainless steel 0Cr18Ni9 in 1 mol/L HCl water solution at room-temperature. When the potential is anodically scanned, no active-passive transition range was observed on the anodic polarization curves of Mo_5Si_3 alloy, indicating that the alloy is passivated immediately. The anodic current density of the alloy increases gradually after a short passivation range on the anodic polarization curve, suggesting transpassive dissolution of the alloy. At higher potential, the anodic current density of the alloy decreases obviously with the increasing potential as a result of secondary passivation of the alloy. The Mo_5Si_3 alloy has higher corrosion potential and much lower corrosion current density compared with the 0Cr18Ni9 stainless steel, implying that the Mo_5Si_3 alloy exhibited excellent corrosion resistance than the 0Cr18Ni9 stainless steel in 1mol/L HCl solution.

As shown in Fig. 3(b), the potentio-dynamic anodic polarization curves of the Mo_5Si_3 alloy in 1 mol/L H₂SO₄ solution has the similar shape with that of the alloy in 1 mol/L HCl solution. Although the austenitic stainless steel has a wide passivation region, the present alloy has considerably higher corrosion potential and much lower corrosion current density compared with the stainless steel 0Cr18Ni9, showing that the Mo_5Si_3 -based alloy exhibits high corrosion resistance in 1 mol/L H₂SO₄ solution.

As indicated in Fig. 3(c), the Mo_5Si_3 alloy has a lower corrosion potential and a higher current density than 0Cr18Ni9 at the initial stage. Meanwhile, the corrosion potential of the alloy in 1 mol/L NaOH solution is obviously negative than that in the other two solutions, which also indicates the relatively high susceptibly of the alloy to electrochemical corrosion in alkaline medium.



Figure 4. XPS survey spectra of the Mo₅Si₃-based alloy after passivation at 0.1 V vs. SCE for 10 min in 1 mol/L HCl solution



Figure 5. High-resolution XPS spectra of Mo₅Si₃-based alloy after 10 min potentiostatic polarization at 0.1 V vs. SCE in 1 mol/L HCl solution: (a) Mo 3d, (b) Si 2p



Figure 6. Surface morphologies of the Mo₅Si₃ alloy after anodic potentiodynamic polarization in 1mol/L HCl(a), 1 mol/L H₂SO₄(b) and 1 mol/L NaOH(c).

Corrosion behavior of material is often controlled by the properties of surface passive film. Passive films of Mo_5Si_3 -based alloy after passivation at 0.1 V vs. SCE in 1 mol/L HCl solution were

studied by XPS (as shown in Fig. 4), exhibit peaks of Mo, Si, O and C. The C 1s peak possibly arose from a contaminant hydrocarbon layer covering the specimen surface [17]. In order to further determine the film components, the high-resolution XPS spectra of Mo 3d and Si 2p regions were recorded, as shown in Fig. 5. The Mo 3d spectrum consist of two peaks at 231.79 eV and 235.1 eV, which are designated as MoO₃ and MoO₂, respectively. The Si 2p spectrum with a binding energy of 101.8 eV, corresponded to Si in silicon oxides form (SiO_x). This is close to the results obtained by Jiang [11], who reported that Si 2p peak was made up of oxidized components (SiO_x) in the passive film on the (Mo_xCr_{1-x})₅Si₃ films in NaCl solution. According to the XPS analysis showed that the main component in the passive film is silicon oxide (SiO_x) coexisting with molybdenum oxide (MoO₃ and MoO₂) in HCl solution.

Fig. 6 shows the corrosion surface morphologies of Mo_5Si_3 alloy after anodic potentiodynamic polarization in three solutions. Compared with Fig. 2(b), it could be observed that the surface of the alloy was obviously destroyed, and become coarse and porous after anodic polarization corrosion in HCl solution, as shown Fig. 6(a). This is mainly attributed to the dissolution of the surface passive film. The surface of the alloy after anodic polarization corrosion in 1mol/L H₂SO₄ solution has the similar morphology with that of alloy in 1 mol/L HCl solution, as shown Fig. 6(b). However, it is evident from Fig. 6(c) that Mo_5Si_3 -based alloy has been suffered from the severe attack of OH⁻¹ ion and a large area of spalling occurs on the corroded surface, and the degree of surface damage dependent on the Si content in Mo_5Si_3 alloy. In general terms, the phases with lower silicon contents were least corrosion resistant. For instance, as shown in Fig. 6(c) the Mo_3Si phases were preferentially corroded with respect to the Mo_5Si_3 matrix. Meanwhile, preferential corroded at the interface of the cluster of grains were found in the case of Mo_5Si_3 alloy in 1 mol/L NaOH solution.

3.3 Immersion corrosion test

The mass loss of the alloy and the stainless steel 0Cr18Ni9 induced by immersion corrosion in the HCl, H₂SO₄ and NaOH solutions open to air at the room temperature for 100h are shown in Table 1. Meanwhile, the corrosion rates are also calculated according to the mass loss of the alloy and stainless steel. In 1 mol/L HCl and 1 mol/L H₂SO₄ solutions, stainless steel 0Cr18Ni9 dissolves actively, showing a high corrosion rate of 12.04 mm/a and 12.791 mm/a, respectively. On the other hand, the corrosion rate of Mo₅Si₃-based alloy only is 0.064 mm/a and 0.011 mm/a, respectively. Therefore, it is clear that the Mo₅Si₃-based alloy has much high corrosion resistance than the reference material in 1mol/L HCl and 1mol/L H₂SO₄ solutions. In addition, after immersion in HCl, H₂SO₄ and NaOH solutions for 100 h, the mass loss of alloys is so slight that it could be almost ignored. All the samples maintain good metallic shinning after immersion for 100 h in HCl and H₂SO₄ solutions excluding NaOH solution. As shown in Fig. 7, the surfaces morphologies of alloy specimens and the reference materials are observed by scanning electron microscopy (SEM). No change could be seen on the surface of the alloy after immersion tests in HCl and H₂SO₄ solutions. Only a slight pitting could be observed on the sample surface after immersion for 100h in NaOH solution. However, the reference material completely loses metallic luster, pitting, ditches and grain boundary corrosion are observed everywhere throughout the surface after immersion in three solutions for 100h, as shown Fig. 7(b), (d) and (f). Results of mass losses and surface morphologies are consistent and indicate the excellent corrosion resistance of the Mo_5Si_3 -based alloy during immersion in the HCl, H_2SO_4 and NaOH solutions.

Table 1. Results of immersion corrosion tests of the Mo₅Si₃-based alloy and austenitic stainless steel0Cr18Ni9 in 1 mol/L HCl, 1 mol/L H₂SO₄ and 1 mol/L NaOH solutions for 100 h.

| Electrolytes | Test materials | Corrosion mass loss(mg) | Corrosion rate (mm)year |
|--|--|----------------------------|----------------------------|
| 1 mol/L HCl | Mo ₅ Si ₃ -based alloy | 0.6 | 0.064 |
| | Austenitic stainless steel 0Cr18Ni9 | 123.4 | 12.040 |
| 1 mol/L H ₂ SO ₄ | Mo ₅ Si ₃ -based alloy | 0.1 | 0.011 |
| | Austenitic stainless steel 0Cr18Ni9 | 131.1 | 12.791 |
| 1 mol/L NaOH | Mo ₅ Si ₃ -based alloy | 0.1 | 0.011 |
| | Austenitic stainless steel 0Cr18Ni9 | 1.2 | 0.117 |



Figure 7. SEM images showing the surface morphologies of the Mo₅Si₃-based alloy(a),(c),(e) and austenitic stainless steel(b),(d),(f) after immersion for 100h in 1 mol/L HCl(a),(b), 1 mol/L H₂SO₄(c),(d), and 1 mol/L NaOH solutions(e),(f)

4. DISCUSSIONS

The present experimental results indicated that the Mo_5Si_3 -based alloy exhibited excellent corrosion resistance both in the anodic polarization and immersion corrosion tests in HCl and H_2SO_4 solutions. In comparison to austenitic stainless steel 0Cr18Ni9 which was widely applied in industries for its outstanding corrosion resistance, the Mo_5Si_3 -based alloy was much more corrosion resistance. The considerably higher corrosion potential, much lower corrosion current density and a secondary

passivation region were observed under the anodic polarization test conditions in HCl and H_2SO_4 solutions. Meanwhile, the alloy displayed relatively low immersion corrosion rates in three solutions. As indicated in Fig. 3(c), though the Mo_5Si_3 alloy has a lower corrosion potential and a higher current density than 0Cr18Ni9, the mass loss of alloy was much lower in NaOH solution.

As shown in Fig. 7(b), the pits and ditch appeared on the surface of austenitic stainless steel. The micro-pits were gradually connected with each other during the immersion test as a result of the breakdown of the passive film. While, no significant changes were observed on the surface of the Mo₅Si₃ alloy and the breakdown mechanism of passive film indicating the gradual dissolution mechanism, instead of an abrupt breakdown mechanism of passive film. Two models are used to describe the mechanism of the passive film in HCl solution. For instance, the adsorption of Cl- on the passive film and the ion migration or penetration of Cl- ion through the passive film to metal surface [6, 22]. While, no signals of chloride ions were detected in the passive film of the Mo₅Si₃ alloy according to the XPS results. Thus, the absorbed Cl- on alloy surface was very low and the passive film was more insensitive to pitting corrosion than n-type film [23]. Therefore, the Mo₅Si₃ alloy displayed excellent corrosion resistance in HCl solution.

It is well known that Mo and Si are all strong passive elements in aggressive environments. As indicated by the XPS results in Fig. 4 and Fig. 5, the passive layer formed on the surface of the Mo_5Si_3 -based alloy is composed mainly of silicon oxide (SiO_x) and molybdenum oxide (MoO_3 and MoO_2). The higher molybdenum and silicon contents in this alloy and the high oxygen affinity of molybdenum and silicon would promote the rapid formation of a compact and electrochemically stable oxide passive film on the surface of the alloy, protecting the alloy from further attacks under an aggressive environment was responsible for the high corrosion resistance of the present alloy. Meanwhile, the silicon oxide in the passive film has a significant corrosion inhibition effects, due to its good corrosion resistance and almost insolubility in acidic and neutral media. Furthermore, the chemical stability and strong inter-atomic bonds inherent to Mo_5Si_3 also make an important contribution to the excellent corrosion-resistance of the Mo_5Si_3 alloy.

The Mo₅Si₃ alloy displayed relatively low electrochemical corrosion resistance in 1 mol/L NaOH solution due to the lack of a stable passivation state compared with that in acidic environments. XPS results indicated that the passive film mainly composed of silicon oxide (SiO₂ or SiO). In NaOH solution, SiO₂ reacts with NaOH and formed Na₂SiO₃ when polarized to a certain anodic potential according to the reaction SiO₂+OH⁻¹ \rightarrow SiO⁻³+H₂O [17]. Na₂SiO₃ was dissolved and damaging the integrity of SiO₂ preservative in NaOH solution. In addition, owing to a lack of passive film (SiO₂), the grain boundary has negative effect on corrosion behavior of the alloy, accelerating corrosion by forming micro-electrochemical cells between grains boundaries and the matrix and by increasing the electrochemical reactivity during the corrosion process, as shown in Fig. 6(c).

5. CONCLUSIONS

Mo₅Si₃-based alloy was fabricated by hot press sintering with Mo-Si elemental powder blends. Microstructure of Mo₅Si₃-based alloy consists of small amount of Mo₃Si uniformly distributed in a Mo_5Si_3 matrix. The alloy exhibited excellent electrochemical corrosion resistance compare with OCr18Ni9 stainless steel in 1 mol/L HCl and 1 mol/L H₂SO₄ solutions due to the formation of a stable and compact passive film (SiO_x, MoO₃ and MoO₂). Meanwhile, the chemical stability and strong bonds with large covalent component inherent to Mo_5Si_3 -based alloy are also beneficial to its excellent corrosion resistance. However, the alloy displayed relatively low electrochemical corrosion resistance in 1 mol/L NaOH solution due to the formation and dissolution of Na_2SiO_3 and damaging the integrity of SiO₂ preservative. Results of mass losses and surface morphologies indicate the excellent corrosion resistance of the Mo_5Si_3 -based alloy during immersion in three test solutions. Only a slight pitting could be observed on the sample surface as a result of selective corrosion of the Mo_3Si phases with respect to the Mo_5Si_3 matrix after immersion for 100 h in NaOH solution.

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References

- 1. J.G. Gonzalez-Rodriguez, I. Rosales, M. Casales, S. Serna, L. Martinez, *Mater. Sci. Eng.* A. 371 (2004) 217
- 2. H.M. Wang, G. Duan, Intermetallics. 11 (2003) 755
- 3. S. Tao, D.Y. Li, Wear. 263 (2007) 363
- Yanqiu Xia, Junhong Hu, Feng Zhou, Yimin Lin, Yulin Qiao, Tao Xu, Mater. Sci. Eng. A. 402 (2005) 135
- 5. Shizhong Wei, Jinhua Zhu, Leujue Xu, Mater. Sci. Eng. A. 404 (2005) 138
- 6. L. Yuan, H.M. Wang, *Electrochem Acta*. 54 (2008) 421
- 7. F. Neppl, G. Menzel, U. Schwabe, J. Electrochem. Soc. 130 (1983) 1174
- 8. M. Herranen, A. Delblanc Bauer, J.O. Carlsson, R.F, Surf. Coat. Tech. 96 (1997) 245
- 9. K Yoshimi, S. Nakatani, N. Nomura, S. Hanada, Intermetallics. 11 (2003) 787
- 10. C.L. Yeh, W.H. Chen, J. Alloys Compd. 438 (2007) 165
- 11. Jiang Xu, Chenghou Zhou, Shuyun Jiang, Intermetallics. 18 (2010) 1669
- 12. Erik Strom, Sten Eriksson, Hakan Rundlof, Ji Zhang, Acta Mater. 53 (2005) 357
- 13. Sergey A. Kuznetsov, Evgeny V. Rebrov, Martijn J.M. Mies, Mart H.J.M. de Croon, Jaap C. Schouten, *Surf. Coat. Tech.* 201 (2006) 971
- 14. Sharma Paswan, R. Mitra, S.K. Roy, Mater. Sci. Eng. A. 424 (2006) 251
- 15. R. Sakidja, J.S. Park, J. Hamann, J.H. Perepezko, Scripta Mater. 53 (2005) 723
- 16. J.G. Gonzalez-Rodriguez, I. Rosales, M. Casales, S. Serna, L. Martinez, J. Solid State Electr. 9 (2005) 691
- 17. L. Yuan, H.M. Wang, Intermetallics. 16 (2008) 1149
- 18. J.H. Yan, H.A. Zhang, S.W. Tang, J.G. Xu, Mater Charact. 60 (2009) 447
- 19. Q.D. Hu, P. Luo, Y.W. Yan, J. Alloys Compd. 468 (2009) 136
- 20. H.A. Zhang, X.Y. Liu, Int J Refract Met H. 19 (2001) 203
- 21. P.V. Krakhmalev, Int J Refract Met H. 22 (2004) 205
- 22. A. Kocijan, C. Donik, M. Jenko. Corr. Sci. 49(2007) 2083
- 23. G. Bianchi, A. Cerquetti, F. Mazza, S. Torchio, Corr. Sci. 12(1972) 495

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