

Preparation of Oxidation Resistance Coating of Silicide by Pack Cementation

Tao Lin^{1, a}, Huiping Shao¹ and Wenwen Zhang¹

¹Institute for Advanced Material & Technology, University of Science and Technology Beijing, Beijing 100083, China

^aemail: lintao@ustb.edu.cn

Keywords: Pack cementation; Coating; Silicide; Oxidation

Abstract. The application of molybdenum was limited as a candidate material for working at a high temperature because molybdenum has a poor oxidation resistance. MoSi₂ is typically selected to solve the problem since it can form a dense SiO₂ coating to protect the substrate molybdenum. MoSi₂ coating on the surface of the Mo was prepared by pack cementation process in this paper. The silicide coating was formed by controlling the weight ratio of Si/MoSi₂ powders and the pack cementation time. The results showed that the Si is mainly involved in the formation of a silicide layer on the surface of Mo. The MoSi₂ is little participation in the coating formed. Two silicide layers have formed on the surface of Mo, outer layer of MoSi₂ and inner layer of Mo₅Si₃. With the extension of time, the thickness of the MoSi₂ layer and the Mo₅Si₃ layer increases, but the increasing rate slows down.

Introduction

High melting point and high temperature strength of refractory metals has attracted the attention of many researchers, Refractory materials play an important role in national defence industry, aviation, nuclear industry[1,2]. Metals with melting point above 1800 °C, such as tungsten, molybdenum, niobium, vanadium and chromium, have lower prices and wide range of practical applications. Molybdenum has been attended as high temperature performance, high thermal conductivity, specific heat capacity low, and has good thermal shock and thermal fatigue ability. Molybdenum antioxidant performance is poor, because they begin to form oxide above 400°C, and volatilization of the oxide with the increase of temperature rapidly speed up[3], resulting in the failure of materials, but the high temperature anti-oxidation coating can effectively resolve the refractory metals oxidation problem. The development of high temperature anti-oxidation coating has attracted the attention of many researchers at home and abroad. Ryosuke, etc. [4] using the Molten-salt Growth Method in a pure Nb matrix prepared NbSi₂ coating. Tatsuo, etc. [5] has prepared Mo(Si,Al)₂ coating by hot pressing coated niobium alloys. The lack of the antioxidant capacity of these coating systems or service temperature is low (≤1400°C), and difficult to meet the high temperature (≥1600°C) for a long time anti-oxidant requirements.

Excellent high temperature properties of MoSi₂ caused the concern of researchers recently. The glassy SiO₂ phase generated at high temperatures can prevent the further oxidation of the coating, and effectively play a role in filling the crack. As for the formation of MoSi₂ coating, Mo layer was firstly deposited using plasma or arc[6], and then silicified to the MoSi₂ coatings. This MoSi₂ coating has more pores or cracks and it is easy to peel off. Suzuki etc [7] prepared MoSi₂ coatings on the Mo substrate and alloy steel by a molten salt method, the laser cladding method and CVD method, but the cost is high.

The MoSi₂ coatings were prepared by dipping slurry on a molybdenum substrate, and then using the pack cementation method in this study. The coating density, thickness and other factors were analyzed.

Experimental

1mm thick molybdenum plates were cut into 30mm×15 mm samples and the samples surface was ground with sandpaper, and was cleaned by ultrasonic instrument filled with acetone, and then dried. The Si powder, MoSi₂ powder and activator powder were mixed by a certain proportion, and then mixed with organic binder into the slurry on the molybdenum surface. After dried, the mixed powder was covered in a crucible. Lastly, the sample was put into a vacuum furnace for heat treatment at the temperature of 1320°C for 7 hours.

The sample was cut and polished the cross-section after the heat treatment. The organization and structure of the coating were analyzed by using the scanning electron microscope (JSM-5600LV type) and the spectrum analyzer (IE 300 X-type).

Results and Discussion

The effect on the ratio of Si powder and MoSi₂ powder. Si powder is a silicon atom source. MoSi₂ powder could be a diluent and NaF powder plays the role of the activator. The Si atoms spread to Mo atoms vicinity to react with Mo for formation a silicide. The different Si, MoSi₂ weight ratio was designed, and to study the formation of the silicide layer. The total weight of these two materials is 30g.

Fig. 1 is the morphology of samples cross section with heat treatment at the different ratio of Si/MoSi₂. It shows that the molybdenum surface have formed two layers of the darker outer layer and lighter inner layer. Through energy dispersive spectroscopy analysis, the outer layer of Mo / Si atomic ratio close to 1:2, formed the MoSi₂ layer and the inner Mo / Si atomic ratio close to 5:3 formed the Mo₅Si₃ layer. Observed the morphology of the coatings, the outer layer of MoSi₂ prone to cracks, while inner Mo₅Si₃ coating almost no cracks. It shows that the coating have good thermal expansion match between Mo₅Si₃ layer and Mo substrate. The coatings cracks were led by a large internal stress cooling to room temperature.

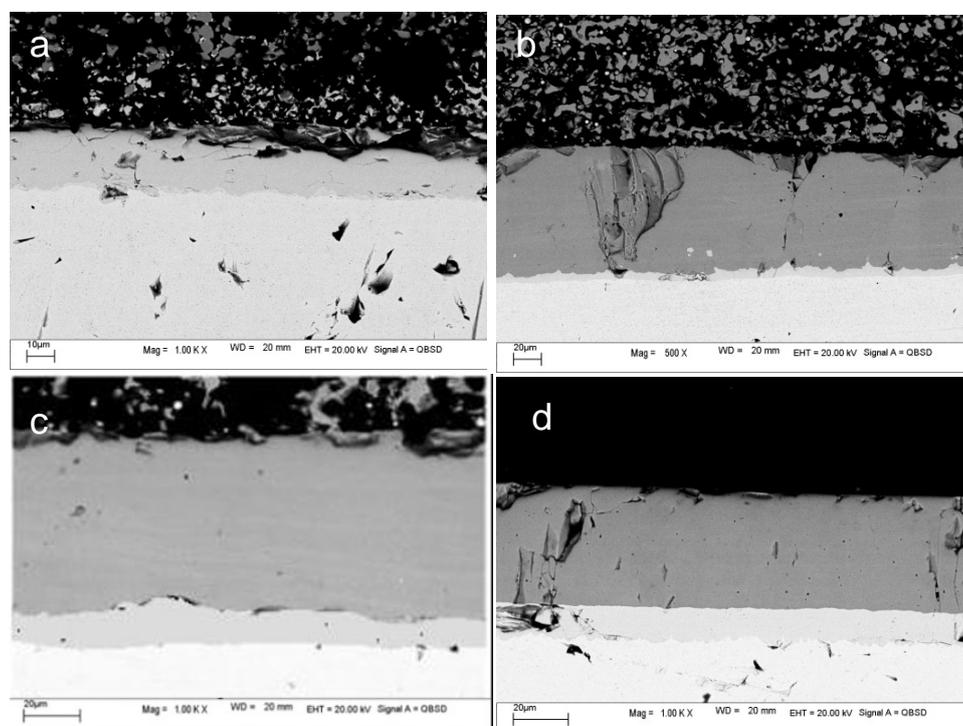


Fig.1. The different Si/MoSi₂ proportion of cross-section diagram (a)0:30; (b)1:4; (c)1:2; (d)30:0

A Mo₅Si₃ transition layer has formed between the MoSi₂ layer and Mo substrate, but it was impossible to reach significant buffering effect because the thickness is too small, and the MoSi₂ layer still have cracks because of the large internal stress.

Table 1 shows the total thickness of the silicide layer under the different ratio of Si / MoSi₂. Silicide layer was also formed when there was no silicon, but it was thin. Although the ingredients of MoSi₂ was a diluents, a small amount of participation in the silicide layer generated in the heating process. At this point, the Mo₅Si₃ layer was very thin. Mo₅Si₃ and MoSi₂ layer thickness increased significantly with the silicon appear in the ingredients, it is the main reason that the silicon and activator interaction for the formation of the silicide layer. The outer layer thickness decreases, while the inner layer thickness was significantly increased without the MoSi₂ powder. It indicates that the silicon powder can conducive to the form the inner layer, and the MoSi₂ powder can conducive to form the outer layer.

Table 1. Different Si/MoSi₂ proportion of the coating thickness

Si/MoSi ₂		0:30	1:4	1:2	30:0
Coating thickness / μm	Outerlayer MoSi ₂	19.2	60.0	61.5	42.3
	Innerlayer Mo ₅ Si ₃	0.8	5.1	10.0	12.3
	Total thickness	20.0	65.1	71.5	54.6

The effect of the pack cementation time. Fig. 2 shows the coating cross-section images while increasing the pack cementation time. The MoSi₂ outer layer, Mo₅Si₃ inner and coating total thickness has been shown in Table 2. The thickness of coating increased followed with increasing the sintering time, especially the outer layer of MoSi₂. But the trend of increase of coating thickness slow down followed with increasing time. The Si and Mo layer interface to generate a thin layer of the low-silicide Mo₅Si₃ at the early reaction stages. With the conduct of Si diffusion layer Mo₅Si₃ reacts with Si to generate MoSi₂ layer, the reaction process is controlled by the diffusion rate of Si by the MoSi₂ layer. Low silicide Mo₅Si₃ as a reaction diffusion front of the interface moved to the Mo layer. With increasing sintering time, its thickness increased. However, because the diffusion of Si affect by the new phase layer, the increased trend of the coating thickness was decreased. Xiao Lai-rong etc. also found silicide coating thickness which formed on the niobium alloy and time has a parabolic relationship [8].

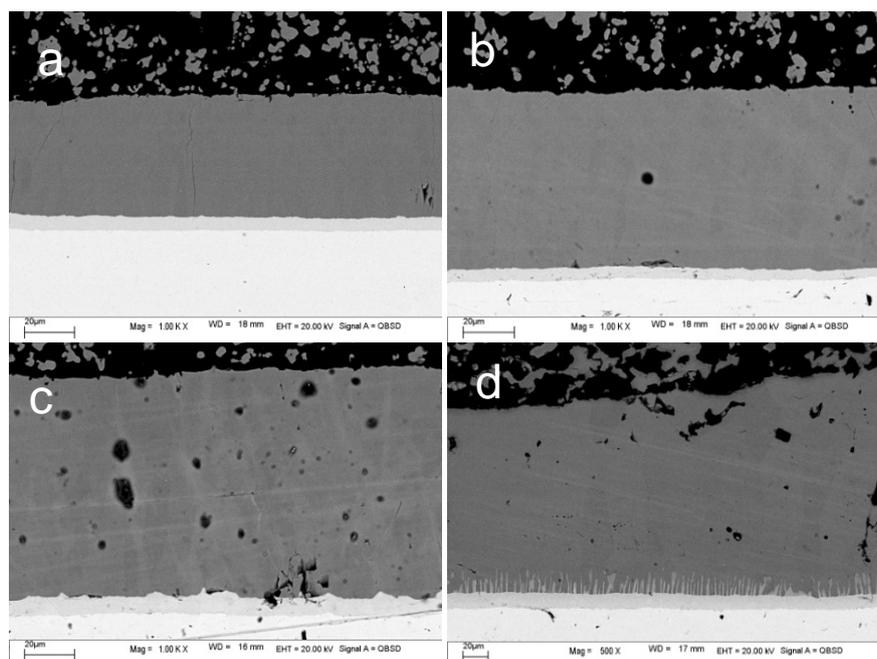


Fig. 2. Different pack cementation time obtained coating cross-section (a)1h; (b)2h; (c) 4h; (d)7h

Table 2. Different pack cementation time obtained coating thickness

time /h		1	2	4	7
Coating thickness / μm	Outerlayer MoSi_2	46.4	66.7	88	157
	Innerlayer Mo_5Si_3	4.8	4.4	8	12.9
	Total thickness	51.2	71.2	96	169.9

Conclusions

Silicide coating on the surface of the Mo was successfully prepared by the pack cementation method in this paper. Si in the ingredients mainly related to the formation of the Mo surface silicide layer, MoSi_2 can also participate in a small amount of coating formation. Two layers of silicide layer formed on the surface of Mo, outer layer is MoSi_2 , and inner is Mo_5Si_3 , the silicide thickness of the outer and inner layers increased with the extension of the pack cementation time, but the trend of increase gradually decreased.

Acknowledgements

This work was financially supported by the Education & Research Project of Guangdong Province (No.2011A090200091).

References

- [1] Ge Qi-Lu, Xiao Zhen-Sheng, Han Huan-Qing. Applications and developing tendency of advanced refractory materials in high-tech fields. *Mater Sci Engin* Vol. 18(z1)(2000), p.123.
- [2] S Jia Zhonghua. High-temperature oxidation-resistant coatings for columbium alloy and molybdenum alloy with slurry method. *Powder Metall Tech* Vol. 19(2001), p.74.
- [3] U.S. National Materials Advisory Committee, Coating Committees. High temperature anti-oxidation coating. Beijing, Science Press(1980).
- [4] Ryosuke Suzuki, Masayori Ishikawa, Katsutoshi Ono. NbSi_2 coating on niobium using molten salt. *J Alloys Compounds* Vol. 336(2002), p.280.
- [5] R Tatsuo T, Kim J H. Development of $\text{Mo}(\text{Si},\text{Al})_2$ base oxidation-resistant coating on Nb-base structure materials. *Metall Mater Trans A* Vol. 36A (2005), p.617.
- [6] Zhang Zhongwei, Wang Junshan, Xu Zhenghui Li. Preparation processes affecting anti-oxidation property of MoSi_2 layer on SiC coated C/C composites. *Aerospace Mater Tech* Vol. 37(2007), p.58.
- [7] Suzuki R, Ishikawa M, Ono K. NbSi_2 coating on niobium using molten salt. *J Alloys Compounds* Vol. 336(2002), p.280.
- [8] Xiao Lai-rong, Yi Dan-qing, CAI Zhi-gang. Microstructure and formation mechanism of silicide coating prepared by pack cementation. *J Central South University* Vol. 39(2008), p.49.
- [9] Kook C K, Yu T H. Pack cementation coating on Ti3Al-Nb alloys to modify the high-temperature oxidation properties. *Surf Coating Tech* Vol. 126(2000), p.171.
- [10] Deevi S C. Diffusional reactions between Mo and Si in the synthesis and densification of MoSi_2 . *Inter J Refract Metals Hard Mater* 13(1995), p.337.