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Silicide coating on refractory metals in molten salt

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Abstract

For better oxidation resistance of refractory metals in air, the electroless coating of silicide in the molten salt was developed in open air at 973–1173 K. The molten salt consists of NaCl, KCl, Na₂SiF₆ and Si powder, where the proportional reaction between Si and Si⁴⁺ ions forms Si²⁺ ions. Si²⁺ deposits on the metal substrate and forms the metal silicide. The deposited silicide layers were classified into two categories depending on the metal substrates: (1) Nb, Mo and Cr mainly formed silicon-rich disilicide (MSi₂) layer. (2) Fe, Ni and Co formed silicon-poor silicide layer (MSi_n, n < 2), such as Fe₃Si. This difference was described by the diffusivity of Si through the silicide layer into the metal. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Molten salt; Electroless plating; Transition metal compounds; Coating materials

1. Introduction

The resistance to corrosion and oxidation of pure metals can be improved by adding appropriate amount of silicon [1,2], whereas the workability of the metals is damaged by silicon alloying because their strength and toughness decrease. Supposing that silicon could permeate only into the metal surface, the chemical properties of alloys would be improved without any damage to mechanical property of the bulk [1,2].

Since the early time, various methods for silicide coating have been studied, such as vacuum deposition, chemical vapor deposition, or solid reaction with silicon powder. For example, the pack-cementation method has been extensively studied as low cost, good adhesion coating [3,4]. Because this process is based on the chemical vapor deposition from the dilute halide gas phase, as shown in Fig. 1(a), it requires encapsulation, long reaction time and a high vapor pressure at temperatures as high as 1273–1473 K.

The molten salt is the media also suitable to carry Si to the metallic substrate. The coating techniques using molten salt are classified into the two categories: electrolytic and electroless plating. Ueda et al. [5] applied the electrolytic plating of an iron substrate in the molten LiCl–KCl–LiF– K_2SiF_6 bath impressing 0.6–1.0 V (vs. Li⁺/Li) at 723 K. They reported that the deposits were dendritic or powdery. It was reported, however, that the non-electrolytic plating could deposit about 200 µm thick smooth silicide on metal surface, simply by immersing the iron substrate into the molten salt composed of KCl–NaCl–NaF–Na₂SiF₆–Si (–SiO₂) below 1273 K [6–13]. This method does not require any external electrical energy, and it was operable in air at 973–1173 K, lower than the pack cementation processing temperature [3,4].

The purpose of this work is to find the applicability of the electroless silicide coating on the refractory metals, and to know experimentally their preferable phase of silicide in this technique.

2. Silicide deposition on metal substrate

The detailed principle of the electroless deposition was reported in [7–13]. A brief outline will be given here. When Na_2SiF_6 and Si powder are added to the supporting chloride salt, the proportional and disproportional reactions between Si and Si⁴⁺ ions deposit a siliconized layer on the metallic

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Fig. 1. Silicide formation on the metallic substrate using vapor deposition (a) and molten salt (b).

substrates, M, as:

Si (source particles in the molten salt) $+ 6F^{-}$

 $+\operatorname{SiF}_{6}^{2-} \to 2\operatorname{SiF}_{6}^{4-} \tag{1}$

 $2SiF_6^{4-} + M(substrate) \rightarrow M-Si(siliconized layer)$

$$+6F^{-}+SiF_{6}^{2-}$$
 (2)

The deposited Si from Si^{2+} penetrates into the metal surface, and forms an alloy (M–Si) with the metal substrate. The total reaction

Si(particle in the molten salt) + M(substrate)

$$\rightarrow$$
 M-Si(siliconized layer) (3)

shows that the reaction is driven by the difference between the thermodynamic activity of pure silicon and that of the siliconized layer. In this thermodynamic sense, the deposition reactions are fundamentally the same as both the pack cementation in the gaseous state (Fig. 1(a)) and the electroless plating in the molten salt (Fig. 1(b)). The former uses gaseous species as silicon carrier, and the latter the ionic SiF₆⁴⁻. The amount of silicon atoms in the media, however, is much larger in the molten salt than in the gaseous phase. It can enhance silicide formation even at lower temperatures.

This method was fundamentally applied to the coating on the refractory metals, such as Mo [12], Nb [13], Ni [6,7], Cr and Co, which are main components of the refractory commercial alloys.

3. Experimental

The salt was composed of 36.58 mol% NaCl-36.85 mol% KCl-21.95 mol% NaF-4.89 mol% Na₂SiF₆. About 150-200 g salt mixture and Si powder (21.85 mol% for salt mixture) was filled into the alumina crucible, and melted in open air or Ar gas atmosphere. Pure Cr, Fe, Co, Ni, Nb or Mo plate was immersed into the molten salt. After removal of the adhered salt, the cross-section of the sample was observed by the scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) analyzer.

4. Results

Figs. 2 and 3 show the cross sectional views of the deposited samples. The amount of deposit, i.e. the layer thickness, for all the substrates increased commonly at the higher temperature and for the longer time.

The deposited silicides were classified into two groups: the substrate on which the di-silicide (MSi_2) precipitated and that on which the lower silicide (MSi_n , n < 2) was formed. The former (Group A) consists of Mo, Nb and Cr. The latter (Group B) consists of Fe, Co and Ni.

The single phase of metal di-silicide (MSi₂) was deposited on Mo, Nb and Cr substrates (Group A) at 973–1173 K, as identified by X-ray diffraction (XRD) measurements and EDX analysis (Fig. 2). They were the Si-richest phase in the binary systems, as listed in Table 1. For example, the two other silicides, α -Nb₅Si₃ and Nb₃Si, are stable at the studied temperatures, but their formation was never detected. The hexagonal MoSi₂ deposited at



Fig. 2. SEM images of the silicide layer deposited on Mo at 1073 K for 10.8 ks (a), on Nb at 1173 K for 7.2 ks (b), and on Cr at 1073 K for 57.6 ks (c).



Fig. 3. SEM images of the silicide layer deposited on Fe at 1173 K for 10.8 ks (a), on Ni at 973 K for 57.6 ks (b), and on Co at 1173 K for 57.6 ks (c).

973 K on Mo because the tetragonal MoSi₂ is unstable below 1073 K [14]. A faint amount of CrSi phase ($<1 \mu m$ thick) was found by EDX at the interface between CrSi₂ and Cr when the reaction time was longer than 57.6 ks at 1173 K (Fig. 2(c)).

On the Fe, Ni and Co substrates (Group B), the lower silicides were deposited as shown in Fig. 3. For example, γ -Ni₅Si₂, δ -Ni₂Si and ϵ -Ni₃Si₂ were deposited on Ni plate (Fig. 3(b)), while the higher silicides, NiSi and α -NiSi₂,

Table 1

Phases detected after the reaction with the substrate in the molten salt, in comparison with the stable phases in the binary system of M–Si

Group	Substrate	Stable silicides in the binary system	Identified phases ^a
	Мо	MoSi ₂ , Mo ₅ Si ₃ , Mo ₃ Si	MoSi ₂
A	Nb	NbSi ₂ , Nb ₃ Si, Nb ₅ Si ₃	NbSi ₂
	Cr	CrSi ₂ , CrSi, Cr ₅ Si ₃ , Cr ₃ Si	CrSi ₂ , (CrSi)
	Fe	FeSi ₂ , FeSi, Fe ₃ Si	Fe ₃ Si
В	Ni	NiSi ₂ , NiSi, Ni ₃ Si ₂ , Ni ₂ Si, Ni ₅ Si ₂	$(Ni_3Si_2),$ (Ni_5Si_2)
	Ca		$(N_2SI),$ N_5Si_2
	Co	$C031_2, C031, C0_231$	$(CO_2SI),$ CoSi

^a The phases in the bracket were detected only at the higher temperature and/or for the longer reaction time.

were not found, which agreed with the previous work [7]. At the early stage of coating, the lowest silicide was formed on the substrate and the second or third silicide deposited outside the lowest silicide layer as shown in Fig. 3(b). The α -Co₂Si layer was thicker than the CoSi layer for 0.9 ks at 1173 K, however, the thickness of the CoSi layer became larger than that of the α -Co₂Si layer for the longer time, as shown in Fig. 3(c). α -Co₂Si precipitated at the lower temperature and for the shorter time, while CoSi became dominant at the higher temperature and for the longer time.

5. Discussion

Fig. 4(A) shows the formation model (A) of the disilicide formers. The deposited Si from the proportional reaction between Si and Si⁴⁺ ions (Eq. (1)) forms MSi₂ phase first on the surface. Then the subsequently deposited Si diffuses into this MSi₂ phase and reacts with the substrate. After the thick layer formation of MSi₂ phase, the Si supply to the interface delays and the lower silicide, MSi_n (n < 2) is formed as:

$$MSi_2 + M(substrate) \rightarrow MSi_n(at interface)$$
 (4)

There was no quantitative report on the reactivity with Si of Nb and Cr. The diffusivities in the phases, Mo, Mo₃Si and Mo₅Si₃, were studied that the Si diffusion controlled the growth of these Mo silicides [15,16]. The preferential growth of MoSi₂ from the molten salt may be explained by the diffusivity of Si if we can assume that Si diffuses faster in the MoSi₂ phase, although the data for MoSi₂ is unknown.

Fig. 4(B) shows the formation model (B) of the lower silicides. The deposited Si forms MSi_2 phase first, but this di-silicide decomposes to the lower silicides, MSi_m . Then the base metal diffuses through the thin MSi_m layer toward the surface and reacts with Si to subsequently deposit. After the thick layer formation of the lower silicide, then the metal supply to the surface delays and the higher



Fig. 4. Mechanisms of silicide layer formation.

Table 2 Growth constant, k^2 , of the cobalt silicides

	Temperature (K)	$k^2 (10^{-16} \text{ m}^2/\text{s})$		
		a-Co ₂ Si	CoSi	CoSi ₂
Barge et al. [17]	1119	7.1	64	2.5
	1206	40	1000	2.8
	1273	186	743	67
Jan et al. [18]	1173	85	160	3.2
	1273	430	2000	19
	1323	850	3700	47
This work	1173	35.8	149	-

silicide, MSi_n (m < n), is formed as:,

 $MSi_m + Si(deposited) \rightarrow MSi_n (at surface)$ (5)

Table 2 lists the growth constants, k^2 , determined by the diffusion couples in the Co–Si binary system [17,18]

$$k^2 = d^2/t \tag{6}$$

where *d* and *t* are thickness of the silicide layer and the reaction time, respectively. When we assumed the solid reaction of Eq. (5), the k^2 values deduced from this work agreed well with the reported ones. Therefore, we may conclude that the reactions of lower silicide formation are diffusion-limited, although the silicon deposition on the surface, the electrochemical reactions in the salt and the dissolution of Si were suspected as the other possible rate-determining steps.

In the case of Fe, we detected only Fe_3Si phase formation even after the long reaction time. This is consistent with the significant diffusion of Fe that formed the Kirkendal voids at the interface, as shown in Fig. 3(a). The precise analysis on Fe was reported previously [10,11].

Further understanding of the silicide formation mechanism and the coating design will be done when the diffusivity is clarified.

6. Conclusion

The molten salt consisting of NaCl, KCl, Na_2SiF_6 and Si formed the silicide layer on the refractory elements, Cr, Fe, Co, Ni, Nb and Mo. The silicide formation was classified as two groups; (A) di-silicide formers and (B) lower silicide formers. Nb, Mo and Cr mainly formed the silicon-rich

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References

- A.V. Byalobzheskii, M.S. Tsirlin, B.I. Krasilov, High-Temperature Corrosion and Protection of Superrefractory Metals, Atomizdat, Moscow, 1977.
- [2] B.J. Saldanha, M.A. Streicher, Mater. Perform. 25 (1986) 25.
- [3] R. Bianco, M.A. Harper, R.A. Rapp, JOM 11 (1991) 68.
- [4] Y. Li, W. Soboyejo, R.A. Rapp, Met. Mater. Trans. B 30B (3) (1999) 495–504.
- [5] T. Ueda, T. Goto, Y. Ito, Surf. Finish. Soc. Jpn (Hyohmen Gijutsu) 46 (12) (1995) 1173–1179 (in Japanese).
- [6] G.I. Belyaeva, A.I. Anfinogenov, N.G. Ilyushchenko, Metalloved. I Term. Obrabotka Metal. Sb. Statei 13 (1971) 63–65 (in Russian).
- [7] A.J. Gay, J. Quakernaat, J. Less-Commun. Metals 40 (1975) 21-28.
- [8] T. Oki, J. Tanikawa, J. Metal Finishing Soc. (Kinzoku Hyohmen Gijutsu) 31 (10) (1980) 561–566 (in Japanese).
- [9] T. Oki, J. Tanikawa, Molten Salt (Yoyuen) 25 (2) (1982) 115–137 (in Japanese).
- [10] R.O. Suzuki, T. Nishibata, K. Nakanishi, M. Ishikawa, K. Ono, Steel Res. 71 (4) (2000) 130–137.
- [11] R.O. Suzuki, Y. Nagaso, K. Nakanishi, K. Ono, Steel Res. 71 (4) (2000) 138–143.
- [12] R.O. Suzuki, M. Ishikawa, K. Ono, J. Alloys Comp. 306 (1/2) (2000) 285–291.
- [13] R.O. Suzuki, M. Ishikawa, K. Ono, J. Alloys Comp. 336 (1/2) (2002) 280–285.
- [14] J. Aubry, R. Duval, B. Roques, C.R. Acad. Sci. Paris, Comput. Rendus 261 (1965) 2665.
- [15] A.I. Nesterenko, M.S. Tsirlin, V.I. Korshun, N.G. Nesterenko, Inorg. Mater. 21 (3) (1985) 347.
- [16] J.-Y. Byun, J.-K. Yoon, G.-H. Kim, J.-S. Kim, C.-S. Choi, Scr. Mater. 46 (7) (2002) 537–542.
- [17] T. Barge, P. Gas, F.M. d'Heurle, J. Mater. Res. 10 (5) (1995) 1134–1145.
- [18] C.H. Jan, C.P. Chen, Y.A. Chang, J. Appl. Phys. 73 (3) (1993) 1168–1179.