Study of Corrosion Resistance of Ni-W-B Amorphous Alloy Deposits

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Corrosion resistance of Ni-W and Ni-W-B amorphous alloy electrodeposited respectively from solutions of HNO_3, HCl, H_2SO_4, and 5-percent NaCl have been studied. The difference among corrosion resistance of the Ni-W amorphous alloys deposited on substrates of A3 steel, copper, 18-8 stainless steel and nickel-based alloys has been investigated. Corrosion resistance of deposits on 18-8 stainless steel and nickel based alloys is better than that for A3 steel or copper. It has been found that the corrosion resistance of the deposits was further increased because of enrichment of W in Ni-W and Ni-W-B amorphous alloy deposition during the corrosion tests using the H_2SO_4 solution.

Amorphous films deposited on metal substrates have been studied by electrochemical deposition method.[1,2] Amorphous deposits of Ni-P, Fe-Mo, Ni-W and Ni-Mo etc. were used.[3-7] Amorphous Ni-W alloys showed some remarkable properties. Glassy alloys can be made extremely hard and highly wear resistant, but microcracks were produced easily in the surface of Ni-W amorphous alloys electrodeposited on carbon steel or Cu substrates.[8-10] In this paper, the Ni-W-B amorphous alloy films made by adding boron into the Ni-W plating solution were investigated. It was found that boron eliminated and reduced microcracks in deposits and improved corrosion resistance.

Experimental Procedure

The solutions and operating conditions for Ni-W and Ni-W-B electrodeposits are listed in Table 1. Carbon steel, 304 stainless steel, copper and $Ni_{80}Cr_{20}$ alloy were used as cathodes (40 x 40 x 1 mm). The anode was Ni sheet.

The tungsten ion was prepared by using $Na_2WO_4 \cdot 2H_2O$. The fractured cross sectional morphology and microcracking of plated films was observed by SEM. The film composition was measured by ESCA analyzer. Corrosion tests of the substrates deposited with Ni-W or Ni-W-B coating were carried out according to immersed solution method.[11] Nitric acid, 5-pct NaCl and 1 mol/L H_2SO_4 were used as the immersion solution. Dissolution time after immersion of samples in nitric acid was measured to determine corrosion resistance of the coatings. Corrosion times in 5-pct NaCl and 1 mol/L H_2SO_4 showed the desquamation times of the coatings and were measured as evidence of the corrosion resistance.

All anodic polarization curves were obtained by using the coatings with and without carbon steel substrates. The films were prepared by the method of desquamation, coating films from the surface of the stainless steel substrates after deposition of a Ni-W layer.

The amorphous structure of Ni-W and Ni-W-B coatings was measured by X-ray. Figure 1 shows the X-ray diffraction graph for three different contents of tungsten in the coating.

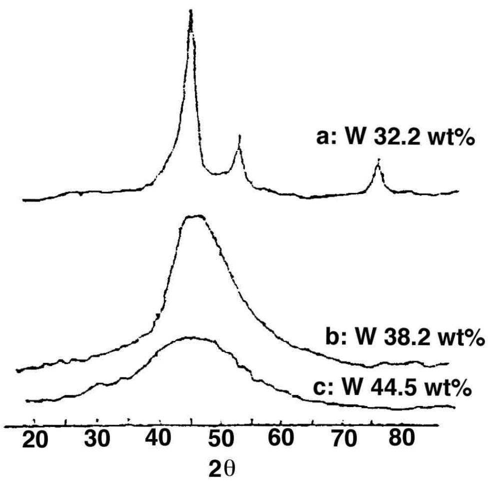

Fig. 1—X-ray diffraction curves for Ni-W coating.

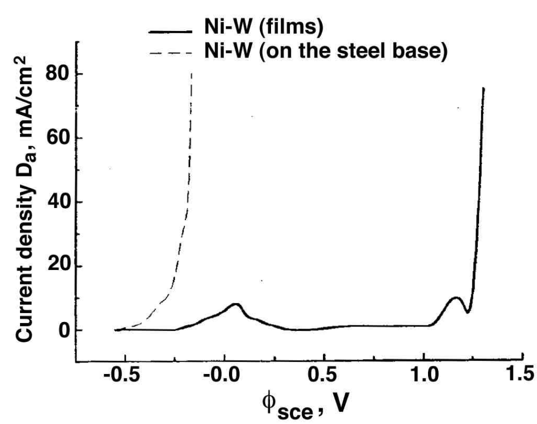

Fig. 2—Anodic polarization curves of Ni-W amorphous deposit in 5% NaCl.

Results & Discussion

Corrosion Resistance of Ni-W Amorphous Deposits On Different Substrates

The corrosion test results of Ni-W and Ni-W-B amorphous deposits in HNO_3, 5-pct NaCl and 1 mol/L H_2SO_4 solutions are listed in Tables 2, 3 and 4. It was found that the corrosion resistance of amorphous Ni-W and Ni-W-B deposits was better than that of crystalline Ni-W deposits and that the corrosion resistance of amorphous Ni-W-B deposits was better than that of amorphous Ni-W deposits. Obviously, it is because of its non-defective structure. Additionally, boron eliminates and reduces microcracking in Ni-W-B deposits, thus improving their corrosion resistance.

The corrosion resistance of amorphous Ni-W and Ni-W-B deposits on different substrates in HNO_3, 5-pct NaCl and 1 mol/L H_2SO_4 solutions were different. The microcracks in deposits on copper and carbon steel resulted in low corrosion

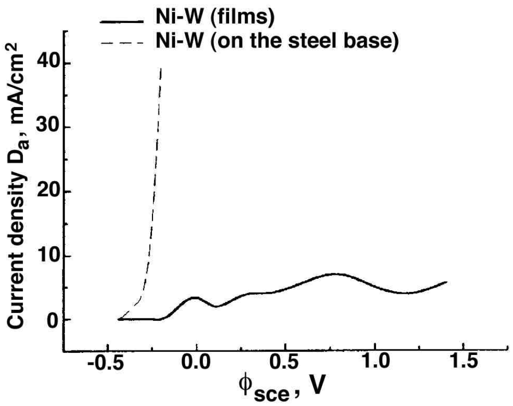

Fig. 3—Anodic polarization curves of Ni-W amorphous deposit in 1 mol/L HCl.

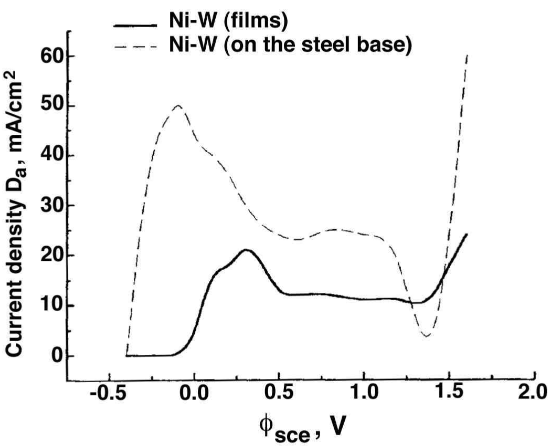

Fig. 4—Anodic polarization curves of Ni-W amorphous deposit in 1 mol/L H_2SO_4.

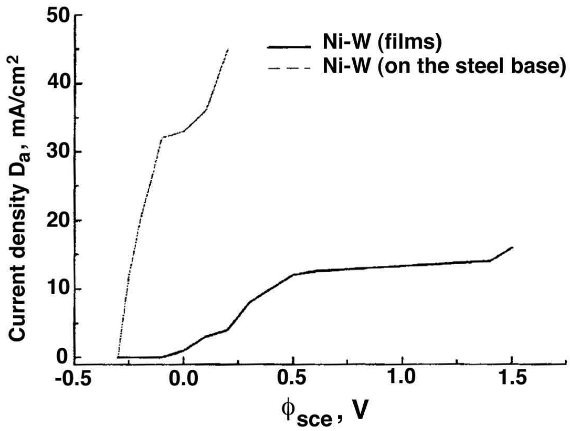

Fig. 5—Anodic polarization curves of Ni-W amorphous deposit in 1 mol/L HNO_3.

resistance, but the corrosion resistance of the deposits on stainless steel and Ni-based alloys were much better. The corrosion resistance of deposits on copper, stainless steel and Ni-based alloys in 1 mol/L H_2SO_4 solutions were similar, but the corrosion resistance of deposits on carbon steel was much lower.

Corrosion Resistance of Amorphous Ni-W Film Deposit

Anodic polarization curves of Ni-W amorphous film deposit and of carbon steel deposited with amorphous Ni-W were measured in 5-pct NaCl, 1 mol/L HCl, 1 mol/L H_2SO_4 and 1 mol/L HNO_3 solutions, respectively.

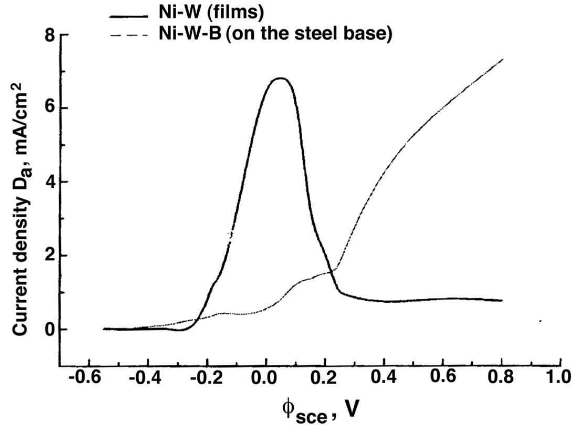

Fig. 6--Anodic polarization curves of Ni-W-B amorphous deposit on carbon steel substrate in 5% NaCl.

Table 1
Bath Composition & Operating Conditions
For Ni-W Amorphous Coating

	Ni-W	**Ni-W-B**
$NiSO_4 \cdot 6H_2O$ (g/L)	20	20
$Na_2WO_4 \cdot 2H_2O$ (g/L)	80	80
$C_6H_8O_7 \cdot H_2O$ (g/L)	50	50
$Na_2B_4O_7 \cdot 10H_2O$ (g/L)	—	10 - 40
pH	5.7	5.7
t (°C)	45	45
D_k (A/dm^2)	4 - 10	4 - 10
W content (wt%) in coating	44.5 - 45.3	45 - 53.6

It was found that the corrosion resistance of the Ni-W film was very good. The anodic polarization curves of the Ni-W film and carbon steel with Ni-W amorphous alloy in 5-pct NaCl are shown in Fig. 2. The curve shows that the electrode potential of the Ni-W deposit is about 0.00 V and a reactive current occurs within 0.2 V. The film is passivated in the range of 0.2 ~ 1.05 V, which resulted in good corrosion resistance. Carbon steel is reactive, however, in the anodic process. Obviously, the reactive anodic current is not a result of the Ni-W amorphous deposit. It is the result of the direct corrosion between the medium and the carbon steel substrate.

The same results in 1 mol/L HCl are also shown in Fig. 3. In l mol/L HCl solution, HCl corrodes the substrate directly through microcrack and higher corrosion currents. Contrary to the state of the Ni-W amorphous deposit, it is shown that amorphous deposit film has good corrosion resistance. The key, therefore, to applying amorphous deposits is to eliminate microcracks.

The anodic polarization curves of Ni-W amorphous alloy film on substrate and film with carbon steel substrate in 1 mol/L H_2SO_4, 1 mol/L HNO_3 solutions are shown in Figs. 4 and 5. It was demonstrated that the corrosion resistance of Ni-W amorphous alloy films in 1 mol/L H_2SO_4 and 1 mol/L HNO_3 solutions was very good (Fig. 4), and that microcracks result in poor protection and higher anodic current (Fig. 5).

Corrosion Resistance of Ni-W-B Amorphous Deposit

It is clear from Tables 2, 3 and 4 that the corrosion resistance of the Ni-W-B amorphous deposits was better than that of Ni-W amorphous deposits. It can be concluded that boron eliminates the microcracks on the deposit surface and improves its corrosion resistance and protection of the substrate. Under the same anodic polarization conditions, the anodic polarization current of the Ni-W-B deposit was much lower than that of Ni-W deposit (Fig. 6).

For Ni-W-B amorphous deposits, there was no reactive current occurring between -0.2 V and +0.2 V, and the deposit was always passive in the potential range of -0.2 to +0.2 V. The reason was that a continuous stable and fine passive film formed on the deposit surface. On the other hand, for Ni-W deposits, passive film on Ni-W deposit, formed in higher anodic corrosion current, was not continuous.

The corrosion rate of Ni-W-B amorphous deposits in 1 mol/L H_2SO_4, 1 mol/L HNO_3 and 5-pct NaCl solutions were measured by linear polarization method, respectively. It also showed that the corrosion resistance of Ni-W-B amorphous deposits was better than that of Ni-W amorphous deposits.

Table 5 shows that the corrosion resistance of Ni-W-B amorphous deposits is much better than that of Ni-W amorphous deposits. Boron content in Ni-W-B amorphous alloy deposits improved corrosion resistance, and the corrosion rate decreased incrementally with the amount of boron in the deposit. This was because the high combining energy of boron with nickel eliminated the microcracks in the surface of the passive alloy.

When a Ni-W-B amorphous alloy deposit was immersed in 1 mol/L H_2SO_4 solution, Ni atoms in the deposit were dissolved slowly, so tungsten content in the deposit surface was increased. The increment of W content is useful for surface passivity and the color of the passive film can be observed visually. It was found from Table 6 that the content of W changed from 53.62 wt pct to 63.1 wt pct after the Ni-W-B alloy deposit was corroded in 1 mol/L H_2SO_4 solution. The enriching tungsten expedited the formation of a passive film, promoted the fine, uniform passive film and improved the corrosion resistance of the Ni-W-B alloy deposit.

Table 2
Immersion Test Results of Deposits
On Different Substrates in Concentrated HNO_3
(Time to Observable Corrosion, sec)

Deposit	Substrates: Copper	Carbon Steel	Stainless Steel	Ni-based Alloy
Ni-32 wt% W (crystal)	19	16	120	200
Ni-44.6 wt% W (amorphous)	40	20	220	260
Ni-45.2 wt% W-1.05 wt% B (amorphous)	45	23	230	270
Ni-45.3 wt% W-2.03 wt% B (amorphous)	43	21	230	270

Table 3
Immersion Test Results of Deposits
On Different Substrates in 5% NaCl Solution
(Time to Observable Corrosion, hr)

Deposit	Substrates: Copper	Carbon Steel	Stainless Steel	Ni-based Alloy
Ni-32 wt% W (crystal)	6	0.1	1.8	0.8
Ni-44.4 wt% W (amorphous)	11	0.5	14	16
Ni-46.1 wt% W-1.05 wt% B (amorphous)	13	0.8	17	22
Ni-45.6 wt% W-2.03 wt% B (amorphous)	16	1.1	19	24

Table 4
Immersion Test Results of Deposits
On Different Substrates in 1 mol/L H_2SO_4 Solution
(Corrosion state, hr)

Deposit	Substrates: Copper	Carbon Steel	Stainless Steel	Ni-based Alloy
Ni-31.7 wt% W (crystal)	48 no corr	0.4 corr	24 corr	32 corr
Ni-44.8 wt% W (amorphous)	48 no corr	1.8 corr	48 no corr	48 no corr
Ni-45.8 wt% W-1.05 wt% B (amorphous)	48 no corr	2.2 corr	48 no corr	48 no corr
Ni-46.1 wt% W-2.03 wt% B (amorphous)	48 no corr	2.6 corr	48 no corr	48 no corr

Table 5
Corrosion Rate of Ni-W-B Amorphous Deposit
In Different Corrosion Solutions (mA/cm^2)

Deposit	Corrosion Solution: 1 mol/L H_2SO_4	1 mol/L HNO_3	5% NaCl
Ni-W (W:45.23 wt%)	0.245	0.615	5.3×10^{-3}
Ni-W-B (W: 45 wt%; B: 1.02 wt%)	0.098	0.492	1.7×10^{-3}
Ni-W-B (W: 45.3 wt%; B: 2.1 wt%)	0.053	0.188	1.5×10^{-3}

Table 6
Changes of Surface Composition Before & After Anodic
Polarization Corrosion of Ni-W-B Amorphous Alloy Deposit
(in 1 mol/L H_2SO_4 solution)

W Content (wt%) of Deposit	Before Corrosion	After Corrosion
Ni-W	45.2	55.8
Ni-W-B	53.62	63.1

Findings

1. Corrosion resistance of Ni-W amorphous film deposit was very good in HNO_3, 1 mol/L H_2SO_4 and 5-pct NaCl solutions, but the microcracks in deposits on copper and carbon steel substrates had lower protection.
2. Addition of boron atoms removed microcracks in the deposits and increased corrosion resistance and protection.
3. Enrichment of W in Ni-W and Ni-W-B amorphous alloy deposits occurred during the corrosion tests in a solution of H_2SO_4, and increased further the corrosion resistance of the deposit.

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References

1. T.Omo, H. Yamamoto & H.L. Glass, *J. Electrochem. Soc.*, **119**, 168 (1972).
2. A. Budniok & J. Kupka, *Electrochim. Acta*, **34**, 871 (1989).
3. M. Donten & J. Osteryoung, *J. Appl. Electrochem.*, **21**, 496 (1991).
4. L. Zhu, T. Watanabe, *J. Japan Inst. Metals*, **56**, 664 (1992).
5. T. Agladze, S. Bagaev, D. Gabe, V. Kudryavtsev, Ch. Raub, S. Schachameyer, N. Spyrelis & T. Tsupak, *Trans. IMF*, **75**, 30 (1997).
6. E. Chassaing, K. Vuquang & R. Wiart, *J. Appl. Electrochem.* **19**, 839 (1989).
7. K. Wikiel & J. Osteryoung, *J. Appl. Electrochem.*, **22**, 506 (1992).
8. C-H. Huang, *Plat. and Surf. Fin*., **84**, 62 (April 1997).
9. N. Atanassov, K. Gencheva & M. Bratoeva, *Plat. and Surf. Fin.*, **84**, 67 (Feb. 1997).
10. N. Isaev &J. Osteryoung, *J. Appl. Electrochem*., **25**, 1091 (1995).
11. C-Y. Zhu, *Electroplat. & Finish. (China)*, **17**(2), 19 (1998).

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