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HARDNESS AND WEAR RESISTANCE OF ELECTROLESS NICKEL DEPOSITS①

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ABSTRACT The hardness and wear resistance of electroless nickel deposits with two types of P contents have been investigated. The results indicate that Ni-1.5%P deposit possesses as-deposited hardness and wear resistance superior to Ni-10.5%P deposit. Their hardness and wear resistance can be further improved by proper heat treatment. The optimum wear resistance of Ni-1.5%P deposit corresponds to its peak hardness (annealing at 375 ℃ for 1 h), whereas for Ni-10.5%P deposit the optimum wear resistance is obtained after annealing at 650 ℃ for 1 h.

Key words electroless Ni-1.5%P deposit Ni-10.5%P deposit hardness wear resistance

1 INTRODUCTION

Electroless Ni-P deposits have been widely used in diverse fields for their unique combination of properties such as corrosion resistance, wear resistance, non-magnetism and uniformity of coating thickness[1-3]. In the early 1960s, proprietary electroless nickel process suitable for commercial use entered the U.S. market. There existed some limitations in corrosion resistance for these products, which were medium phosphorus deposits (5% ~ 8% P) and commonly used sulfur-containing or heavy-metal stabilizers. In the late 1970s and the 1980s, substantial emphasis was placed on high phosphorus electroless nickel coatings (9% ~ 12% P). This was due to their amorphous microstructure, improved corrosion resistance, and non-magnetism characteristics[4-6]. The recent development of low phosphorus electroless nickel (1% ~ 5% P) has offered an excellent alternative to hard chromium and nickel-boron coatings due to its superior as-deposited hardness and outstanding corrosion resistance in hot alkaline environment, especially suitable for heat sensitive materials such as Al and Al alloys[7, 8]. Based on systematic study on the formulation of electroless Ni-P plating baths, high phosphorus electroless nickel with higher deposition speed and bath stability[9] and new low phosphorus electroless nickel deposits[10] have been successfully developed (with phosphorus content of 10.5% and 1.5% respectively). In this work, special attention has been focused on the hardness and wear resistance of these two deposits under different heat treatment conditions.

2 EXPERIMENTAL PROCEDURE

The hardness of deposits was measured by Micromet-II type microhardness tester with a load of 0.5 N for 15 s. The data were obtained for each specimen by averaging five measurements. The wear resistance were determined with a ball and flat machine in dry condition. The flat samples of d 50 mm made from $45^{\#}$ steel were plated with 40 μm thick Ni-P coatings. The counterpart was a GCr15 steel ball of d 5 mm, with hardness of HRC62. The rotating radius is 15 mm and the rotating speed is 45 r/min.

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The load series are 5, 10, 20, 40 and 80 N, with a testing time of 15 min. The wear rate was expressed by specimen's mass loss after test. The wear tracks were examined in a scanning electron microscope (SEM).

3 RESULTS AND DISCUSSION

3.1 Hardness of deposits

The microhardness of these two deposits annealed at various temperatures between 200 ℃ and 600 ℃ for 1 h is plotted in Fig. 1. The results show that the as-deposited electroless Ni-P coatings exhibit much higher hardness than that for conventional electrodeposited nickel (250~350HV). The TEM and XRD results[11] indicated that as-deposited Ni-10.5% P deposits were amorphous, while deposits containing 1.5% P could be represented as an fcc NiP supersaturated solid solution of 5~ 10 nm microcrystallites. Ni-1.5% P coating has as-deposited hardness of HV700, higher than that of Ni-10.5% P coating (HV520) mainly due to their structural differences. It was shown by DSC[12] that crystallization for amorphous Ni-10.5% P deposits occurred at about 300 ℃. By XRD it was found that annealing caused the formation of finely dispersed Ni_3P precipitates, which act as the function of second phases or precipitation hardening because Ni_3P particles possess higher strength and shearing modulus. The maximum hardness reaches HV 1 050 after 400 ℃ annealing for Ni-10.5% P coating, corresponding to the state of optimum distribution for Ni_3P particles. Above 400 ℃, the hardness of Ni-10.5% P decreases slowly mainly due to the recrystallization of Ni and coarsening of Ni_3P precipitates. While microcrystalline Ni-1.5% P deposits reach maximum hardness of HV 1 100 after annealing at lower temperature (350 ℃). At higher annealing temperature, the hardness decreases rapidly, even lower than the as-deposited sample (e. g. above 500 ℃). It was known from the grain growth behavior of Ni-1.5% P deposits[13], the rapid decrease in hardness has a relation to the grain growth and coarsening of Ni_3P. Compared with Ni-1.5% P deposit, Ni-10.5% P possesses higher hardness after annealing at a higher temperature and its decrease tendency in hardness after reaching maximum is somewhat gentle due to their difference in fraction of Ni_3P phases within the coatings. After crystallization, the matrix for Ni-10.5% P deposit is Ni_3P (about 70% (in volume) Ni_3P), which acts as the function of volume strengthening, whereas the matrix for Ni-1.5% P is Ni (containing about 10% (in volume) Ni_3P).

Fig. 2a shows the relationship of hardness vs annealing time at various temperatures for Ni-10.5% P deposits. It can be seen that, the hardness increases gradually with increasing annealing time at a temperature below 400 ℃ and thereafter keeps at a certain level for longer annealing. The lower the annealing temperature, the longer the time for reaching the peak of hardness. When annealed above 400 ℃, the deposits reach a maximum hardness within shorter time and further annealing will cause the slow decrease in hardness. Fig. 2b shows the situation for Ni-1.5% P deposit. Ni-1.5% P deposits reach peak of hardness after longer annealing time under a temperature below 350 ℃, and when the annealing temperature is low (e. g. 300 ℃), the maximum hardness reached is also lower because Ni_3P phase precipitate somewhat difficultly. In the case of Ni-1.5% P deposit heat treated at 500 ℃, it seems that the maximum hardness actually occurs at a time shorter than the shortest annealing time (10 min).

It can be seen from the above results and analyses that these two deposits with different P

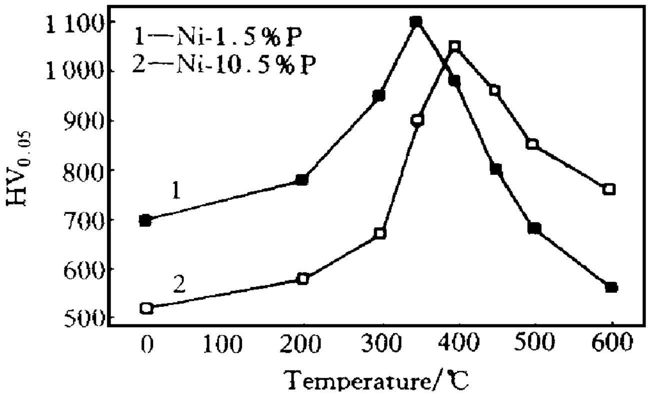

Fig. 1 Relationship between annealing temperature and hardness of deposits

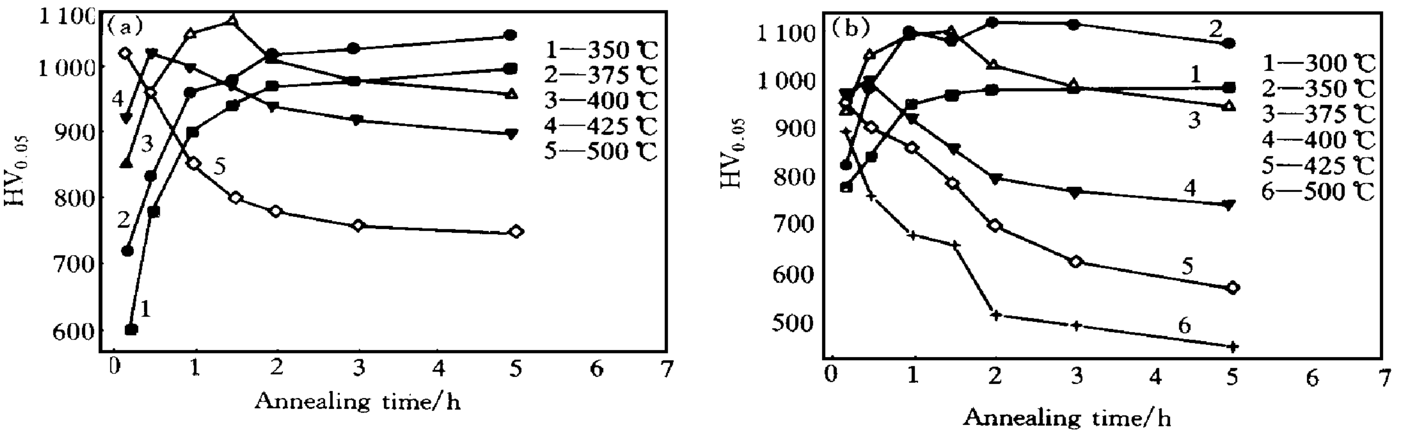

Fig. 2 Relationship between hardness and annealing time at different temperatures
(a) —Ni-10.5% P; (b) —Ni-1.5% P

contents show different hardening and softening behaviors during annealing. It seems that the finely dispersed crystallites of Ni_3P and Ni initially formed progressively aggregate, particularly at higher temperature and longer time. For deposits containing high phosphorus content, this process does little to the reduction of hardness, since the majority of the heat-treated deposit is Ni_3P. However low phosphorus content deposit shows obvious softening after annealed at a higher temperature for a longer time mainly due to lack and coarsening of Ni_3P precipitates. Thus, in order to reach maximum hardness, 400 ℃, 1 h and 375 ℃, 1 h heat treatments are suitable for Ni-10. 5% P and Ni-1. 5% P deposits, respectively.

3. 2 Wear resistance of deposits

Fig. 3 shows the variation in wear rate with load for as-deposited Ni-10. 5% P and Ni-1. 5% P deposits. The wear rate increases with increasing load, and the wear rate for Ni-10. 5% P is much higher than that for Ni-1. 5% P. When the load is increased to above 40 N, the wear rate for Ni-10. 5% P increases rapidly, while that for Ni-1. 5% P increases only slightly. This indicates that the wear resistance of Ni-1. 5% P is much better than that of Ni-10. 5% P deposits at heavy load.

Fig. 4 shows the worn surface morphology of as-deposited Ni-10. 5% P deposits under different loads. Torn patches of coating elongated along the wear direction can be seen on worn surface (Fig. 4a), which indicates the phenomena of adhesive wear. Increasing load will cause heavier adhesive wear and obvious plastic deformation within the coating. Further wear causes larger region of the coating to crack and detachment of coating in local areas (position *A* in Fig. 4b), indicating the worse interface bonding between the coating and the substrate.

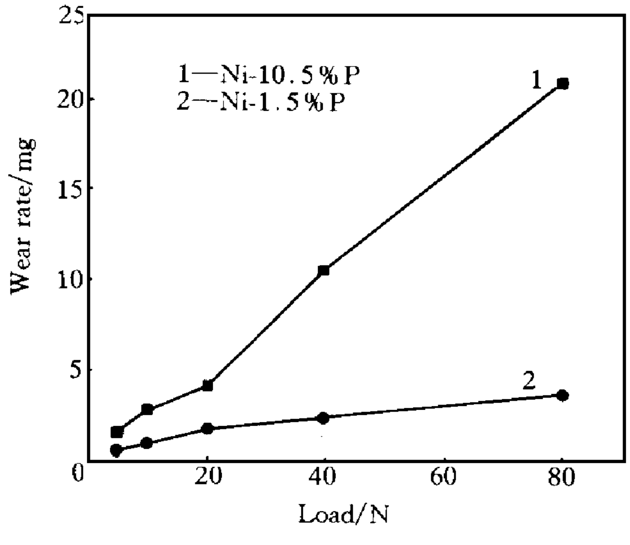

Fig. 3 Relationship between wear rate and load for as-deposited electroless nickel deposits

Fig. 5 shows the worn surface of Ni-1. 5% P deposits. Within the range of loads tested, adhesive wear has not taken place, which may primarily correspond to their higher hardness and microcrystalline structure.

Fig. 6 shows the relationship between wear

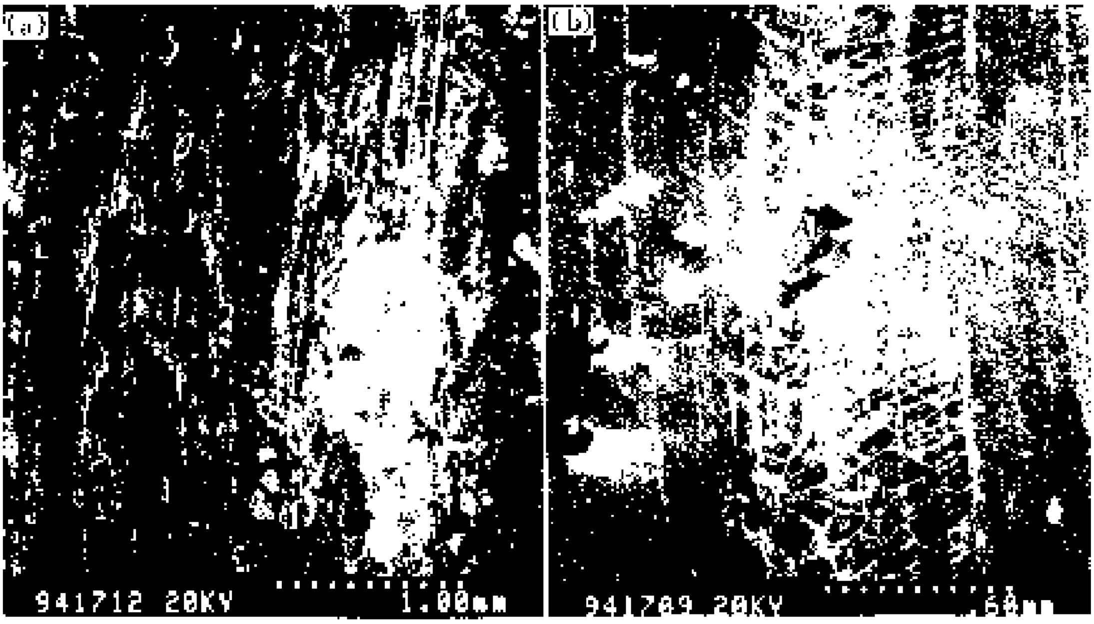

Fig. 4 Worn surface morphology of as-deposited Ni-10. 5% P deposits under different loads
(a) —20 N; (b) —40 N

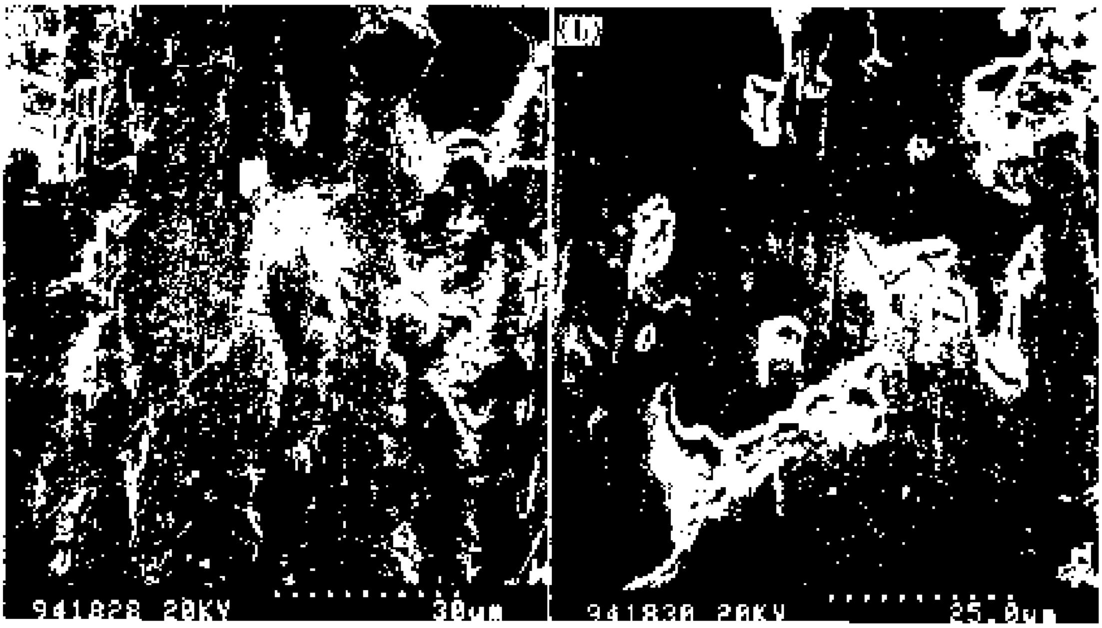

Fig. 5 Worn surface morphology of as-deposited Ni-1. 5% P deposits under different loads
(a) —20 N; (b) —80 N

rate and load for Ni-10. 5% P deposits annealed at various temperatures for 1 h. It indicates that the coating annealed at 650 ℃ for 1 h possesses optimum wear resistance under different load levels. For samples after annealing at 200 ℃, severe adhesive wear will take place under a higher load (above 40 N) due to the coating's lower hardness and amorphous structure. After annealed at 400 ℃ for 1 h, the coating reaches the peak of hardness, but owing to the increase in brittleness, the coating tends to crack and even detach (Fig. 7a). After heat treatment at 650 ℃ for 1 h, the coating's hardness decreases somewhat, but the coating's ductility can be improved due to the recrystallization of Ni and coarsening of Ni_3P, as well as the interface bonding, which enhances the coating's wear resistance. Fig. 7b shows the worn surface of Ni-10.5% P deposit under 80N after heat treatment at 650 ℃ for 1 h. Although there are a number of network cracks on the worn surface, no debris and adhesive phenomena are found.

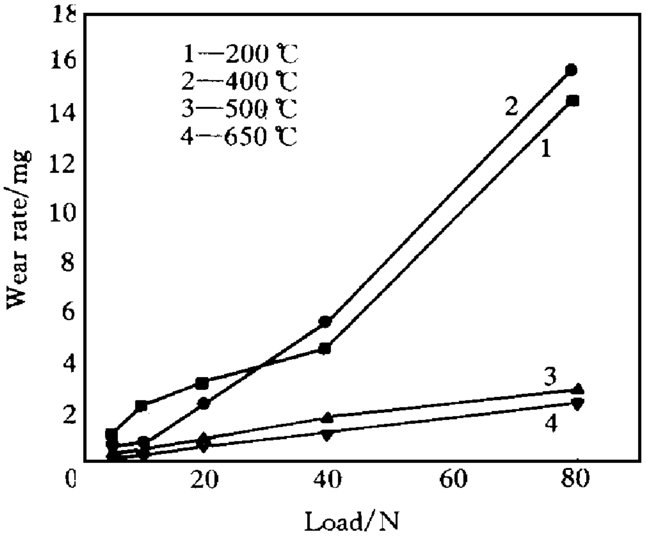

Fig. 6 Relationship between wear rate and load for Ni-10.5% P deposits annealed at different temperatures for 1 h

Fig. 8 shows the wear rate of Ni-1.5% P deposits annealed at different temperatures. The optimum wear resistance of Ni-1.5% P deposit corresponds to heat treatment at 375 ℃ for 1 h. The higher hardness and the existence of primary phase of ductile Ni within the coating may prevent the coating's cracking during wearing. Annealing at a higher temperature will cause rapid increase in wear rate because of the abrupt decrease in hardness caused by grain growth and agglomeration of Ni_3P. The lower strength will bring about ploughing phenomena during wearing.

3 CONCLUSIONS

(1) Ni-1.5% P deposit possesses a much higher as-deposited hardness than Ni-10.5% P deposit does. Proper annealing will cause obvious increase in hardness due to the precipitation of Ni_3P phase within the coating.

(2) The optimum hardness of Ni-10.5% P deposit corresponds to heat treatment at 400 ℃ for 1 h. The decrease in hardness after annealing at a higher temperature is somewhat gentle for Ni-10.5% P deposit due to the existence of numerous hard phase (Ni_3P), while the optimum hardness of Ni-1.5% P deposit corresponds to heat treatment at 375 ℃ for 1 h. Higher temperature annealing will cause rapid decrease in hard-

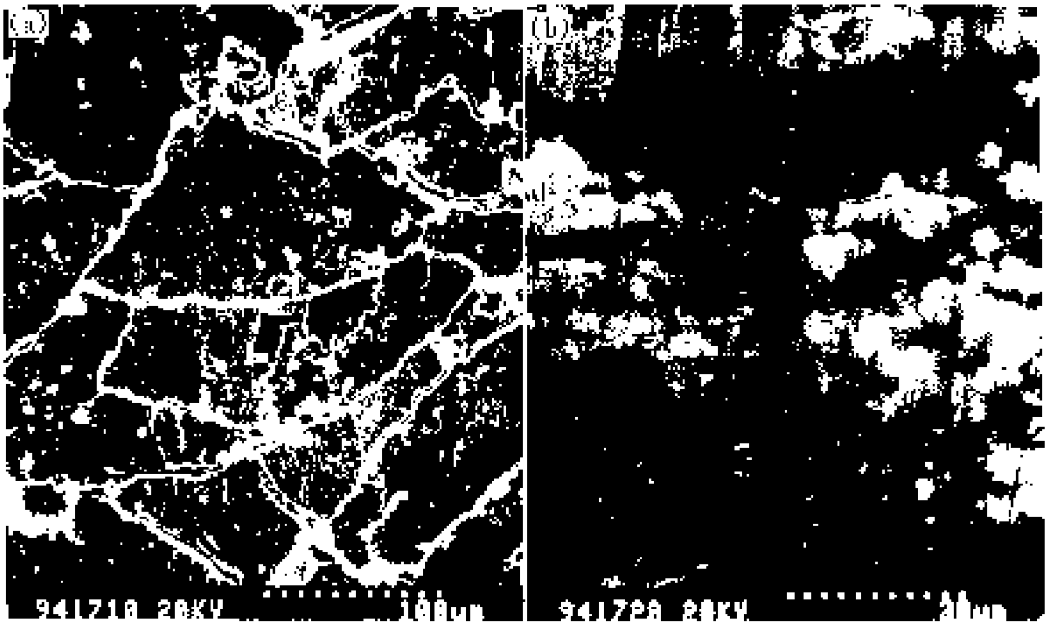

Fig. 7 Worn surface morphology of Ni-10.5% P deposits under 80N after different heat treatments
(a) —400 ℃, 1 h; (b) —650 ℃, 1 h

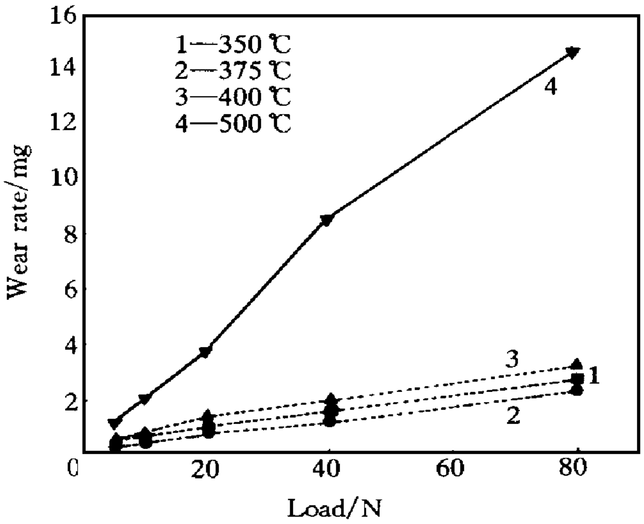

Fig. 8 Relationship between wear rate and load for Ni-1.5% P deposits annealed at different temperatures for 1 h

ness due to the recrystallization of Ni and coarsening of Ni_3P.

(3) The wear results of deposits under different loads indicate that, Ni-1.5% P deposit possesses an as-deposited wear resistance superior to Ni-10.5% P deposit. The adhesive transfer and ductile tearing are primary mechanisms in the wear of the Ni-10.5% P deposit.

(4) The wear resistance of deposits can be further improved by proper heat treatment. The wear resistance of Ni-1.5% P deposit varies identically with its microhardness, while for Ni-10.5% P deposit its optimum wear resistance is obtained after annealing at 650 ℃ for 1 h. This indicates that not only the coating's hardness but also ductility and adhesion strength will affect the wear resistance for Ni-10.5% P deposit.

REFERENCES

1 Miller R E. Plat & Surf Finish, 1987, 74(12): 52 - 56.

2 Keene R H. Plat & Surf Finish, 1988, 75(12): 22 - 25.

3 Guo Zhongcheng *et al*. Electroplating & Pollution Control, (in Chinese), 1996, 16(5): 8- 13.

4 Tracy R P and Shawhan G J. J Mater Perform, 1990, 29(7): 65- 70.

5 Bayes M *et al*. Trans IMF, 1991, 69(4): 140- 144.

6 Hajdu J B. Plat & Surf Finish, 1996, 83(9): 29- 33.

7 Jackson B, Macary R and Shawhan G. Trans IMF, 1990, 68(3): 75- 83.

8 Bleeks T and Shawhan G. Metal Finishing, 1989, 87 (10): 21- 27.

9 Zhang Yongzhong *et al*. Aerospace Materials & Technology, (in Chinese), 1998, 28(1): 52- 56.

10 Zhang Yongzhong *et al*. Electroplating & Pollution Control, (in Chinese), 1995, 15(6): 18- 20.

11 Zhang Yongzhong *et al*. J Mater Sci & Technol, 1996, 12(5): 342- 346.

12 Zhang Yongzhong. PhD Dissertation, (in Chinese). Harbin: Harbin Institute of Technology, 1997: 63 - 76.

13 Zhang Yongzhong *et al*. J Mater Sci Letters, 1998, 17(1): 37- 40.

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