Effects of Heat-Treatment Processes on the Electroless Ni-B Coating and its Natural Aging Mechanism

Rao Qunli[a], *Wang Haowei*[a], *Zhang Kun*[b], *Fan Xiaolan*[c], *Zhou Yoahe*[a]

[a]*State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiaotong University, Shanghai 200030, P.R. China*
[b]*Institute of Mechanics, Chinese Academy of Sciences, Beijing 100081, P.R. China*
[c]*School of Mechanical Engineering, Taiyuan University of Technology, Taiyuan 030024, P.R. China*

SUMMARY – A Ni-B coating was prepared with EN using potassium borohydride reducing agent. The as-plated micro-structure of the coating was confirmed from XRD to be a mixture of amorphous and supersaturated solid solution. Three kinds of phase transformation were observed from the DSC curve. Different from the previous works, the formation of Ni_4B_3 *and* Ni_2B *was found during some transformation processes. The key factors which influence the variation of micro-hardness and micro-structure in deposits are the formation, the size and amount of* Ni_3B, Ni_4B_3 *and* Ni_2B*. Aging of the deposits treated under some heat treatment conditions occurred at room temperature. Changes of micro-hardness indicated aging phenomena evidently. The natural aging phenomena are concerned with various kinds of decomposition of borides, especially with* Ni_4B_3 *phase. The extent of natural aging depends on the formation and the quantity of* Ni_4B_3 *and* Ni_2B*.*

Key Words: Ni-B alloy, Electroless Nickel, Natural aging, Ni_2B, Ni_3B, Ni_4B_3

INTRODUCTION

Electroless plating with its many advantages, such as uniform deposition on complex and intricately shaped parts, the possibility of metallizing non-conductors, and the ability to plate selectively draws world wide attention. Compared with electroless Ni-P alloy, Ni-B alloy has features of higher hardness, good wear-resistance and solderability, etc. It has been widely used in the fields of automotive, aerospace and electronic industry. As an efficient and cheap method to prepare surface protection coatings with high properties, electroless Ni-B has promising future prospects.

Dimethylamineborane (DMAB) and sodium borohydride are two common reducing agents for electroless Ni-B alloy[1,2]. DMAB is used for plating from weak acidic to strong alkaline conditions. The deposits made from this reductant contain boron within the range of 0.1~5 wt%, and possess some specific characteristics such as good solderability and electrical conductivity. This kind of deposit is mainly applied in the electronics industry[3]. Sodium borohydride reductant is used under strong alkaline conditions[4]. Deposits with 3~8 wt% boron content can be obtained. This kind of deposit is known for high hardness, good wear-resistance and corrosion-resistance. Although numerous papers about the properties and micro-structures of electroless Ni-B deposits have been published[5-7], few of them have described the transformation mechanism of the deposits under heat-treatment, especially with relatively long duration. In the present paper, the deposits with 3.5~6.5 wt% boron content were prepared by electroless nickel using borohydridge reductant. The as-plated deposits with micro-hardness 750~800 VHN_{100} comprised of microcrystalline and amorphous phases. The phase transformation of the deposits through various heat-treatment processes, its mechanism as well as natural aging characteristics are discussed in detail.

EXPERIMENTAL

Sample Preparation

The standard composition of the bath was $NiCl_2{\cdot}6H_2O$: 30 g l^{-1}, $NH_2CH_2CH_2NH_2$: 60 ml l^{-1}, NaOH: 50 g l^{-1} KBH_4: 0.8~1.2 g l^{-1}, stabilizer as it required. The pH value of the solution exceeded 13. The operating temperature was 92±1°C. Deposition rate was 10~20 μm/h^{-1}. Deposition time was one hour.

To minimise substrate effects, 7Cr7Mo2V2Si alloy steel blocks with hardness of Hv 700~800 were used. The size of a coupon was 18 × 10 mm. All substrates were polished, alkaline cleaned, water cleaned, acid activated and de-ionized water rinsed before plating.

Sample Testing

The boron content of samples was determined with an HITACHI 180 86 type atomic absorption spectrometer. The micro-structure of coatings was analyzed with a D/MAX A X-ray diffractometer. The micro-hardness of samples was measured with an HXD-1000 micro-hardness tester. The thermal analyses of samples were performed with a differential scanning calorimeter between room temperature and 500°C at a heating rate of 20°C min^{-1}.

RESULTS & DISCUSSION

Phase Transformation under Thermal Action

The micro-structure of an as-plated coating was explored with X-ray diffraction. The XRD pattern (Figure 1) of an as-plated deposit, consists of a broad peak and a superimposing sharp one. Accordingly, the micro-structure of the coating is a mixture of micro-crystalline and non-crystalline, and the main constitution of the micro-crystalline was probably a supersaturated solid solution of B in nickel[5].

The phase transformations in the coating were characterized by differential scanning calorimeter (DSC) testing. A DSC curve of the deposit sample is shown in Figure 2. It has three manifest peaks on the curve which indicate three kinds of phase transition respectively. According to a previous paper[1], Ni_3B is formed at 350°C, Ni_7B_3 is formed at 405°C, Ni_2B formed at 425°C. The DSC results in the present paper show three peaks occurring at 302.15°C, 307.65°C and 421.5°C. Further XRD analyses indicate that Ni_3B, Ni_2B and Ni_4B_3 are formed at these temperatures, respectively.

The XRD patterns of coatings after 300°C, 400°C and 500°C heat treatment are shown in Figure 3. These patterns are very different from each other. Diffraction lines corresponding to Ni_3B and {111}Ni are observed evidently in all three patterns. There are discernible peaks corresponding to {110} and {200} Ni_2B planes in Figure 3(b) and (c) except those confused with Ni_3B peaks. An unlapped peak of {202} plane Ni_4B_3 in Figure 3(c) is marked. Therefore, the micro-structure of the 300°C heat treatment coating consists of fcc Ni and Ni_3B (Figure 3(a)), while that of the 400°C consists of fcc Ni, Ni_3B and Ni_2B (Figure 3(b)) and that of the 500°C consists of fcc Ni, Ni_3B, Ni_2B and Ni_4B_3 (Figure 3(c)). It should be noted that the Ni_4B_3 phase appears among the nickel borides instead of the Ni_7B_3 phase when the heat treatment temperature

---

R. Qunli, W. Haowei, Z. Kun, F. Xiaolan, Z. Yoahe, *Trans. IMF*, 2001, 79(2), 56

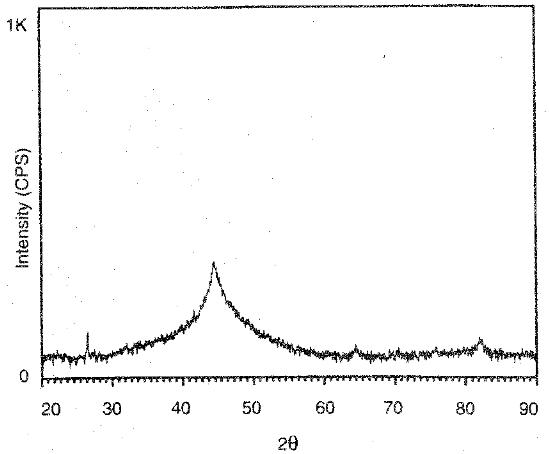

Figure 1. The XRD pattern of as-plated sample.

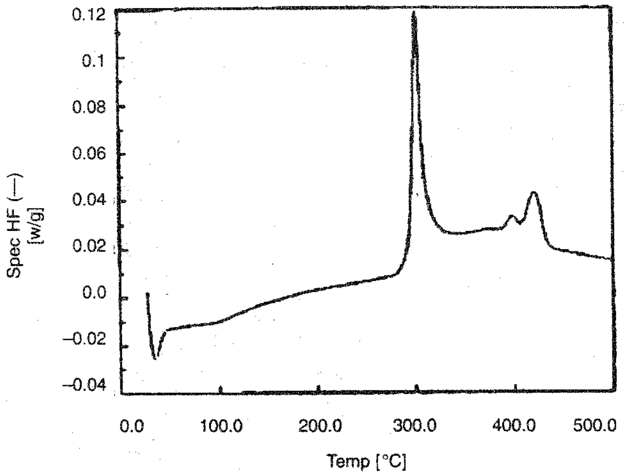

Figure 2. The DSC curve of Ni-B deposits.

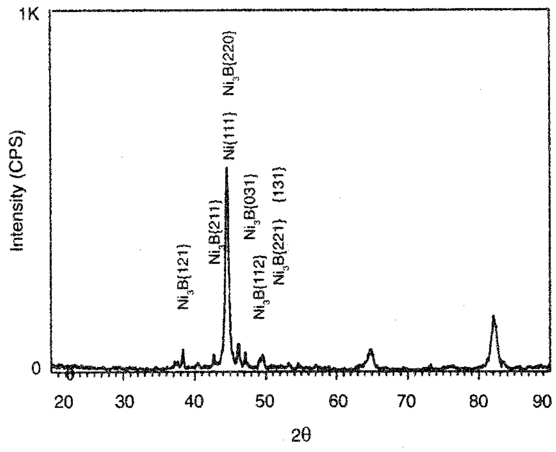

Figure 3(a). XRD pattern of a sample after 300°C × 1 h heat treatment.

was high enough. So combined with the DSC results, it can be confirmed that Ni_3B is formed at about 302.1°C, Ni_2B at about 397.65°C, and Ni_4B_3 at about 421.5°C.

Heat Treatment Process and its Influence on the Micro-Structure and Micro-Hardness

From the DSC results, 300°C, 350°C, 400°C and 500°C were selected as heat treatment temperatures. These treating temperatures were chosen near to the three crystallization temperatures of Ni-B alloy. Diversity of treatment duration was selected corresponding to different heat treatment temperatures. Longer duration was adopted for lower temperature treatments. The processing scheme is listed in Table I.

The variations of coating micro-hardness under different heat treatment conditions are shown in Figure 4. In general, micro-hardness variability of this kind of deposit relates to its micro-structure which is determined by the type of crystallization reactions in the heat treatment process. When 300°C and 350°C were selected as heat treatment temperatures, Ni_3B formation was the main transition in the heat treatment process because these temperatures are below that of Ni_2B formation. At 400°C, Ni_3B and Ni_2B formation was the main process, while after 500°C treatment, all the three kinds of borides appeared in the deposits. Therefore, the micro-hardness of deposits varied with their micro-structure and constitution, i.e. boride types and their congregation.

The main distinction between 300°C and 350°C treating processes was in the speed of Ni_3B formation. When the treatment temperature was fixed at 300°C (Figure 4(a)), the crystallization reaction took place in a short time. As a result, a great deal of fcc Ni was generated in deposits. This improved the micro-hardness of the deposit greatly. As the duration extended further, the micro-hardness of deposit increased owing to Ni_3B precipitation. When the heat treatment temperature reached to 350°C, more complicated changes were shown in the micro-hardness curve. Quite a high value was obtained just after 1 h treatment because of the rapidly forming fcc Ni. Then it decreased over 2 h duration due to the congregation of fcc Ni. But this trend was inhibited by Ni_3B forming. As the amount of Ni_3B increased, another maximal value of 1230 VHN_{100} or so was obtained within 5~6 h. Then deposits were softened after longer duration, which is ascribed to the growth and congregation of borides. The value of micro-hardness kept nearly a constant beyond 7 h duration of heat treatment.

Variations of micro-hardness under 400°C and 500°C heat treatment are illustrated in Figure 4(b). Both of the two temperatures are higher than that of Ni_3B and Ni_2B formation, but differ in that 500°C is above the Ni_4B_3 formation temperature. For the temperature 400°C, it is much higher than the temperature of Ni_3B formation and just around the Ni_2B formation temperature. Ni_3B can be formed after a short duration, while Ni_2B formation needs a long one. Thereby the curve for 400°C rises markedly before 1 h duration, for a large amount of Ni_3B precipitation. Then the curve almost becomes level within 1 to 3 h duration. This may be ascribed to both the precipitation of Ni_2B and congregation of Ni_3B. Although the congregation of Ni_3B lowers the micro-hardness, the increment of Ni_2B in deposits compensates for this action. When the duration extended to 4~5 h, the micro-hardness came to a peak caused by the precipitation of a large amount of Ni_2B. It seems that due to congregation of borides and Ni_2B decomposition the micro-hardness of deposits decreases as a consequence of further long duration heat treatment. As for 500°C, the micro-hardness is higher than for all the three borides formation temperatures. Hence crystallizing proceeds strongly at this temperature, and nickel borides can be formed promptly. The micro-hardness curve reaches 1200 VHN_{100} after only 0.5 h duration on account of Ni_2B and Ni_3B precipitating in the deposits. A peak occurs after 3 h duration corresponding to an increasing amount of borides. Compared to that of 400°C, this peak point advanced by two hours. It is also remarkable that the peak value in this figure

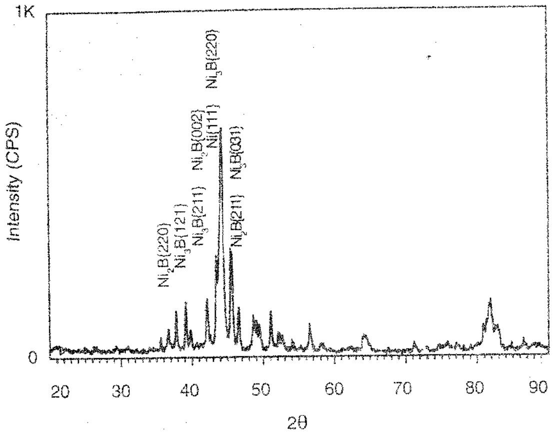

Figure 3(b). XRD pattern of a sample after 400°C × 1 h heat treatment.

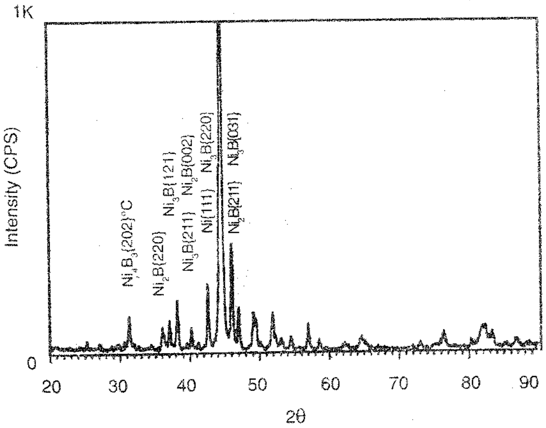

Figure 3(c). XRD pattern of a sample after 500°C × 1 h heat treatment.

surpasses other temperatures, reaching 1400 VHN_{100}. This is possibly due to Ni_4B_3 precipitation.

To sum up the results above, it is evident that the changes of micro-hardness relate intimately with nickel borides formation. When borides appeared in deposits, micro-hardness increased markedly. Micro-hardness also related to the specific borides. It reached 1100~1200 VHN_{100} with Ni_3B existing in deposits, 1200~1300 VHN_{100} with Ni_2B, attaining 1400 VHN_{100} with Ni_4B_3. Therefore the decline in micro-hardness after long duration of heat treatment is owing to some kind of borides disappearance in addition to borides congregation. For instance, the amount of Ni_4B_3 decreases when the duration of heat treatment at 500°C exceeds 6 h (Figure 4(b)); very little Ni_4B_3 is found in deposits after 10 h treatment. This is due to the unstability of these borides. From this figure, it can be also recognised that formation of nickel borides is determined not only by the heat treatment temperature, but also by its duration. If only the duration is sufficient, Ni_2B precipitation can take place at 300°C and 350°C which is below its forming temperature. A similar case occurred for Ni_4B_3 at 400°C.

Natural Aging Phenomena after Heat Treatment and its Mechanism

Natural aging phenomena in deposits prepared under the current experimental conditions were discovered after some heat treatment processes. They are mainly reflected in variations of micro-hardness. Curves of micro-hardness *in situ* after some kinds of process and those after 5 and 25 days natural aging are shown in Figure 5. It can be seen from this figure that the natural aging trend is weak for treatment below 350°C. When the temperature fixed at 300°C, natural aging hardly occurred (Figure 5(a)). As for 350°C (Figure 5(b)), some extent of aging occurred after a very long duration. In contrast to these, natural aging phenonmena become rapid above 350°C. For instant, aging softening was severe even after a short duration 400°C treatment (Figure 5(c)). These phenomena are thought to be concerned with the occurrence of metastable boride phases in deposits. It has been reported[8] that Ni_2B is a metastable compound. It probably transfers to the stable Ni_3B or fcc Ni phase at room temperature, from XRD analysis. This suggests that natural aging phenomena in some cases in Figure 5 can be interpreted as Ni_2B transferring to Ni_3B or fcc Ni.

The aging softening mechanism of 500°C treatment (Figure 5(d)) differs somewhat from that of 400°C. Besides transition of Ni_2B, another key factor affecting aging in deposits is transformation of Ni_4B_3. This has been confirmed by XRD analysis. XRD patterns of coatings treated at 500°C for 3 h are shown in Figure 6. Figure 6(a) and (b) are patterns obtained immediately after 500°C treating and thereafter 5 days aging respectively. Comparing the two patterns, it is clear that the intensity of {111}Ni and {121}Ni_3B peaks increases while that of the {200}Ni_2B and {202}Ni_4B_3 unlapped peaks decreases in Figure 6(b). This proves sufficiently that the decomposition of Ni_2B and Ni_4B_3 is the principal cause of natural aging.

It also can be found from Figure 5 that the maximal drop in micro-hardness appears in different places on different curves. These maximal points tend to shift in the long duration direction as the treatment temperature is lowered. For instant, the point on the 500°C curve locates at about 3 h, while 400°C is close to 5 h, 350°C close to 10 h. The maximal effect is of 500°C × 3 h. This is brought by Ni_4B_3 decomposition because in this case Ni_4B_3 is a key to improve micro-hardness in the deposit. When treated under 500°C, a great deal of Ni_4B_3 was formed originally besides Ni_2B and Ni_3B. The natural aging occurring

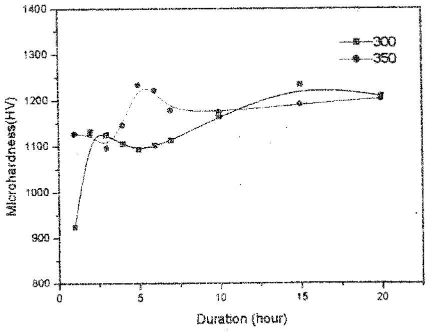

Figure 4(a). Variation of microhardness under different durations 300°C and 350°C.

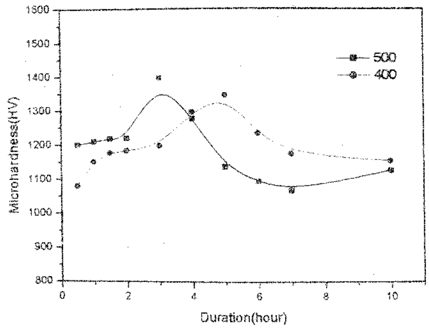

Figure 4(b). Variation of microhardness under different durations at 400°C and 500°C.

Table I. Schedule of Heat-treatment Processes

Temperature °C	*Heat treatment time (hours)*									
300	1	2	3	4	5	6	7	10	15	20
350	1	2	3	4	5	6	7	10	15	20
400	0.5	1	1.5	2	3	4	5	6	7	10
500	0.5	1	1.5	2	3	4	5	6	7	10

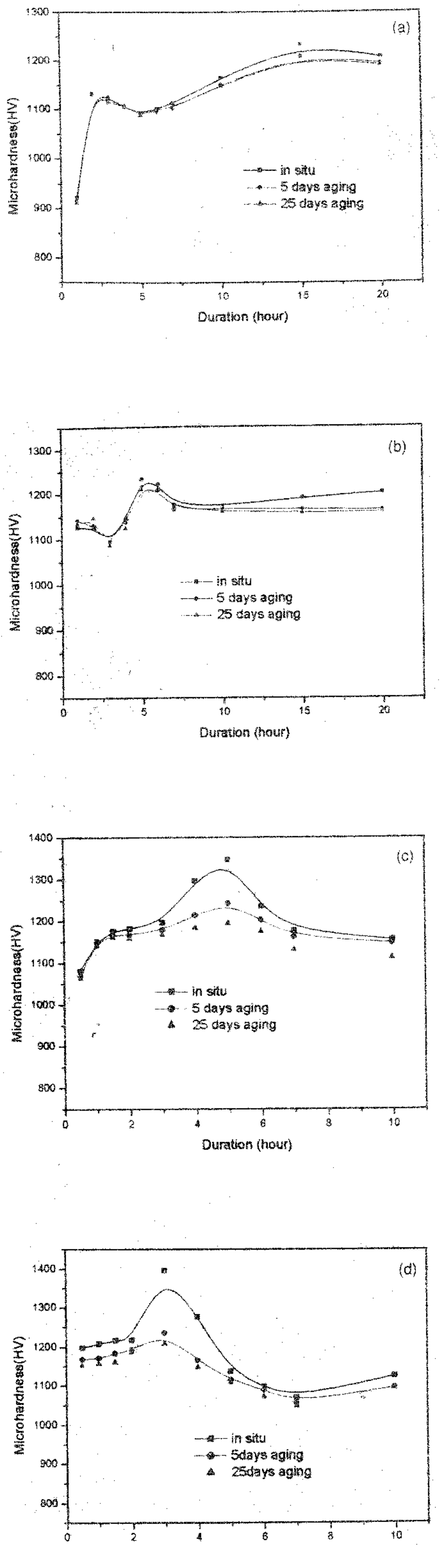

Figure 5. Influence of heat treatment processes and their 5 & 25 days natural aging on microhardness of deposits

(a) Heat treat at 300°C
(b) Heat treat at 350°C
(c) Heat treat at 400°C
(d) Heat treat at 500°C

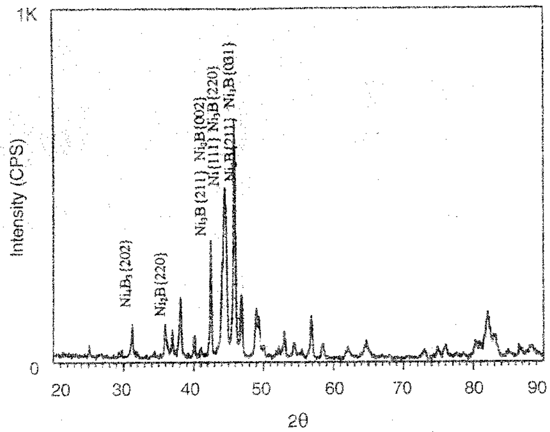

Figure 6(a). XRD pattern of a sample after 500°C × 3 h heat treatment.

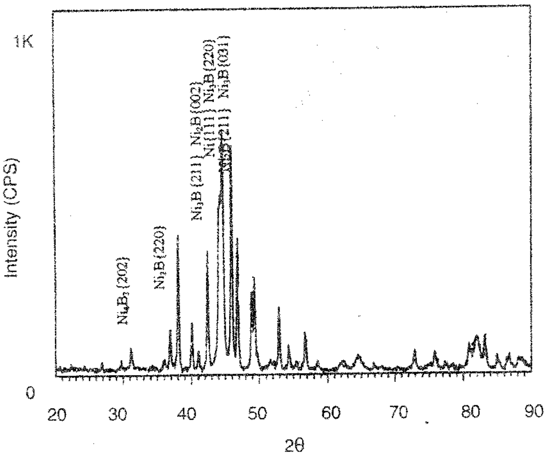

Figure 6(b). XRD pattern of the same sample after 500°C × 3 h heat treatment and 5 days aging.

thereafter is caused not only by Ni_2B decomposition, but also chiefly by Ni_3B_4 decomposition. Consequently, natural aging after 500°C treatment is most noticeable.

CONCLUSIONS

1. As-plated coatings with mixed micro-structure of non-crystalline and boron supersaturated solid solution in nickel were prepared in the present research. Nickel borides such as Ni_2B and Ni_4B_3 were found following several different heat treatment processes.
2. Nickel borides can be precipitated at the temperatures below their forming temperature as long as the duration is long enough. These borides are the key factors affecting coatings micro-hardness. The time necessary for a certain boride precipitation becomes shorter as higher treatment temperature is selected.
3. A large amount of Ni_4B_3, which greatly improved coatings micro-hardness was found in deposits after 500°C heat treatment. It is a metastable phase, whose decomposition was found to occur at room temperature.
4. Natural aging phenomena were found in deposits after some heat treatment processes. They were proved to be concerned with the decomposition of Ni_2B and Ni_4B_3.

REFERENCES

1. K. M. Gorbunova, *et al.*, *J. Electrochem. Soc.*: 1973, **120**, 613.
2. N. Hedgecock *et al.*, *J. Electrochem. Soc.*: 1975, **122**, 866.
3. Man Kim, Atsushi Iizuka, *et al.*, *Plating & Surface Technology* (in Japanese): 1999, **50**(3), 294.
4. Yi Ling Lo, *et al.*, *Ind. Eng. Chem. Res.*: 1994, **33**, 56.
5. P. B. Beldingfield, *et al.*, *Trans. IMF*: 1992, **70**(2), 19.
6. W. T. Evans, *et al.*, *J. Electrochem. Soc.*: 1994, **141**, 78.
7. Hongzhe Zhang, *et al.*, *Plating & Surface Finish*: 1993, (4).
8. He Liu, *et al.*, *Electroplating & Pollution Control* (in Chinese): 1999, **19**(3), 5.