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Effect of imides on nickel-tungsten alloy electroforming

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Electroformed nickel-tungsten alloy with low internal stress has been obtained in a sulfamate solution by using organic imides namely bis(benzene-sulfonyl)imide and ortho-benzosulfimide as stress-reducing agents. Concurrently, the hardness of the alloy electroforms thus obtained was increased by these imides, especially the ortho-benzosulfimide. The effect of imides on hardness after thermal treatment of the alloy electroforms is also studied. © *1999 Kluwer Academic Publishers*

1. Introduction

Owing to its advantages of better chemical and physical properties, electroformed nickel alloy is replacing nickel in several practical applications. Due to the unusual mechanical properties of tungsten, nickel-tungsten alloy electroform is considered to be worth detailed investigation [1]. Unfortunately, the nickel alloy electroforms usually exhibit greater stress than that of the corresponding nickel electroform, thus making the addition of stress-reducing agents in the nickel alloy electroforming bath is necessary. In the present work, the effect of two soluble organic imides on the induced nickel-tungsten alloy electroforming [2] has been studied with the aim of developing low-stress alloy electroforms. The influence of these imides on the cathode current efficiency, hardness, and tungsten content in the alloy electroforms have also been investigated. As tungsten retains a considerable degree of hardness at high temperatures [3], the effect of these imides on hardness change of thermally treated alloy electroforms is also studied.

2. Experimental procedure

An alloy electroforming bath containing 400 $\mathrm{g\,l^{-1}}$ of nickel sulfamate [$Ni(NH_2SO_3)_2 \cdot 4H_2O$], 40 $\mathrm{g\,l^{-1}}$ of sodium tungstate ($Na_2WO_4 \cdot 2H_2O$) and 36 $\mathrm{g\,l^{-1}}$ of citric acid ($C_6H_8O_7 \cdot H_2O$) was used in this study (Bath-A). Two organic imides, viz. bis(benzene-sulfonyl)-imide (Imide-1) and ortho-benzosulfimide (Imide-2), were selected as stress-reducing agents. Based on the preliminary experiments in a 267 ml Hull Cell, along with the result of our previous studies [4], the added concentration of these imides was 0.4 $\mathrm{g\,l^{-1}}$. Nickel-tungsten alloy was electroformed on bright, flat, 3×3 cm stainless steel specimens in a 1-litre solution at 60 °C. Owing to a lower anode current efficiency is needed to keep the nickel concentration in the alloy solution, electrolyzed nickel anodes were used. When the deposit reached the required weight of about 0.8 g (90 μm thickness), the electroformed layer was separated mechanically. The surface morphology of the alloy electroforms was observed using a Topcon Model ABT-32 scanning electron microscope (SEM). A Kevex X-ray energy dispersive spectroscopy (EDS) system was used for determination of tungsten and oxygen contents in the alloy electroforms. The results of six tests were averaged. Hardness was measured on a Vickers microhardness tester under 200 g load. The thermal treatments of the nickel-tungsten electroforms were performed using a Mettler TG-50 thermoanalyzer in a dry helium atmosphere at 300, 400, and 500 °C for 1 hour, at the heating rate of 20 $\mathrm{^\circ C\,min^{-1}}$. The thermally treated electroforms were tested for hardness at room temperature. Internal stress was determined by a QCI spiral contractometer [4] when the thickness of the deposit was about 25 μm.

3. Results and discussion

3.1. Internal stress

Stress control is important in nickel-tungsten alloy electroforming in order to prevent deformation of the electroforms when separated from the mandrel. As shown in Fig. 1, nickel-tungsten alloy electroforms with tensile stress were obtained by using Bath-A. The stress was noticeably increased when the current density in the bath was greater than 5 $\mathrm{A\,dm^{-2}}$. On the other hand, stress in the alloy electroforms was obviously decreased when Bath-A contained these imides mentioned above, especially the Imide-1. Alloy electroforms obtained from the Imide-1 containing solution exhibited zero-stress when the current density was equal to, or less than, 10 $\mathrm{A\,dm^{-2}}$. Moreover, the stress in these alloy electroforms was still less than 20 MPa even for the current density of 30 $\mathrm{A\,dm^{-2}}$. Therefore, addition of Imide-1 offers a wide range of current density to obtain an alloy electroform with low stress.

For addition of Imide-2, perhaps due to the greater amount of adsorption on the cathode [5] than that of Imide-1 when the current density exceeded 20 $\mathrm{A\,dm^{-2}}$, much greater stress was obtained. As shown in Fig. 1, low-stress alloy electroforms ($<$20 MPa) were obtained from Imide-2-containing solutions only for the current densities equal to, or less than, 20 $\mathrm{A\,dm^{-2}}$.

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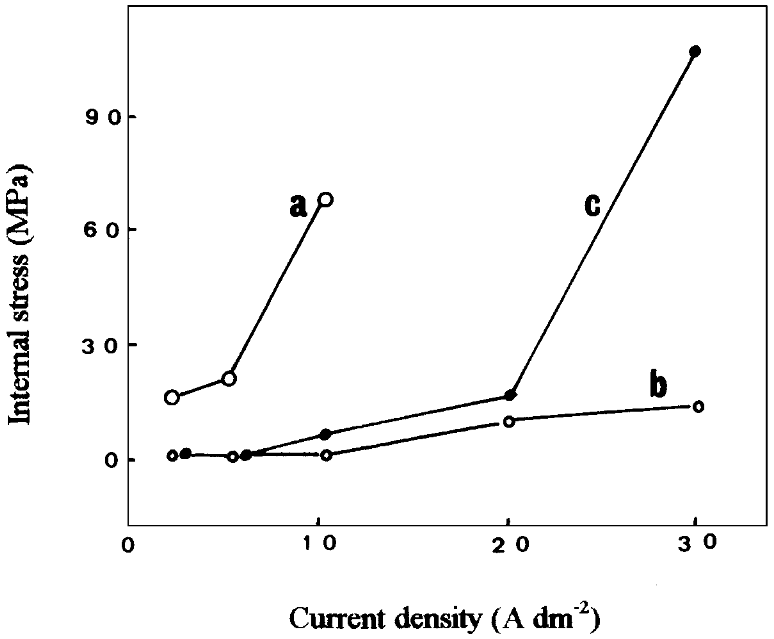

Figure 1 Internal stress of electroformed nickel-tungsten alloys obtained from following solutions: (a) Bath-A, (b) Imide-1-containing solutions, (c) Imide-2-containing solutions.

3.2. Tungsten content

Owing to the polarization effect [6], the tungsten content in the alloy electroform was affected by the nature of stress-reducing agent. The tungsten content of the alloy obtained from the Imide-2-containing bath was greater than that obtained by using Imide-1. As shown in Fig. 2, no significant variation in the tungsten content of the alloy electroforms as a function of current density was found. Perhaps greater amount of hydrogen reduced tungstate at the cathode at lower current density, resulting in a slightly higher tungsten content in the alloy electroforms at lower current density [7]. This fact is supported by the results plotted in Fig. 3, that a greater amount of hydrogen evolved at lower current density, resulting in low current efficiency [8]. Although higher current density may cause alkalization of the solution layer adjacent to the cathode and the hydroxo-compounds of tungsten produced may be codeposited to increase the tungsten content of the alloy electroforms thereby [9, 10], due to the effect of these imides, no occluded oxygen in the alloy electroforms was found when the current density was increased to 30 A dm^{-2}, as evidenced by EDS measurements. The tungsten content of the alloy electroforms was therefore not increased with increasing current density. Although electrodeposited nickel-tungsten alloy coatings containing a high percentage of tungsten often exhibit high internal stress, a better optimization with respect to the tungsten content and internal stress was obtained due to the effect of these imides. Consequently, nickel-tungsten alloy electroforms with lower stress and higher tungsten content was obtained from the imide-containing electrolyte at a lower current density.

The variation of current efficiency with current density coincides with the change of internal stress in the alloy deposits. According to Fig. 3, owing to the greater

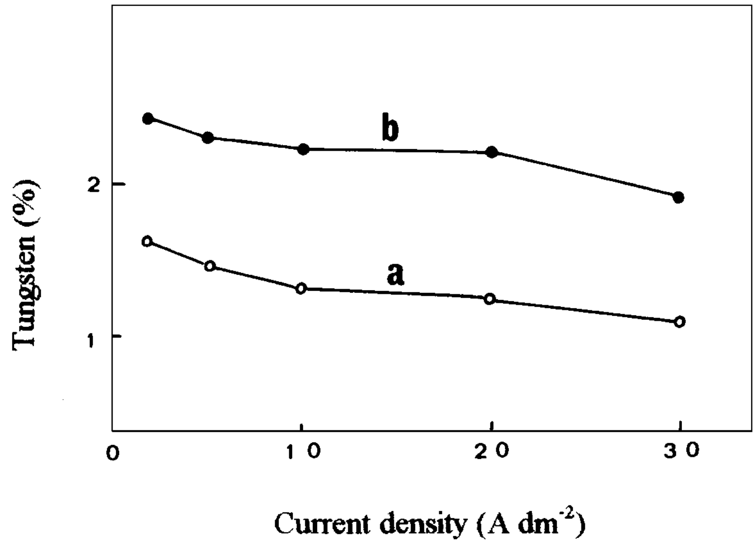

Figure 2 Tungsten content of electroformed nickel-tungsten alloys obtained from following solutions: (a) Imide-1-containing solutions, (b) Imide-2-containing solutions.

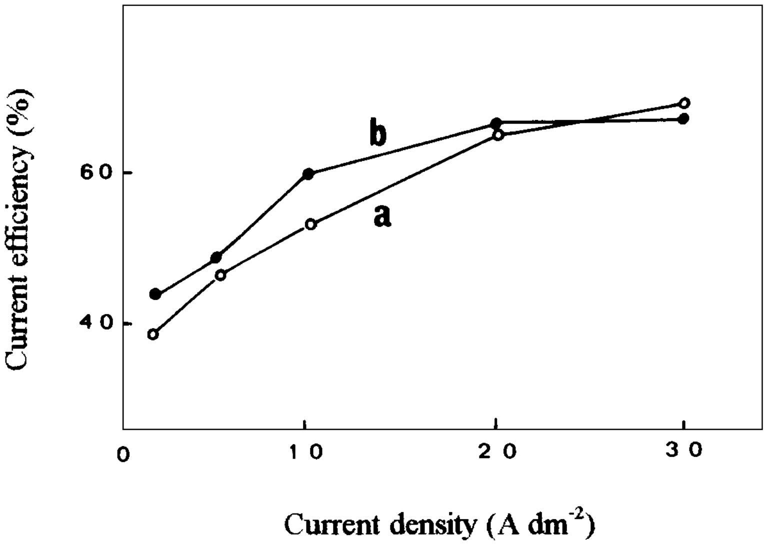

Figure 3 Current efficiency of the nickel-tungsten alloy electroforming conducted in the following solutions: (a) Imide-1-containing solutions, (b) Imide-2-containing solutions.

amount of adsorption of Imide-2 on the cathode, current efficiency of Imide-2 containing solutions is lower than that of Imide-1 containing solutions when the current density is greater than 20 A dm^{-2}. The adsorbed amount of Imide-2 is associated with the variation of the stress. Perhaps this is a reason to explain why greater stress were obtained at higher current density when Imide-2 was added in Bath-A (Fig. 1).

3.3. Hardness

Although the pH of the solution was only 1.6, owing to the influence of tungsten component, the alloy electroforms obtained from the Imide-2-containing solution exhibited hardness greater than HV 500 over the current density range of 2 to 30 A dm^{-2}, can be seen from Fig. 4. The variation in hardness with current density was small. As a result, when the current density is below 20 A dm^{-2}, addition of Imide-2 provides favorable condition for preparation of alloy electroforms with higher hardness, greater tungsten content, and very low stress.

The alloy electroforms obtained from the imide-free Bath-A exhibited lower hardness and became increasingly softer with elevated temperature (about 18% decrease in hardness was found after thermal treatment at 300 °C). Whereas, as can be seen from Fig. 4, the alloy electroforms obtained from the Imide-2 containing solution showed increase in hardness after the thermal treatment at 300 °C. Hardness decreased after the thermal treatment at 400 or 500 °C, especially the hardness of deposits obtained at a lower current density. Owing to a greater amount of hydrogen evolved and then occluded in the deposits at a lower current

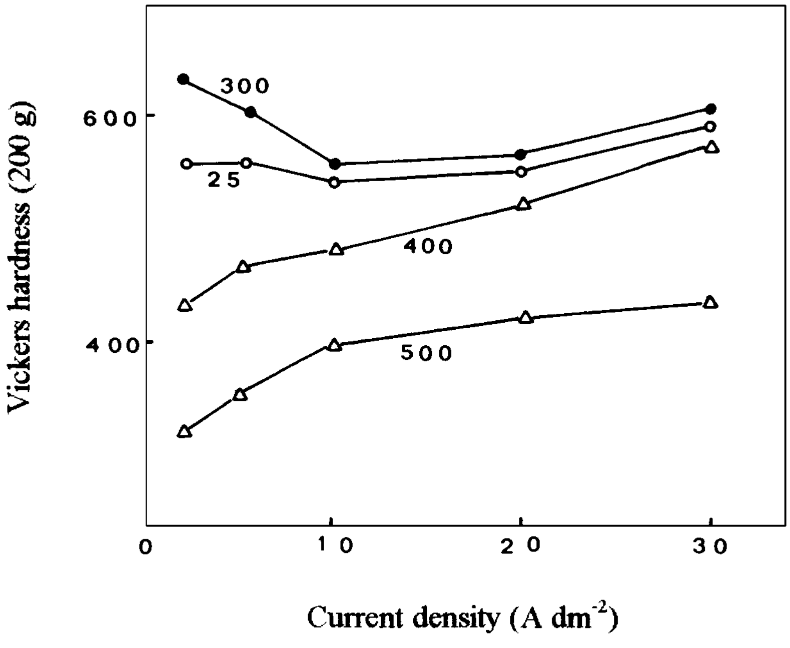

Figure 4 Hardness of the nickel-tungsten alloy electroforms obtained from Imide-2-containing solutions. Numbers adjacent to curves are the treated temperature in °C. Number 25 means no thermal treatment.

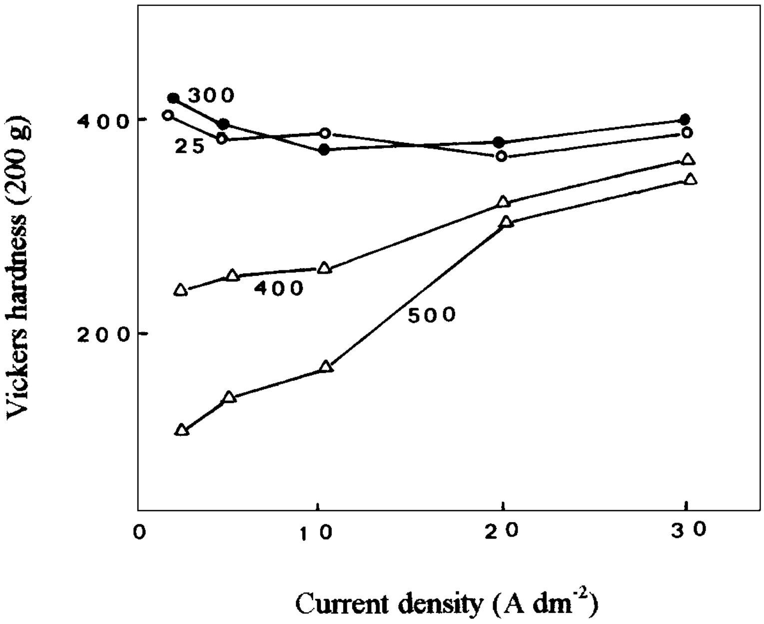

Figure 5 Hardness of the nickel-tungsten alloy electroforms obtained from Imide-1-containing solutions. Numbers adjacent to curves are the treated temperature in °C. Number 25 means no thermal treatment.

density; therefore, a greater amount of hydrogen will be escaped after a higher temperature treatment, causing a greater recrystallization of the alloy electroforms [11]. Perhaps this is a reason to explain why a considerable decrease in hardness was observed for the alloy electroforms obtained from Imide-2 containing solutions at a lower current density after thermal treatment at 400 or 500 °C.

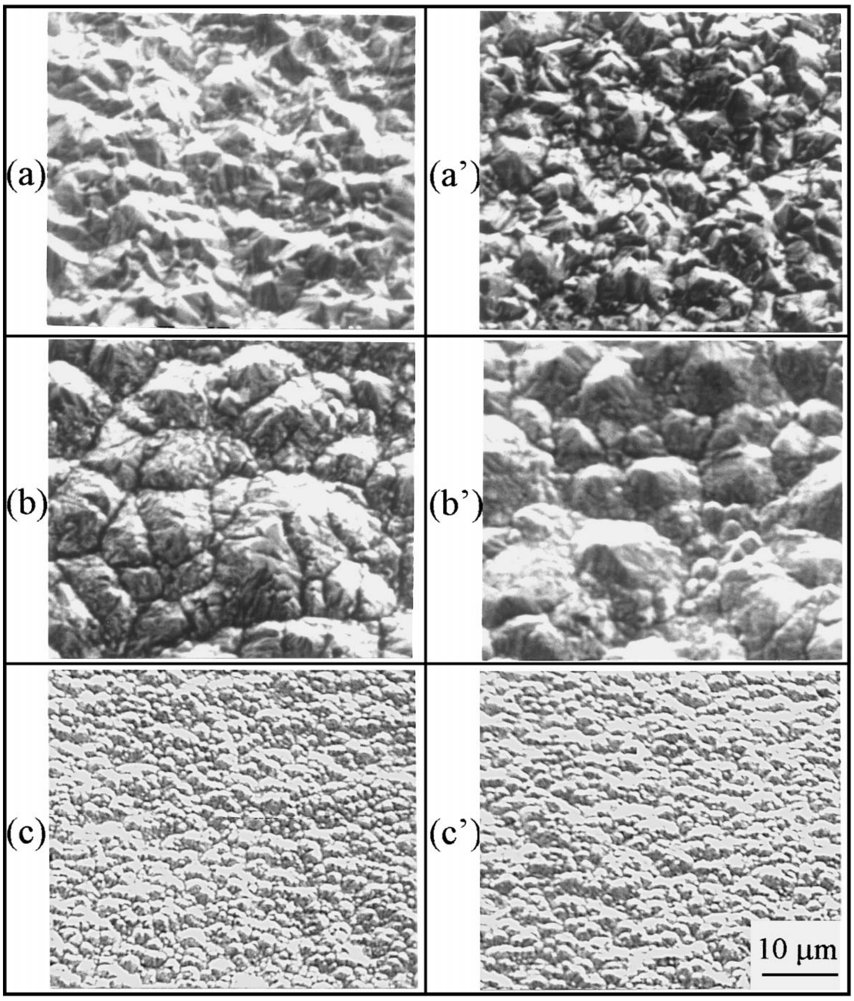

Figure 6 Scanning electron micrographs of nickel-tungsten alloy electroforms obtained at 10 A dm^{-2} from following solutions: (a) Bath-A, (b) Imide-I containing solution, (c) Imide-2 containing solution. After thermal treatment at 500 °C, the micrographs of these electroforms are (a′), (b′), and (c′) respectively.

Although the hardness of alloy electroforms obtained from the Imide-1 containing bath was less than those obtained from Imide-2, as can be noted from Fig. 5, higher hardness was still obtained at low current density. Besides, the variation in hardness as a function of current density was very small and the hardness was still retained even after the thermal treatment at 300 °C. Similar to the results in Fig. 4, the alloy electroforms obtained from the Imide-1 containing solution at low current density became softer after thermal treatment at 400 or 500 °C, due to the escape of occluded hydrogen from the heated alloy deposits.

3.4. Morphology

The low-stress alloy electroforms obtained in this work exhibited a uniform surface, displaying no cracks. Larger granular electrodeposits were obtained at higher current densities. The alloy electroforms obtained from the Imide-1 containing baths had larger grain morphology, while fine grains were obtained from the Imide-2 containing solutions. The surface morphology of these tested deposits was not changed after 500 °C thermal treatment. Typical scanning electron micrographs of the alloy electroforms obtained from Bath-A and the imide-containing solutions are shown in Fig. 6.

4. Conclusion

Nickel-tungsten alloy electroforms with very low stress and high hardness have been obtained by adding bis(benzene-sulfonyl)imide and ortho-benzosulfimide to the electroforming solution. Due to the effect of these of two imides, not only that the variations in hardness of the alloy electroforms as a function of current density was significantly small, the hardness of these alloy electroforms was retained or even increased after the thermal treatment at 300 °C.

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