JOURNAL OF MATERIALS SCIENCE **36** (2001) 4385–4391

Study of sulfur embrittlement in electroformed Ni-Re alloy

CHEIN-HO HUANG*, JONG-RONG JAN
Chemistry Department, Soochow University, P.O. Box 86-18, Taipei, Taiwan
E-mail: cchhuang@mail.scu.edu.tw

WEN-YUNG SHU, HSIEN-MING WU
Materials & Electro-Optics Research Division of Chung Shan Institute of Science and Technology, Lung Tan, Taiwan

Although the amount of cathodic absorption sulfur (sulfur content) was enhanced by the presence of rhenium in electroformed nickel, superior ductility of the Ni-Re alloy deposits obtained from saccharin-free baths was determined, even when the deposits were treated at 400°C. On the other hand, owing to the presence of saccharin in the alloy baths changed the banded microstructure of the alloy deposit to granular microstructure after 400°C thermal treatment, resulting in sulfur embrittlement even the sulfur content was only about 100 ppm. Deposit microstructures, X-ray diffraction patterns, and ductility data were investigated to evaluate the effect of rhenium and saccharin on sulfur embrittlement in the alloy deposits. In addition, the effect of rhenium and sulfur on deposit hardness was also studied.

1. Introduction

Saccharin, a typical organo-sulfur compound, enhances the sulfur content in nickel electrodeposits [1]. The incorporated sulfur refines grain size and greatly increases the hardness of the nickel deposit. This is important for applications such as electroformed molds and dies, where the hardness of pure nickel is insufficient [2]. However, Dini *et al.* [3] indicated that there is a high rate of sulfur diffusion along the grain boundaries, where the low-melting-point, nickel-nickel sulfide eutectic is formed, thus destroying cohesion between grains. Therefore, this sulfur mobility causes the nickel deposits to lose ductility rapidly as the temperature increases [4, 5].

Manganese is known to be a sulfur scavenger and is alloyed in most wrought nickels to prevent hot shortness at high temperatures, hence manganese is codeposited with nickel to prevent the sulfur embrittlement. Some of this improvement has been attributed to manganese forming a relatively inactive phase of manganese sulfide and preventing the formation of nickel sulfide [6, 7], which wets intergranular surfaces, causing brittle failure. However, most Ni-Mn alloy baths are unstable and MnO_2 build-up during their use limits the bath life [8].

Rhenium is in the same family of the periodic table as manganese, but rhenium in an acid perrhenate solution has a standard electrode potential more noble than that of manganese, hence no oxides of rhenium will build up during electrolysis. In addition, a Ni-Re alloy will be obtained of higher hardness than the Ni-Mn alloy [4]. Accordingly, to avoid the disadvantages of the unstable Ni-Mn alloy baths and sulfur embrittlement in electroformed nickel, we decided to investigate the codeposition of rhenium in further depth. Because the hardness of the deposits is associated with the sulfur content and the percentage of rhenium, therefore we studied the effects of rhenium and sulfur content on the changes in hardness of the alloy deposits.

2. Experimental procedure

Rhenium-free control deposits were prepared from the nickel bath which containing 300 $g\,l^{-1}$ of nickel sulfamate $[Ni(NH_2SO_3)_2 \cdot 4H_2O]$ and 25 $g\,l^{-1}$ of boric acid. Electroformed nickel-rhenium alloys were prepared by adding potassium perrhenate to the nickel bath. Saccharin ($C_7H_4NO_3S \cdot Na$) was added to the baths to enhance the sulfur content in the deposits. Electroforming was conducted on bright, flat, 3 × 3 cm stainless steel specimens in a 0.5-litre solution from 5 to 30 A dm^{-2} at 60°C, using electrolyzed nickel anodes. When the deposit reached the required weight of around 1 g, the electroformed layer was separated mechanically. The sulfur content was determined using a combustion analyzer, and the rhenium content was determined by photometry using dimethylgloxime. The thermal treatment of the deposits was performed using a thermogravimeter in a dry helium atmosphere for 1 hour. The crystallographic structure of the deposits was examined with an X-ray diffractometer (XRD). After polishing, the cross-section of the deposits was etched in a 1 : 1 : 2 mixture of nitric acid, acetic acid

---

[*] Author to whom all correspondence should be addressed.

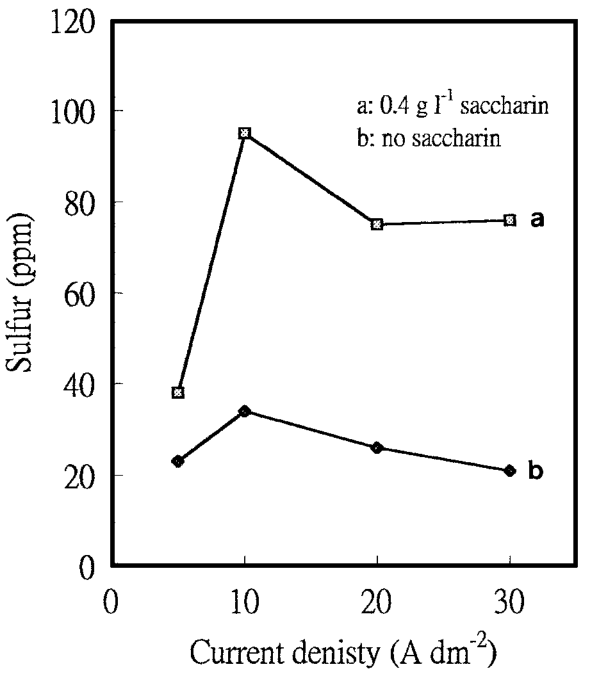


Figure 1 Sulfur content in the nickel deposits obtained from the nickel baths.

and acetone, after which the microstructure of the deposits was examined using a scanning electron microscope (SEM). Hardness measurements were performed on polished cross sections using a Vickers microhardness tester with a 200 g load. Ductility was measured in accordance with ASTM Standard Practice B-490.

3. Results and discussion

3.1. Sulfur embrittlement in nickel deposits

Nickel deposits obtained from the nickel baths was found to have a sulfur content of less than 35 ppm (0.0035 percent). There is an increase in the sulfur content in deposits with the addition of saccharin to the nickel bath; therefore, a higher sulfur content is characteristic of nickel obtained from baths with 0.4 g l^{-1} saccharin, as can be seen from Fig. 1. Because the refined structure of deposits resulting form the influence of saccharin in the nickel bath involves an increase in hardness; therefore, as shown in Table I, higher hardness values of nickel deposits obtained from saccharin-containing baths. Moreover, as shown in Fig. 2, the sulfur content in the nickel deposits increases with the concentration of saccharin in the nickel baths. Accordingly, as shown in Table II, the hardness of the nickel deposits also increases with the concentration of saccharin in the nickel bath. The results of Table II also show that the nickel deposits softened appreciably when treated at or greater than 300°C.

TABLE I Hardness of the nickel deposits obtained from the nickel baths

Saccharin	Hardness (HV)			
(g l^{-1})	5 (A dm^{-2})	10 (A dm^{-2})	20 (A dm^{-2})	30 (A dm^{-2})
0	233	253	223	158
0.4	406	455	489	450

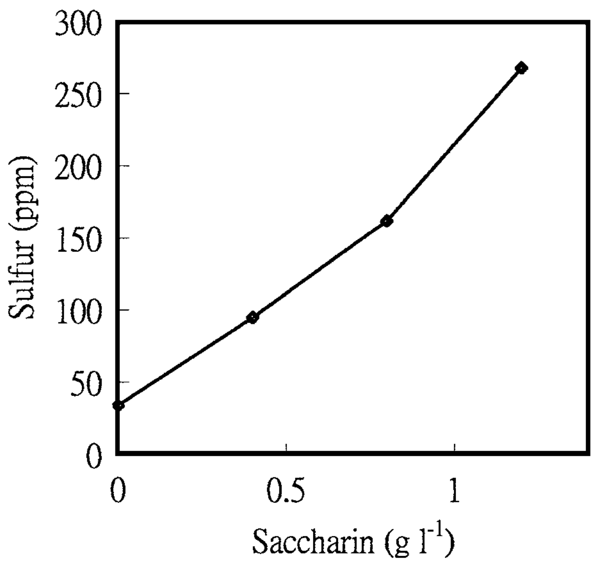


Figure 2 Sulfur content in the nickel deposits obtained from the nickel baths at 10 A dm^{-2}.

However, the incorporated sulfur causes the nickel deposits to lose ductility rapidly as the temperature increases. Therefore, Table III shows that the ductility of nickel deposits obtained in saccharin-containing baths decreases with increasing the temperature of thermal treatment, along with the concentration of saccharin. Although previous study [3] indicated that 200 ppm of sulfur in nickel deposits was needed to have severe embrittlement, due to the presence of saccharin in the bath the sulfur content is not a critical point. For instance, although the sulfur content of the nickel deposit obtained from the bath with 0.4 g l^{-1} saccharin is about 100 ppm at 10 A dm^{-2} (Fig. 2), the nickel deposit completely loses its ductility when treated at 300°C (Table III).

TABLE II Hardness of the nickel deposits obtained from the nickel baths at 10 A dm^{-2}

	Hardness after thermal treatment (HV)			
Saccharin (g l^{-1})	As plated	200°C	300°C	400°C
0	253	228	207	155
0.4	451	455	269	245
0.8	477	517	318	300
1.2	514	523	318	306

TABLE III Ductility of the nickel deposits obtained from the nickel baths at 10 A dm^{-2}

	Ductility after thermal treatment (%)			
Saccharin (g l^{-1})	As plated	200°C	300°C	400°C
0	100	100	100	100
0.4	76.2	45.3	0	0
0.8	61.7	31.6	0	0
1.2	61.0	23.4	0	0

TABLE IV Ductility of the Ni-Re alloy deposits obtained from the nickel baths with 0.6 g l^{-1} potassium perrhenate

	Ductility after thermal treatment (%)			
Current density (A dm^{-2})	As plated	200°C	300°C	400°C
5	100	100	100	100
10	100	100	100	100
20	100	100	100	100
30	100	100	100	100

TABLE V Hardness of the Ni-Re alloy deposits obtained from the nickel baths with 0.6 g l^{-1} potassium perrhenate

	Hardness after thermal treatment (HV)			
Current density (A dm^{-2})	As plated	200°C	300°C	400°C
5	426	341	284	275
10	318	279	271	250
20	278	273	262	225
30	252	262	247	198

Accordingly, a further study of the effect of saccharin on the sulfur embrittlement in the electroformed Ni-Re alloy was conducted.

3.2. Ni-Re alloy deposits obtained from saccharin-free baths

The percentage of codeposited rhenium in nickel deposits is higher than that of manganese because the highly positive potential of rhenium in aqueous solutions facilitates codeposition with nickel. The percentage of rhenium in the alloy deposits increases with an increase of the concentration of potassium perrhenate in the alloy bath. When the concentration of potassium perrhenate was equal to or greater than 0.6 g l^{-1}, more than 1 percentage of rhenium in the alloy deposit was obtained. Therefore the rhenium content was stoichiometrically sufficient to bind sulfur in nickel deposits, preventing the high-temperature embrittling effect. This fact is supported by the results of Table IV, which shows that no sulfur embrittlement at 400°C was observed when the alloy deposits obtained from the nickel bath containing 0.6 g l^{-1} of potassium perrhenate, even though some of these alloy deposits containing about 200 ppm of sulfur (curve "e" in Fig. 3). Accordingly, although greater sulfur content was determined in the deposits obtained form the nickel bath with 0.6 g l^{-1} of potassium perrhenate than with 0.4 g l^{-1} saccharin, owing to the role of rhenium in preventing the formation of brittle grain-boundary film of nickel sulfide, Ni-Re alloy deposits with a greater ductility still obtained after thermal treatment.

Comparing the results of Tables I and V, the hardness of the alloy deposits is superior to the corresponding nickel deposits over the range of studied current density. Because there is a lower pH in the depletion layer at low current density, the reduction of perrhenate ions was enhanced [9], causing a significant increase of the percentage of rhenium in the alloy deposits. Therefore there is a higher hardness value of the alloy deposits obtained at low current density (Table V). Most

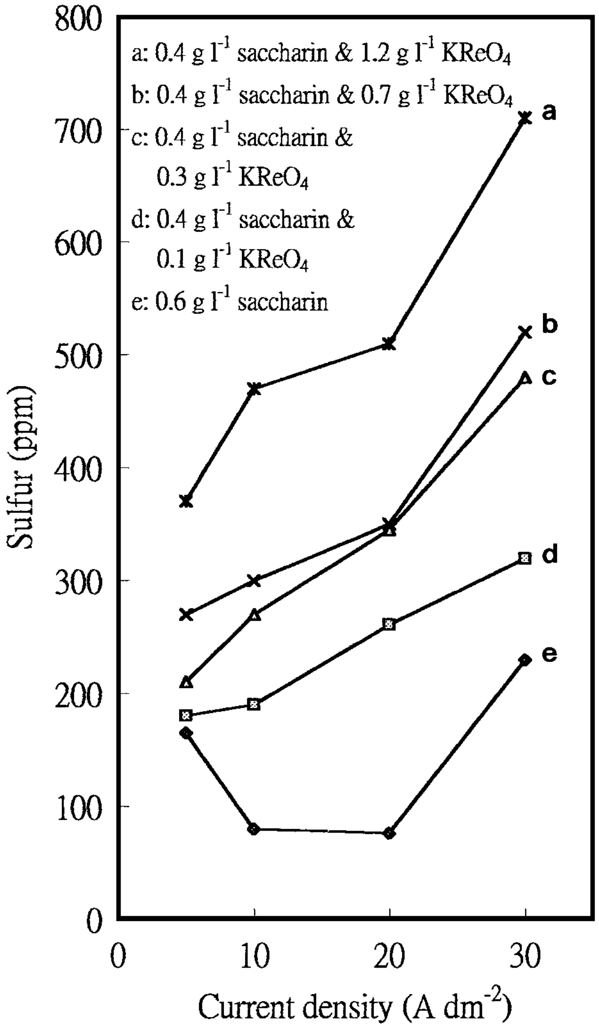


Figure 3 Sulfur content in the Ni-Re alloy deposits obtained from the nickel baths with potassium perrhenate and saccharin.

TABLE VI Ductility of the Ni-Re alloy deposits obtained from the nickel baths with potassium perrhenate and 0.4 g l^{-1} saccharin

KReO$_4$ (g l^{-1})	Current density (A dm^{-2})	Ductility after thermal treatment (%)			
		As plated	200°C	300°C	400°C
0.1	5	100	100	100	0
	10	100	100	0	0
	20	76	0	0	0
	30	62	0	0	0
0.3	5	100	100	100	0
	10	100	100	0	0
	20	100	60	0	0
	30	100	42	0	0
0.7	5	100	100	100	0
	10	100	100	0	0
	20	100	65	0	0
	30	100	41	0	0
1.2	5	100	100	100	0
	10	100	100	0	0
	20	100	86	0	0
	30	56	46	0	0

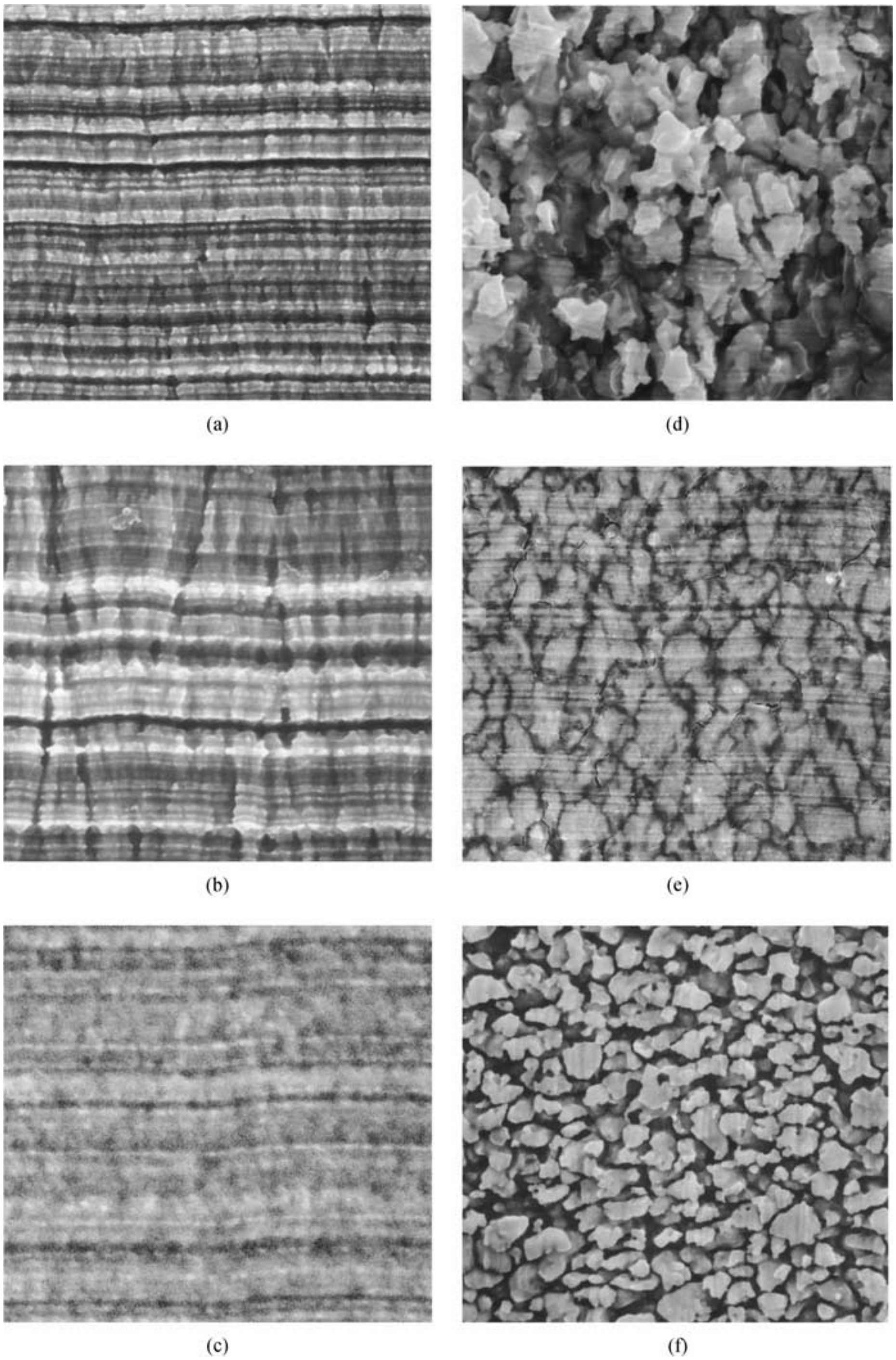


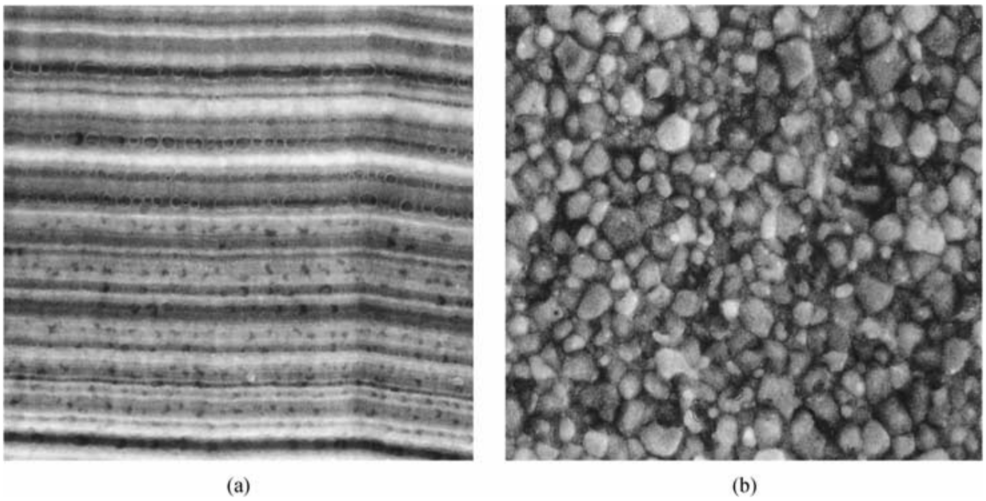
Figure 4 Scanning electron micrographs of microstructure of the Ni-Re alloy deposits obtained from the nickel baths with 1.2 g l^{-1} potassium perrhente and 0.4 g l^{-1} saccharin at following current densities: (a) 5 A dm^{-2}, (b) 10 A dm^{-2}, (c) 20 A dm^{-2}. After 400°C thermal treatment, the corresponding micrographs of these deposits are (d), (e), and (f) respectively.

of the alloy deposits softened appreciably after 300°C or 400°C thermal treatment.

3.3. Ni-Re alloy deposits obtained from saccharin-containing baths

With the synergetic effect of saccharin and rhenium, as shown in Fig. 3, greater sulfur content in the alloy deposits was obtained from the alloy baths containing 0.4 g l^{-1} saccharin. In addition to the concentration of saccharin, the sulfur content also increases with increasing current density and the concentration of potassium perrhenate in the alloy baths.

With the effect of rhenium, the ductility of the alloy deposits obtained from baths with saccharin is greater than their corresponding nickel deposits. For instance, comparing the results of Tables III and VI, when the added concentration of saccharin is 0.4 g l^{-1} and at 10 A dm^{-2}, there was still superior ductility (100%) for the alloy deposits after 200°C thermal treatment, whereas the ductility of the corresponding nickel deposit is only 45.3%. Accordingly, when 0.4 g l^{-1} saccharin was added in the studied baths, the embrittling effect of nickel deposits at 200°C was decreased by the codeposition of rhenium.

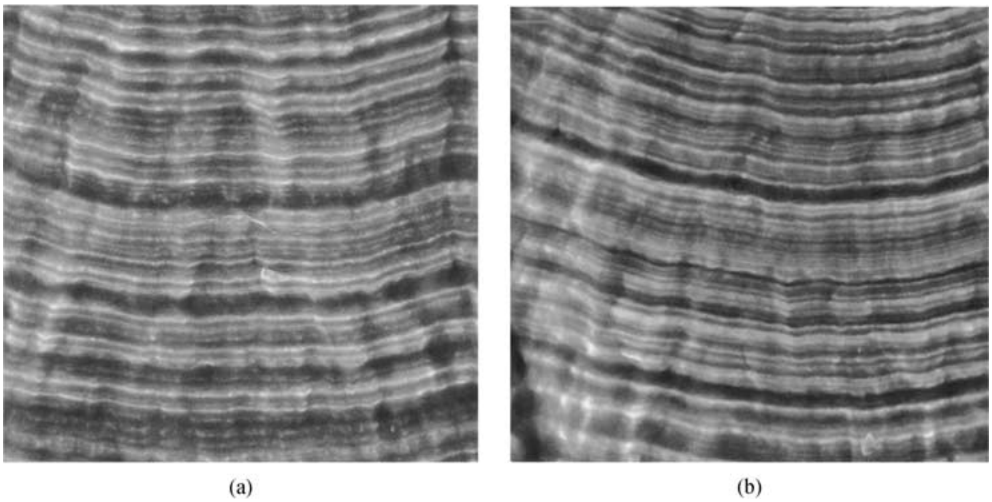


(a) (b)

Figure 5 Scanning electron micrographs of microstructure of the nickel deposits obtained from the nickel bath with 0.4 g l^{-1} saccharin at 10 A dm^{-2}. (a) Before thermal treatment, (b) after 400°C thermal treatment.

However, as shown in Table VI, all the alloy deposits obtained from baths with saccharin exhibit severe embrittlement after thermal treatment at 300°C and 400°C, especially at 400°C. In addition to the effect of greater sulfur content (Fig. 3), a better explanation is the microstructural change of the deposit after thermal treatment. When the alloy baths contained saccharin, as shown in Fig. 4, the banded microstructure of the obtained Ni-Re alloy deposits changed to a granular microstructure after thermal treatment at 400°C, resulting in severe embrittlement. In addition to the alloy deposits, owing to the presence of saccharin in the nickel bath, ductility of the nickel deposits was also changed from 100% to 0% after 400°C thermal treatment, as can be seen from Table III. For instance, as shown in Fig. 5, although the sulfur content in the nickel deposit obtained from the nickel bath with 0.4 g l^{-1} saccharin at 10 A dm^{-2} was only around 100 ppm, the banded microstructure of the nickel deposits also changed to granular microstructure after thermal treatment at 400°C, resulting in severe embrittlement. As a result, both nickel and Ni-Re alloy deposits obtained from baths with saccharin changed their deposit microstructure after thermal treatment, resulting in sulfur embrittlement. This may be explained by the effect of saccharin on the crystal orientation of the deposits. During electrolysis, adsorption of this organic compound at the metallic surface involves an increase in the frequency of nucleation, blocking crystalline growth [10], resulting in a different microstructure of deposits after thermal treatment.

In contrast, when the alloy deposits obtained from saccharin-free baths, the alloy deposits exhibit a banded microstructure both before and after thermal treatment at 400°C (Fig. 6); therefore no sulfur embrittlement was found in the alloy deposit (Table IV) even the sulfur content is around 200 ppm. Consequently, in addition to the effect of a greater sulfur content, SEM results provide clear evidence that severe embrittlement in Ni and Ni-Re deposits was still observed when the deposit microstructure was changed after thermal treatment.



(a) (b)

Figure 6 Scanning electron micrographs of microstructure of the Ni-Re alloy deposits obtained from the nickel bath with 0.6 g l^{-1} potassium perrhenate at 5 A dm^{-2}. (a) Before thermal treatment, (b) after 400°C thermal treatment.

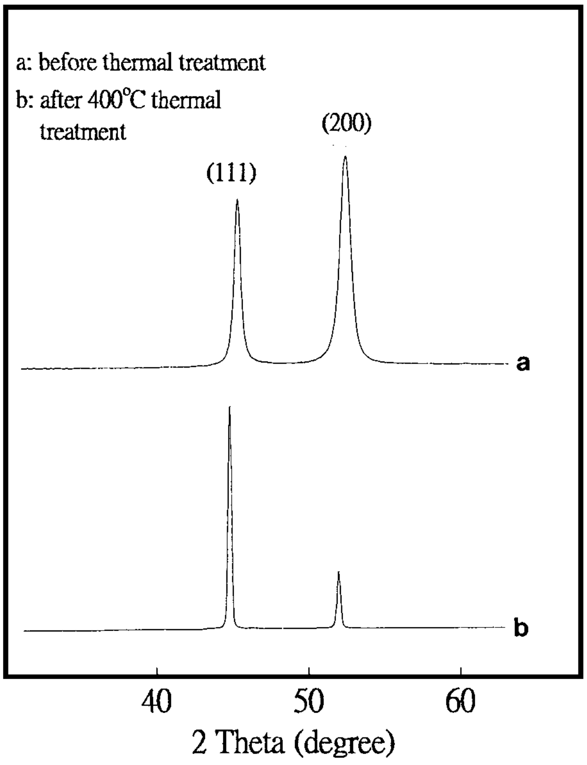


Figure 7 X-ray diffraction patterns of the Ni-Re alloy deposit obtained from the nickel bath with 1.2 g l^{-1} potassium perrhenate and 0.4 g l^{-1} saccharin at 10 A dm^{-2}.

The SEM results indicating the change of deposit microstructure are supported by the XRD patterns of the deposits before and after thermal treatment at 400°C. As shown in Figs 7a and 8a, XRD studies show that both the nickel and alloy deposits obtained from baths with saccharin exhibit a higher (111) orientation, as well as peak broadening in comparison to that obtained from saccharin-free bath (Fig. 9a). Whereas, after thermal treatment at 400°C, as shown in Figs 7b and 8b, in addition to the narrowing of diffraction peaks, the (111) peak increased in intensity while the (200) peak weakened. Therefore, these XRD patterns also indicate that the deposit microstructures of both the nickel and Ni-Re alloy deposits obtained from baths with saccharin were changed after 400°C thermal treatment, resulting in sulfur embrittlement. In contrast, as Fig. 9 clearly shows, although the sulfur content in the alloy deposit obtained in bath without saccharin is almost 200 ppm, the relative intensity of (111) and (200) narrow peaks was unchanged after thermal treatment at 400°C, hence no deposit microstructure was changed resulted in superior ductility. On the basis of SEM and XRD studies it would be appropriate to conclude that the change of deposit microstructure after thermal treatment is an important factor to predict the sulfur embrittlement in nickel and Ni-Re alloy deposit.

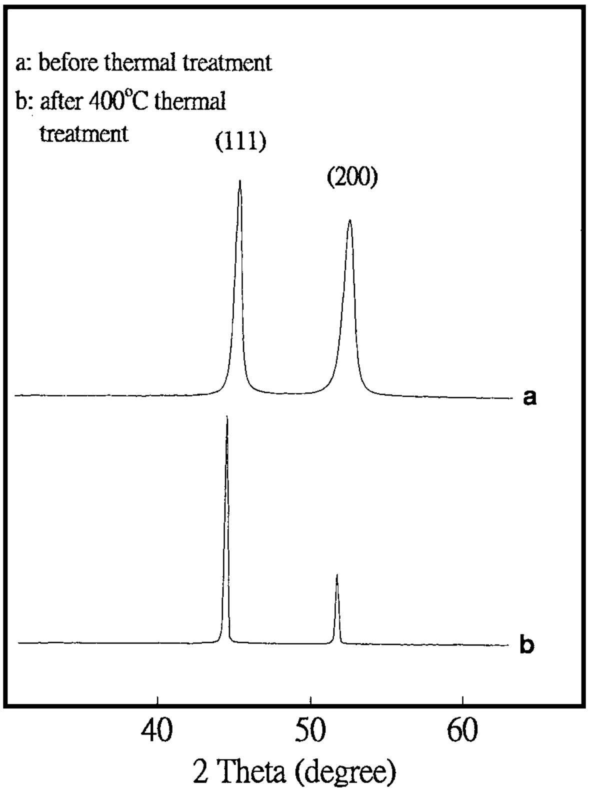


Figure 8 X-ray diffraction patterns of the nickel deposit obtained from the nickel bath with 0.4 g l^{-1} saccharin at 10 A dm^{-2}.

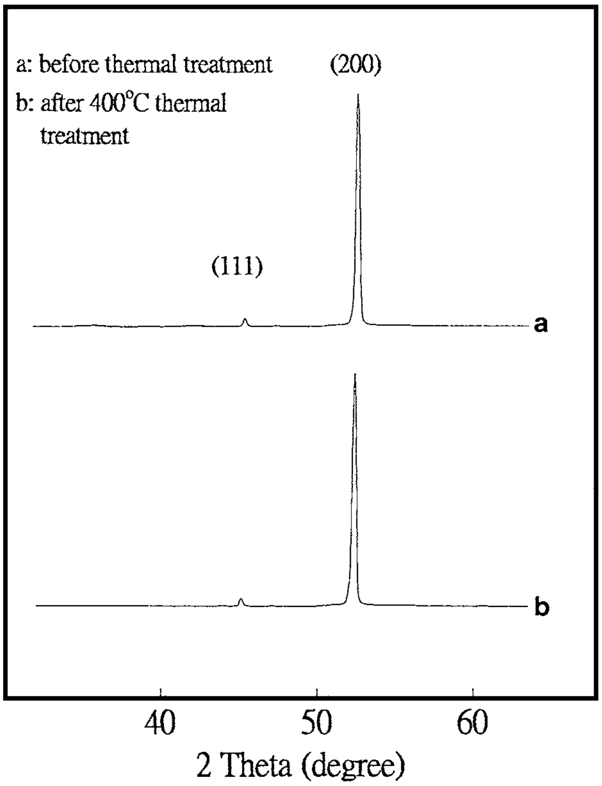


Figure 9 X-ray diffraction patterns of the Ni-Re alloy deposit obtained from the nickel bath with 0.6 g l^{-1} potassium perrhenate at 5 A dm^{-2}.

The hardness of the nickel deposits obtained from the saccharin-containing baths was enhanced by the presence of potassium perrhenate in the nickel baths. As shown in Table VII, the hardness value of the alloy deposits increases with the increase of the concentration of potassium perrhenate. This behavior may be due to the dispersion and size characteristics of the rhenium sulfide particles. The hardness of these alloy deposits

TABLE VII Hardness of the Ni-Re alloy deposits obtained from the nickel baths with potassium perrhenate and 0.4 g l^{-1} saccharin

$KReO_4$ (g l^{-1})	Current density (A dm^{-2})	Hardness after thermal treatment (HV)			
		As plated	200°C	300°C	400°C
0.1	5	425	435	247	156
	10	460	458	250	219
	20	496	482	254	277
	30	518	486	376	243
0.3	5	428	406	222	196
	10	465	447	290	231
	20	501	478	354	297
	30	527	500	358	268
0.7	5	431	470	315	255
	10	452	475	303	263
	20	516	525	337	309
	30	528	558	347	315
1.2	5	420	508	332	268
	10	461	518	353	324
	20	514	525	355	340
	30	536	584	361	337

was clearly decreased after 300°C and 400°C thermal treatment.

4. Conclusion

In addition to enhancing the hardness of the nickel deposits, the presence of rhenium in nickel electroform has the advantage of preventing sulfur embrittlement at high temperature. Therefore, although sulfur content was about 200 ppm, superior ductility of Ni-Re alloy deposits was still obtained even with thermal treatment at 400°C.

In addition to the influence of sulfur content, results of this study indicate that the change of deposit microstructure after thermal treatment plays a prominent role in sulfur embrittlement of nickel and Ni-Re alloy deposits. Accordingly, because the deposit microstructure changed from a banded microstructure to a granular microstructure, both nickel and Ni-Re deposits obtained from the saccharin-containing baths exhibited sulfur embrittlement after thermal treatment at 400°C, even though the sulfur content of some deposits was only about 100 ppm.

References

1. C. H. HUANG, *Metal Finishing*, **91**(6) (1993) 107.
2. C. H. HUANG, H. M. WU and Y. H. HON, *Plat. Surf. Fin.* **77**(4) (1990) 56.
3. J. W. DINI, H. R. JOHNSON and L. A. WEST, *ibid.* **65**(2) (1978) 36.
4. W. R. WEARMOUTH and K. C. BELT, *ibid.* **66**(10) (1979) 53.
5. W. D. BONIVERT, H. A. JOHNSEN and J. T. HACHMAN, AESF Electroforming Symposium, Las Vegas, NV, 1989, Session IV.
6. P. A. KORZHAVYI, I. A. ABRIKOSOV and B. JOHANSSON, *Acta Mater.* **47**(5) (1999) 1417.
7. G. A. MALONE, *Plat. Surf. Fin.* **74**(1) (1987) 50.
8. Y. NAKAMURA, N. KANEKO, M. WATANABE and H. NEZU, *J. Appl. Electrochem.* **24** (1994) 227.
9. J. JI, W. C. COOPER, D. B. DREISINGER and E. PETERS, *ibid.* **25** (1995) 642.
10. J. P. BONINO, P. POUDEROUX, C. ROSSIGNOL and A. ROUSSET, *Plat. Surf. Fin.* **79**(4) (1992) 62.

Received 24 August 2000
and accepted 24 April 2001