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Formation of composition-modulated alloys by electrodeposition

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A method has been developed to produce composition-modulated alloys by electrodeposition. The method was demonstrated for the copper–nickel couple. Salts of the two component metals are dissolved in a common electrolyte and the potential is alternately pulsed for fixed durations between values above and below the reduction potential of the less noble component. Co-deposition of the nobler metal into the other metal layer is diminished by setting unfavourable diffusion conditions during the more cathodic pulse. Modulation was achieved down to 0.8 nm thick layers. The resulting composition-modulated alloys were analysed by Auger spectroscopy and X-ray diffraction.

1. Introduction

In some early investigations Bradley [1], Daniel and Lipson [2], Hillert [3] and Cahn [4, 5] studied modulated structures by X-ray diffraction and the effect of interfacial energy on spinodal decomposition. Subsequently, effects were made to artificially develop modulated alloys in order to obtain new and unpredictable properties of materials. Tsakalakos [6] has produced such structures by alternate vapour deposition of copper and nickel, following earlier work by Dumond and Youtz [7] and Dinklage and Frerichs [8]. The alloys prepared by Tsakalakos were modulated with a cycle of 0.5 to 5 nm with a copper content of between 33 and 77 wt %. He measured the modulus of elasticity and found an appreciable enhancement with a maximum at modulation of about 1.7 nm at an average composition of 50% Cu–50% Ni. The enhancement of the modulus diminished at modulations of over 5 nm. These results were confirmed by Testardi *et al.* [9]. Similar results were also reported by Hilliard and co-workers [10–13] for composition-modulated alloys of other metals. These authors [13] have also reported unexpected magnetic properties of such films, which were further studied by Dillon, Gyorgi, Testardi and co-workers [14, 15].

In view of the exceptional properties of the modulated alloys, it was of interest to try and produce such alloys with a modulation of less than 5 nm by electrodeposition. Such an electrochemical method should lend itself to more variation in shape and size of deposits than that of vapour deposition. It should also enable the production of engineering parts by electroforming which would have the extraordinary properties of modulated alloys.

Electrodeposition of composition-modulated films was attempted many years ago by Brenner [16] using two separate baths for the two components and periodic transfer of the deposit from one bath to the other. Such a method is too cumbersome for practical use. On the other hand, deposition from a single bath containing the salts of the two components of the modulated alloy is far more promising. There is, however, a fundamental problem with deposition from a common solution. While a layer of the more noble component can be deposited by maintaining the potential between the reduction potentials of the two components, one would expect that upon switching the potential to a value sufficient to reduce the less noble component, both metals would deposit simultaneously to form a layer made of an alloy rather than of pure metal. For this reason, Cohen *et al.* [17] were only able to deposit a layered structure of two alloys of Ag–Pd rather than that of pure metals. Furthermore, they raised doubts whether a modulation cycle of less than 100 nm could be attained by electrodeposition. An improvement in modulation was obtained by Tench and White [18] who deposited composite structures down to tens of nanometres. The resulting structures showed increased tensile strength due to the hard nickel plates embedded in a soft copper matrix. The range of modulation was not short enough to attain the enhancement of the modulus of elasticity or the other effects which require modulations of the order of 1 to 3 nm.

It was the purpose of the present work to develop an electrochemical method that would produce modulated foils with modulations of the order of 1 to 5 nm and which would have unique properties similar to those produced by vapour deposition. The principle of this method is schematically illustrated in Fig. 1. Traces of Metal A ions are introduced into a concentrated solution of Metal B (if Metal A is nobler than Metal B). At a sufficiently low polarization potential (Point B), the rate of reduction of Metal A is slow and controlled by diffusion, while Metal B is deposited fast at a rate determined by its activation polarization constants. At Point A, however, only Metal A is reduced. The potential is thus switched between Points A and B to form a modulated structure composed alternately of pure layers of Metal A and

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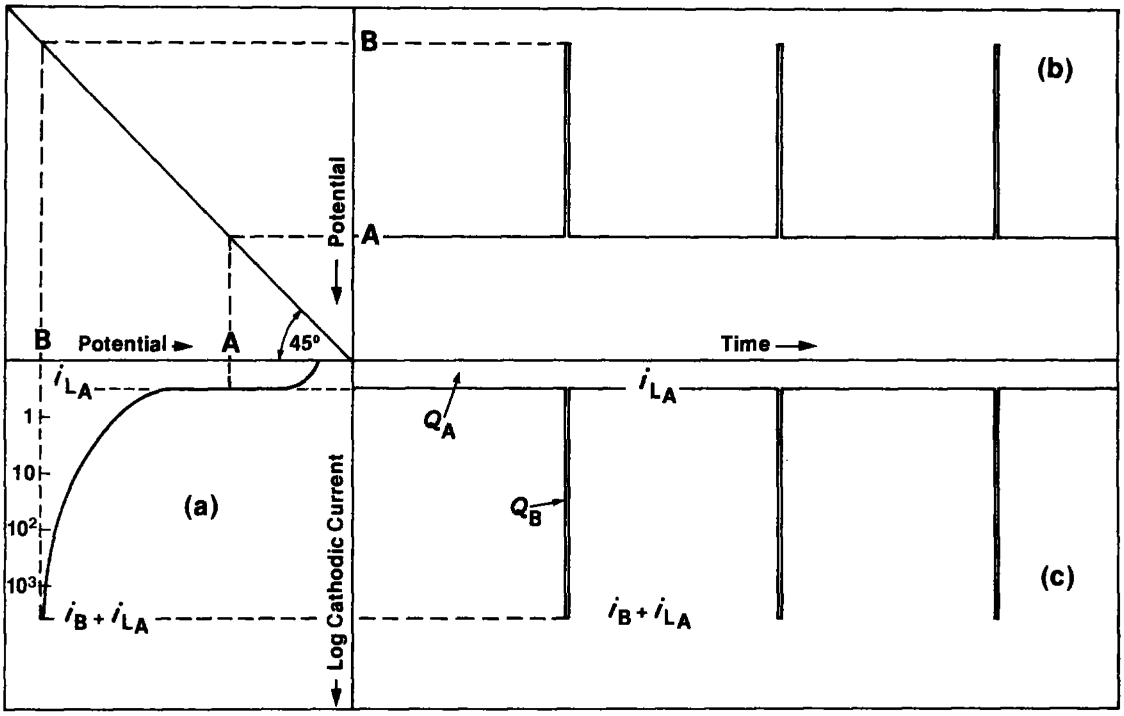

Figure 1 Schematic representation of deposition method for composition-modulated alloys: (a) cathodic polarization curve; (b) potentiostatic deposition; (c) galvanostatic deposition.

layers of B with traces of A at a level of alloying determined (assuming similar efficiencies) by $i_{L_A}/(i_B + i_{L_A})$, where i_{L_A} is the limit current density of A and i_B is the partial current density for the reduction of B. The dilution of A in the B layer can be brought to negligible values by a proper selection of concentrations, hydraulic conditions and potentials. The deposition of the modulated alloys can be carried out either by potential control (Fig. 1b) or by current control (Fig. 1c). A pulsed polarization curve has to be constructed for the latter case. The composition modulation cycle is determined coulometrically by setting Q_A and Q_B with a suitable feed-in to the function generator regulating the pulsing.

This method is suitable for numerous combinations of metals provided both components can be deposited from similar baths. It was first tried on the Cu–Ni system, taking into account the sufficient difference in reduction potentials, the similarity in crystal structure and the proximity of lattice parameters enhancing coherency between the layers. It was also important to choose a system on which extensive data exist in the literature concerning the mechanical and magnetic properties of vapour-deposited composition-modulated alloys in order to compare the modulated alloys produced by electrodeposition.

2. Experimental procedure

The basic electrolyte was a standard nickel Watts solution with the following composition:

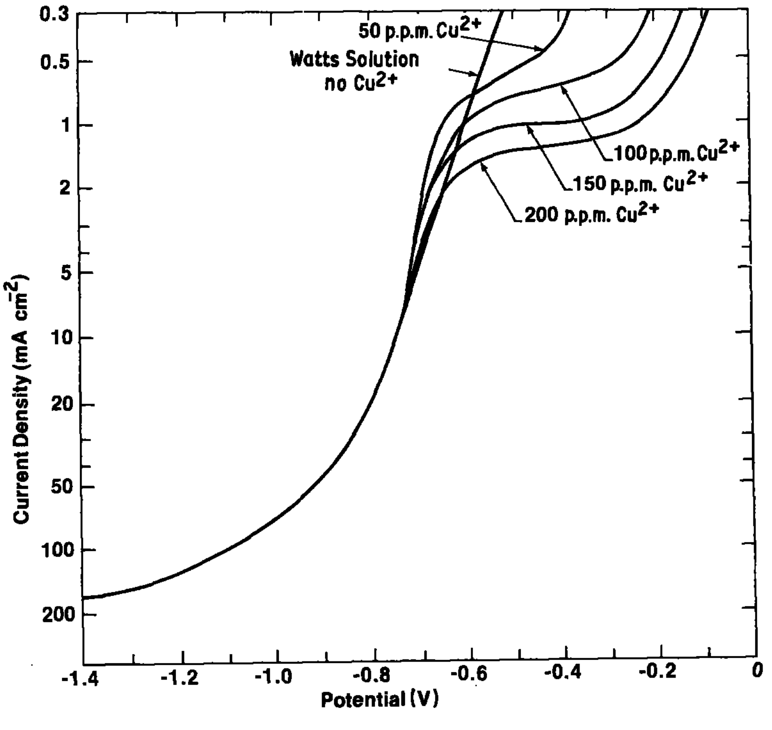

Figure 2 Cathodic polarization curves in Watts solution (pH 2) with varying additions of $CuSO_4 \cdot 5H_2O$. Potential measured against SCE.

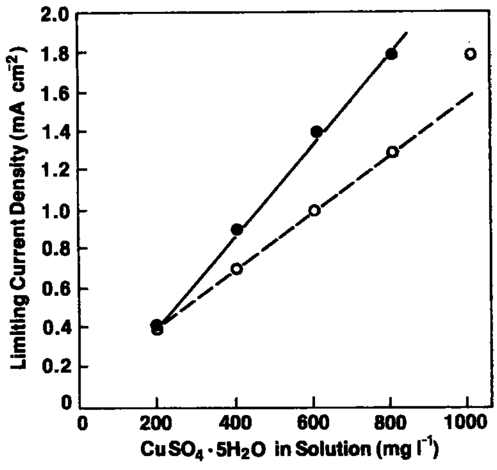

Figure 3 Limiting current density against copper sulphate concentration in (○) Watts and (●) blank solutions.

$330\,g\,l^{-1}\,NiSO_4 \cdot 6H_2O \quad 45\,g\,l^{-1}\,NiCl_2 \cdot 6H_2O$

$35\,g\,l^{-1}\,H_3BO_3 \quad 0.1\,g\,l^{-1}$ coumarine

$0.1\,g\,l^{-1}$ sodium dodecyl sulphate (SDS)

Coumarine was added to minimize dendrite formation and SDS in order to prevent hydrogen sheathing. $CuSO_4 \cdot 5H_2O$ was added in varying quantities of between 10 and 1000 p.p.m. Deposition was carried out at 58° C. A blank solution containing equivalent concentrations of sulphate and chloride, but no nickel, was used for comparison with the following composition:

$178\,g\,l^{-1}\,Na_2SO_4 \quad 22\,g\,l^{-1}\,NaCl$

$35\,g\,l^{-1}\,H_3BO_3 \quad 0.1\,g\,l^{-1}$ coumarine

$0.1\,g\,l^{-1}$ SDS

The substrates usually consisted of electrolytic copper or nickel-plated copper discs. The discs were mechanically polished to 0.05 μm by wet alumina and degreased in sequence in methanol, acetone, n-hexane and then in reverse order. They were then activated in 1 : 1 HCl for 1 min. The discs were either rotated (usually at 240 r.p.m., mercury contact) or polarized without agitation. Cathodic polarization was carried out with a horizontal platinum counterelectrode facing the disc with a saturated calomel electrode (SCE) reference through a luggin capillary at a scan rate of 2 mV sec^{-1} using a PAR (Princeton Applied Research Model) 170 electrochemical system.

3. Results and discussion

Fig. 2 shows cathodic polarization curves in Watts solution with varying additions of $CuSO_4 \cdot 5H_2O$. From these curves it is obvious that copper deposition is diffusion-controlled over several hundred millivolts above the potential range for nickel deposition. There is therefore no difficulty in depositing a pure copper layer potentiostatically between -100 and -500 mV (SCE). The potential is then switched to say -1.0 V (SCE) pulse to deposit a nickel layer of about 99% purity, if the solution contains up to 100 p.p.m. Cu^{2+}. The purity of the nickel layer can be increased by either lowering the Cu^{2+} concentration in the bath or

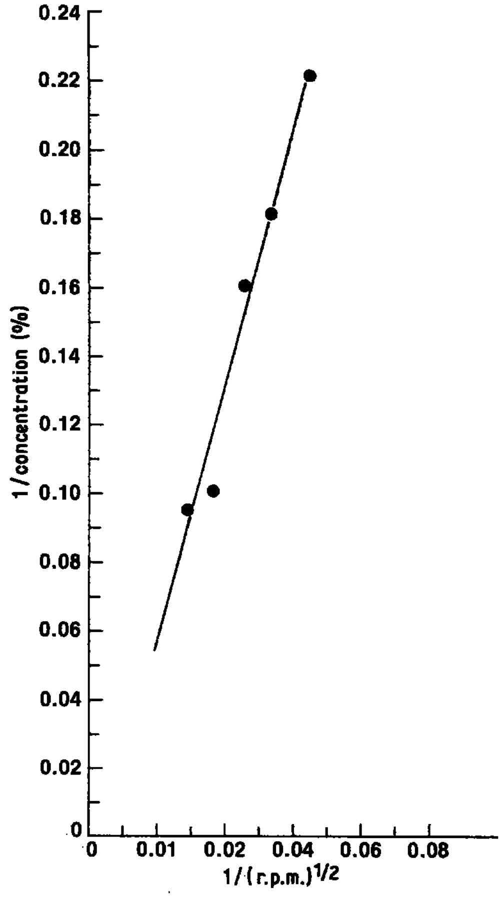

Figure 4 Reciprocal of copper content in nickel layer against reciprocal of square root of rotation speed.

by avoiding agitation during the nickel pulse. With a proper control of these variables, the copper content in the nickel layer can be brought to a negligible value. It should also be pointed out that the limiting current density for copper in the nickel solution was found to be lower than in a nickel-free solution, as can be seen in Fig. 3 for solutions containing more than 50 p.p.m. Cu^{2+}. The cathodic current efficiency for nickel deposition was 93 ± 1% and did not change significantly with pH or current density. The copper content in the nickel can be controlled using the Levich equation, as can be seen from the linear relationship in Fig. 4 between the reciprocal of copper content in the nickel layer and the reciprocal of the square root of the rotation speed. No nickel content was found in the copper layer at 200 p.p.m. Cu^{2+} solution at 7.6 mA cm^{-2}, 240 r.p.m. The current efficiency for copper deposition in the Watts solution was 100 ± 1%.

Auger spectroscopy was used to determine the composition of deposits with 25 nm modulation (as determined coulometrically) with varying total thicknesses. The external layer, as determined by the last applied pulse, was either nickel or copper. The spectrum for the surface of a 475 nm thick film (19 layers) with an outer modulation layer of copper is shown in Fig. 5. The same spectrum was found on a 50 nm thick film with just one layer of copper on top of one layer of nickel. Analysis of this spectrum with respect to the location and shape of the peaks at 725 and 920 eV, as discussed by Pamler and Roll [19], shows that the outer layer is indeed composed of pure copper. The spectrum on a 125 nm thick film with an outer layer of

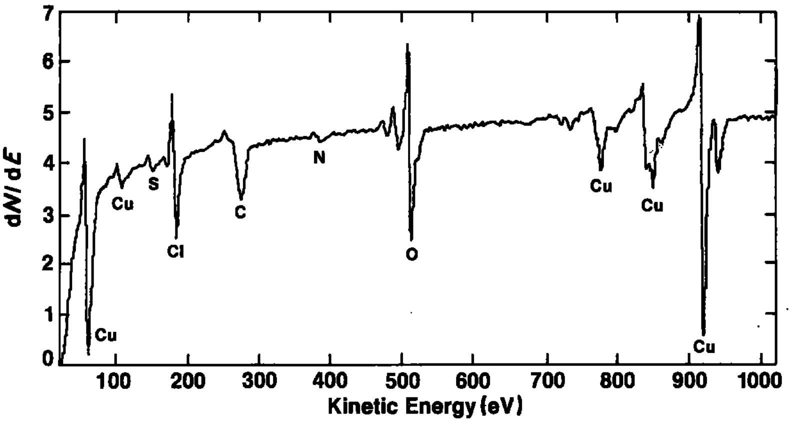

Figure 5 Auger spectrum of 475 nm thick film, 25 nm modulation with an outer copper layer.

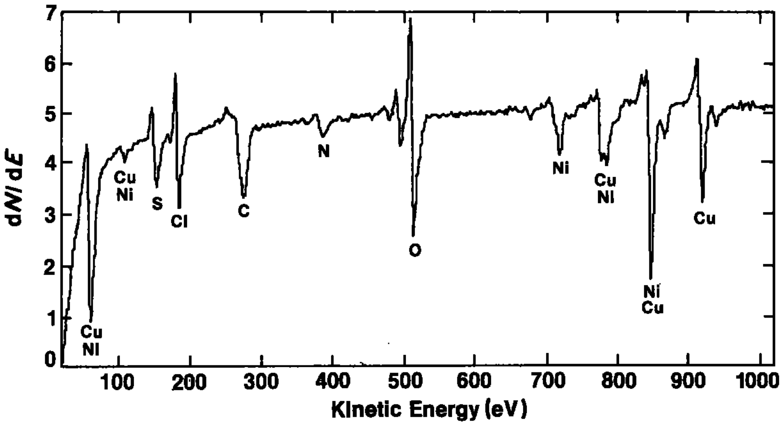

Figure 6 Auger spectrum of 125 nm thick film, 25 nm modulation with an outer nickel layer.

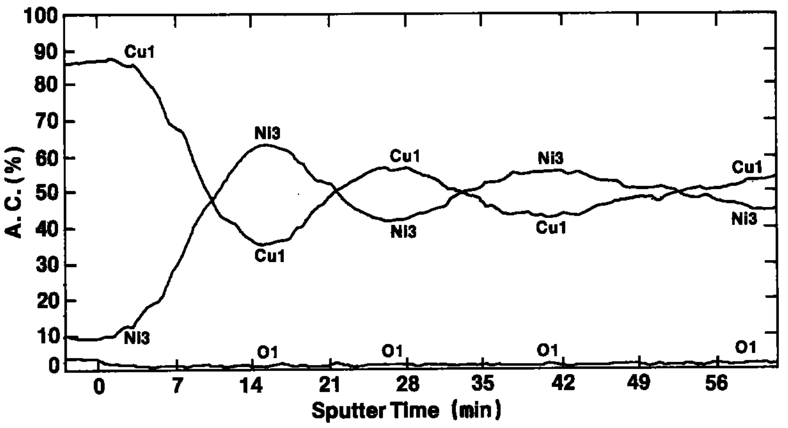

Figure 7 Auger depth profile for the film shown in Fig. 5.

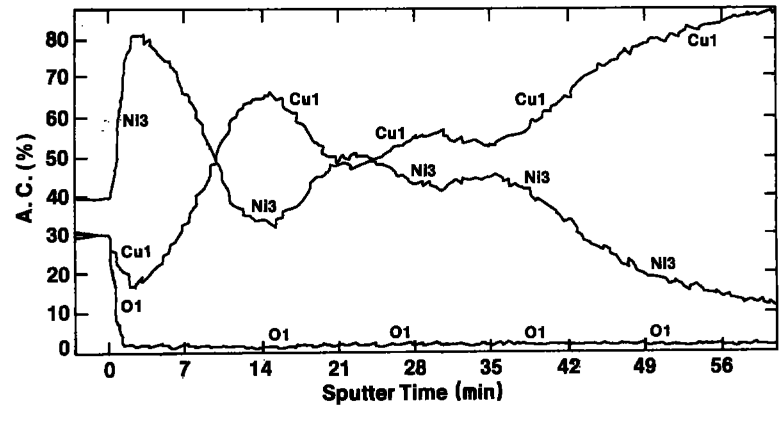

Figure 8 Auger depth profile for the film chosen in Fig. 6.

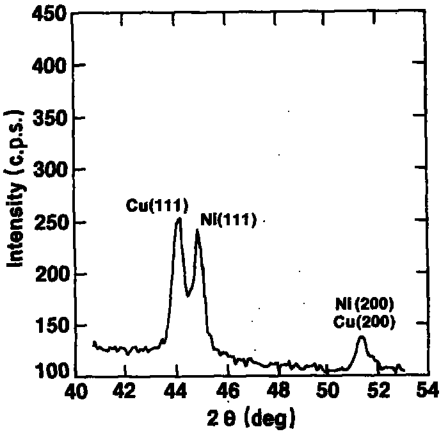

Figure 9 X-ray diffraction for 1.5 nm modulated film (copper radiation).

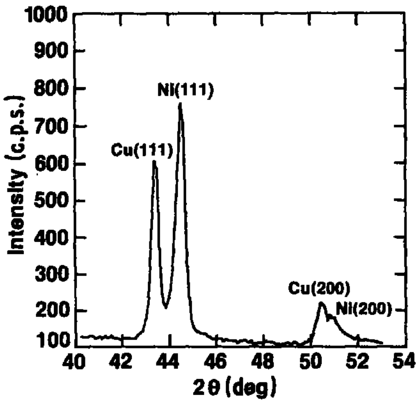

Figure 10 X-ray diffraction for 25 nm modulated film (copper radiation).

nickel is shown in Fig. 6. As in the previous case, this spectrum is the same as that obtained on a 50 nm thick film with an outer modulation of nickel. The spectrum shows the outer layer to be composed of nickel with a small amount of copper. From the limiting current data for this particular film, the copper content in the nickel was calculated to be 3%. Sputtering was applied to the samples at a rate of 2.5 nm min^{-1}. On the walls of the crater produced by sputtering, it was possible to observe rings corresponding to the individual layers. Local Auger analysis revealed spectra like Figs 5 and 6.

Auger depth profiles are shown in Fig. 7 (for the 475 nm film shown in Fig. 5) and in Fig. 8 for the 12.5 nm film with an outer nickel content (cf Fig. 6). The substrate was copper in all these samples. The modulation in composition of copper and nickel is obvious from these profiles. There is a good correlation between the peaks of the copper and nickel contents. The decay in wave amplitude for longer sputtering times is explained by a decrease in depth resolution due to surface roughness as was shown by Hoffman *et al.* [20], and is attributed to re-deposition of sputtered atoms from valleys. This effect becomes particularly important for modulation layers thinner than 30 nm.

X-ray diffraction analysis was carried out on films with a modulation of 1.5 and 25 nm and the spectra are shown in Figs 9 and 10, respectively.

A copper source was used at a scan rate of 0.1° per 10 sec. The results indicated the presence of two distinct phases of nickel and copper in both modulations. No mixing was noticeable when the diffraction was repeated 10 days after formation. Transmission electron microscopy and magnetic measurements confirmed the layered nature of the structure down to less than 1 nm.

It can be said in conclusion that the electrochemical method made it possible to produce composition-modulated alloys with modulation cycles as low as 0.8 nm. These structures compare favourably with similar structures produced by vapour deposition that exhibit enhanced elastic and magnetic properties.

Acknowledgements

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