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Electron micrographic examination of electrodeposited dispersion-hardened nickel

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Dispersion-hardened nickel has been produced by electrodepositing Ni from a Watts' bath containing Al_2O_3, TiO_2 and ZrO_2 particles (0·005–0·06 μm) in suspension. The effect of these particles on the onset of recrystallization at elevated temperatures (up to 1400°C) has been studied and it has been shown that Al_2O_3 is the most effective in stabilizing the electrodeposited structure. Thin films of Ni-Al_2O_3 examined by transmission electron microscopy showed a high dislocation density and restricted twinning, the Al_2O_3 particles being present both within the grains and at the grain boundaries.

For optimum thermal stability the oxide should be present in the nickel matrix as discrete particles, but electron microscopy has shown that in all cases agglomeration occurs and that the particles are present as large clusters. Attempts to avoid this difficulty have proved unsuccessful.

1. Introduction

The improvement in the high-temperature strength of metals by incorporating a dispersed phase of oxide, carbide or boride is well known, and there is considerable scope for the use of dispersion-hardened materials in engineering. A number of methods exist for the preparation of dispersion-hardened metals and alloys e.g. internal oxidation, powder metallurgy, surface oxidation of powders followed by extrusion etc. and each method has its advantages and limitations.

It is well known that oxides are unintentionally introduced into metal deposits during electroplating, and that these inclusions can markedly affect the properties of the metal; for example, an increase in pH during the electrodeposition of Ni results in the inclusion of $Ni(OH)_2$ in the deposit with a subsequent increase in hardness and loss of ductility. Thus the possibility exists that dispersion-hardened metals could be produced by the deliberate additions of finely divided oxides to a plating bath. The method is attractive technologically, since the material could be produced in one operation, and control of the plating variables could provide a means of controlling particle distribution and orientation as well as the properties of the metal.

This concept was applied by Grazen [1] who described an electroplating process for producing coatings of Ni, Cu, Ag, etc., containing finely divided particles of oxides and carbides, which were claimed to greatly improve the wear resistance of gauges and tools.

Withers [2] used electroplating with periodic reversal of the current to prepare Ni cermets containing dispersions of Al_2O_3, ZrO_2, etc. He suggested that particles of sizes up to 44 μm could be included in the deposit, but considered that those of 1–3 μm gave the best properties. Sautter [3] found that the Al_2O_3 content of Ni

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deposited from a Watts' bath containing various concentrations of suspended Al_2O_3 (particle size 0·01–0·3 μm) was affected only slightly by temperature, pH and current density. Tensile strength measurements on some of the specimens showed an increase in yield strength from 7·85 MNm^{-2} for pure Ni to 34·3 MNm^{-2} for alloys containing 3·5 to 6 vol. % Al_2O_3. Sautter suggested that this increase was attributable to dispersion strengthening similar to that observed in sintered or internally oxidized metal-oxide systems.

Williams and Martin [4] described a novel method of preparing composite coatings by electrodeposition. Metals investigated were Fe, Cu and Ni while the dispersoids (0·5–30 μm diameter) included SiO_2 fibres and Al and W carbides. The effects of bath agitation, current density and particle and fibre concentrations were studied, and it was shown that there was an optimum current density for producing the greatest concentration of particles in the matrix.

Recently, Saifullin [5] codeposited Al_2O_3 with Ni and found that the Al_2O_3 content increased somewhat with increasing oxide concentration in the bath. The deposit was harder than Ni and its chemical resistance to 10% HNO_3 was independent of oxide inclusions.

The mechanism of entry of particles into the electrodeposit has not received a great deal of attention. Martin [6] pointed out that the fields involved in electroplating (0·1 to 0·3 Vcm^{-1}) were too low to invoke a mechanism based on electrophoresis, and concluded that agitation of the bath caused the suspended particles to impinge and adhere momentarily to the cathode surface with consequent entrapment in the crystals of the growing electrodeposit. Hoffman and Mantell [7] studied the mechanism of alumina entry into Cu during electrodeposition at 32 mA cm^{-2} in a bath containing 25 g l^{-1} Al_2O_3 in suspension. The three possible controlling factors investigated were mechanical inclusion, electrophoresis and adsorption.

In the present study, the factors which influence the concentration of Al_2O_3 in Ni deposited from a Watts' bath containing a suspension of Al_2O_3 have been investigated using electron microscopy to assess the size, content and distribution of these particles. A comparison has been made of the stability of Ni-Al_2O_3 with Ni-TiO_2 and Ni-ZrO_2 prepared in a similar manner. Other properties of Ni-Al_2O_3 such as its structure and tensile strength have also been examined.

2. Experimental

The modified Watts' bath, prepared from high purity chemicals, contained 300 g l^{-1} $NiSO_4.6H_2O$, 45 g l^{-1} $NiCl_2.6H_2O$ and 30 g l^{-1} H_3BO_3 and this was maintained at pH 3·5–4·0. Oxide particles (supplied by Bush Beach and Segner Bayley Limited) had the following dimensions:

Al_2O_3 (Type Cl)	0·005–0·05 μm
TiO_2 (Type P25)	0·01–0·06 μm
ZrO_2 (Type RV 294)	0·005–0·05 μm

Deposition was carried out at 50° ± 1°C at various current densities and N_2 was bubbled through the solution (pH 3·5 to 4) to keep the particles in suspension; in all experiments the duration of plating was adjusted to give Ni deposits 0·01 cm thick. The anode was high purity Ni enclosed in a nylon bag to prevent impurities entering the bath. It was necessary to remove the electro-deposit from the substrate, and for this reason a rotating cylinder of stainless steel (5 cm × 3·8cm diameter) was used as cathode. During deposition hydrogen bubbles adhered to the surface of the nickel with the consequent formation of pits, but this difficulty was overcome without the use of addition agents by means of a foam rubber pad that pressed lightly against the surface of the rotating cathode.

After each run, the deposit was readily detached in one piece from the stainless steel. The oxide content in the deposit was determined using a similar method to that adopted by Sautter [3].

Thin films for transmission examination were prepared by chemically polishing the deposit (4 × 1 × 0·01 cm) using a solution composed of 60 vol. % glacial CH_3COOH, 35 vol. % HNO_3 and 5 vol. % HCl. Squares 2–3 mm^2 were carefully cut out from suitable areas, placed in the specimen holder of the electron microscope (A.E.I., Model EM6G) and examined using an accelerating voltage of 100 kV.

3. Results

Fig. 1 shows the effect of current density on the Al_2O_3 concentration of Ni, and it is evident that increasing the current density results in an increase in Al_2O_3 to a maximum at 20 mA cm^{-2}, followed by a decrease. The concentration of Al_2O_3 in the Ni was determined gravimetrically (curve B) and by counting the particles in the electron-micrographs (curve A), and it can be seen that both curves follow a similar pattern.

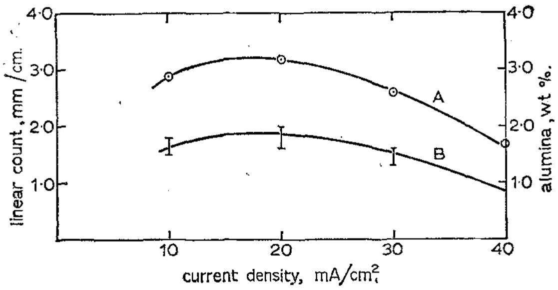

Fig. 1. Effect of current density on Al_2O_3 concentration of electrodeposited Ni. Curve A, Al_2O_3 estimated from electron micrographs. Curve B, Al_2O_3 estimated gravimetrically.

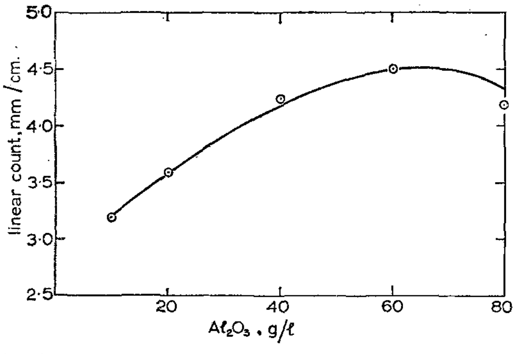

Fig. 2. Effect of Al_2O_3 concentration (gl^{-1}) in plating bath on Al_2O_3 in Ni deposit. Al_2O_3 estimated from electron micrographs.

Fig. 2 shows that increasing the concentration of Al_2O_3 in the bath increases the Al_2O_3 content of the deposit up to a maximum followed by a decrease.

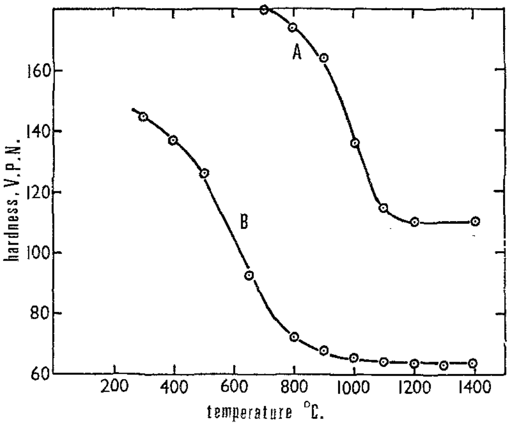

Fig. 3. Micro-hardness versus annealing temperature (1 h anneal). Curve A, $Ni-Al_2O_3$ deposit. Curve B, Ni deposit.

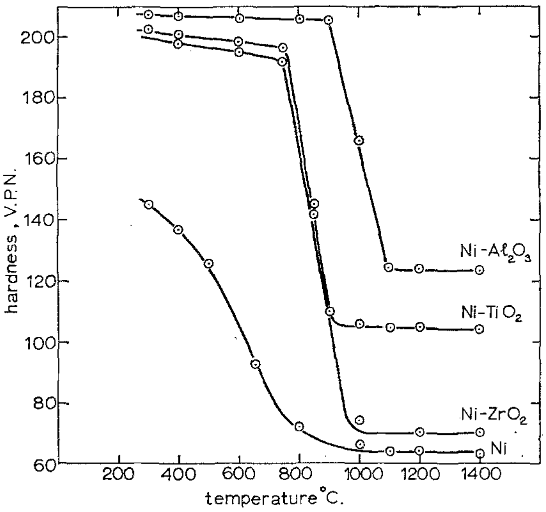

Fig. 4. Micro-hardness versus annealing temperature (1 h anneal) for electrodeposited Ni containing various oxides.

Micro-hardness values for specimens that were annealed for 1 h at various temperatures are given in Figs. 3 and 4. A comparison between Ni (curve B) and $Ni-Al_2O_3$ (curve A) deposited from a bath containing 10 g l^{-1} Al_2O_3 (Fig. 3) shows that with the latter recrystallization occurs at ~800°C when there is a sudden fall in the hardness. Fig. 4 gives a comparison of the effect of various oxides on recrystallization of Ni (deposited from a bath containing 20 g l^{-1} of oxide), and it can be seen that an increase from 10 to 20 g l^{-1} Al_2O_3 in the bath increases the recrystallization temperature to ~1000°C. It is also evident that Al_2O_3 is more effective than

TiO_2 or ZrO_2 in controlling recrystallization.

Figs. 5 and 6 are electron replica micrographs for Ni-Al_2O_3 unannealed and after 1 h heat treatment at 800°C, respectively. It can be seen that the particles have coarsened, and studies at higher temperatures (up to 1400°C) showed that with increase in temperature the coarse particles coalesced to a more compact form.

The tensile strength of deposits (1·25 × 0·6 × 0·01 cm.) determined after 1 h anneal at 750°C were 17·6 MNm^{-2} for Ni and 76·4 MNm^{-2} for Ni-Al_2O_3 (20 mA cm^{-2}, 20 g l^{-1} alumina) i.e. a four-fold increase in tensile strength was produced by the Al_2O_3.

Twinning, when formed, appeared to be restricted in length and width by the oxide particles (Fig. 7). Alumina particles were present at both the grains and grain boundaries, but more so in the grains.

Heat-treatment in the range 1000 to 1400°C resulted in particles coalescing to form discrete ones, as previously noted, and there was a reduction in dislocation density.

4. Discussion

The main problem of electrodeposition as a method of producing dispersion-hardened materials is the tendency of the particles to form clusters. Ideally, the deposit should consist of a Ni matrix with a uniform dispersion of discrete particles of alumina with a spacing less than 0·01 μm, which is considered to be the most effective size for pinning down dislocations. However, owing to the high surface energy of the particles, they tend to form agglomerates in the bath and all attempts to disperse them proved unsuccessful. The formation of agglomerates was indicated by the size and shape of the particles within the deposit, as assessed by electron microscopy and confirmed by sedimentation studies.

The mechanism of particle entry into the deposit is not clear. Hoffmann and Mantell [7] studied the deposition of Cu from acid copper sulphate and copper formate containing alumina in suspension, and considered mechanical entrapment, adsorption and electrophoresis in relation to particle entry. However, no definite conclusion was arrived at from their studies, although they preclude electrophoresis on the grounds that no zeta potential on the alumina particles could be detected. It should be noted that in certain of their plating baths they introduced thiourea, a substance that is known to be strongly adsorbed at a cathode surface, and found a pronounced increase in particle inclusion.

It has been found in the present studies that particles are distributed throughout the deposit, with little tendency to segregate at grain boundaries. Under the conditions of electrodeposition in which the bath is vigorously agitated and a foam rubber brush is placed at a point in contact with the rotating cathode surface to remove hydrogen bubbles, particles will impinge on the growing deposit, adhere momentarily and either become entrapped or re-enter the bath. Whether entrapment occurs will depend on the size of the particle and the time of contact with the surface; the latter in turn will be related to the velocity and angle of impact and to the precise site on the growing deposit at which impact occurs. The surface of the growing deposit will not be uniform, and it is possible that preferential entrapment could occur at certain sites, e.g. steps, kinks in a step and vacancies.

The agglomerates consist of a number of irregularly shaped particles which, if they adhere momentarily on the surface, could be included by a thickness of deposit very much less than their overall individual sizes. Under these circumstances, adherence of the agglomerate onto the surface need only be for a very short time, probably a fraction of a second, for entrapment to occur. At 20 mA cm^{-2} the rate of thickening of the deposit is 0·007 μm s^{-1} and the size of the individual particles range from 0·005–0·06 μm. Thus if an agglomerate is assumed to consist of the smaller particles, then mechanical entrapment could occur if the particle adhered to the surface for about 0·005/2 ÷ 0·007 i.e. 0·36 s or probably less.

The decrease in alumina content with decrease in pH [3] is possibly due to the decrease in the efficiency of nickel deposition and the increase in the viscosity of the solution. The decrease in efficiency lowers the rate of deposition with a consequent decrease in the rate of entrapment

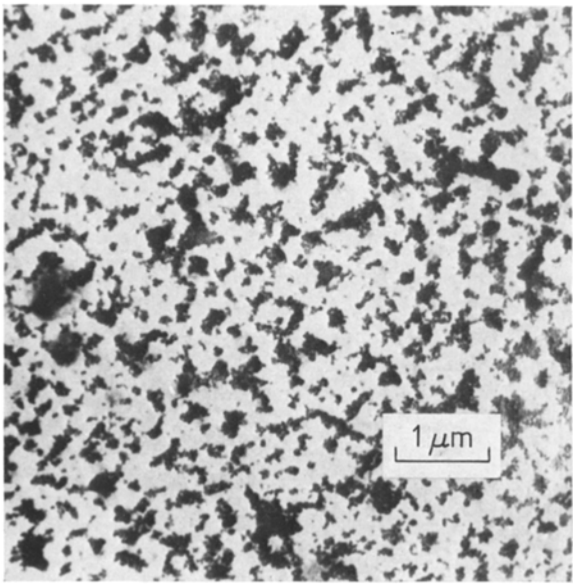

Fig. 5. Extraction replica micrograph of Al_2O_3 distribution in unannealed electrodeposited Ni (20 gl^{-1} Al_2O_3, 20 $mAcm^{-2}$).

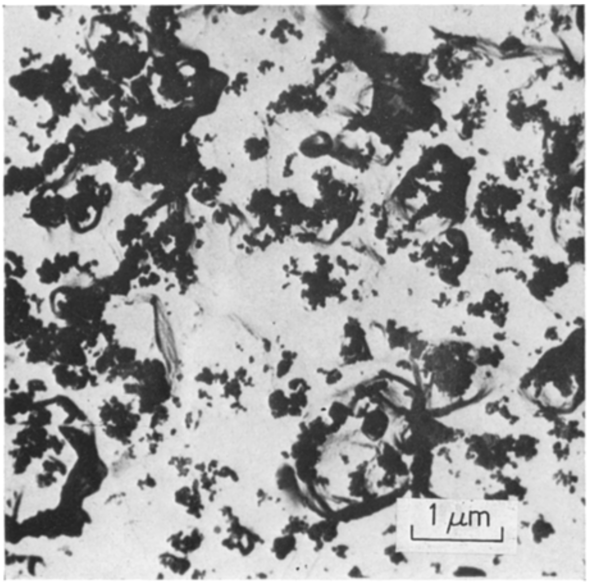

Fig. 6. Extraction replica micrograph of Al_2O_3 distribution in electrodeposited Ni (20 gl^{-1} Al_2O_3, 20 mA cm^{-2}, annealed for 1 h at 800°C)

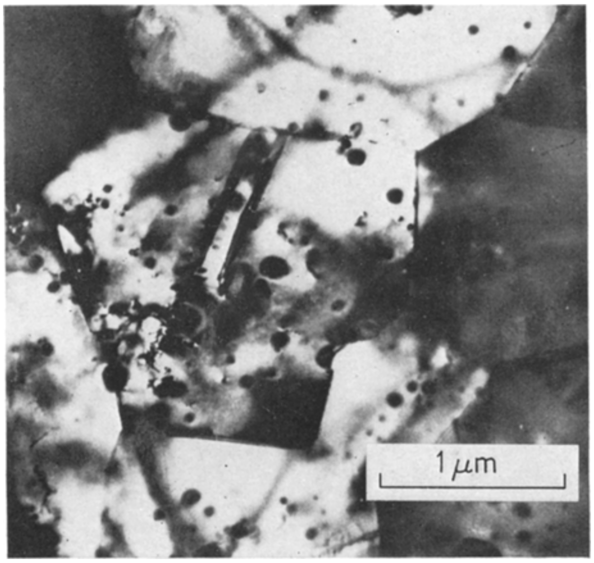

Fig. 7. Twinning and grain growth restriction by alumina particles (annealed for 3·375 h at 1200°C.)

and, in addition, the increase in hydrogen evolution results in mechanical dislodgement of particles.

Maximum particle entry was attained at 60 g l^{-1} alumina added to the bath and at higher concentrations there was a decrease in particle content; the latter is presumably due to the inability to maintain all the solid particles in suspension and to the greater degree of agglomeration in the bath.

The structure of Ni-Al_2O_3 deposits was examined after etching by optical microscopy and it was evident that the agglomerated particles were randomly distributed; however, there was no evidence of grain boundaries. Transmission electron microscopy examination revealed that there was no segregation at grain boundaries; in fact, the density of distribution appeared to be greater within the grains than at grain boundaries, which showed that entrapment of particles within the interstices of growing crystals (grain sizes 0·5 to 3·0 μm) is not significant in the mechanism of particle inclusion. The dislocation density of electrodeposited Ni-Al_2O_3 (Fig. 7) was far greater than that observed in pure electrodeposited Ni.

Annealing at elevated temperatures (1200–1400°C) resulted in a reduction of dislocation density, and the dislocations were annihilated after a prolonged time of annealing. At elevated temperatures, particles became more compact, and particle size increased with time of annealing; however, twinning and grain growth were restricted (Fig. 7).

Grain size has measurable effects on a number of mechanical properties e.g. hardness, yield strength, tensile strength, fatigue strength and impact resistance all increase with decreasing grain size [8], but in the present studies the grain sizes of Ni and Ni-Al_2O_3 deposits were found to be similar. However, grain size is not the sole factor that determines mechanical properties and the increase in strength observed for Ni-Al_2O_3 deposits is due to the blockage of dislocation movement during deformation.

5. Conclusions

1. Electrodeposition can provide a method of preparing dispersion-hardened nickel, but a major difficulty arises from the fact that the particles form agglomerates in the bath and do not therefore enter the deposit as discrete particles.

2. Appreciable concentrations of alumina can be introduced into nickel by this technique with a consequent increase in tensile strength. Studies of hardnesses of Ni-Al_2O_3, Ni-TiO_2 and Ni-ZrO_2 at various temperatures up to 1400°C have shown that alumina particles are the most effective in stabilizing the structure.

3. As deposited, the structure of Ni-Al_2O_3 is complex and has a high dislocation density, presumably due to the presence of the alumina particles. Although annealing reduces the dislocation density, the particles restrict twinning and grain growth.

4. The particle-entry mechanism is not clear, but is is possible that preferential entrapment occurs at defective sites on the surface of the growing deposit.

Acknowledgements

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