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Microstructure and hardness of brush plated Ni–Fe–W–P–S alloy

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1. Introduction

Various techniques have been used to deposit coatings for tribological applications. Electrodeposited chromium has been popular for many years due to its high hardness, low coefficient of friction, good wear resistance and good corrosion resistance. However, chromium baths based on the metal's hexavalent form have serious technical, health and environmental disadvantages [1]. It is now considered that there is a risk of cancer of the lung and nose being caused by certain electrolytic Cr(VI) processes [2], including deposition of chromium from chromic acid baths. The UK COSHH Approved Code of Practice for Carcinogenous Substances has been amended recently [3] to make mandatory from 1992 a maximum exposure limit (MEL) of Cr(VI) of 0.05 mgm^{-3} in the air near chromium plating baths on an 8 h time-weighted average. Other countries may have different limits and methods of determination of Cr(VI) in the atmosphere. The current problems associated with the use of electrodeposited chromium have stimulated an extensive search for alternative coating processes and materials [4, 5]. Although each alternative has advantages for specific applications, no one process can be considered as a universal replacement for electrodeposited chromium when wear resistance, corrosion resistance, complexity of the process and cost are considered.

An alloy of Ni–Fe–W–P–S has been developed which can be deposited by brush plating. This has been shown to have good wear resistance and hence to be a possible replacement for hard chromium in some applications [6]. In this paper its microstructure has been investigated in the 'as-plated' condition and after heat treatment up to 700^{0}C.

Brush plating is a specialized electrodeposition technique in which an absorbent pad is wrapped around an inert anode, soaked with electrolyte and rubbed over the surface to be plated. It can range from a very simple manual process to a fully automated one. The advantages and limitations of the process have been reported by previous authors [7–9], but the main advantages are that the work does not have to be immersed in a plating vat and selective areas can be plated. Very good adhesion can be achieved which is essential in wear situations.

2. Experimental methods

2.1 *Materials and microanalysis*

Plain carbon steel test-pieces 100 mm × 20 mm × 3 mm were used as substrates and coatings 30μm thick were deposited. The composition of the plated layer was Ni 65%, Fe 30%, W 4%, P 0.5% and S 0.5%. The plated samples were cut into pieces 15 mm × 10 mm for X-ray analysis and transmission electron microscopy.

2.2 *Plating conditions*

The solution composition is shown in Table 1. A range of concentrations is listed which give sound deposits and also specific values are stated which result in the alloy composition quoted above.

The coating was deposited by a manual brush plating operation using stylus movement of 14 - 22 $m\,min^{-1}$, voltage of 6–12 V and current density of 8000–10 000 $A\,m^{-2}$. The anode was prepared by inserting a graphite rod, 1 cm diameter, into a holder connected to a power supply and the rod was wrapped in cotton wool. The plating solution was replenished in the pad by regular dipping in a beaker of solution. Provided that the pad around the stylus was not allowed to dry or become depleted of metal ions, this technique had no adverse effects on the structure or properties of the deposit. Examination of a cross-section by optical microscopy revealed a fine banded structure. However, the banding is not due to periodic changes in composition of the plating solution absorbed in the pad. It is typical of a very fine grained

Table 1. Composition of plating solution

Compound	*Concentration range* $g\,dm^{-3}$	*Concentration to deposit alloy containing* Ni 65%, Fe 30%, W 4% $g\,dm^{-3}$
$NiSO_4.7H_2O$	200–330	330
$FeSO_4.7H_2O$	10–80	20
$Na_2WO_4.2H_2O$	3–25	15
Citric acid	50–100	50
Boric acid	30–50	40
Na_2SO_4	10–30	20
Additive	100 ml	100 ml

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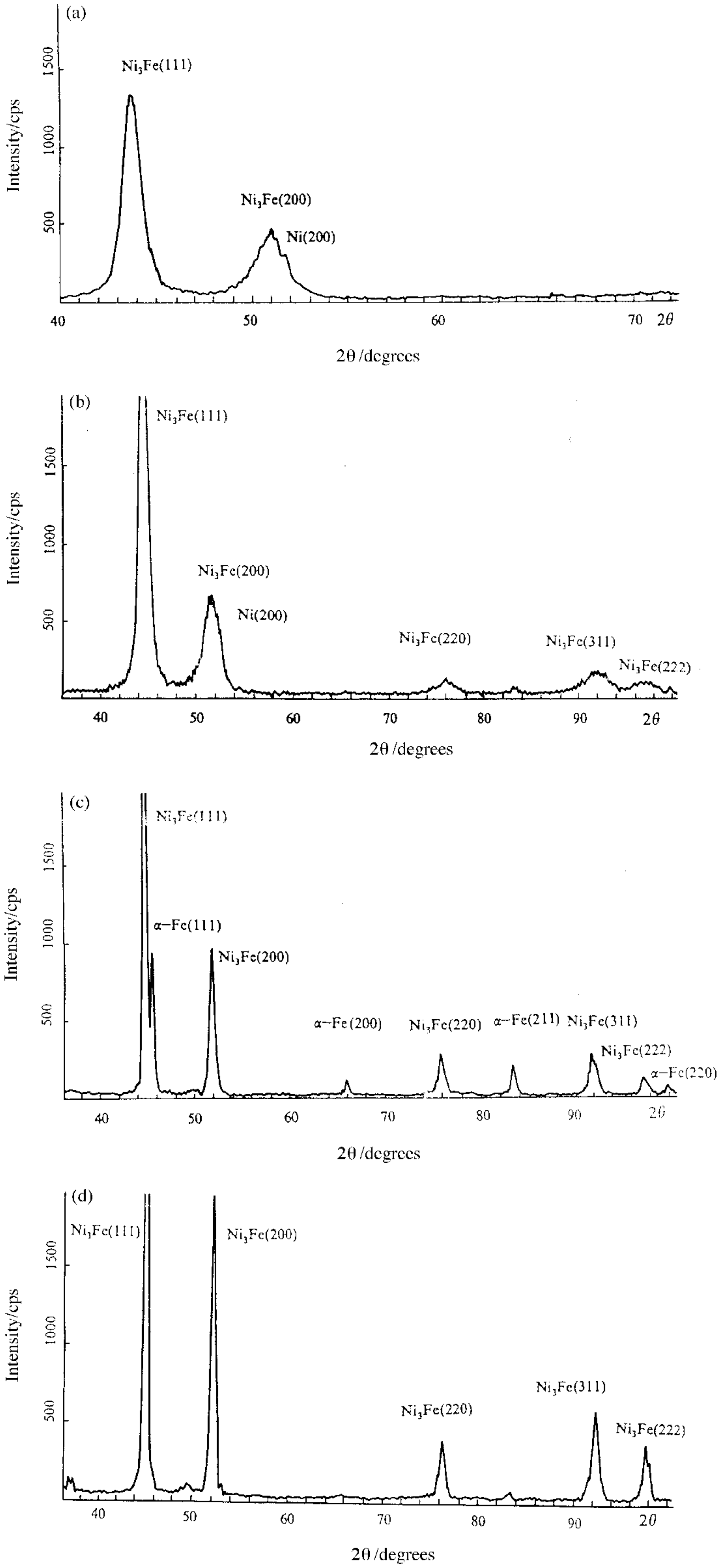
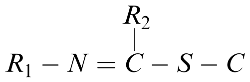


Fig. 1. X-ray diffraction patterns of alloy layers after heat-treatment at various temperatures: (a) room temperature, (b) 300C, (c) 500 °C and (d) 700 °C.

deposit plated from an electrolyte containing an organic additive. A recent paper by Gering *et al.* [10]. showed that the structure of a deposit from a proprietary nickel plating solution could be either columnar or banded, depending on the brush plating conditions employed. A banded structure occurred when the pad was replenished by dipping, but a columnar structure was produced when a 'flow through' technique was used to replenish the solution in the pad. The same paper referred to the deposition of a nickel tungsten alloy but its structure was not shown. As proprietary solutions were used, only metal contents were quoted. There was no indication whether the solution contained organic additives and so a direct comparison with the present work is not possible.

Brush plating is a high speed deposition process and so the solution must contain a relatively high concentration of metal salts in order to prevent burning. Nickel sulfate, ferrous sulfate and sodium tungstate are the sources of the metallic elements. Boric acid is present as a buffer to control pH and sodium sulfate is included to increase the conductivity of the solution. The organic additive is present to facilitate codeposition of the three metallic elements. Its presence results in a brighter and smoother fine grained deposit with lower internal stress. It also inhibits the oxidation of Fe^{2+} to Fe^{3+} in solution. The general formula is:



$$R_1 - N = \overset{\displaystyle R_2}{\overset{|}{C}} - S - C$$

where R_1 is H or C and R_2 is N or C.

Tungsten cannot be deposited from aqueous solution on its own but it can be electrodeposited by induced codeposition with iron group elements [11]. The sulfur and phosphorus present in the deposit results from the addition agent.

2.3. *Heat treatment and hardness determination*

Samples were heat treated at seven temperatures (100, 200, 300, 400, 500, 600 and 700°C) for 1 h under vacuum. Hardness (HV_{50}) was determined at room temperature after heat treatment. Each value is the average of five readings.

2.4 *X-ray examination and surface analysis*

A diffractometer was employed for the analysis of phase constitution (Cu target, $\lambda = 154.18$ pm, tube potential 40 kV, beam current 50 mA) and a JEM 200-EX model transmission electron microscope was used to examine the microstructure. The surface concentration of nickel, iron, tungsten, sulfur, phosphorus and oxygen were determined using Auger emission spectroscopy (AES).

3. Results and discussion

Figure 1 shows X-ray diffraction results for samples after heat treatment at various temperatures. Figure 1(a), 'as-plated' sample, is shown to consist of nickel base solid solution plus the intermetallic compound Ni_3Fe. The nickel base solid solution shows the characteristic diffuse scattering produced by an amorphous structure. The Ni_3Fe peak is also quite broad.

The 'as-plated' deposit had an extremely fine grain size so that its structure was not clearly defined by transmission electron microscopy, see Figure 2(a). A fine dispersion of particles approximately 10 nm in size was observed in the matrix. These particles exhibited a twin-petal effect which indicates coherency of the second phase with the matrix and is likely to result in good wear resistance.

Figure 2b shows the electron diffraction pattern of a selective area at a Ni_3Fe particle. This was found to be f c c with a lattice parameter of 0.375 nm

Heat treatment at 100°C did not result in any noticeable changes in the structure of the deposit. However, changes were observed at higher heat treatment temperatures. Figure 1(b) shows the effect of heat treatment at 300°C. Several small diffraction peaks are visible. They are not nickel, iron or Ni_3Fe and could not be identified using the ASTM index. A high magnification of a diffraction ring from the sample heat treated at 300°C is shown in Figure 3 and illustrates that the structure consists of several

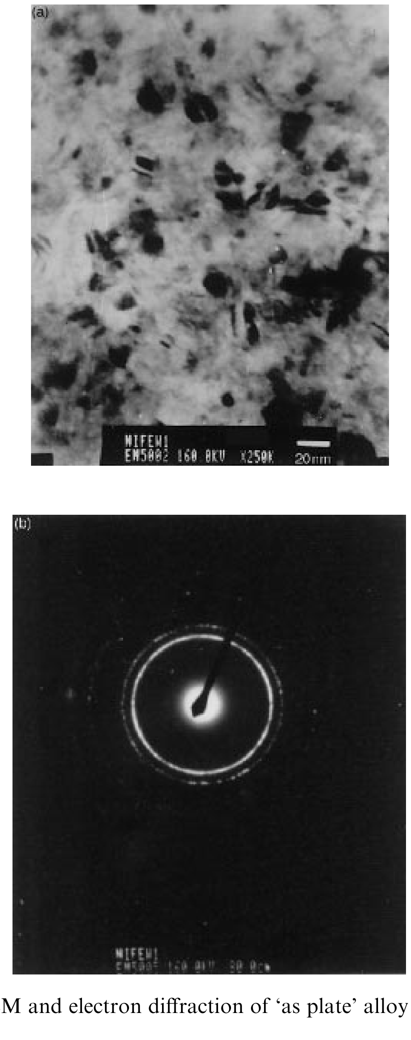


Fig. 2. TEM and electron diffraction of 'as plate' alloy layer.

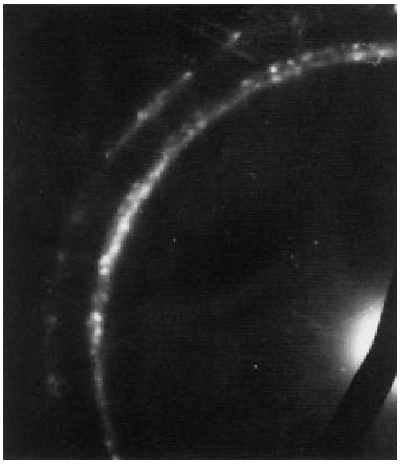


Fig. 3. Enlarged photograph of electron diffraction pattern of alloy layer after heat treatment at 300°C.

Table 2. Hardness of alloy electrodeposits after heat treatment at various temperatures in vacuum

Heat treatment Temp °C	None	100	200	300	400	500	600	700
Hardness HV_{50}	750	780	780	930	802	703	691	440

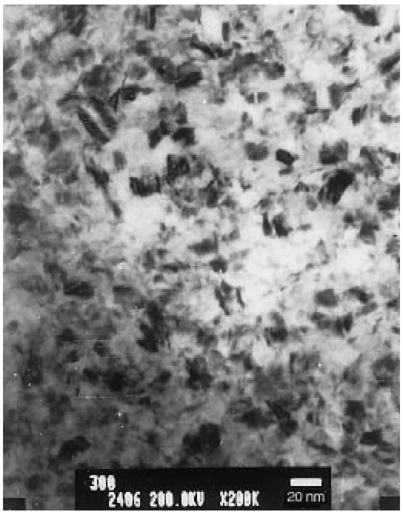


Fig. 4. TEM of alloy layer after heat treatment at 300°C.

phases, the lattice constants of which differ only by about 5%. The crystallization process of an amorphous structure commences from the formation of a substable transition phase [12] and so the small diffraction peaks in Fig. 1(b) or the diffraction spots in Fig. 3 probably result from the formation of a substable phase Ni_xFe_y.

When the alloy was heated at 500°C, Fig. 1(c), peaks resulting from α-Fe(1 1 1) and (2 1 1) were observed. The plated deposit had been transformed into a compound of nickel base solid solution, Ni_3Fe and α-Fe after this heat treatment.

The X-ray diffraction pattern of a plated layer heat treatment at 700 °C shown in Fig. 1(d) illustrates that the peaks of α-Fe have almost disappeared due to resolution of iron atoms in the nickel matrix. The crystallization of the alloy was virtually complete after heat treatment at 700 °C.

Hardness measurements were used as a means of illustrating changes in properties as a result of changes in structure after heat treatment. The results obtained are shown in Table 2. Maximum hardness was achieved after heat treatment at 300°C which corresponds to the formation of precipitates coherent with the matrix as shown in Fig 4. As the heat-treatment temperature was increased, the hardness of the alloy decreased with the growth of precipitates and the occurrence of recrystallization. It must be emphasized that the hardness values quoted were obtained at room temperature after heat treatment. Consequently, these figures do not give an indication of the hot hardness properties.

4. Conclusions

(i) The microstructure of the brush plated Ni–Fe–W–P–S is composed of nickel base solid solution and dispersive precipitated intermetallic compound Ni_3Fe. The matrix is composed of amorphous and microcrystalline substructure.

(ii) The hardness of the alloy is about 600 –750 HV_{50} at room temperature. It can be increased to about 900–950 HV_{50} by heat treatment at 300 °C. The relatively high hardness is due to the small grain size and coherent precipitation with the matrix.

5. References

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