The broad diffused band in the region 750 to 700 cm^{-1} may represent the aluminate and ferrite phases, as is evident from a pronounced peak in sample no. 635 containing about 20% C_3A + C_4AF.

The sharp and weak bands at 620 and 600 cm^{-1} arise from calcium sulphate which is corroborated by the development of a better defined peak in sample no. 635 which contains considerably higher proportions of sulphate than the others.

The bands in the range 550 to 500 cm^{-1} are produced as a result of superposition of characteristic bands of almost all the major cement minerals and hence have little value in the characterization of the composite material.

Based on this study, therefore, the following conclusions may be drawn.

(1) The ATR technique is suitable for infra-red spectrometry of cement materials.

(2) The ATR spectra of cements are resolved and reproducible.

(3) The splitting of the broad band in the frequency range 1000 to 800 cm^{-1} could be used as a satisfactory qualitative index regarding the relative proportions of the tricalcium and dicalcium silicate phases. It appears that the relative proportions of alite and belite may be predicted by matching in a computer any unknown cement spectra with the spectra of the constituent phases superimposed in different ratios.

(4) The shifting of the high frequency band may be accounted for by the different polymorphic forms of C_3S which are known to be stabilized by small amounts of impurities compared to β-C_2S.

Reference

1. S. N. GHOSH and A. K. CHATTERJEE, *J. Mater. Sci.* **9** (1974) 1577.

Received 14 February
and accepted 19 March 1975

S. N. GHOSH
A. K. CHATTERJEE
Cement Research Institute of India,
M-10 South Extension II, Ring Road,
New Delhi, 110 049, India

Observation of twin faults in sputter-deposited high-purity nickel

Columnar grains with stacked microtwins were first observed in sputter-deposited copper [1]. Here, the conditions for formation of the microtwins in nickel and a comparison of the twinned microstructures in nickel and copper are described.

Nickel and copper deposits were made by d.c. triode sputtering, which is described elsewhere [1, 2]. The nickel sputtering target was made from a 3.8 cm diameter Materials Research Company MARZ Grade (99.995% pure) nickel rod. A 1.9 cm diameter rod of ASARCO Grade (99.999 + % pure) copper was pressed into a 4 cm diameter disc for the copper target. Nickel and copper deposits were made at nearly the same rate (average rate ~ 0.75 μm min^{-1}) and at the same homologous deposition temperature $T_H = 0.275$, where $T_H = T_D/T_M$; T_D is the deposition temperature (K) and T_M is the melting temperature (K). The substrate temperatures corresponding to $T_H = 0.275$ were 473 K for nickel and 373 K for copper. The nickel and copper deposits were formed on metallographically polished copper and aluminium substrates, respectively, which were 3.8 cm diameter. The deposits were made 2 to 4 mm thick so that cross-sections normal to the substrate plane could be studied.

Deposits were sliced normal to the substrate into 0.5 mm thick strips. A series of 3 mm diameter discs were punched from the strips so the deposits could be examined normal to the deposition direction by transmission electron microscopy. The nickel discs were thinned with 20% perchloric acid in ethyl alcohol at − 10°C, and the copper discs were thinned with 60% phosphoric acid in water at 5°C both using the jet thinning technique.

Columnar grains with stacked microtwins in sputtered nickel are shown by a dark-field micrograph obtained from a (002) diffraction spot (Fig. 1). Grain boundaries, such as A-A, were parallel to the growth direction. As with the copper deposits, the columnar grains in nickel grew with the [111] direction perpendicular to the substrate. The average grain-boundary spacing was 0.38 μm which was about the same as the average spacing (0.4 μm) observed for sputter-deposited copper shown in Fig. 2. Occasionally, as in copper [1], large spacings (> 2 μm) were found for nickel. The similar grain-boundary spacings for nickel and

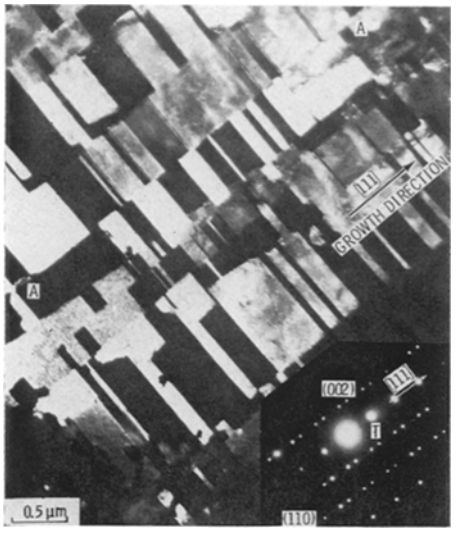

Figure 1 Columnar grains and microtwins in high-purity nickel sputter-deposited at 473 K (T_D/T_M = 0.275) and average rate ~ 0.75 μm min^{-1}. A-A, columnar grain boundary. Dark-field micrograph was made from the (002) reflection.

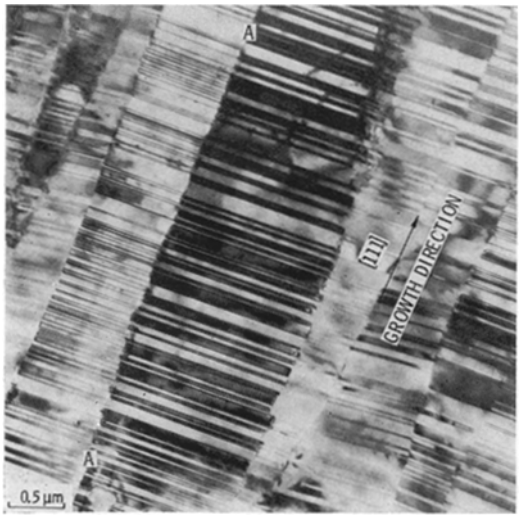

Figure 2 Columnar grains and microtwins in high-purity copper sputter-deposited at 373 K (T_D/T_M = 0.275) and average rate ~ 0.75 μm min^{-1}.

copper may be due to approximately similar diffusion lengths parallel to the substrate for two metals at the same homologous temperature.

Although nickel had about the same grain-boundary spacing as copper, the twin plates in nickel were almost six times thicker than the twin plates in copper. The average thickness of the twin plates obtained from Fig. 1 for nickel was about 0.17 μm, which was considerably larger than the 0.03 μm average thickness reported [3] and observed for copper (Fig. 2). In nickel many fine twins as small as 0.015 μm, and some large twins nearly 0.75 μm, were observed, but the most predominant twin plate thicknesses were between 0.08 and 0.25 μm. The greater thickness of the twins in nickel correlates with a higher twin-boundary energy for nickel (41 erg cm^{-2}) than for copper (27 erg cm^{-2}) [4], that may cause a correspondingly reduced probability for twin-boundary formation during columnar growth.

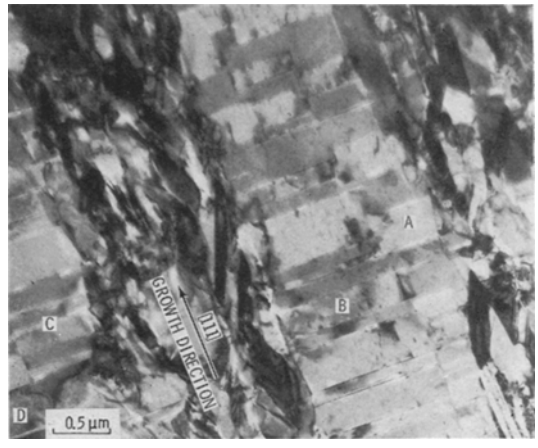

Figure 3 Simultaneous observation of both columnar grains A, B, C and D and regions of fine random grains in the nickel deposit.

Long columnar grains and stacked microtwins of nickel were observed only over an area about 1.5 cm diameter at the central region of the deposit. Micrographs obtained near the boundary of the central region showed fine random grains about 0.1 μm diameter between the twinned columnar grains (e.g. Fig. 3). The probability of twinned columnar grains reduced rapidly outside the 1.5 cm diameter central region. Apparently the formation of twinned columnar grains in nickel is extremely sensitive to the small variation of the sputtering geometry and conditions across the deposit.

This study has led to the following significant observations.

(1) Columnar grains with stacked microtwins formed in high-rate sputter-deposited nickel and copper.

(2) At the same deposition rate, the grain-boundary spacings are essentially the same for the two metals at the same homologous temperature.

(3) At the same homologous temperature, nickel has a thicker average twin spacing than copper due to the higher twin-boundary energy of nickel.

(4) Observation of fine random grains in nickel indicated that small variations in unspecified sputtering conditions can change the microstructure.

References

1. S. D. DAHLGREN, *J. Vac. Sci. Technol.* **11** (1974) 832.
2. S. D. DAHLGREN, E. D. MCCLANAHAN, J. W. JOHNSTON and A. G. GRAYBEAL, *ibid* **7** (1970) 398.
3. M. D. MERZ and S. D. DAHLGREN, to be published.
4. L. E. MURR, "Electron Optical Applications in Material Science" (McGraw-Hill, New York, 1970) p. 397.

Received 24 February
and accepted 10 March 1975

R. WANG
S. D. DAHLGREN
Battelle North West,
Richland, Washington, USA

Isochronal annealing studies on quenched aluminium–manganese alloys

The solid solubility of Mn in Al decreases with decrease in temperature from a maximum value of 1.55 wt% at 658°C [1]. Lattice parameter measurements suggest that decomposition of the splat cooled Al–6.7 wt% Mn alloy occurs in a single stage above 350°C [2]. The annealing stages obtained by electrical resistivity measurements in two alloys quenched from the solid-state are reported here.

The alloys prepared by melting 99.999% pure Al and 99.999% Mn were drawn into wires 0.9 mm diameter. Spectroscopic analysis showed that the two alloys contained 0.35 and 1.0 wt% Mn with traces (< 0.001 wt%) of Mg and Cu. Fe, Ni, Cr and Cd were not detected in the alloys. The samples for resistance measurements were in the form of coils, the current and potential leads were of the same composition as the alloy wires. Electrical resistivity measurements were carried out at liquid nitrogen temperature with a Leeds and Northrup precision Kelvin bridge. By suitably adjusting the length of the wires forming the specimen it was possible to detect changes in resistivity of 10^{-10} Ωcm. The experimental details are reported elsewhere [3].

The samples were heated to 620°C and quenched in a bath of calcium chloride solution at −2°C. Isochronal annealing was carried out in the temperature range 0 to 500°C for two annealing times of 5 and 15 min. The difference in the resistivity of the sample immediately after quenching (ρ_Q) and after annealing at a particular temperature, T (ρ_T) is plotted against temperature in Figs. 1 and 2 for the 0.35% and 1.0% alloys respectively.

The following features are observed in the annealing curves. (1) the first recovery stage occurs in the temperature range 0 to 40°C in both the alloys. (2) The second stage is observed in the temperature range 120 to 200°C in both the alloys; the resistivity recovery in this stage is about 18% of the total quenched-in resistivity. (3) A peak is observed in the Al–1% Mn alloy only at about 290°C. (4) The peak in the concentrated alloy is followed by an annealing stage showing a marked fall in resistivity. The effect of the longer annealing time is essentially to shift the annealing stages to lower temperatures.

The first two stages have also been observed in pure Al and a number of Al alloys [4]. For example, quenching of 99.995% pure Al from 600°C gives rise to the first stage at − 50 to 0°C, while the second stage corresponding to a resistivity recovery of about 20% of the total quenched-in resistivity occurs in the range 100 to 200°C. Alloying elements shift these stages to slightly higher temperatures; this is also observed in the present investigation. Consequently the first stage of the Al–Mn alloys correspond to the annealing of vacancies to permanent sinks and the formation of secondary sinks like Frank and prismatic dislocation loops. The second stage is associated with the annealing of the dislocation loops.

A resistivity peak corresponding to the third stage in the Al–1% Mn alloy has been observed in quenched Al–Cu and Al–Zn alloys at temperatures of about 0°C, particularly when the solute content exceeds 1% [4]. These peaks are associated with the formation of clusters and have widths of the order of a few hundred nΩcm. However, the peak in the 1% Mn alloy is rather