The Vapour-Phase Growth of Thin Nickel Crystal Platelets

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The growth of nickel platelets and whiskers by thermal and chemical decomposition of NiI_2 and $NiBr_2$ has been investigated. The various factors affecting the transport of nickel were examined. For best growth of platelets the amount of nickel transported must be kept low. Hence reactions with low $|\Delta H^\circ|$ are necessary and growth must proceed at the lowest temperature possible.

1. Introduction

Near perfect crystals of ferromagnetic materials in whisker or platelet form are of importance for magnetic domain studies, both under static and dynamic conditions. Remarkable domain patterns have been observed on crystals of this type by DeBlois [1] and Gemperle [2] using colloid techniques; their switching properties are now being investigated using magneto-optic techniques. For this work a reliable method of preparation for crystals with uniform properties in sizes up to 1 mm was required.

Although the growth of crystals of various materials in abnormal morphological form (i.e. whiskers and platelets) was investigated as long ago as 1877 [3], the conditions of formation and the mechanism of growth are in most cases still obscure. Sears [4-6] investigated the growth of whisker and platelet crystals of Hg, Cd, Zn, Ag and CdS by vapour deposition and concluded that these grew if the supersaturation at the growth temperature was below a critical value characteristic of the material. He also postulated that whiskers grew by deposition on a single screw dislocation, while platelets grew by a set of screw dislocations in a grid formation. Brenner [7] grew whiskers of Fe, Cu, Ni and Co by halide reduction, and of Pt and Ag by thermal decomposition of their compounds. He concluded that in the case of Cu at least, the crystals grew under conditions of high supersaturation.

Cech [8, 9] investigated the mechanism of growth of Ni whiskers on NiO and deduced the most probable reactions which took place in the growth zone, concluding that the nucleation of a whisker was initiated by the reduction of NiO. More recently DeBlois [1] grew ferromagnetic whiskers and platelets using Brenner's techniques, but using a low hydrogen concentration by dilution with argon. However, insufficient experimental details were given to enable this growth to be easily reproduced, and no attempt was made to define the important factors affecting growth.

Following unsuccessful initial attempts to reproduce Deblois' results a critical examination of the method was undertaken. The results of the investigation are presented below.

2. Experimental

The resistance winding of the tubular furnace was centre-tapped to allow independent control of the two halves and consequently choice of a range of temperature gradient in the growth region. Temperatures in each zone were controlled by Eurotherm PID/SCR controllers operated by Pt/Pt-13% Rh thermocouples positioned close to the windings. Internal temperatures were monitored by additional thermocouples positioned inside the apparatus.

A 3 cm diameter silica tube accommodated a glazed porcelain boat of dimensions $7 \times 1.5 \times 0.8$ cm. The usual experimental procedure was to place 10 g of the Ni compound inside the boat which was then covered by a second inverted boat to form a lid. This arrangement was not intended to seal the enclosed vapours, but to provide a convenient

TABLE I

Transport system	Calculated optimum transport temperature (°C)	Calculated transport rates (mg/min)
Ni acetylacetonate; thermally decomposed in H_2	400	10
NiI_2; thermally decomposed in dry, O_2-free argon	650	10^{-3}
$NiBr_2$; reduced by hydrogen diluted with argon	600	2×10^{-5}

These values were derived according to the methods described by Schafer [10]

nucleation surface which could be removed with the crystal products intact.

The chemicals used were of laboratory reagent grade supplied by British Drug Houses Ltd. The gases were generally used unpurified, apart from the argon used in the decomposition of NiI_2; this was deoxygenated by passing over heated Ti chips, and dried by passage through a bed of molecular sieve.

Formation of the metal was effected either thermally or chemically at selected temperatures. The furnace temperature rise time was 30° C per min. Growth periods were usually of several hours duration although shorter runs were carried out to check the extent of transport and growth.

Three starting materials were chosen to give a wide variation of transport rates. Calculated values for the three materials are given in table I.

At a later stage, some experiments were carried out in a hot-stage microscope to investigate the behaviour of small quantities of Ni halide under comparable experimental conditions. This proved to be a useful means of checking the minimum reduction temperature and detecting the formation of oxide during the reduction of $NiBr_2$.

3. Results

The decomposition of nickel acetylacetonate yielded only continuous nickel films irrespective of the temperature conditions used, indicating a high transport rate for Ni in conjunction with a cold substrate. Attempts to produce crystals by increasing the temperature of the deposition zone to 600° C produced quantities of carbon mixed with Ni, but no faceted crystals. This system appeared to be totally unpromising because of the difficulty in reducing the rate of formation of Ni while retaining a reasonably high temperature to promote crystallisation. Subsequent work therefore was concentrated on the halide systems.

The thermal decomposition of NiI_2 gave various forms of Ni crystals, as shown in fig. 1. The whiskers and platelets were usually few and small (~ 100 μm), while growth in equant cubic and pyramidal forms was dominant. Variation of the temperature, temperature gradient and flow rate had little or no effect on the products, excepting for flow rates ~ 100 cm^3 min, for which no Ni crystals were obtained. Transport of Ni occurred only over small distances, although large numbers of hexagonal NiI_2 crystals were formed in the cool zone at the end of the tube.

Much better results were obtained by reducing $NiBr_2$ with diluted wet hydrogen. The majority of crystals produced were platelet and whiskers which grew perpendicularly to the boat's surface. Rectangular platelets of up to 500 μm across, right triangular plates of up to 2 mm a side, and whiskers up to 1 cm in length were commonly obtained. The platelets ranged from 500 Å to over 10 μm in thickness. In later experiments crystals were grown on different substrates, including flame-polished silica and sapphire, with similar results. Examples of crystals formed on the surface of the upper porcelain boat are shown in fig. 2.

The optimum conditions of growth for $NiBr_2$ reduction were:* temperature 600° C; temperature rise time 20 min; temperature gradient 4° C/in†; flow rate of argon 12 cm^3/min; flow rate of hydrogen 1 cm^3/min; duration of reduction 7 h. To avoid the formation of a cloudy layer on the crystals, heating was continued in argon alone for a further period of 6 to 7 h. This surface contamination, observed in "quenched" crystals, is presumably a disordered film of Ni deposited as the crystals cooled.

4. Discussion

The best Ni platelets were obtained at very low rates of formation of the metal. In general the

*DeBlois uses different growth conditions namely: Argon flow rate 100 cm^3/min, hydrogen flow rate 0.1 cm^3/min and temperature 700° C.
†1.0 in. = 2.5 cm.

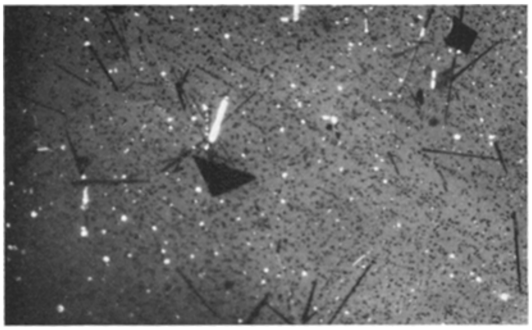

Figure 1 Nickel crystals grown by decomposition of NiI_2 (×70)

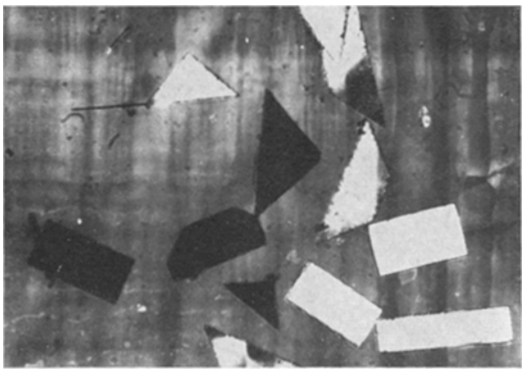

Figure 2 Nickel crystal platelets formed by reduction of $NiBr_2$ (×10)

rate of transport is related to the thermodynamical quantities $\Delta H°$, $\Delta S°$ and the equilibrium constant K_p, of the reaction involved [10, 11]. Thus a suitably low rate of generation from the gaseous phase is obtained provided that: (i) the reaction has a small but finite $\Delta H°$; (ii) the reaction proceeds with a small change in volume of the gases involved (low $\Delta S°$); (iii) the flow rate is low since this limits the concentration of reactants; (iv) the reaction proceeds at the lowest temperature commensurate with finite transport, since the rate varies rapidly with K_p [11]. Applying these considerations to the possible reactions occurring in the systems studied we have:

(i) $Ni_{(s)} + 2I_{(g)} \rightleftharpoons NiI_{2(g)}$, $\Delta H° = -17$ kcal/mole

(ii) $NiBr_{2(g)} + H_{2(g)} \rightarrow Ni_{(s)} + 2HBr_{(g)}$, $\Delta H° = -18.2$ kcal/mole

(iiia) $NiBr_{2(g)} + H_2O_{(g)} \rightarrow NiO_{(s)} + 2HBr_{(g)}$, $\Delta H° = -17.9$ kcal/mole

(iiib) $NiO_{(s)} + H_{2(g)} \rightarrow Ni_{(s)} + H_2O_{(g)}$, $\Delta H° = -0.3$ kcal/mole.

Of the two possible reactions for the reduction of $NiBr_2$, (iiib) has the lowest $|\Delta H°|$; the steps (iiia) and (iiib) have no overall volume change, unlike reaction (i). Experimentally the formation of Ni by reactions (iiia and b) is favoured by keeping the gas-flow rate low (i.e. low hydrogen concentration) and passing the gas mixture through 6 in. of water.

These considerations indicate that DeBlois' procedure is particularly suited to the formation of Ni platelets, and it is thus of interest to consider the experimental variables that can affect growth by this process. These are (i) the concentration of gaseous components, H_2, A and H_2O; (ii) temperature and temperature gradient; (iii) gas flow rates; (iv) substrate texture or composition. The necessity of working with low hydrogen and high water contents at the lowest possible temperature has already been discussed. In practice it was found that the temperature gradient in the region of the growth zone was relatively unimportant since it mainly determined the position at which formation of the Ni occurred. Since in all cases the transport distance was small the gradient becomes unimportant.

The gas flow rate controls two effects. At high flow rates material is transported further in a given time. Secondly, reactant concentrations are increased by the more rapid arrival of fresh gas, while reaction products are swept away more rapidly. This situation leads to a higher transport rate of Ni, and consequently gas flow rates should be kept low. Substrate textures of the various types studied included: new glazed porcelain; acid-etched porcelain; sintered alumina, silica glass, quartz and sapphire crystals. Under optimum growth conditions very little difference in crystal size or yield was noted, and the substrate texture is considered to be of minor importance. Of greater significance is the relative yield of whiskers, triangular platelets, rectangular platelets and equant crystals formed. However, an adequate explanation of the development of the different forms of crystals has still to be derived from studies in progress.

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