DISLOCATION SUBSTRUCTURES IN DEFORMED AND RECOVERED CHROMIUM

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Summary

In an attempt to correlate the degree of plastic deformation of chromium with the physical properties associated with its antiferromagnetism, a study has been made by thin-foil electron microscopy of the dislocation substructures in polycrystalline chromium sheet after deformation by rolling and subsequent annealing. The original hot-rolled sheet exhibited a typical cell structure. Annealing at 900°C produced regular hexagonal networks and simple tilt boundaries. Complete recrystallization was achieved by annealing at 1250°C. 1·5% deformation of this material at room temperature produced a non-uniform substructure of sharply kinked dislocation lines and irregularly shaped closed loops. Annealing at temperatures below 650°C had little effect. However, at that temperature there was some recovery and large circular loops lying in the slip planes appeared. The beginnings of regular networks appeared and the closed loops annealed out at 900°C. Comparison with the annealing characteristics of dislocation loops in iron allowed an estimate of the activation energy for the process in chromium to be made. It is shown that the elastic stress induced by plastic deformation, which critically affects the physical properties associated with the antiferromagnetism, is consistent with the experimental observations of the influence of an applied magnetic field on the elastic properties of chromium.

I. Introduction

Previous work (Bacon 1961; Street 1963) has shown that the physical properties of chromium associated with its antiferromagnetism are strongly dependent upon its state of plastic deformation. In an attempt to correlate the degree of plastic deformation with the observed antiferromagnetic properties, the dislocation substructures in annealed and plastically deformed chromium have been studied by thin-foil electron microscopy.

II. Experimental Procedure

The specimens were made from 99·97% pure chromium supplied in the form of hot-rolled sheet 0·002 in. thick. All annealing treatments were carried out in a vacuum of approximately 10^{-5} mmHg. The specimens were furnace cooled.

Thin foils suitable for transmission electron microscopy were prepared by electropolishing in a solution of 65 ml perchloric acid (sp. gr. 1·54), 300 ml acetic acid, and 300 ml butyl cellosolve at about 1°C, in an apparatus similar to that described by Presland (1961). The cathodes were stainless steel and a current of 1·5 A from a current-stabilized rectified a.c. power supply was used. The thinned foils were examined in a JEM-6A electron microscope operating at 100 kV.

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III. Results and Discussion of Microscope Observations

(a) *The Original Rolled Sheet and the Effects of Subsequent Annealing*

The dislocation substructure of the original rolled sheet is shown in Figure 1 (Plate 1). The characteristic cell structure indicates the heavily deformed state of the sample. The cells vary in size from about 2 to 4 μ.

The effects of annealing this material at 900°C for 2 hr are shown in Figure 2 (Plate 2). It will be seen that the tangled dislocations have become straightened and rearranged into regular sub-boundaries, most of which consist of hexagonal networks. However, simple tilt boundaries are also seen. The well-developed hexagonal network at A in Figure 2(*a*) (Plate 2) is similar to the networks observed in a number of body-centred cubic metals (Keh and Weissmann 1963). It will be seen that the network contains $\langle 100\rangle$ dislocation segments which probably resulted from the reaction

$$\tfrac{1}{2}\mathbf{a}[111]+\tfrac{1}{2}\mathbf{a}[1\bar{1}\bar{1}] \rightarrow \mathbf{a}[100].$$

Annealing at 1250°C for 2 hr produced complete recrystallization (see Fig. 3, Plate 3). The average grain size was about 25 μ. The grains were generally free of substructure, although very occasionally remnants of sub-boundaries were observed. The dislocation density was therefore of the order of 10^6–10^7 cm/cm^3. The grain boundaries were usually featureless, but ledges similar to those observed in iron and tungsten (Li 1963) were sometimes seen.

(b) *Deformation at Room Temperature of Fully Recrystallized Chromium and the Effects of Subsequent Annealing*

The fully recrystallized sheet was extremely brittle. However, it was found that at room temperature it could be deformed plastically up to about 2% by rolling it between two mild steel plates 0·05 in. thick.

The dislocation substructure after 1·5% increase in length is shown in Figure 4 (Plate 3). The most notable features were (1) the sharp kinks and cusps on the individual dislocation lines, (2) the hairy appearance of the grain boundaries, (3) the small closed loops, generally of irregular shape, and (4) the many black dots.

Li (1963) has suggested that the ledges observed on the grain boundaries (Fig. 3, Plate 3) in the fully recrystallized samples, could act as sources of dislocations. The hairy appearances of the grain boundaries after deformation suggests that they are a major source of dislocations.

Occasionally dislocations were seen to move under the influence of the electron beam but no traces were left behind. The dislocations were not uniformly distributed throughout the specimens, but the average dislocation density was 5×10^9 cm/cm^3. Dark-field observations were consistent with the dislocations having a Burgers vector of the type $\tfrac{1}{2}\mathbf{a}\langle 111\rangle$.

It is possible that the black dots are simply loops which are too small to be resolved, but this is not certain. Benson, Thomas, and Washburn (1962) and Low and Turkalo (1962) observed similar loops in molybdenum and silicon-iron respectively, and have suggested that they arise from the "pinching off" of cusps. The loops observed in chromium appear to have formed in a similar way. An example of this process near completion can be seen at A in Figure 4 (Plate 3).

The effects of annealing this deformed material for a period of 15 min (and then furnace cooling) at temperatures of 400, 650, and 900°C are shown in Figures 5 and 6 (Plate 4) and Figure 7 (Plate 5). The average density of black dots and closed loops for each annealing temperature is given in Table 1. The foil thickness was assumed to be 2000 Å.

The effect on the dislocation lines of annealing at 400°C is small, but the features already noted in the as-deformed specimen appear to have become clearer. In foils such as that shown in Figure 5 (Plate 4), with (001) parallel to the surface, the dislocations appeared to lie along ⟨110⟩. These are probably screw dislocations. The density of black dots was significantly decreased, but there was an increase in the density of closed loops.

TABLE 1

AVERAGE DENSITY OF BLACK DOTS AND CLOSED LOOPS IN UNITS OF 10^{10}/CM^3

Annealing Temperature (°C)	25	400	650	900
Black dots (< 250 Å diameter)	859±5	614	251±23	0
Closed loops (> 250 Å diameter)	34±1	62±10	72±21	2±2

The effects of annealing at 650°C are shown in Figure 6 (Plate 4). There was some evidence of recovery, but the dislocation line density did not change significantly. There was a further reduction in the density of black dots, although no significant increase in the density of closed loops. There was, however, an increase in the number of closed loops greater than 750 Å in diameter, and they were more regular in shape. Similar loops have been observed in molybdenum annealed at 300°C by Benson, Thomas, and Washburn (1962), and in vanadium annealed at 750°C by Edington and Smallman (1963). The latter workers also showed that the loops were vacancy in character. Examples of very nearly circular loops were observed in a ($\bar{2}$13) foil. This was the only foil examined whose surface was parallel to one of the probable slip planes. In all the (001) foils examined the loops were elliptical, as would be expected if the loops were circular and lay on planes inclined to the foil surface, such as the probable slip planes {110}, {112}, and {123}.

Benson, Thomas, and Washburn (1962) have suggested that these loops are formed by double cross-slip of close dislocation pairs, but a pinching-off process may also operate.

Heating at 900°C caused all the black dots and most of the closed loops to anneal out. The dislocation lines straightened out considerably, but the dislocation line density dropped only to 3×10^9 cm/cm^3. As will be seen from Figure 7 (Plate 5), many of the dislocation lines have interacted to produce threefold nodes and the beginnings of regular hexagonal networks. Note the [010] dislocation segments at A.

(c) *Annealing Out of Dislocation Loops*

Silcox and Whelan (1960) showed that the annealing out of dislocation loops in aluminium is an activated process in which the time taken is proportional to the square of the loop diameter.

In chromium the black dots annealed out completely at 900°C, but there was a significant reduction in their density even at 400°C. If the black dots are loops too small to be resolved, then it is reasonable that they should anneal out at lower temperatures than the larger closed loops.

It was observed that most of the closed loops in chromium annealed out after heating at 900°C. An estimate of the activation energy E for the process has been made by assuming the relation

$$E_1/T_1 = E_2/T_2$$

to hold for two different metals in which loops anneal out in the same interval of time (Segall 1963). Keh and Weissmann (1963) found that the 500-Å diameter loops in deformed iron annealed out after 1 hr at 550°C with an activation energy of 2·39 eV. Substituting these values in the above equation, it is found that for chromium E is equal to 3·4 eV.

Hagel (1962) found the activation energy for self-diffusion in chromium to be 3·18 eV. The reasonable agreement between the activation energies for the two processes supports the view that loops anneal out by a climb process controlled by the production and diffusion of vacancies.

(d) *Deformation by Rolling at Liquid Nitrogen Temperature*

Attempts were made to deform plastically the fully recrystallized chromium sheet by rolling it between mild steel plates at liquid nitrogen temperature. Even the lightest rolling caused the specimen to crack severely. The average distance between cracks was about 100 μ.

The preferential attack which occurred at the cracks during subsequent electropolishing is probably the reason why it was found impossible to prepare really satisfactory thin foils for electron microscopy. Examination of the few thin areas in a specimen which had probably been deformed about 0·5% indicated that the substructure was not obviously different from that observed in specimens deformed at room temperature.

IV. Influence of Dislocation Density on Physical Properties associated with Antiferromagnetism

Measurements of Young's modulus Y and susceptibility χ as a function of temperature in chromium, which had been annealed at 1250°C, showed that there are marked anomalies at 120°K and at 312°K (the spin-flip and Nèel temperatures, T_{sf} and T_n, respectively). However, specimens which had been deformed plastically by about 1% showed no anomalies in Y and the temperature variation of χ was entirely similar to that observed in unannealed specimens. Deformed specimens, which were subsequently annealed at 400, 650, and 900°C, behaved in a similar way.

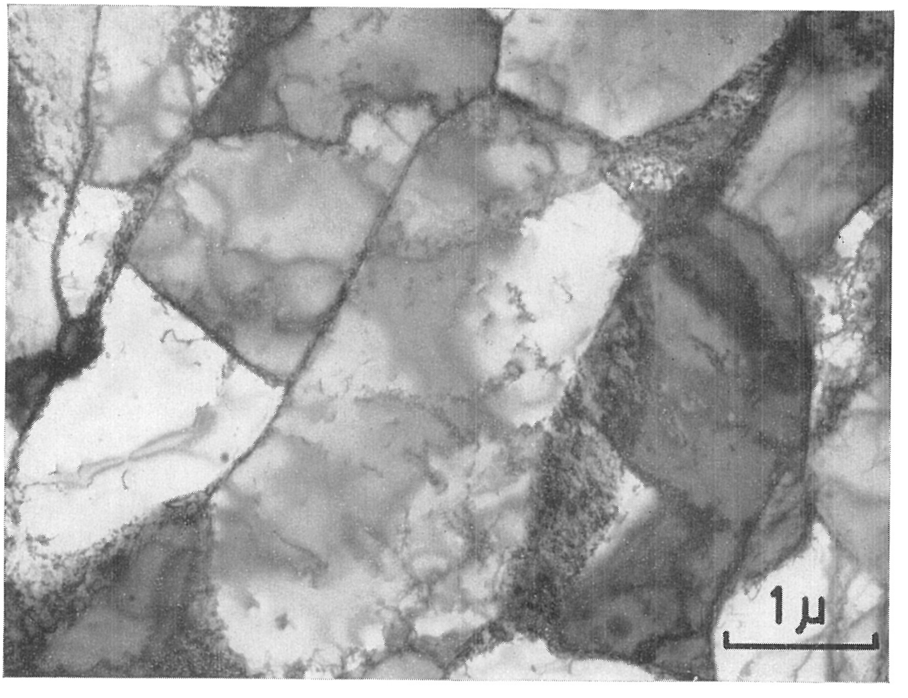

Fig. 1.—Cell structure in the original rolled sheet.

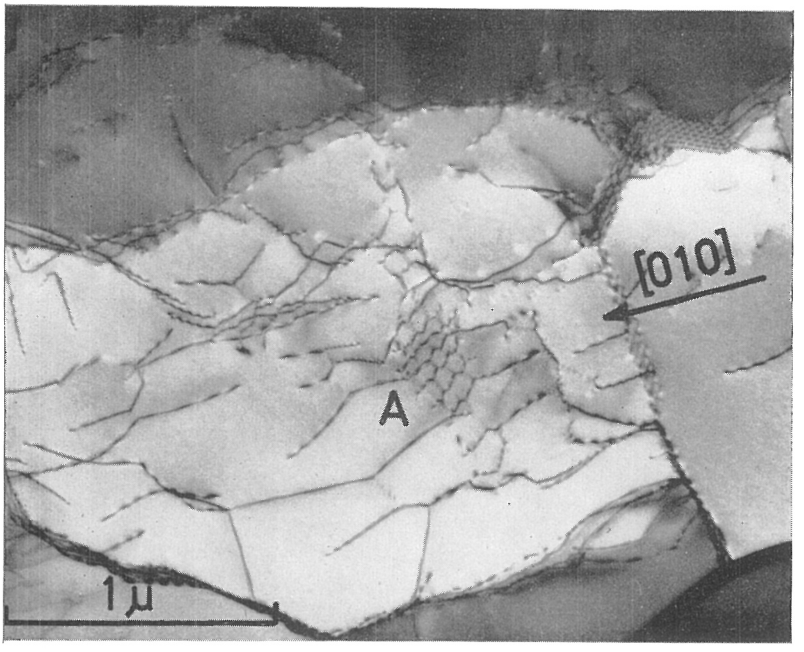

Fig. 2(*a*).—Sub-boundaries consisting mainly of hexagonal networks in the original rolled sheet after annealing at 900°C for 2 hr. The plane of the foil is (001).

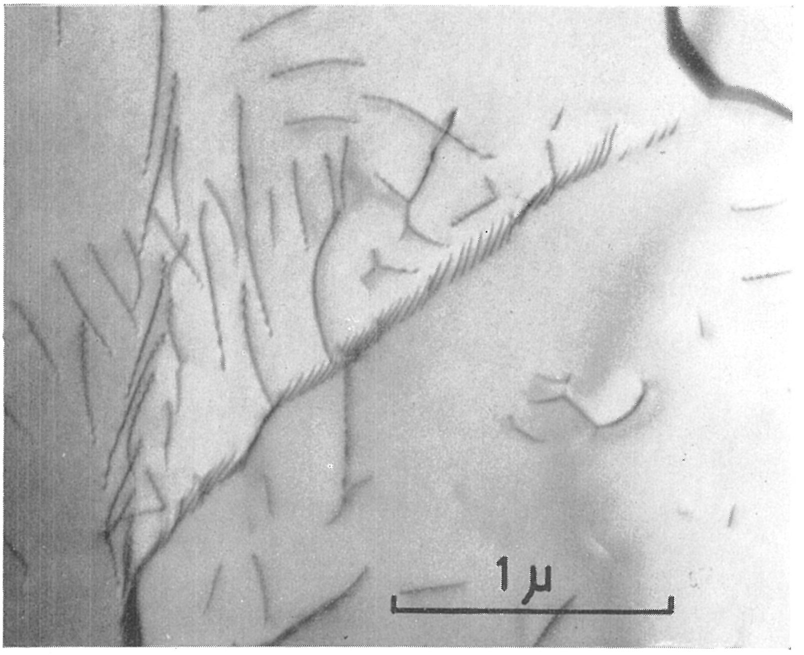

Fig. 2(*b*).—Simple tilt boundaries in another part of the same specimen.

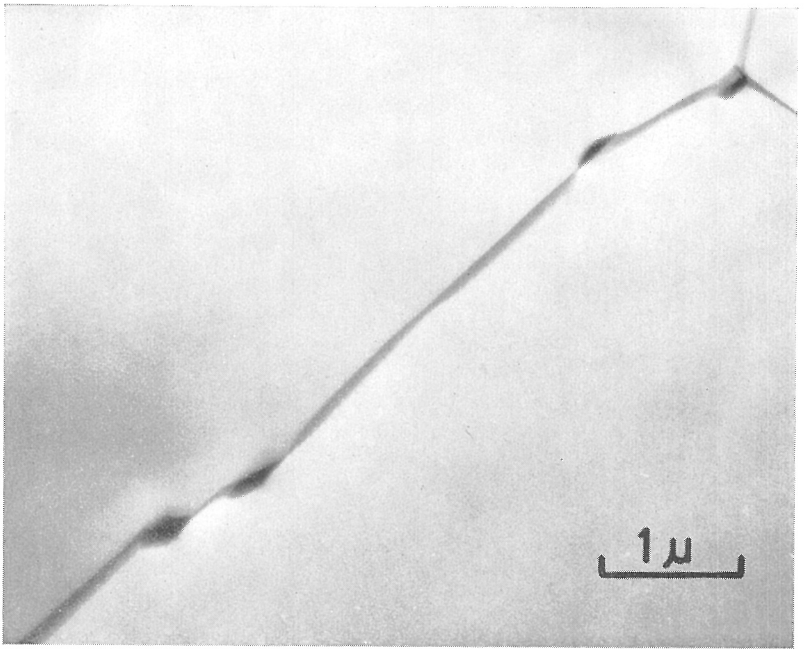

Fig. 3.—Structure of recrystallized chromium.

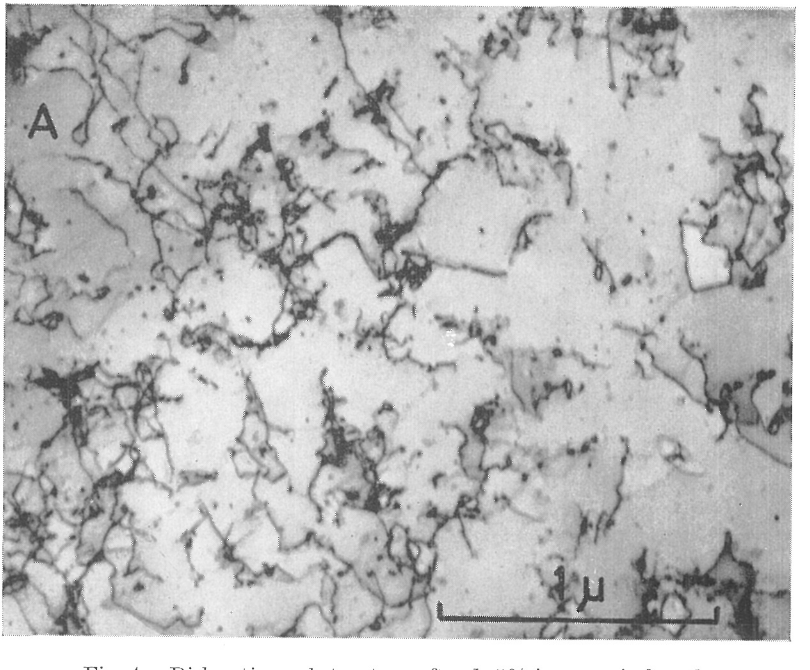

Fig. 4.—Dislocation substructure after 1·5% increase in length.

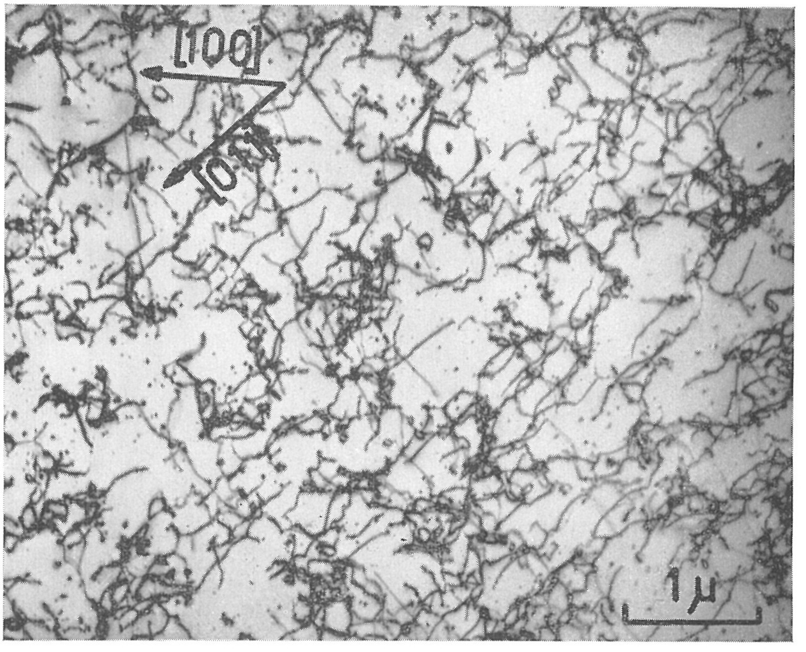

Fig. 5.—Dislocation substructure after 1·5% deformation, annealed at 400°C. The plane of the foil is (001).

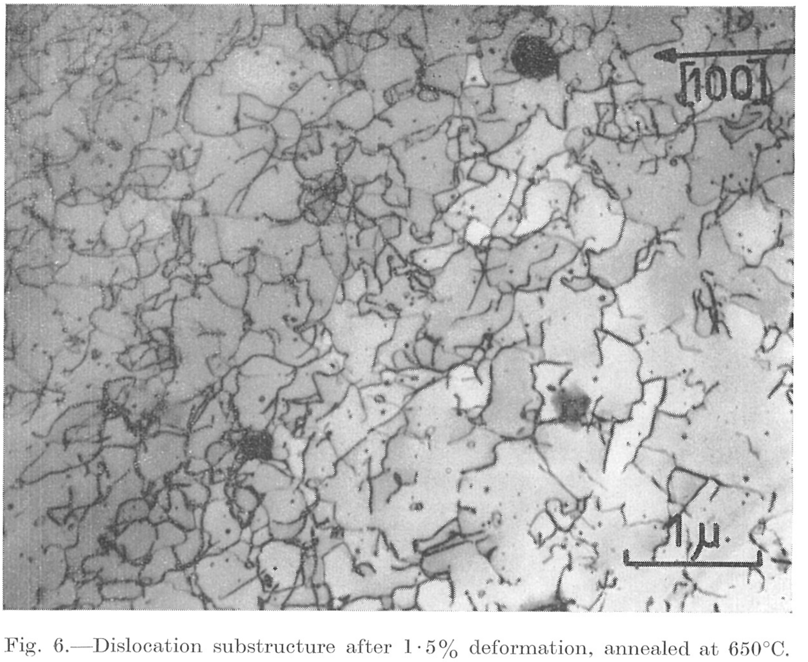

Fig. 6.—Dislocation substructure after 1·5% deformation, annealed at 650°C. The plane of the foil is (001).

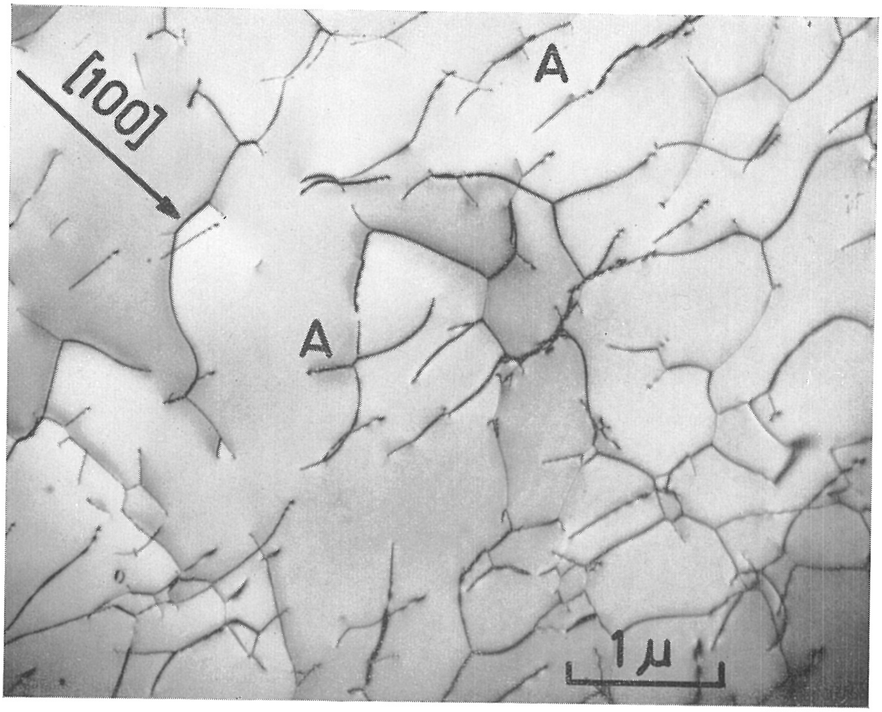

Fig. 7.—Dislocation substructure after 1·5% deformation, annealed at 900°C. The plane of the foil is (001).

In a crystal the stress associated with a screw dislocation has magnitude $(G/2\pi).b/r$ at distance r, where G is the rigidity modulus and **b** the Burgers vector (Read 1953). For a dislocation density of the order of 10^{10} cm/cm³, the average distance between dislocations will be 10^{-5} cm. Taking $G = 10^6$ kg/cm², $b = \frac{1}{2}a = 1 \cdot 44 \times 10^{-8}$ cm, and $r = 5 \times 10^{-6}$ cm, the stress becomes approximately 500 kg/cm². The electron microscope observations indicate, therefore, that the stress throughout the crystal will be of this order of magnitude after about 1% deformation, and that it will not be significantly reduced by subsequent annealing at temperatures up to 900°C.

Street (personal communication) has shown that a magnetic field of 50 kOe will smooth out the anomalies in Y at T_{sf} and T_n in polycrystalline specimens; that is, for $T_{sf} < T < T_n$ only those spin density distributions with lowest magnetostatic energy are present in fields of 50 kOe. From the measured values of anisotropy of χ in specimens cooled in a field of 50 kOe, the magnetostatic energy density difference between energetically favourable and unfavourable spin density distributions was estimated to be 100 erg/cm³.

The magnetostrictive strain energy density associated with an applied elastic stress Z is of the order of $Z\lambda$, where λ is an "antiferromagnetostriction" coefficient associated with the spin density distributions. In a field of 26 kOe, λ was estimated to be 10^{-7}.

It follows that the stress Z which will smooth out the anomalies at T_{sf} and T_n is about 1000 kg/cm². This is only a factor of two greater than the stress associated with a dislocation density of the order of 10^{10} cm/cm³. In view of the assumptions made, the agreement is reasonable.

V. Acknowledgments

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