the process is fundamental and occurs to some extent at all stages of deformation.

No evidence of spontaneous recrystallisation after rolling was found for any specimen, nor was there any evidence of self-recovery in copper specimens. Thus the texture formed in these metals during or immediately after deformation at room temperature is quite stable, in sharp contrast to the behaviour of the softer metals which are to be discussed in the next paper.

The authors are indebted to Prof. Sir Lawrence Bragg and Dr W. H. Taylor for their constant help and encouragement. They would also like to thank their colleague Dr P. B. Hirsch for much valuable advice and criticism. The work was carried out while the authors were in receipt of maintenance grants from the Department of Scientific and Industrial Research.

References

GAY, P., HIRSCH, P. B., THORP, J. S. & KELLAR, J. N. (1951). *Proc. Phys. Soc.* B, **64**, 374.
HIRSCH, P. B. (1950). Ph.D. Dissertation, University of Cambridge.
HIRSCH, P. B. (1952*a*). *Acta Cryst.* **5**, 168.
HIRSCH, P. B. (1952*b*). *Acta Cryst.* **5**, 172.
HIRSCH, P. B. & KELLAR, J. N. (1951). *Proc. Phys. Soc.* B, **64**, 369.
HIRSCH, P. B. & KELLAR, J. N. (1952). *Acta Cryst.* **5**, 162.
MEGAW, H. D. & STOKES, A. R. (1945). *J. Inst. Met.* **71**, 279.
STOKES, A. R., PASCOE, K. J. & LIPSON, H. (1943). *Nature, Lond.* **151**, 137.
WOOD, W. A. (1939). *Proc. Roy. Soc.* A, **172**, 231.

Acta Cryst. (1953). **6**, 172

X-ray Studies of Polycrystalline Metals Deformed by Rolling. II. Examination of the Softer Metals, Tin, Zinc, Lead and Cadmium

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The examination of the softer metals, tin, zinc, lead and cadmium after deformation by rolling, is described. X-ray back-reflexion methods, employing both beams of normal diameter and micro-beams, have been used.

In the initial stages of deformation a mosaic structure is found within the deformed grains of the metal and the size of the mosaics reaches a lower limiting value, dependent on the particular metal. At heavy deformations these metals spontaneously recrystallize. The effects upon the mosaic structure of annealing at low temperatures and of recovery at room temperature have been studied. Some evidence is presented concerning the nature of recrystallization nuclei.

1. Introduction

Most of the previous investigations of the structure of cold-worked metals have been concerned with the behaviour of the harder metals of high melting point; little attention has been devoted to the deformation of those melting at lower temperatures (~300–400° C.). The experiments to be described in this paper are complementary to those described for the harder metals in a previous paper (Gay & Kelly, 1953).

In these experiments, the soft metals selected for examination were cadmium and zinc, representatives of the hexagonal metals; the tetragonal modification of tin; and lead, a face-centred cubic metal. It is found that the behaviour of these metals at heavy deformation differs from that of the harder metals, in that they exhibit spontaneous recrystallization. However, the experiments to be described here have been mainly concerned with the textures of the materials before the onset of recrystallization. The authors have attempted to determine the processes by which deformation, recovery and recrystallization occur, and to this end three main groups of experiments have been carried out.

First, the metals have been examined immediately after deformation for various degrees of reduction (cf. § 3). Then the changes which occurred, with time after deformation, within the same volume of a particular specimen were observed, and finally the effects of annealing at low temperatures were studied. Complete investigations of this type have been carried out for the m als tin, zinc and lead, but for cadmium such detailed studies have not been undertaken since it appears that its behaviour is similar to that of the other metals.

In this paper, the results of the experiments and a

preliminary discussion of their interpretation are given; the similarities between these and other cold-worked metals will be discussed in a later publication.

2. Experimental methods

Throughout the work described in this paper X-ray back-reflexion methods have been used. When using beams of normal diameter (~ 1 mm.) the mosaic structure can in most cases be resolved and it is only occasionally necessary to use the X-ray microbeam technique (Hirsch & Kellar, 1951; Gay *et al.*, 1951). Thus, for tin, resolution can be obtained throughout the complete range of deformation by normal methods, but at small deformations narrower beams are required with the other metals.

The main features of the methods of interpretation have been described earlier (Gay & Kelly, 1953). Measurements of mean particle size and misorientations have been made; no systematic investigation of spot shapes could be carried out owing to the large diameter of the X-ray beam used in most cases and to the large particle size. Ordinary metallographic examination of the specimens revealed little to supplement the information from the X-ray photographs; it has, however, been possible to confirm some of the deductions from the X-ray evidence by the use of phase-contrast microscopic methods.

3. Preparation of specimens

All the specimens were in the form of bars; the initial annealed grain size was large (~ $\frac{1}{2}$–1 mm.). The percentage deformations are quoted throughout as the ratio of the thickness after deformation to the original thickness of the material. Except for lead specimens, rolling was used as the method of deformation.

The specimens of tin were of 99·995% purity (Johnson, Matthey Ltd, J.M. 530). After deformation the specimens were etched with a solution of one part hydrochloric acid to two parts of water saturated with ferric chloride so that the surface layers (~ 0·1–0·2 mm.) were removed.

The specimens of zinc were of 99·999% purity (Johnson, Matthey Ltd, J.M. 150). After deformation, the specimens were etched to a similar depth with a solution of chromic oxide and sodium sulphate in water.

The specimens of lead were of 99·99% purity (Johnson, Matthey, Ltd, J.M. 561). After deformation, in this case by compression, etching was carried out with a solution of ammonium molybdate in nitric acid.*

The specimens of cadmium were of 99·99% purity (Johnson, Matthey Ltd, J.M. 170). After deformation, the specimens were etched in a mixture of hydrochloric acid and nitric acid.

* Owing to the softness of the material, compression instead of rolling was used as the method of deformation since the reduction may then be more easily controlled.

4. Experimental results

(*a*) *Tin*

(i) *Examination immediately after deformation.*— Photographs taken of the annealed specimens show reflexions from large grains randomly distributed within the material (Fig. 1(*a*)). Even after the smallest deformations (1–3%) entirely different diffraction patterns are obtained (Fig. 1(*b*)); most of the Laue reflexions seen in the previous photograph have disappeared, and the main reflexions are clustered into short arcs around the Debye–Scherrer rings. The spots within the arcs are very often joined by a continuous background. As the amount of deformation is increased, it is found that the total angular extent of each arc increases, and that the number of spots on each becomes greater. Heavier deformations are marked by the frequent occurrence of large sharp isolated reflexions and the reappearance of Laue spots (Fig. 1(*c*)). The frequency of occurrence of these randomly oriented reflexions is greater the heavier the deformation. Finally, after a limiting deformation, no trace of the arcs remains immediately after deformation; the pattern is very similar to that obtained from the annealed material, except that at very heavy deformations the photographs show grains of much smaller dimensions than the initial grain size.

From this description of the diffraction patterns at various deformations, it is seen that two types of 'grain' are apparently produced during or shortly after the deformation. The reflexions which are clustered into spotty arcs must come from mosaics produced within the original grain during the deformation. The large, sharp isolated reflexions come from recrystallized grains. The phenomenon of spontaneous recrystallization during the deformation of tin has been noted before (Schmid & Boas, 1950). After severe deformations, the tin specimens have completely recrystallized.

It is possible to obtain values of the particle size and angular misorientations by the methods described in an earlier publication (Gay & Kelly, 1953). It is found, after about 20% deformation of the annealed specimen (grain size ~ 1 mm.), that the particle size has fallen sharply to about 25 μ. For further deformations up to about 35% reduction, a slight decrease in particle size to about 20 μ is found. At heavier deformations, complete spontaneous recrystallization occurs, the size of the recrystallized grains decreasing with increasing deformation. Fig. 4 shows the variation of particle size plotted as a function of the amount of deformation; a smooth curve has been drawn through the experimental points. The points plotted in the diagram are averaged values for several specimens; it cannot be expected that the

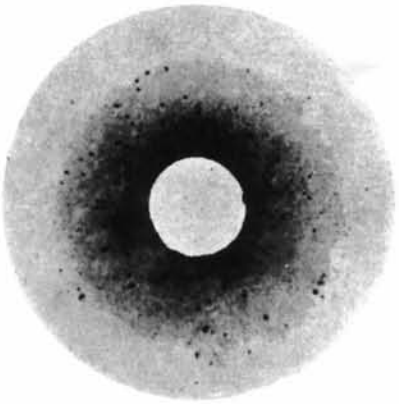

Fig. 1 (*a*).

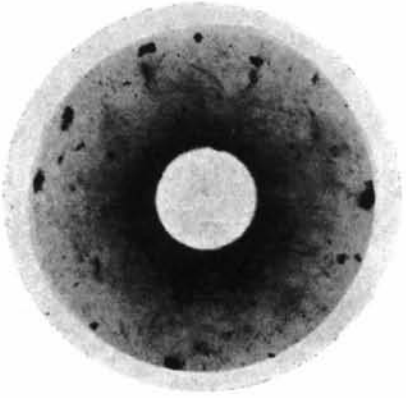

Fig. 1 (*b*).

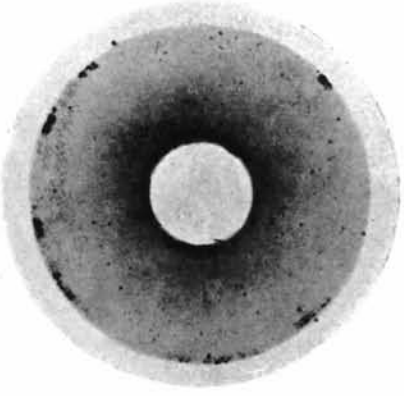

Fig. 1 (*c*).

Fig. 1. (*a*) Ordinary back-reflexion photograph of an annealed tin specimen (grain size 1–2 mm.). Cu $K\alpha$ radiation. (*b*) Ordinary back-reflexion photograph of a 3% rolled specimen of tin taken immediately after deformation. The inner ring is the 701 reflexion. Cu $K\alpha$ radiation. (*c*) Ordinary back-reflexion photograph of a 20% rolled specimen of tin taken immediately after deformation. The inner ring is the 701 reflexion. Cu $K\alpha$ radiation.

Fig. 2. Phase-contrast micrograph of the electro-polished surface of a 10% rolled specimen of tin taken 10 days after rolling (magnification $\times 200$).

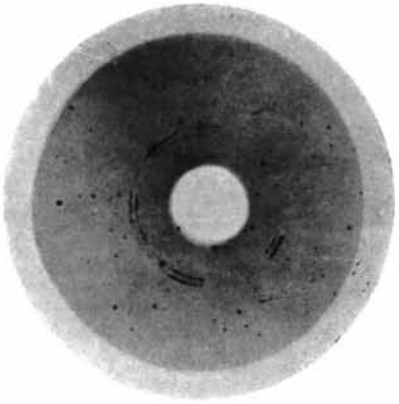

Fig. 3 (*a*).

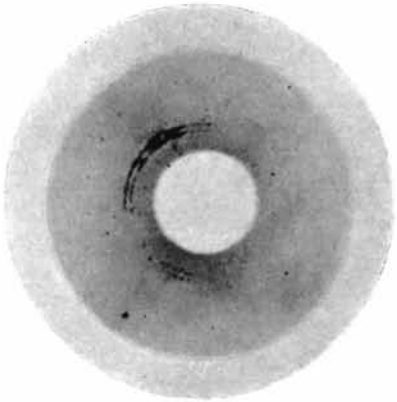

Fig. 3 (*b*).

Fig. 3. (*a*) Ordinary back-reflexion photograph of a 20% rolled specimen of tin taken immediately after deformation. The inner ring is the 701 reflexion. Cu $K\alpha$ radiation. (*b*) Ordinary back-reflexion photograph of the same volume of the same specimen as (*a*) after an anneal of ¼ hr. at 50° C.

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texture of specimens deformed by nominally the same amount will be exactly similar when rolling is the method of deformation.

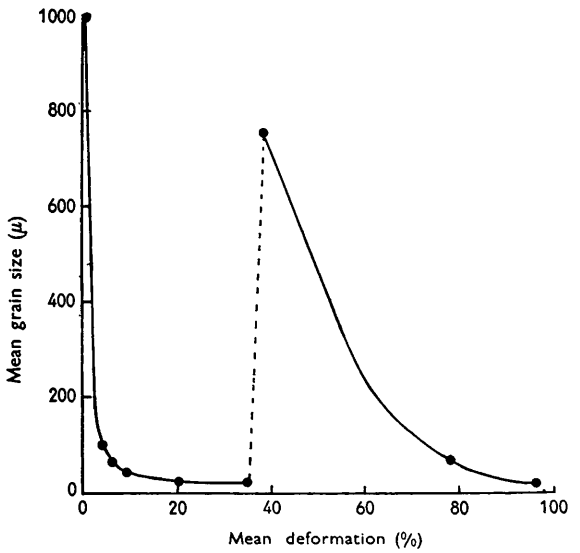

Fig. 4. Variation of particle size with the amount of deformation for tin.

Independent confirmation of the existence of a mosaic structure within the deformed initial grains was provided by an examination of several specimens using phase-contrast microscopy; this examination was kindly carried out by Mr E. C. W. Perryman (British Non-Ferrous Metals Research Association). Fig. 2 shows a micrograph of the electropolished surface of a 10% rolled specimen; the mosaics within the original grains are clearly visible. However, it was not possible to obtain conclusive evidence of the mosaic structure in a 3% rolled specimen by this technique; this is probably due to the fact that the method is insufficiently sensitive to reveal the boundaries between mosaics which have relative misorientations of only a few minutes of arc (Gay & Hirsch, 1951).

Table 1. *Misorientations in tin, zinc and lead as a function of deformation*

	Deformation (%)	Total range of misorientations with an original grain (°)
Tin	3	½
	6	1
	10	2½
	20	7½
	35	31
Zinc	2·6	2
	5·0	4¼
	9·0	9
	15·0	9½
	19·8	6
Lead	2	3
	5	6½
	9	7
	12	7½
	15	3½

Measurements have been made of the extreme range of orientation of the material present within the deformed original grain. The variation of averaged measurements of this quantity as a function of deformation is given in Table 1. It can be concluded that the material within a deformed initial grain covers an appreciable range of orientation; the misorientations within the grains increase with increasing deformation.

Thus the deformation of annealed polycrystalline tin produces a mosaic structure; the size of the mosaics is dependent on the amount of deformation. However, after about 20% reduction, the particle size decreases only slightly; the misorientations within an original grain, however, increase rapidly with further deformation.

As has been mentioned earlier, the more heavily deformed specimens of tin show reflexions from recrystallized grains, in contrast to the behaviour of similar specimens of the harder metals. The increased frequency of occurrence of this type of reflexion at heavier deformation, and the decrease in the recrystallized grain size with increasing deformation, imply that the ease of recrystallization increases with increasing deformation. The occurrence of complete recrystallization of the material at a value of the deformation slightly greater than that needed to produce the lower limiting mosaic size suggests that recrystallization may be connected with the instability and growth of the mosaics.

The stability of the mosaic structure has been investigated by experiments on the recovery and annealing effects in tin.

(ii) *Examination after various intervals of time after deformation.*—When the specimens were examined immediately after deformation they were mounted rigidly on the camera. Photographs were then taken with the X-ray beam incident on the same volume of specimen after various intervals of time after deformation.

For specimens deformed up to 5% reduction, little change is found in the spotty arc pattern on photographs taken at periods up to a month after rolling. Some of the background between the spots disappears, but no reflexions from recrystallized grains appear during this time.

For greater deformations, some reflexions from recrystallized grains are observed, together with the spotty arcs, immediately after deformation. Such specimens show marked changes over short periods of time. The recrystallized grains which are present initially grow rapidly; new reflexions of this type appear and grow. The rate of growth of these grains seems to be dependent on the initial deformation; it is faster for the more heavily deformed specimens.

As the recrystallized grains grow, some of the arcs on the Debye–Scherrer ring disappear; the reflecting material contributing to these parts of the ring has been consumed by the expanding grains. Sometimes this process is carried to completion and the final photographs show only a recrystallized structure; sometimes equilibrium is reached with traces of the spotty arcs still present on the photographs. From an examination of the photographs it is not possible to say whether a recrystallized grain giving rise to a reflexion at a particular point on the Debye–Scherrer ring may be associated with the disappearance of the adjacent mosaic reflexions on the ring.

The rate of growth of the mosaic structure is, in general, slow compared with that of the recrystallized grains (but see § 4*a*(iii), below). Whilst there is no change in the total range of orientation within a deformed original grain, a slight sharpening of the spots removes some of the continuous background between them.

The rate of growth of the recrystallized grains is relatively rapid; for a 20% reduced tin specimen showing some recrystallization after deformation, complete recrystallization of the material occurs within a period of three days.

It is apparent from these experiments that the mosaic structure found in the deformed tin specimens is stable provided that no recrystallization has occurred. If recrystallization has occurred to any degree during or immediately after deformation, the recrystallized grains grow rapidly and consume most of the mosaic structure.

(iii) *The effect of annealing.*—The specimens were heated *in situ* in a low-temperature furnace for short periods. An examination of the diffraction patterns from the same volume of specimen after different annealing treatments has been made; only specimens showing sub-structure within the deformed original grains were examined.

The stability of the structures of specimens showing no recrystallization was confirmed by these further experiments; more severe annealing conditions were required to induce complete recrystallization for these specimens than for those which showed some recrystallization immediately after deformation. For example, a 3% rolled tin specimen required ½ hr. at 100° C. for complete recrystallization; for a 20% rolled specimen an anneal of ½ hr. at 50° C. was sufficient to complete the recrystallization.

For some specimens, showing initial recrystallization, a rapid growth rate of the mosaic structure was found. Fig. 3(*a*) shows a photograph obtained for a 20% deformed specimen taken immediately after deformation. After an anneal of ¼ hr. at 50° C. it can be seen that the reflexions on one of the arcs have grown so large that they form an almost continuous thick black arc (Fig. 3(*b*)). It will be noticed that one of the arcs has disappeared completely; this material has probably been incorporated into a growing grain. Further, the sizes of several of the reflexions from recrystallized grains have diminished; this suggests that the recrystallized material is being removed by the growth of the mosaic structure. On further annealing, the arcs consisting of coarsened sub-structure reflexions disappear, leaving only the usual pattern from recrystallized material.

This remarkable behaviour has been observed for several tin specimens, though rapid growth of only the recrystallized grains occurred in some others.

(*b*) *Zinc*

(i) *Examination immediately after deformation.*—As with tin, after small deformations of the annealed specimens (grain size $\sim 300\ \mu$) the initial spots spread into arcs around the Debye–Scherrer ring. It is found that the angular extent of the arcs increases with increasing deformation, which also causes a decrease in the size of the mosaics until a lower limiting value is reached. Photographs taken at deformations greater than about 2–5% show the presence of some recrystallized grains; for deformations greater than about 40% reduction, complete spontaneous recrystallization occurs. The marked recovery of zinc in normal mechanical tests is well known (Haase & Schmid, 1925).

Measurements of particle size plotted as a function of deformation are shown in Fig. 5. After a rapid initial decrease, the particle size determined by the use of X-ray beams of $\sim 150\ \mu$ diameter reaches an approximately constant value of $\sim 12\ \mu$. Measurements of the misorientations for specimens showing a mosaic structure are given in Table 1; the trend shown

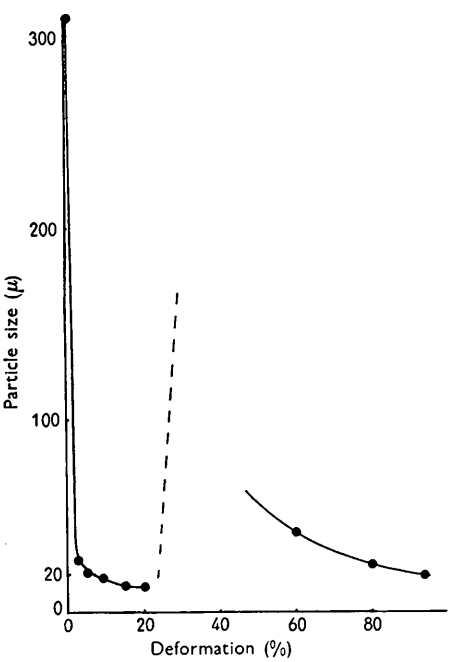

Fig. 5. Variation of particle size with the amount of deformation for zinc.

is similar to that found for tin. At heavy deformations (> 60%) the material consists solely of recrystallized grains, the size of which decreases with increasing reduction, and is much less than the initial grain size of the annealed metal.

(ii) *Examination after various intervals of time after deformation.*—The textural conditions produced by deformations of less than 2% are very stable and are almost unchanged for periods of up to a month after rolling. However, the spots within the arcs become more clearly resolved in this time, the background between them disappearing.

For heavier deformations, as with tin, the sharp spots due to the recrystallized grains grow rapidly, the rate of growth being greater for heavier deformations. The recrystallization may be carried to completion, or it may reach equilibrium with traces of the mosaic structure still present.

(iii) *The effect of annealing.*—The stability of specimens with a purely mosaic structure was again demonstrated by the relatively severe annealing conditions needed for their complete recrystallization; specimens showing recrystallized grains required less severe annealing conditions to promote complete recrystallization.

For this metal, no evidence was found of the rapid growth of the mosaic structure to give a pattern similar to that described for tin. Preliminary results similar to these have been reported by Ramsay (1950).

(*c*) *Lead*

(i) *Examination immediately after deformation.*—The initial annealed grain size of the material was $\sim \frac{1}{2}$ mm. and the deformation was carried out by compression. At the smallest deformations the photographs show an angular spread in the reflexions from each initial grain which increases with increasing deformation. At deformations greater than about 4% reflexions from recrystallized grains are found, and complete recrystallization takes place at deformations of about 30%. After small deformations the diffraction arcs, representing the spread in reflexions from one initial grain, may be resolved using X-ray beams of $\sim 150\ \mu$ diameter, and the limiting mosaic size is found to be $\sim 6\ \mu$. The angular spread of the arcs increases up to about 12% deformation, as shown in Table 1. At heavy deformations (> 80%) the recrystallized grain size ($\sim 40\ \mu$) is much smaller than that found in the annealed material.

(ii) *Examination after various intervals of time after deformation.*—Little change is seen on the photographs taken of the same volume of lead specimens after various periods of time, apart from a slight sharpening of the reflexions clustered into arcs, which occurs at small deformations. It appears that the greater part of the recovery and recrystallization takes place during deformation or before the X-ray photographs have been taken.

(iii) *The effect of annealing.*—The stability of the mosaic structure is again demonstrated by the fact that for specimens showing little recrystallization on deformation annealing for 1–2 hr. at 200° C. is required to obtain photographs showing no traces of arcs, while specimens showing marked evidence of recrystallization immediately after deformation recrystallize completely after more gentle annealing. No evidence of the rapid growth of the mosaic structure has been found for this metal.

(*d*) *Cadmium*

(i) *Examination immediately after deformation.*—In general, the photographs from cadmium are similar to those obtained from the other metals, and complete quantitative measurements have not been made.

At very small deformations, a mosaic structure only is found. At deformations larger than about 2% reduction, reflexions from recrystallized grains begin to appear in the photographs; the frequency of their appearance increases with increasing deformation until, at about 15% reduction, complete recrystallization occurs.

Measurements of the particle size are shown in Table 2. The value of 40 μ at 3% reduction represents the smallest particle size which has been measured. The appearance of the photographs at slightly greater reductions, taken with an X-ray beam of normal diameter, suggests a limiting particle size of about 10 μ. The rapid decrease corresponding to the formation of the mosaic structure is quite clear. No detailed measurements of the changes in misorientations within the deformed grains have been made; however, it is clear from the photographic evidence that the changes are similar to those in the other metals, namely that the range of orientation of the material within a deformed grain increases with deformation.

Table 2. *Mean particle size of deformed cadmium specimens*

Deformation (%)	Mean particle size (cm. $\times 10^{-4}$)
0	~ 1000 (initial grain size)
1	250
3	40
15	~ 600

(ii) *Examination after various intervals of time after deformation.*—For cadmium the mosaic textures of the very lightly rolled specimens are stable over relatively long periods of time. In addition, the growth rate of the recrystallized grains for the more heavily deformed specimens is very much greater than that of the mosaic structure, which tends to disappear with time after rolling.

(iii) *The effect of annealing.*—The stability of specimens showing a mosaic structure without recrystallization is again demonstrated by the effect of the annealing treatments as before.

The rapid growth of the mosaic structure during annealing, which was found in some specimens of tin, was not observed for any cadmium specimen.

5. Physical interpretation

The experimental evidence presented in this paper shows that, at least up to a limiting deformation, a mosaic structure is formed within the grains of the cold-worked polycrystalline metal; this mosaic structure consists of particles slightly misorientated with respect to one another and joined by regions of distorted material. Discussion of possible models for the formation of this structure is given in the third paper of this series.

The disappearance of the background between the diffraction spots in the arcs, with time after deformation, corresponds to a removal of the distorted material between the particles. This is essentially a recovery process and may be due to the polygonization of the heavily distorted boundary regions (Cahn, 1949). Further, the observations carried out with time after deformation and the annealing experiments show that in these metals the mosaic structure is quite stable at room temperature if it is produced by a small deformation.

The occurrence of complete spontaneous recrystallization after the attainment of a limiting mosaic size, and of a maximum angle between particles, suggests that recrystallization commences after maximum distortion of the boundary material. The rapid growth of the mosaic structure in some tin specimens on annealing indicates that it would be difficult by ordinary metallographic methods to distinguish these coarsened sub-structure grains from other recrystallized grains, and suggests that there may be some relationship between the mosaics and the 'recrystallized' grains.

A fuller discussion of recrystallization, and the possible processes by which deformation and recovery can occur, and of the obvious similarities in the behaviour of these metals to those described earlier, is given in a later paper.

The authors would like to express their gratitude to Prof. Sir Lawrence Bragg and Dr W. H. Taylor for their constant help and encouragement. They would also like to thank their colleague, Dr P. B. Hirsch, for much helpful criticism and advice. The work was carried out during the tenure of maintenance grants from the Department of Scientific and Industrial Research.

References

Cahn, R. W. (1949). *J. Inst. Met.* **76**, 121.
Gay, P. & Hirsch, P. B. (1951). *Acta Cryst.* **4**, 284.
Gay, P., Hirsch, P. B., Thorp, J. S. & Kellar, J. N. (1951). *Proc. Phys. Soc.* B, **64**, 374.
Gay, P. & Kelly, A. (1953). *Acta Cryst.* **6**, 165.
Haase, O. & Schmid, E. (1925). *Z. Phys.* **33**, 413.
Hirsch, P. B. & Kellar, J. N. (1951). *Proc. Phys. Soc.* B, **64**, 369.
Ramsay, J. A. (1950). *Nature, Lond.* **166**, 867.
Schmid, E. & Boas, W. (1950). *Plasticity of Crystals*, chap. 6. London: Hughes.