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A Stroboscopic Effect in the X-ray Analysis of Crystalline Aggregates

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An X-ray diffraction technique is described, based on the observation of a stroboscopic effect which results from synchronism between the speed of specimen rotation and the pulse frequency of the incident X-ray beam. The effect consists in regular striations occurring at inclinations varying amongst diffraction spots; these striations can be caused to disappear by heat-treatment. Structural details of a crystalline mass are revealed, which would otherwise not be apparent. A photograph showing striations gives simultaneously the orientation and lattice spacing of a given crystallite, and allows a differentiation between different crystal sizes. Contributions to the background intensity from individual reflecting planes can be distinguished, thus helping the determination of the true width of a given line, visually or by photometry. One potential application is to distinguish between strain and small particle size as causes of line broadening.

Introduction

It is known that in X-ray powder photography the use of a synchronous a.c. motor for rotating the specimen can give rise to anomalous line intensities; the reason is that the X-ray beam is generated in pulses of 50 c./s., so that synchronism occurs between the incident beam and the period of rotation of the specimen. As a result the Bragg reflexion produced by any crystallite in the sample, when passing through the correct angular position, may be suppressed, since no primary intensity is received at periodic intervals corresponding to the blank half-cycle of the rectified a.c. across the X-ray tube. For this reason it is generally recommended to use either a d.c. or an asynchronous a.c. motor drive for specimen rotation, or a belt-and-pulley mechanism.

Some observations have however, been made, which not only show that the effect of synchronism can be turned to good account, but which also disclose structural features of the crystalline mass, believed to be of considerable metallurgical interest.

Experimental observations

The method

The technique employed was that of normal Debye–Scherrer photographs, using either the 9 cm. diameter powder or back-reflexion camera, and specimens in form of small rods (0·3 mm. thick, 5 mm. long). The specimen was rotated by an a.c. (clock) motor at 4 rev./min., and use was made of the synchronism between this period and the primary X-ray beam pulses. These pulses are illustrated in Fig. 1, showing records of the beam on a film moved past a pinhole slit at various speeds.

The specimen materials used were permanent-magnet alloys of the Alnico and Alcomax types, on which a detailed X-ray analysis had been carried out (Oliver & Goldschmidt, 1947). These alloys reveal the effect to advantage, owing to varied transitional states of lattice distortion in which they can exist, but the effect is a general one, not restricted to them. The radiation used was cobalt $K\alpha$, and it is the high-angle reflexion (310) of the body-centred cubic pattern which shows the effects most prominently.

Results

Some examples of the resulting photographs are shown in Figs. 2, 6 and 7 obtained from samples of the same alloy after different heat treatments.

The lines are subdivided, throughout their width, into a series of parallel striations of constant spacing. The striations disappeared when the synchronous motor was replaced by an asynchronous or d.c. drive, as shown in Fig. 7 (*b*).

Two characteristics show that the effect is not a mere experimental 'curiosity', but that it is intimately related to the fine-structure of the material proper: (1) The striations can be made to appear or disappear by different heat-treatments of the same alloy sample. (2) Their inclination varies, not only amongst different samples, but also on the same picture from one diffraction spot to the other, along a given Debye–Scherrer line.

It may further be observed that the striations can be followed far into the background to points which, in their absence, would visually have been considered as lying 'well outside the line'. The existence of the striations therefore permits the interpretation of the apparent background intensity in terms of characteristic Bragg reflexions; evidently a large proportion of the background had been reflected simultaneously with a spot.

A further remarkable feature is that the same sample can produce striated *and* non-striated patterns simultaneously (see Fig. 6, example *J*, where a uniform body-centred cubic pattern envelops a striated one, and example *I*, *J*, *K* and *L*, where a non-striated face-centred cubic pattern also appears).

It is necessary to explain here briefly that in the

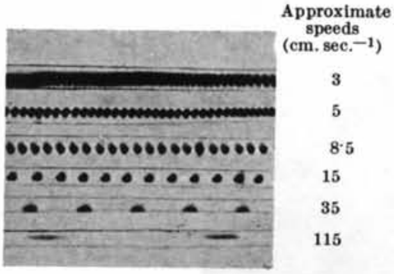


Fig. 1. Periodic image of X-ray beam (pin hole) on a film moved normally to it at different speeds.

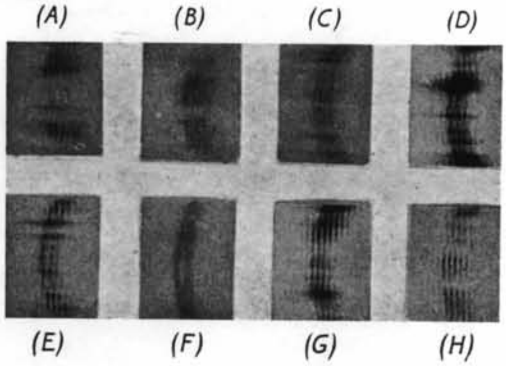


Fig. 2. Examples of end doublets (Co $K\alpha$ radiation, 310 reflexion) illustrating the occurrence of 'striations' on X-ray powder photographs. The samples were thin rods of Alcomax throughout (synchronous motor used), after various heat-treatments. (*A*) As cast. (*B*) Air-cooled 1250° C., without external field; tempered 580° C. (*C*) Air-cooled 1250° C., magnetic field applied parallel to rod axis. (*D*) Air-cooled 1250° C., without magnetic field. (*E*) Air-cooled 1250° C., magnetic field applied normal to rod axis. (*F*) Same rod as *E*, after 4 days 'ageing' at room temperature. (*G*) As cast (further sample). (*H*) As cast (further sample).

The above examples are chosen to illustrate the technique; they should not be regarded as a set typical of Alcomax alloys. In samples (*G*) and (*H*) note discontinuities in otherwise parallel striation sets.

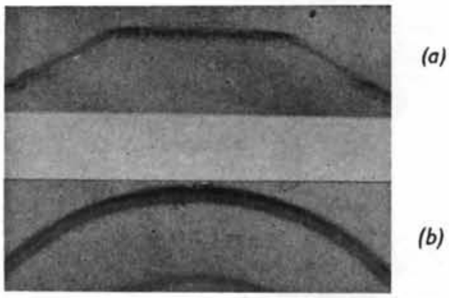


Fig. 3. Striations produced by (*a*) rocksalt, (*b*) aluminium.

Fig. 4. Microradiograph of Alcomax. Cobalt radiation; ×50.

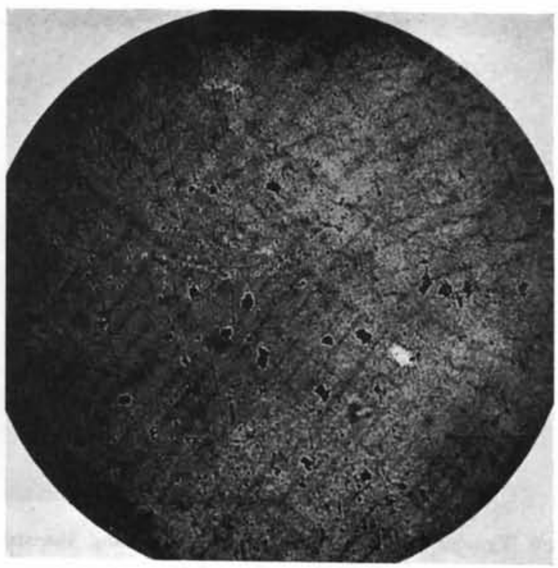
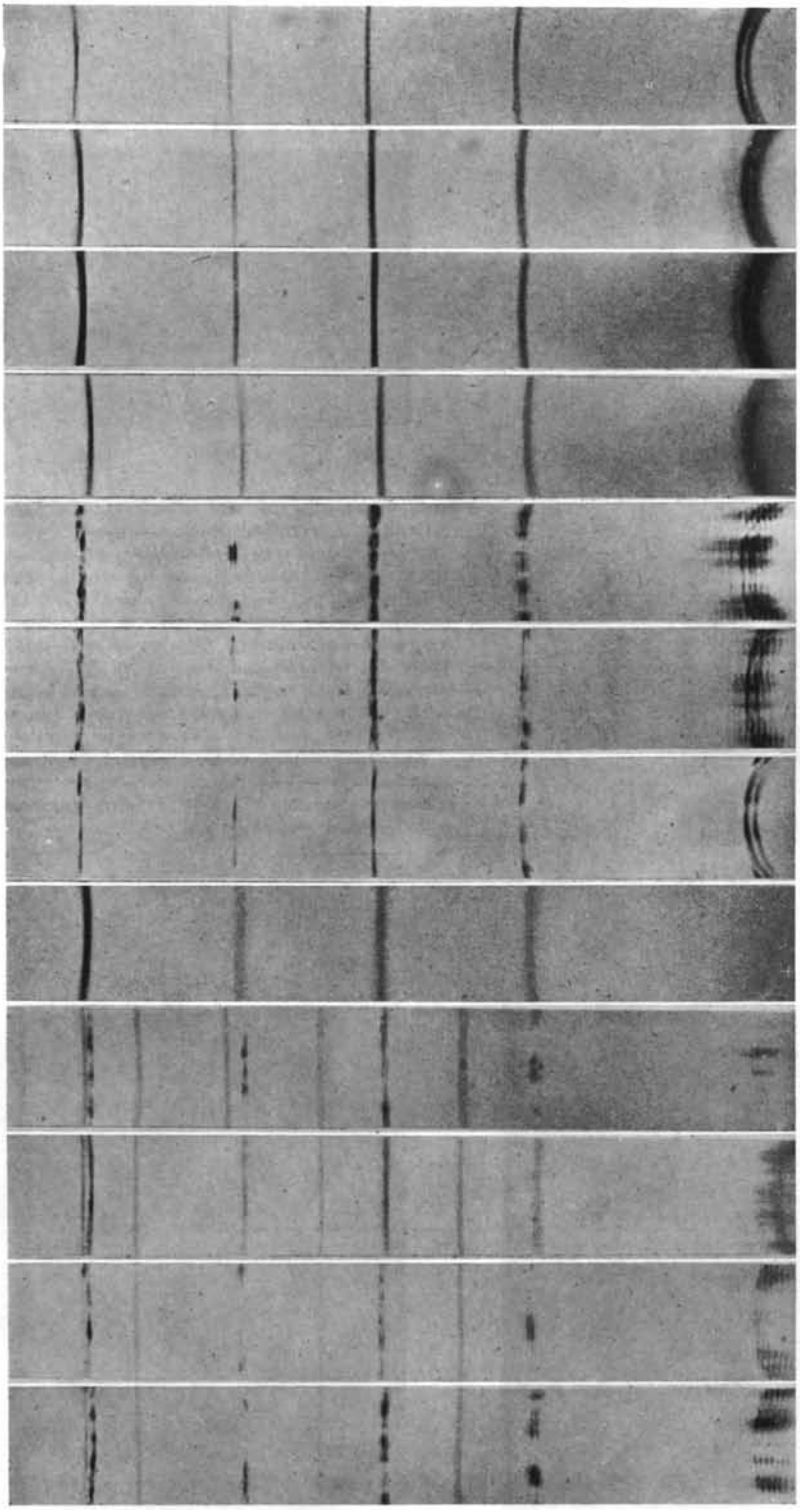


Fig. 5. Microradiograph of Alcomax. Tungsten radiation; ×50.



(A) Quenched 1270° C.

(B) Quenched 1270° C., tempered 690° C.

(C) Quenched 1270° C., tempered 790° C.

(D) Quenched 1270° C., tempered 910° C.

(E) Arbitrary heat treatment.

(F) Arbitrary heat treatment.

(G) Quenched 1270° C.

(H) Same sample as (G), subsequently annealed 1150° C.

(I) Air cooled 1250° C., magnetic field applied normal to rod axis, tempered 580° C.

(J) Air cooled 1250° C., magnetic field applied parallel to rod axis, tempered 580° C.

(K) Further sample, treated as (I).

(L) Air cooled 1250° C., annealed 1000° C.

Fig. 6. Typical powder photographs illustrating the striation effect (Co $K\alpha$ radiation). Synchronous motor used throughout.

(A)–(D) Finely divided powders of Alcomax. (E)–(L) Thin rods of same alloy.

Pictures (A)–(D) (no striations) represent typical line shapes in this alloy, upon which the striations superimpose in the subsequent photographs.

(E) and (F) show the effect extending across the total line-complex, well into the (apparent) background; also the fact that both the sharp and the diffuse lines are contributed by the same crystal, although on the evidence of the non-striated pictures they might have been due to two separate

(G) and (H) are off the identical sample, but (H) as annealed at a lower temperature, causing crystal break-up and absence of striations.

(I)–(L) show the co-existence of phases giving and not giving striations, namely, (I), (K), (L) striated b.c. pattern, non-striated f.c. pattern with superlattice lines; (J) striated b.c. pattern, non-striated second b.c. and f.c. patterns.

The above examples are chosen to illustrate the technique; they should not be regarded as a set typical of Alcomax alloys.

(a)

(b)

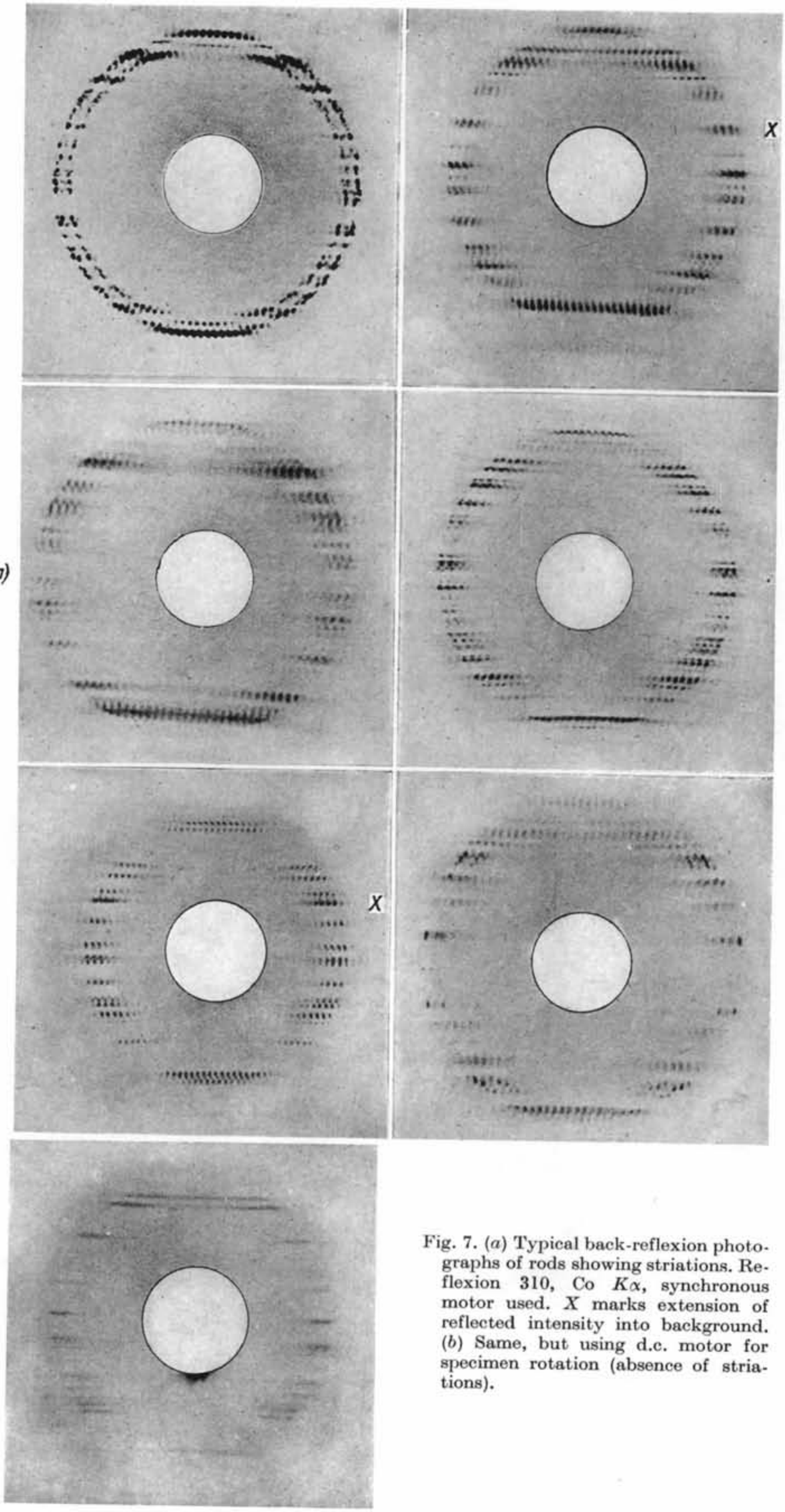


Fig. 7. (*a*) Typical back-reflexion photographs of rods showing striations. Reflexion 310, Co $K\alpha$, synchronous motor used. X marks extension of reflected intensity into background. (*b*) Same, but using d.c. motor for specimen rotation (absence of striations).

present Alcomax-type alloys two body-centred cubic phases of different lattice-constants are liable to be formed, as well as a number of intermediate stages of precipitation and lattice-distortion; lattice-segregates sometimes occur on an atomic scale, manifested by 'side-band' formation adjacent to the principal line (Oliver & Goldschmidt, 1947). After certain heat-treatments the alloy may adopt the face-centred cubic structure, and the diffuse-line complexes observed are often due to martensite-like transition stages. Pictures *A–D* in Fig. 6 illustrate some normal patterns given by the alloy, for comparison with the striated ones underneath. However, the salient fact, for the present purpose, is that the line-width and complexity can vary considerably in this alloy, providing a 'background-canvas' upon which the striations superimpose.*

Three types of striation groupings may be observed

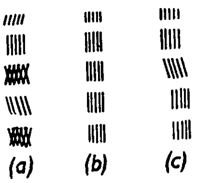


Fig. 8. See text.

as shown diagrammatically in Fig. 8. Case (*a*) is a general one, case (*b*) one of alignment, case (*c*) one of near-alignment. Types (*b*) and (*c*) were found, for instance, in alloys as cast (Fig. 2, *G* and *H*), while various degrees of misalignment are caused by heat-treatment.

It might be queried whether all the striations are produced by the characteristic Co $K\alpha$ wavelengths, or whether the background on either side of the line is due to white radiation. For this purpose, a test was carried out using *monochromatized* radiation (reflexion from bent quartz crystal), with the result that the striations were *still* present and persisted on to apparent background areas. The possibility of white radiation being partly responsible for the spread of striations into the background is thus eliminated.

The origin of striations

A simple general calculation shows that the striations may be quantitatively explained by assuming reflexions from rotating crystal planes, irradiated by periodic X-ray pulses. If a rotating crystalline aggregate such as a fibre-specimen takes t seconds per revolution and receives pulses at a rate of n per second, then the angle δ subtended at the specimen by two succeeding reflexions on a concentric film is given by $\delta = 2\times 360/nt$ (the reflected beam travelling at twice the angular velocity of the specimen); the spacing s between two such reflexions for a camera radius R is

$$s = \frac{\delta \pi R}{180} = \frac{4\pi R}{nt}.$$

In the present case $n = 50$ c./s. (a.c. half-wave rectification is used on the Raymax X-ray set employed), $t = 15$ sec., $R = 45$ mm., which gives

$$\delta_{\text{calc.}} = 0{\cdot}96^\circ \text{ and } s_{\text{calc.}} = 0{\cdot}75 \text{ mm.}$$

The *measured* spacing between successive striations, determined on numerous diffraction spots and on various films, was constant, namely,

$$s_{\text{obs.}} = 0{\cdot}78 \pm 0{\cdot}04 \text{ mm.},$$

giving

$$\delta_{\text{obs.}} = 0{\cdot}99 \pm 0{\cdot}04^\circ.$$

Thus, without detailing the nature of the reflecting elements, the existence and period of striations can be attributed to reflecting planes in individual crystals acting in mirror-like fashion. But this does not explain the physical nature of the 'mirror-facets', nor the length or varying inclination of the striations.

Two alternatives must be considered:

(1) The small crystal blocks form a mosaic of slightly misaligned units, and the varying orientation of (in this case) their (310) planes introduces varying angles of tilt (see Fig. 9(*d*)).

(2) The lattice planes are bent. A curved crystal can be approximated by a fragmented one (as in Fig. 9(*a*) and (*b*)), and in this case the sample may be visualized as a series of cylindrical mirrors, the axes of curvature of which vary in direction (Fig. 9(*c*)). We may consider this as a type of polygonization,

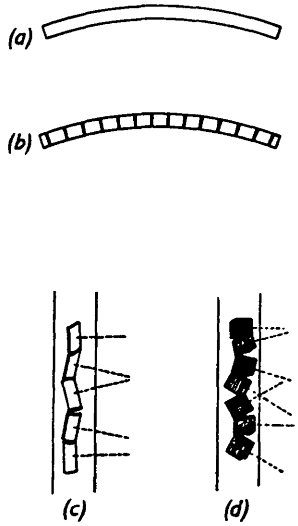


Fig. 9. See text.

* Orowan (1942), by his rotating grid method of crystal analysis, has obtained X-ray photographs resembling the present striation patterns, although of course, the method used and the reason for the striations were entirely different. They were shadow lines inscribed on each reflection spot by a grid of fine copper wire rotating in front of the film in synchronism with the specimen, but some of the information Orowan is able to obtain from the resulting photographs is similar to that given by the present method.

a term used first by Orowan (1947) and by Cahn (1948, p. 136), in a number of French papers (Lacombe & Beaujard, 1947; Guinier & Lacombe, 1948; Lacombe & Berghezan, 1948; Guinier & Tennevin, 1949), and in many subsequent ones.

As defined so far, polygonization is generally regarded as produced by external bending forces upon single-crystal lamellae, with subsequent fragmentation on annealing; although the present permanent-magnet alloys have not been subjected to mechanical work, it is nevertheless possible to account for such bending forces upon the lattice planes by internal stresses developed during the manifold transformations known in these alloys (Oliver & Goldschmidt, 1947). For instance, anisotropic changes in atomic volume of neighbouring crystals caused through the f.c.c./b.c.c. transformation observed can well exert a bending moment, and the resultant fragmented crystal can then be considered as polygonized. Fragments in a curved and polygonized crystal would contribute to a single diffraction spot or group of spots of the type observed by Cahn (1949).

Laue photographs taken on some of the present rods show asterism, which would also be consistent with the presence of lattice curvature. No intensity maxima within the asterism spots were, however, seen.

According to the present evidence both explanations (1) and (2) may be correct, and both actually apply in different cases; but one factor adverse to the lattice-bending theory being the exclusive one is the fact that the striation effect is a general one observed also on other materials in which there was no reason to suppose the existence of lattice curvatures. For example, a single crystal of rocksalt gave the striations shown in Fig. 3(*a*), while an aluminium rod (kindly provided by Mr Hirsch of the Cavendish Laboratory), consisting of a large crystal embedded in a fine particle-size debris, produced the striation pattern superimposed on a continuous reflection shown in Fig. 3(*b*). Furthermore, in the case of a bent lattice, it should be possible to detect a focusing effect on the image produced by the curved reflector planes, i.e. sharp striations should appear only for a specific specimen–film distance, the determination of which would facilitate the actual measurement of the curvature. Photographs taken for this purpose at five different distances showed, however, a simple enlargement of striation size and distance, which would be consistent with the assumption of plain mosaic blocks rather than a curved lattice.

The varying inclinations would thus be due essentially to the varying orientation of a small number of crystal blocklets, either undistorted or curved (as in Figs. 9(*d*) and (*c*)).

The length of the striations is readily explained. A given Debye–Scherrer line is inherently discontinuous along its length, owing to the fact that the rod sample was coarsely crystalline. Each individual diffraction spot is associated with a single crystal within the specimen, and the striations, both in length and spread, delineate the reflected area of intensity contributed by this crystal. Coarse crystallinity does not, of course, itself account for the striations, except in so far as it it helps to reveal them. For a polycrystalline powder, the striations would, in all probability, also occur, but be obliterated through random orientation and overlap of spots.

Evidence in support is obtained from the fact that, whereas a finely divided powder of Alcomax gives perfectly uniform lines without striations (always using a synchronous motor, see Fig. 6(*A*)–(*D*)), there are some exceptional powder photographs of the same alloy, for which the powder contained a few coarse grains of a size just sufficient to cause normal uniform lines to be resolved into spots. In this case striations are already discernable, as such crystals would simulate a small 'rod sample' within the powder.

A single set of striations is thus produced by a single crystallite, or by two or more smaller aligned ones of the same orientation. It is a special feature of the present permanent-magnet alloys that precisely aligned but distinct crystal fragments sometimes occur, able to cohere in brick-like fashion, and such a sequence of aligned fragments would, in effect, behave like a single crystal. A slight misalignment would then show itself in a change in direction as sketched in Fig. 8(*c*) and, for instance, in Fig. 2(*G*). This parallelism, with occasional breaks, is pronounced in as-cast alloys. In some cases, in which two sets of striations may be seen to overlap (giving a cross-hatching effect), these will be due to two different crystals or crystal groups.

Suggested applications

Applications based on crystal size

The fact that the striations are associated with large crystal size also explains why, by heat-treatment, it is possible to remove them and sometimes actually to obtain on one photograph two simultaneous patterns with and without striations. Their absence would indicate crystallite sizes of an order less than 10^{-3} cm., their presence sizes of a greater order.

Thus, as may be seen in examples of Fig. 6(*I*) and (*J*), for coarsely and finely crystalline phases co-existing in the same sample, they automatically mark themselves as of a greater or lesser order of magnitude by the presence or absence of striations.

A further suggested application lies in the field of determination of internal stress by X-rays. Line broadening caused by either lattice strain (variation in spacing) or very fine particle size can be distinguished through the presence or absence of striations. If striations superimpose upon a broad line, small particle size could not have been the cause of this broadening, but only lattice strain or possibly composition fluctuations. The present Alcomax alloys furnish an example of strain broadening, though, *a priori*, and without striations, small crystal size might have been a possible cause of the broadened lines observed for instance in Fig. 6(*B*)–(*F*).

It is true that, once the lines become clearly resolved into spots, this will of course also reveal coarse crystallinity; but the striations are considered a more sensitive and definite criterion, because they appear even in cases where spottiness is not yet discernable or is masked through the merging of spots within the frame of an apparently smooth line.

Visibility of weak intensities

In problems such as that of martensite, in which high-angle reflections are frequently so diffuse that they elude visibility, the striation effect increases the chance of their presence being disclosed by reason of the periodic variations in intensity of the reflections, showing the characteristic separation. The present Alcomax photographs provide an actual instance of this, since the structural changes are martensite-like. Intensity areas such as those marked *X* in Fig. 7 would normally have been considered as 'background', but are here revealed as part of reflexion (310).

In problems, therefore, like stress measurement, where a quantitative measure of overall line width is required, this can be determined more accurately than is otherwise possible by noting the beginning of periodic background fluctuations, however faint. Clearly a large proportion of the seeming background intensity has been reflected simultaneously with a spot, and is revealed through the striations, so that the real extent of the reflection is disclosed and can be included when integrating the intensities.

In microphotometry, the principle can be directly utilised. Intensity figures are frequently inaccurate, because the background level adjoining a line is ill defined, and errors in integration may arise through arbitrariness in deciding where it should be placed. The striations help to distinguish genuine line from true background by locating the 'boundaries' of a line. The total line intensity is then defined by the area between the envelope of periodic maxima and the background level, delineated by the envelope of minima (see Fig. 10). Thus the presence of periodic blank

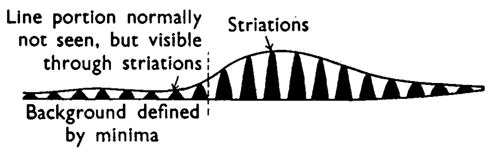


Fig. 10. Diagramatic photometer curve.

portions on the film provides closely spaced reference points of zero intensity against which the adjoining peaks can be calibrated. (Some qualification is however necessary in this respect, as the minima may not in practice reach zero, but remain finite, because the radiation is not strictly monochromatic. The background can however, perhaps more suitably, be deduced by interpolating from the level surrounding the line, itself more accurately defined by the striations.)

Summarizing, it is suggested that the synchronous effect has the following potential uses in the X-ray analysis of the crystalline mass:

(1) For distinguishing between different crystallite sizes, and in some cases, between lattice strain and small particle size as causes of the line broadening.

(2) For distinguishing genuine diffraction line from background in 'labelling' presumed areas of background intensity as associated with a given reflected spot and crystal plane; this would assist for instance, in precision photometry, in stress determination, and in the study of precipitation effects.

(3) For automatically revealing the orientation and lattice spacing of a given crystallite, and varying orientations amongst different crystallites in the same sample.

It is clear that the present effect requires much further study, and this account should be regarded only as in the nature of a first communication.

The writer wishes to express his sincere thanks to Mr D. A. Oliver, Director of Research, the B.S.A. Group of Companies, for his encouragement, and to Dr W. H. Taylor and Dr Audrey M. B. Douglas at the Cavendish Laboratory, for most valuable comments.

APPENDIX

Micro-radiographs of Alcomax

Some direct evidence of a sub-grain structure existing in Alcomax is obtained from X-ray micro-radiographs. These were taken of 0·002 in. thick platelets of the alloy, and two examples are shown in Figs. 4 and 5. The darker lamellae of 2μ width which in Fig. 5 subdivide the grain into lighter blocklets of approximately 10μ width correspond to regions of lower absorption (to the Co and W radiations used), namely to segregates of a composition enriched in aluminium. Families of sub-grains may be seen, in themselves aligned, but abruptly changing direction.

It is hoped to give a more detailed account of this sub-structure which may well be related to the changes in inclination observed amongst the striation groups.

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