The Sulphiding of Mild Steel Surfaces

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Electron-diffraction studies of the reactions between mild steel and sulphur, and mild steel and hydrogen sulphide, are described. All the known forms of iron sulphide were found to be formed under characteristic conditions. In addition a previously unknown cubic iron sulphide was observed. It appears to have a structure analogous to that of γ-Fe_2O_3.

Introduction

In the experiments described below the structure of iron sulphide layers formed on mild steel surfaces under various conditions was investigated by electron diffraction and was compared with the available X-ray data obtained from the known sulphides of iron.

The structure of sulphides of iron deduced from X-ray diffraction experiments are as follows (Wyckoff, 1948):

(1) FeS, which has a hexagonal lattice with $a_0 = 3\cdot438$, $c_0 = 5\cdot880$ Å, or deficit-type variations (of the form FeS_{1+x}, where $x \not> 0\cdot1$), including superlattices of the following types:

(*a*) troilite, for example, having
$a_0' = 5\cdot022$ ($\approx \frac{3}{2}a_0$), $c_0' = 11\cdot748$ Å ($\approx 2c_0$);

(*b*) pyrrotite, having
$a_0'' = 6\cdot87$ ($\approx 2a_0$), $c_0'' = 22\cdot7$ Å ($\approx 4c_0$) .

(2) FeS_2, which occurs in two forms:

(*a*) Marcasite, which is orthorhombic with $a_0 = 4\cdot436$, $b_0 = 5\cdot414$, $c_0 = 3\cdot381$ Å;

(*b*) pyrite, which is cubic with $a_0 = 5\cdot4066$ Å.

Chemical analyses of iron sulphides have been said to indicate the existence also of Fe_2S_3 and Fe_3S_4, but X-ray examination of such preparations was inconclusive (Lipin, 1943).

In the study of reactions occurring on solid surfaces, chemical analysis and X-ray diffraction are of limited usefulness since they cannot yield much information about the early stages of the reaction. Reflexion electron-diffraction techniques, on the other hand, can detect changes in the physical and chemical state of surface regions as thin as 25 Å, and are therefore particularly suitable for this purpose. Although the oxidation of iron and steel surfaces has been studied in detail previously by electron-diffraction methods, it seems that there has been no similar detailed investigation of the sulphiding of iron or steel. In these

experiments the sulphides formed on mild steel by sulphur (at elevated temperatures in vacuum, and in air) and by substances containing active sulphur have therefore been investigated with the aid of reflexion electron diffraction.

Experimental details

1. Surface preparation of mild steel

Mild steel discs of $\frac{1}{2}$ in. and $\frac{1}{4}$ in. diameter were used for these experiments. The following surface finishes were applied:

(*a*) *Lathe turned*.—The surface was machined on an automatic lathe under fixed conditions. After turning, the surface was cleaned with grease-free benzene.

(*b*) *Polished*.—Usual metallographic polishing techniques were applied. The surface was first abraded with successive grades of emery paper from 0 to 0000. Grease-free benzene was used to free the debris during abrasion, and to clean the surface. It was then polished mechanically using levigated alumina with distilled water. The alumina was finally removed by distilled water, and the surface was dried and degreased with grease-free acetone.

2. Methods of sulphiding

(*a*) *Sulphur vapour in vacuum*.—The sulphur and the steel were heated electrically in a silica tube by means of a tungsten strip wound round the outside. The tube was continuously evacuated with a rotary pump and a mercury-vapour pump (with a liquid-air trap in the system).

Great care was taken to ensure that the vacuum was good (i.e. at least 10^{-5} mm. Hg) since a poor vacuum led to the formation of iron oxide even when the sulphur was visibly evaporating and subliming over the steel. An example of an electron-diffraction pattern obtained from an oxide formed in this way at 500° C. is given in Fig. 1. By comparison with X-ray diffraction data from the A.S.T.M. file (1945–53) this has been identified as Fe_3O_4 or γ-Fe_2O_3. In such an arc pattern the intensities of the rings cannot be

specified sufficiently accurately to distinguish between these two very similar structures.

To check the vacuum a Pirani gauge was used, the hot wire being of platinum to minimize corrosion. The temperature of the specimens being sulphided was measured with a platinum platinum–rhodium thermocouple, and sensitive bridge.

(b) *Hydrogen sulphide.*—Hydrogen sulphide, produced by the action of distilled water on aluminium sulphide, and dried by passing through activated alumina, was then passed into a tube containing the mild steel disc. To ensure that all the air was displaced from the apparatus the gas was slowly passed for half an hour. The specimen tube was then heated as quickly as possible to the desired temperature by an external electric heating coil. This temperature was kept constant for the length of time required, by adjustment of the current in the coil, after which the specimens were cooled as rapidly as possible by removing the heating coil and its former (the fume cupboard draught asisted the cooling). The temperature was measured using a mercury-in-glass thermometer.

(c) *Other methods.*—Attempts were made to produce sulphide films on freshly-exposed mild-steel surfaces at room temperature by abrasion of the steel on emery cloth under solutions containing active sulphur, and by simple immersion of freshly abraded mild steel in these solutions for periods of up to 50 hr. The solutions used were

    (i) benzene saturated with sulphur,

    (ii) benzene containing 9% carbon disulphide,

    (iii) carbon disulphide,

    (iv) liquid paraffin containing 0·5% diethyl trisulphide.

The action of molten sulphur on polished mild steel surfaces was investigated at temperatures of up to 300° C.

The action of 62% H_2SO_4, reported by Hemptinne (1898) to produce films of ferrous sulphide on iron, was also investigated at room temperature and at 110 and 140° C.

Results

(a) The action of sulphur vapour in vacuum

(i) *Formation of* FeS *on polished mild steel.*—This occurred when the concentration of sulphur vapour was low, the sulphur at the end of the tube remote from the specimen being heated to a temperature of approximately 40° C. Electron-diffraction patterns of the iron sulphide formed at 150, 250, and 400° C. are shown in Fig. 2 and correspond to a composition approximating to FeS.

The diffraction pattern given by the FeS formed at 150° C. has rather diffuse rings (Fig. 2), from the breadths of which the average crystal diameter was estimated to be in the region of 100 Å. The slightly increased intensity in the plane of incidence of the fourth ring from the central spot—the 110 ring from the hexagonal FeS crystals with $a = 3\cdot43$, $c/a = 1\cdot66$ (Wyckoff, 1948)—shows that the crystals had very slight preferred orientations with their (110) plane parallel (or nearly so) to the mild-steel substrate.

Electron-diffraction patterns taken with specimens sulphided at temperatures between 250 and 400° C. (examples are shown in Fig. 2(b) and (c)) showed that the mean crystal size of the FeS increased with temperature of sulphiding and that in the surface regions of the deposits strong preferential growth of the crystals had occurred. The crystals were orientated with a (110) plane parallel, or nearly so, to the mild-steel substrate surface plane.

In the electron diffraction pattern (Fig. 2(c)) from the sulphide formed at 400° C., a faint extra ring can be seen half-way between the central spot and the (110) ring. This shows the presence of a modification of the normal hexagonal structure, having a true lattice which was a superlattice of the normal structure. Its basal axes were 6·86 Å, twice the normal size for FeS, and its presence was probably due to an excess of sulphur (or defect of iron) in the lattice.

(ii) *Formation of marcasite on polished mild steel.*—This also occurred when the concentration of sulphur vapour was low, being observed after reactions at temperatures of 215 and 225° C. The marcasite formed at 215° C. showed no preferred orientation (Fig. 3(a)). That formed at 225° C. yielded uniform rings, which agreed with the plane spacings in the marcasite lattice, together with intense arcs, which did not all agree with plane spacings due to marcasite (Fig. 3(b)). These arcs are in analogous positions to the main arcs appearing in Fig. 5, and must be due to the presence of the sulphide giving rise to that pattern. The film therefore consisted of a mixture of unorientated marcasite and the other sulphide. The occurrence of both patterns together makes it possible to determine the unit cell dimensions of the second sulphide with high accuracy (see § (iv)).

(iii) *Formation of pyrite on polished mild steel.*—This occurred when the concentration of sulphur vapour was very high, the sulphur quickly evaporating and passing over the hot mild steel. Electron-diffraction patterns of pyrite formed at 200 and 300° C. are shown in Fig. 4. At 200° C. the pyrite showed slight preferential orientation with its (200) plane parallel to the mild-steel substrate surface plane. At 300° C. the (200) orientation was more pronounced, and in addition three extra arcs were observed, corresponding to the cubic sulphide to be described in the following paragraph. A trace of it was therefore present with the pyrite.

(iv) *The formation on polished mild steel of an iron sulphide having a structure similar to that of* γ-Fe_2O_3.—With a high concentration of sulphur vapour, when the sulphur was slowly but visibly evaporating and passing over the hot mild steel, a type of sulphide was formed at 200 and 300° C. that gave electron-diffrac-

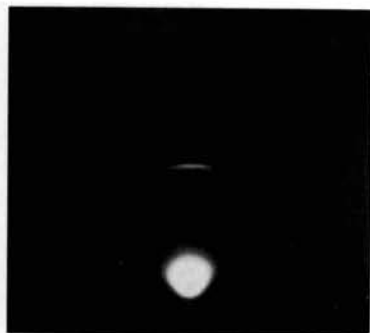Plate 3

Fig. 1. γ-Fe_2O_3 or Fe_3O_4 film formed on mild steel at 500° C. in presence of sulphur vapour in poor vacuum ($\sim 10^{-3}$ mm. Hg.).
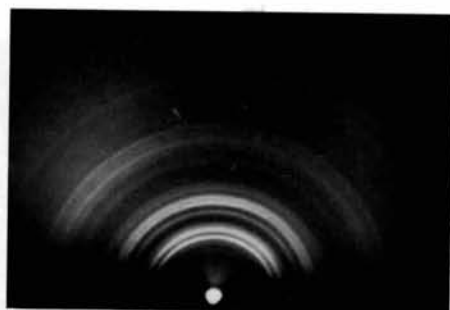

(a)   (b)   (c)

Fig. 2. FeS film formed by action of S (a) at 150° C., (b) at 250° C., (c) at 400° C.

(a)   (b)

Fig. 3. Marcasite film formed by action of S (a) at 215° C., (b) at 225° C.

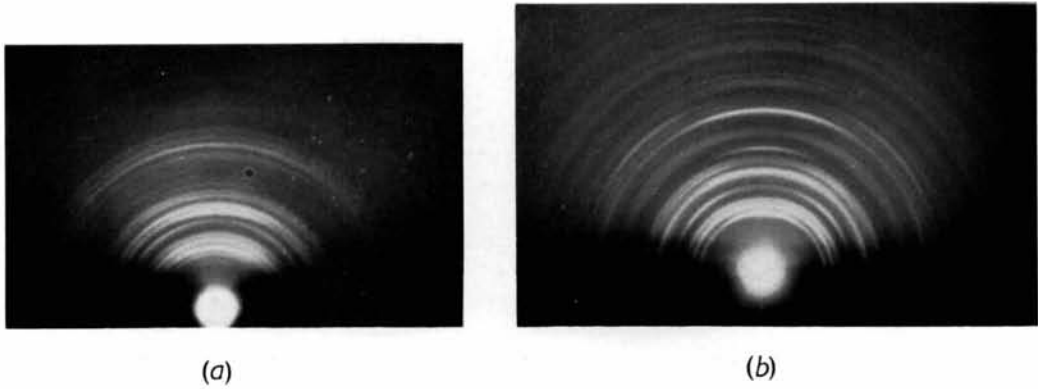(a)   (b)

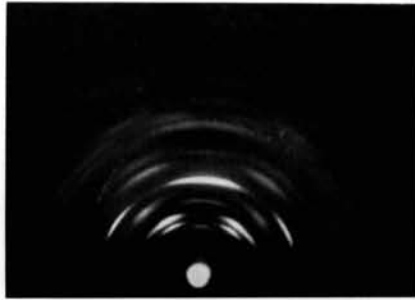Fig. 4. Pyrite film formed by action of S (a) at 200° C., (b) at 300° C.

Fig. 5. Sulphide film formed by action of S at 300° C.
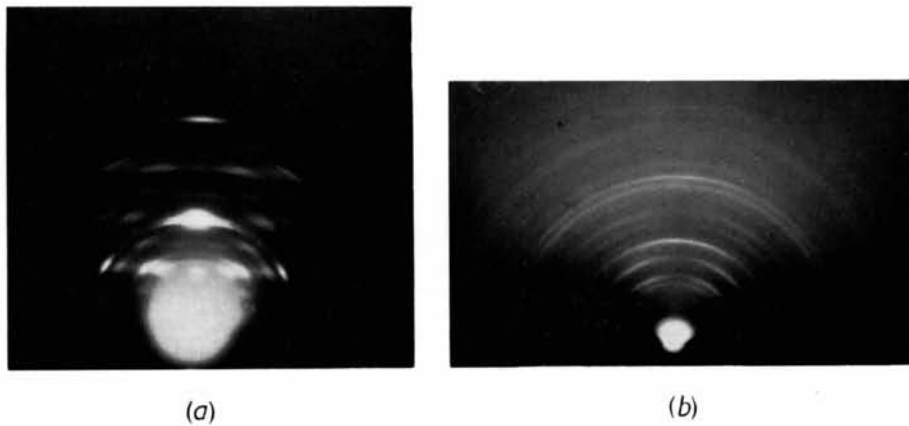

(a)   (b)

Fig. 6. (a) Sulphide formed in H_2S at 250° C.   (b) FeS film formed in H_2S at 250° C.

tion patterns, such as Fig. 5, that could not be completely interpreted in terms of any of the known structures of iron sulphides. The same sulphide was formed by the action of hydrogen sulphide on polished mild steel at temperatures of 250–300° C.

Fig. 5 bears a resemblance to Fig. 2(c) from the hexagonal FeS, with a superlattice having basal axes twice the normal length. Not all the plane spacings associated with the arcs in Fig. 5 can be explained by this superlattice, however. Doubling the c axis makes it possible to account for more of the plane spacings, and approximate quadrupling of this axis makes it possible to explain nearly all of them. The axial ratio in this case is 3·26, the basal axis being 6·86 Å.

To explain the positions of the main arcs the orientation of this lattice would be such that $(11\bar{2}0)$ planes were parallel to the mild steel substrate surface plane. A diagram of the arcs to be expected in this case is shown in Fig. 7(a). By comparison with the arcs
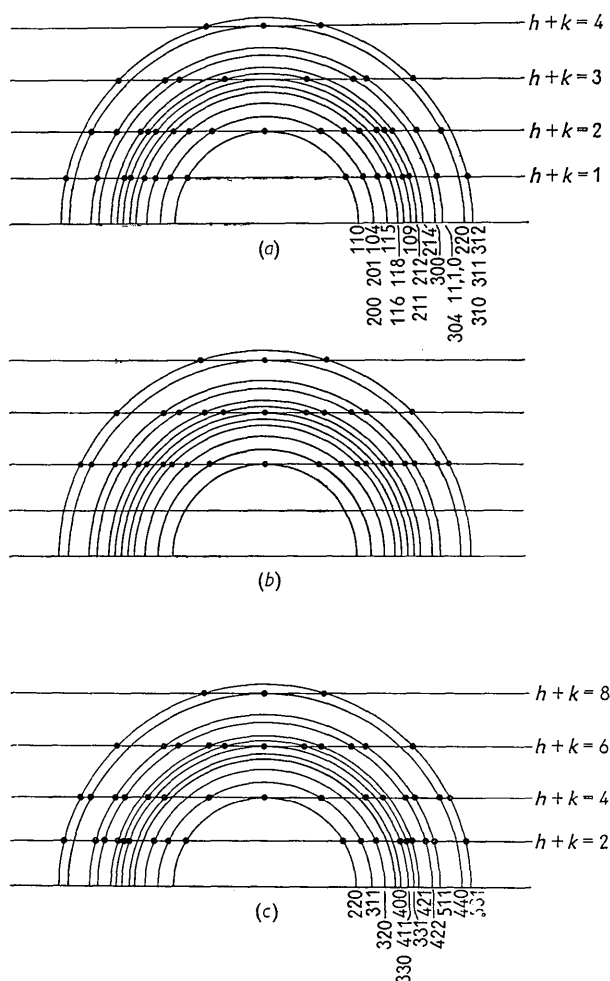

(a)

(b)

(c)

Fig. 7. (a) Arcs expected for hexagonal FeS with superlattice such that $a = 6\cdot86$ Å and $c/a = 3\cdot26$, and orientated with $(11\bar{2}0)$ planes parallel to substrate surface. (b) Arcs observed in Fig. 5. (c) Arcs expected for face-centred cubic iron sulphide with $a = 9\cdot62$ Å, in (110) orientation.

actually observed (drawn to the same scale in Fig. 7(b)) it will be seen that not quite all of the observed arcs are explained. In addition, two arcs on the layer line $h+k = 2$, corresponding to the intersections of the (009) ring and the (330) ring, can be seen in the electron-diffraction pattern. These could not appear in this position from the hexagonal lattice in this orientation.

In considering other values of the axial ratio, good agreement was noted with a value of 2·46. A hexagonal lattice of this ratio can, if rhombohedral, be described as face-centred rhombohedral with $\alpha = 90°$, i.e. face-centred cubic. The pattern had been noted to be similar as regards intensities of diffraction, as well as relative plane spacings, to that of the face-centred cubic form of Fe_2O_3 (γ-Fe_2O_3, see Fig. 1). An explanation of the arcs concerned in terms of the face-centred cubic lattice was therefore considered. With such a lattice, it was possible to assign plane spacings to all but one of the rings, though two of them had indices 330 and 421 respectively which do not appear in diffraction from normal face-centred cubic lattices, their structure factor being zero. They have, however, been observed in X-ray diffraction patterns of γ-Fe_2O_3 (A.S.T.M., 1945–53).

To explain the positions of the main arcs, the orientation of this lattice would be such that (110) planes were parallel to the mild-steel substrate surface plane. A diagram of the arcs to be expected in this case is shown in Fig. 7(c). By comparison with the arcs actually observed it will be seen that three of them, on the layer line $h+k = 4$, are not explained. They are the ones that would lie on intersections of the 330 and 421 rings with this line, and the intersection of the ring that could not be due to this cubic structure at all.

The three unexplained arcs in this case were explained in terms of the hexagonal lattice already considered. It seems very likely, therefore, that the iron sulphide film consisted of a mixture, one constituent being an iron sulphide having a modified FeS structure (probably with excess sulphur). The true lattice of this was a superlattice of the basic FeS structure ($a = 3\cdot43$ Å, $c/a = 1\cdot66$, here with basal axes of 6·86 Å and an axial ratio of 3·26. The other constituent probably approximated in composition to Fe_2S_3 or Fe_3S_4, with a face-centred cubic structure similar to that of γ-Fe_2O_3, or Fe_3O_4, with the positions for iron and sulphur atoms in the lattice similar to those of the iron and oxygen atoms in the γ-Fe_2O_3 lattice. The cube side, determined by reference to the marcasite and pyrite patterns with which it sometimes occurred is 9·62 Å ±2%.

(v) *Formation of iron sulphides on lathe-turned mild steel.*—After prolonged exposure at temperatures of less than 400° C., practically no film could be detected from electron-diffraction patterns, or from visual examination of the specimens. After exposure at 500° C. with a high concentration of sulphur, however, a thin film of FeS was detected. The film was unorientated,

and measurements of the change in weight of the specimen ($\sim 10^{-5}$ g.) showed that the film was about 100 Å thick, assuming uniform sulphiding over the whole surface area of the specimen.

(b) The action of hydrogen sulphide

The action of hydrogen sulphide was studied at temperatures between 220 and 280° C. At temperatures in this range, films giving the same patterns as those shown in Fig. 5 were formed on polished mild steel (Fig. 6(a)) when the mild steel was kept at this temperature for 5–10 min. only. These films must therefore have consisted of Fe_2S_3 or Fe_3S_4. Keeping the specimen at this temperature for longer periods (30–45 min.) resulted in the formation of films of pure hexagonal FeS orientated with (110) planes parallel to the mild steel substrate surface (Fig. 6(b)). No extra rings were observed.

Under the same conditions lathe-turned mild steel heated for 30–45 min. yielded a similar electron-diffraction pattern, though the arcs and rings were broken up into small spots. This indicated that the crystals of sulphide were about 500 Å in diameter. Measurement of the change in weight of the specimens showed that the film was about 2·0 microns thick, assuming uniform sulphiding over the whole surface of the specimen.

(c) Other methods

No trace of sulphide of any sort was observed after abrasion or immersion of the mild steel in any of the active-sulphur-containing solutions described. The surface appeared the same after abrasion and immersion as before, visually and by electron diffraction. (Apparent tarnishing of mild steel abraded under 0·5% diethyl trisulphide in liquid paraffin was explained by other observations on abrasion under pure liquid paraffin, which resulted in the same apparently tarnished appearance, due presumably to the roughening caused by the abrasion.)

Only very slight staining of the surface of polished mild steel was observed after immersion in sulphur at 200–300° C. for up to 6 min. The electron-diffraction pattern then consisted only of diffuse haloes and gave no indication of the chemical nature of the surface film.

No more than slight traces of oxide (γ-Fe_2O_3 or Fe_3O_4), and very slight traces of sulphide, possibly pyrite, were observed after immersion of mild steel in 62% H_2SO_4. The action of the acid was prolonged for periods of up to 45 min. without further evidence of films of FeS being formed.

Conclusions

The reactions of sulphur on mild steel were observed to be inhibited by the presence of air (i.e. oxygen). For example, no reaction was observed when mild steel was abraded under solutions of sulphur in benzene, and there was no reaction between sulphur vapour and mild steel at temperatures of up to 500° C. in a poor vacuum, only oxide films being formed. The difficulty of forming a sulphide film on mild steel that has presumably been slightly oxidized by exposure to air during lathe turning shows that it is the presence of iron oxides covering the steel surface that inhibits the action of the sulphur, even under conditions where a thick sulphide film was formed on polished mild steel.

When oxygen had been almost completely excluded (in a vacuum of the order of 10^{-5} mm. Hg) sulphur vapour was observed to react with mild steel to form one or other of the known iron sulphides (FeS, pyrite and marcasite) under characteristic conditions of temperature and concentration of sulphur. These may be summarized as follows:

1. FeS was formed when the concentration of sulphur vapour was very low, and at temperatures between 150 and 500° C.
2. Marcasite (FeS_2) was formed when the concentration of sulphur vapour was not quite so low, but only in a narrow temperature range, approximately 215–225° C.
3. Pyrite (FeS_2) was formed when there was a high concentration of sulphur vapour, and at temperatures from about 300° C. to 400° C.

The FeS formed by the action of sulphur vapour can have a range of structures, probably due to an excess of sulphur over the stoichiometric ratio. In some cases, although the diffraction pattern shows strong arcs corresponding to the normal hexagonal lattice an additional faint diffraction arc ($\frac{1}{2}\frac{1}{2}0$) showed the presence of a trace of superlattice with basal axes, a, twice the normal value, the third axis, c, being so far undefined. In other cases a large proportion of such a hexagonal superlattice was present, having a twice the normal value, and c about four times the normal value (this is similar to that observed by Bertaut (1952)). Along with this superlattice a quite distinct new form of sulphide occurred, having a face-centred cubic structure, with cube side of 9·62 Å$\pm$2%.

The relative intensities of the arcs were similar to those observed with γ-Fe_2O_3 and Fe_3O_4, and thus this sulphide must have had a composition corresponding approximately to Fe_2S_3 or Fe_3S_4. Such a sulphide has not been observed previously by X-ray diffraction. However, Sinha (1954) in this laboratory, by the action of yellow ammonium sulphide on ferric chloride solution, obtained an iron sulphide (Fe_2S_3) which transmission electron-diffraction patterns showed to have a face-centred cubic lattice with $\alpha_0 = 5\cdot060$ Å (referred to NaCl which was also present), i.e. approximately half the cube side in the present case.

The new cubic iron sulphide was also formed in the present experiments by the action of hydrogen sulphide on mild steel at 220–280° C., if the action was

allowed to proceed for only a short time (about 6 min.). The Fe_2S_3 may be unstable when the sulphide film thickness becomes several thousand Ångströms or more, since further growth (reaction for 30–45 min.) leads to the formation of nearly pure normal FeS. Epitaxial misfit on the substrate may have affected the stability.

As is to be expected, the action of hydrogen sulphide is not inhibited by an oxide film at these temperatures, probably owing to a reaction of the type

$$2\ Fe_3O_4 + 9\ H_2S \rightleftarrows 3\ Fe_2S_3 + 8\ H_2O + H_2$$
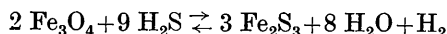
being driven over to the right by the high concentration of hydrogen sulphide.

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A Note on the Measurement of Lattice Spacings from Unannealed Powders or Filings

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A procedure is described for measuring the lattice parameters of cold-worked powder specimens which may, or may not, contain deformation stacking faults.

1. Introduction

The measurement of lattice spacings of annealed powders is now an accepted technique, and an accuracy of the order 1 part in 30,000 to 1 part in 100,000 can be obtained by standard extrapolation methods. In the study of some alloys of high melting point, the measurement of lattice spacings from unnealed powders or filings may be valuable. It is, for example, difficult to anneal and quench filings from temperatures above 2000° C., although lumps of alloy may be quenched satisfactorily, and, from these, filings may be prepared and examined in the cold-worked state. Where the etching of alloys is difficult the determination of phase-boundaries by lattice-spacing measurements is attractive, and should be possible if accurate determinations can be made on cold worked material. The present note describes a method by means of which lattice spacings can be measured to an accuracy of the order 1 part in 3,000 to 1 part in 10,000, using un-annealed powders or filings.

2. General method

Anantharaman & Christian (1953) have described an analytical method based on Rachinger's graphical procedure by means of which the line profile of a diffuse $K\alpha$ line may be resolved into its constituent $K\alpha_1$ and $K\alpha_2$ profiles. The method assumes that the lines are symmetrical about their peaks, and that the intensity ratio of $\alpha_1:\alpha_2$ is 2:1. Subject to this assumption, overlapping doublets which have been broadened symmetrically by cold work may be resolved into their constituent α_1 and α_2 profiles. Variation in background intensity must be allowed for.

In the present work, the line profiles were measured by standard methods on a Philips Geiger-counter X-ray diffraction unit, using flat powder specimens. It was sometimes necessary to apply a dead-time correction for counter losses.

3. Body-centred cubic structures

For these structures the method is straightforward, because stacking faults are not produced by cold-working. All lines are broadened symmetrically, and the peak positions are not affected. It is, thus, necessary only to analyse the profiles of three or more lines, and to follow the normal extrapolation procedure. In order to test the method, experiments were made on pure iron, and on iron–chromium alloys whose lattice spacings had been measured in a 19 cm. Unicam camera by Sutton & Hume Rothery (1955). The results are shown in Table 1, from which it will be seen that the greatest difference between the lattice spacings determined by the two methods is 0·0005 kX.