

*Crystals of artificial cassiterite.*

(With Plate V.)

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THE crystals of artificial cassiterite, described below, were produced by volatilization of South African low-grade tin ores. In the sinter-pot method employed, air was blown through a charge of alternate layers of coke and of a 12% metallic tin concentrate mixed with fine coke. This charge was placed above a basal layer of previously ignited coal. Occasionally sodium chloride was mixed with the concentrate to remove tin as chloride as well as oxide fume. The air-flow was carefully controlled to prevent slagging and was maintained until the evolution of copious fumes of tin oxide, and at times of chloride, ceased.

Optical pyrometer readings on the charges during the experiments gave temperatures of 1050° C. approximately, but it is certain that this value is a grave under-estimate of the actual temperatures in the interior of the sinter-pot. Petrov (1933), in his paper on artificial cassiterite, has given temperatures of 1300° to 1350° C., and it is possible that similar values may have been reached in the present case.

Voids in the loosely sintered residues contained nests of thin, colourless, transparent crystals (pl. V, fig. 1). Where incipient slagging of the charge had taken place the walls of the voids were coated with a dense white deposit of globules. Occasionally this deposit covered larger crystals (pl. V, fig. 2).

Goniometric measurements on the larger crystals were unsatisfactory because of surface imperfections on the faces, but they suggested the presence of the second-order bipyramid and prism faces. The data presented below were therefore obtained by microscopical study only.

The crystals may be divided into the following arbitrary morphological groups:

(a) Lath-shaped crystals either as individuals or in interlaced aggregates. These are 0.5-1.0 cm. long, 10-50  $\mu$  wide, and 4-15  $\mu$  thick.

(b) Hair-like crystals several cm. long but only 1–6  $\mu$  thick. The resolving power of the objective prevented the measurement of the lower limit of thickness.

(c) Elongated skeletal crystals either in rectangular growths or like geniculate twins. They may be up to 1 cm. long with a cross-section of 20–50  $\mu$  but are frequently only 4–8  $\mu$  thick.

(d) Pyramidal crystals 10–30  $\mu$  in width occurring on larger faces of lath crystals.

In addition there was the extremely fine-grained white 'powder'.

Most of the crystals of group (a) rest on one of a pair of well-developed parallel faces. They show straight extinction parallel to the length and give an eccentric uniaxial interference-figure, which suggest a pyramid face. A slice of quartz was cut at an angle of  $34^\circ$  to the plane of the horizontal axes to simulate the (101) face of cassiterite. The eccentricity of the optic picture in this orientated section was practically identical with that of the cassiterite crystals resting on a dominant face. Further, in cassiterite the plane angle formed on the face (101) by the faces (011) and (0 $\bar{1}$ 1) is  $79^\circ 22'$  (calculated). The average of 40 measurements of the corresponding angle on the dominant face of the crystals gave  $78.7^\circ$ . Measurements using a universal stage gave values of  $33^\circ$  to  $36^\circ$  for the inclination of this face to the horizontal axes. When the lath-like crystals were rotated about their length in a viscous medium (for example, Canada Balsam with 5% xylene) the angle of extinction between the plane of the dominant face and that of the horizontal axes was determined as  $34^\circ$  to  $36^\circ$ .

The above methods of measurement have all established that the two dominant faces in the crystals of group (a) and in most of group (b) are of the second-order bipyramid  $e$  (101). The crystallography is simple; two well-developed elongated  $e$  faces with the other six faces of the same form as pyramidal terminations and two faces of the second-order prism  $a$  (100) are present. The idealized form is shown in text-fig. 1a, while text-fig. 1b is a camera lucida drawing which shows the appearance under the microscope. Most of the crystals are flared towards the terminations and where both ends are developed they have a 'dumb-bell' shape (text-fig. 2). Generally, however, only one extremity is present as the crystals have grown from a thicker individual.

Many of the group (b) crystals have the same habit, but the minute cross-sectional area of the majority makes a precise determination impossible. Their dominant form may be simply the second-order prism.

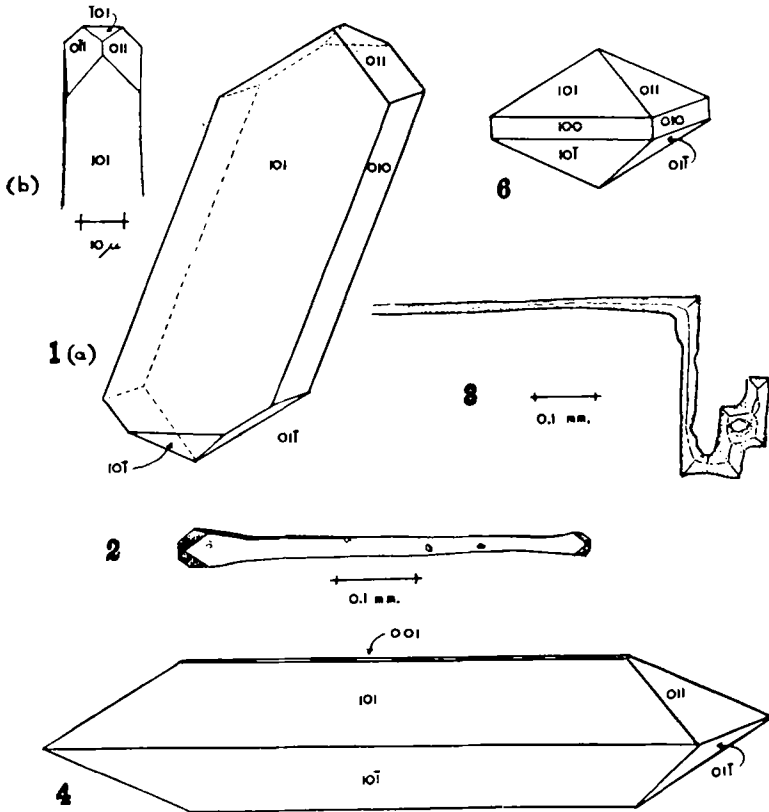
Crystals in group (*c*) exhibit two interesting habits. The first presents elongated prismatic crystals in rectangular or cruciform growths (text-fig. 3). The majority show isotropism or slight anisotropism when in the position they normally occupy on a slide. The almost perfectly centred interference-figure is generally anomalously biaxial, either showing a normal picture with a small optic angle or one centred straight brush in the  $90^\circ$  positions. Straight extinction is shown when the crystals are tilted slightly from the position of isotropism. The form in these crystals is also *e* (101) elongated parallel to one horizontal axis. A very narrow basal pinakoid bevels the crystals on rare occasions. The essentially skeletal nature of these crystals is evident from the holes present where the growth orientation changes through a right angle but remains in the plane of the horizontal axes. The first-order bipyramid, *s* (111) may be present as thin bevels to the *e* faces at these positions. The idealized form is shown in text-fig. 4.

Crystals of the second habit in group (*c*) are also skeletal. They are, in ordinary light, exactly like geniculate twins with two lath-like limbs meeting at  $68^\circ$ . This structure may be repeated several times (text-fig. 5*a*) or a limb may have off-shoots at  $68^\circ$  (text-fig. 5*b*). Text-figs. 5*c* and 5*d* are idealized forms. In polarized light the crystals show high-order colours, a flash interference-figure, and symmetrical extinction. The forms present are the second-order bipyramid and prism. The terminations of the limbs when present are composed of small *e* faces. On some of these crystals each of the *a* faces is replaced by two other pyramid faces, probably *s* faces (text-fig. 5*b*). Many of the crystals are broken and the fragments resting on the broad face show inclined extinction. Very small fragments may have given the erroneous impression of crystallization in systems other than tetragonal. (Hintze, 1904; Groth, 1906.)

The small perfectly formed pyramidal crystals of group (*d*), (text-fig. 6) a combination of the forms *e* and *a* are scattered without any definite orientation on the broad *e* faces of the larger flared crystals. They are sometimes elongated in the direction of a horizontal axis when they have a length of  $50 \mu$ . This habit is identical with that of fig. 17 for cassiterite given by Goldschmidt (1923).

The white powder under moderate magnifications has an opaque appearance, which may obscure the transparent nature of crystals coated with it. Under highest powers it is seen to be composed of minute laths as well as crystals of the second habit of group (*c*), generally  $2 \mu$  and less in length. Interference colours are not always detectable. An X-ray

powder photograph revealed the structure of natural cassiterite, but the extremely small particle size was indicated by the broad lines of the X-ray pattern. This material may be regarded as tin oxide fume which



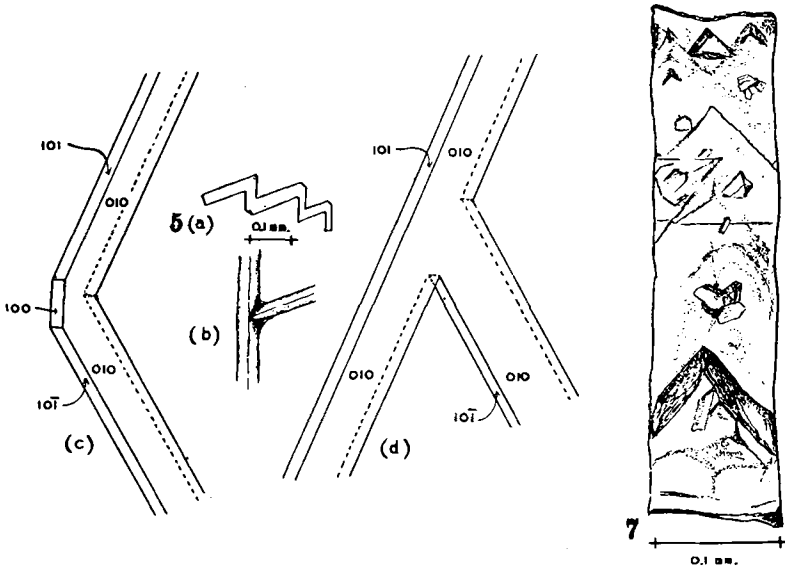
FIGS. 1-4 and 6. Crystals of artificial cassiterite.

was retained in the charge; its appearance is similar to that of fume which was expelled from the sinter-pot and collected.

The combinations of the first-order bipyramid and prism, common to natural cassiterite do not occur on these crystals. The presence of elongated first-order prisms is doubtful, while the  $s$  face is absent except on some crystals of group (c). Although many crystals look like geniculate twins, they are actually simple single individuals; in fact no twin crystals were observed. These observations are similar to those made

by Himmel and Porter (1931). The artificial cassiterite crystals described by vom Rath (1867), which are simple forms of well-developed  $e$  faces, have some features in common with crystals in group (a).

X-ray patterns of aggregates of the present material showed no lines other than those of the natural tetragonal mineral.



FIGS. 5 and 7. Crystals of artificial cassiterite.

Growth accessories are common on the dominant  $e$  faces. They are generally elevated triangular areas on a stepped surface, with edges parallel to the  $e$  or  $a$  faces (pl. V, fig. 3 and text-fig. 7). Fine striations parallel to  $e$  faces are also present. The triangular depressions and hollow crystals found by Himmel and Porter (1931) were absent in these crystals, and no accessories were noted on faces of the other forms present.

A spectrographic analysis was kindly made by Mr. L. H. Ahrens who reported that a spectrographic trace of tungsten was the only significant impurity.

Uniaxial interference-figures are general except in those crystals of group (c) which are anomalously biaxial. In hand-specimen all the crystals appear to be colourless, but under the microscope thicker laths have a very pale purplish-brown colour. Dichroism is just visible in

these with  $\epsilon$  pale purplish-brown and  $\omega$  very pale purple. A West's high refractive index liquid of 2.06 showed that the indices were just above and somewhat below this value for Na light. Crystals which lie perfectly flat on a large  $e$  face show straight extinction and all have positive elongation. Small extinction-angles up to  $6^\circ$  were due to the imperfections on the  $e$  faces, which affected the normal resting position of such crystals on the slide. Strain may have contributed to this extinction-angle as well.

The morphological classification proposed by Shneider (1937) for the estimation of temperatures of formation could not be applied to the cassiterite in the present case, because of vast differences in the conditions and environment of the natural and artificial mineral. It is, however, likely that these artificial crystals were formed above  $600^\circ\text{C}$ ., when the sintered mass cooled after the cessation of the air-flow. The description of crystal growth outlined by Davey (1934) applies very well in this case. Pl. V, fig. 4, shows the growth of secondary on larger primary crystals.

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*Summary.*—Crystals of artificial cassiterite formed by volatilization from the natural mineral are described. Most of the crystals are simple combinations, of a second order bipyramid elongated along either horizontal axis or at right angles to this, with subordinate second order prism faces.

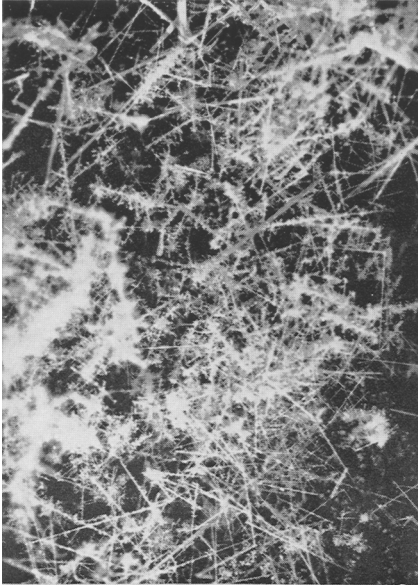
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## EXPLANATION OF PLATE V.

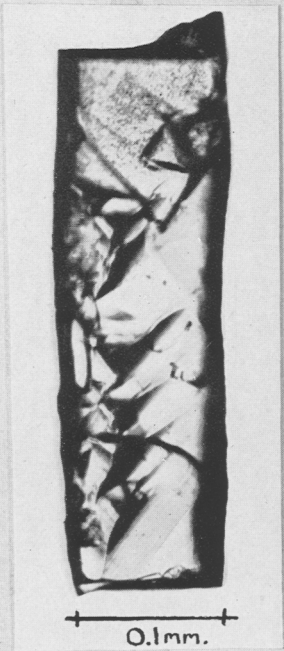
- FIG. 1. Interlaced crystals of artificial cassiterite.  $\times 5$ .
- FIG. 2. Globules of fine white cassiterite 'powder' which also coats the crystals.  $\times 5$ .
- FIG. 3. Growth accessories on an *e* face.
- FIG. 4. Association of primary and secondary artificial cassiterite crystals.  $\times 110$ .
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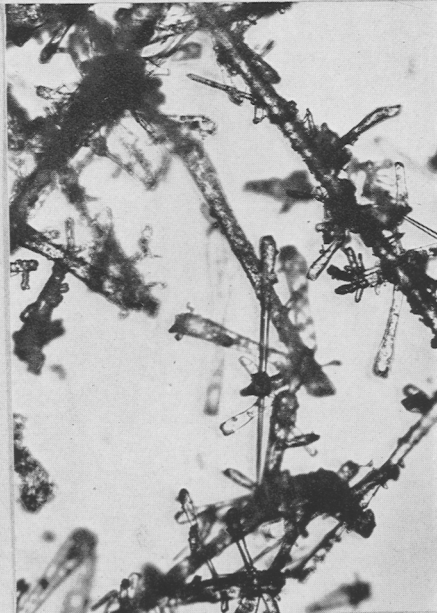
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J. J. FRANKEL: ARTIFICIAL CASSITERITE.