MICROPHOTOGRAPHS OF SINGLE CRYSTALS OF ZINC CONTAINING SMALL KNOWN AMOUNTS OF IRON

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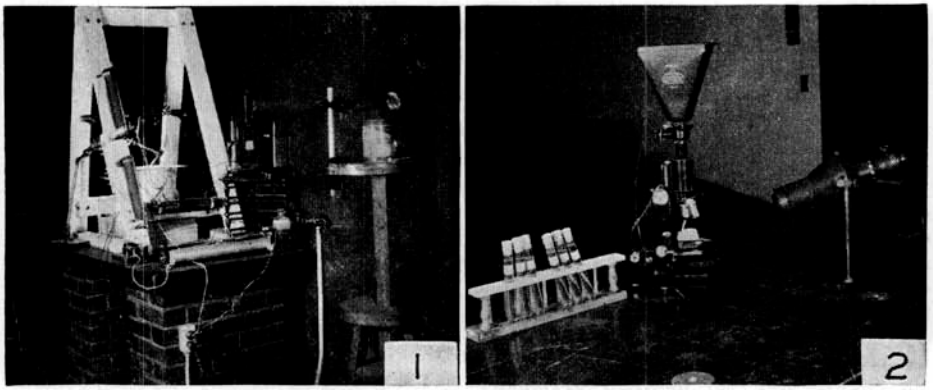
The authors of this paper presented at the 1937 meeting of the Academy a paper on Single Crystals of Zinc (1). This paper dealt with the effects on the zinc by the addition of small known amounts of several elements. The microphotographs showed some rather striking results in the case where iron had been the added impurity. Previous work (2) has shown that the addition of small amounts of iron to zinc in the form of a single crystal gives some very interesting results. The most unexpected effect is that it increases the electrical resistivity almost 50 times as much as the addition of any other impurity had done. When crystals were grown by means of a nucleus in a horizontal oven, the added iron seemed to widen the range of growth and in almost every case, a perfect zinc crystal was obtained. Whenever any of the others were added, mosaics invariably came in and only by very rigid temperature control could they be eliminated.

The growth conditions necessary for single crystals of pure zinc were at one time believed to have been worked out (3). Subsequent work showed that although the zinc had a purity of 99.8 per cent, the small percentage of impurity was an important factor in the successful growth of the crystals. In fact, it seemed necessary to have a small amount of Cadmium to grow single crystals by the Czochralski-Gomperz method. This suggested the possibility of using iron to help the growth conditions for single crystals by this method in preference to the cadmium.

The Czochralski-Gomperz method consists of drawing the crystals from the liquid metal. A glass tube (or copper wire) was immersed in the metal zinc and slowly but steadily pulled out. When the pulling was at a rate of about .5 centimeter per minute, the crystal was about 2 millimeters in diameter. Such a crystal had a so-called 90° orientation. With this as a nucleus for future pulling, any degree could be obtained by setting it at any desired angle when drawing the new crystal. The temperature was measured by means of a chromel-alumel thermocouple placed just under the surface of the liquid and read direct from a Leeds-Northrup manually operated indicator. The temperature of the liquid was controlled to within a degree by a series of heating units surrounding the crucible containing the zinc. The surface of the zinc oxidized rather readily, but could be skimmed off with a glass rod and the nucleus joining readily on the surface of the molten liquid if previously immersed in zinc chloride.

Crystals obtained by this method offered the possibility of studying not only the growth condition of various percentages of iron in the zinc, but also of getting some information of the structure by means of microphotographs. Because of the fact that iron has a very low solubility in zinc, it was necessary to use zinc extremely free of iron in order to measure the real effect. Bunker Hill zinc of extremely high purity was obtained. To check its purity, spectrograms were made on a 10-inch spectrograph and an analysis of its purity made by its comparison with standardized samples. Its resistivity was also measured as a recheck on the amount of iron present. It was found to contain no appreciable amount of iron and a very small amount of cadmium and lead. Because of the absence of iron, this zinc was found to be satisfactory.

To the pure zinc was added enough iron to make a .01 solution by weight. This was diluted down to make a .01 per cent sample; another, .0075 per cent; another, .005 per cent; and another .001 per cent. Spectrograms of each of these were made and growth effects on resistivity likewise made. A number of zinc crystals were grown by the Czochralski-Gomperz method for each concentration. The apparatus used in this is shown in the accompanying picture. Various temperature ranges were tried and limits of growth conditions determined. The crystals were placed in a 6-normal solution of hydrochloric acid for two minutes (other weaker solutions were tried but this proved the most satisfactory). They were maintained with the light falling on them at an angle of



Figs. 1 and 2.—Apparatus used in studying crystals.

about 30° with the horizontal. The microcamera used was a Zeiss mounted on a Spencer, No. 3 microscope with an apochromatic operation giving a magnification of ×80. Supersensitive panchromatic-cut films were found to be most satisfactory. For some of the work a Spencer metallurgical microscope with a direct illuminator and a short mount objective was used. This was found quite satisfactory primarily because the illumination was more uniform and the angle of illumination was constant.

The following table shows the growth conditions for the several percentages of iron used.

TABLE I

Per cent of Iron in zinc	Orientation (Degrees)	Range of growth (Degrees C above M. P.)
.0010	0 to 10 10 to 50 50 to 70 70 to 90	10 — 40 10 — 20 uncertain 10 — 40
.0050	0 to 10 10 to 50 50 to 70 70 to 90	10 — 35 10 — 20 10 — 15 10 — 40
.0075	0 to 10 70 to 90	10 — 30 10 — 30
.0100	0 to 10 70 to 90 75 to 90	10 — 20 10 — 20 10 — 20

The values given in table I are only approximate. Within these ranges over 50 per cent of the crystals attempted were successful. Outside of this range much less than 50 per cent were successful. In general, when .01 per cent iron was added to the zinc there was a wide range of growth conditions. For 0° to 10° orientation, the temperature range was extremely wide, being from 10 to 40 degrees above the melting point of the zinc. While this was also true of the 70° to 90° orientation, that is to be expected, for 90° are always easiest to grow. When crystals were started at an orientation of 50° to 70° they would grow only a short distance and then slip to a 0° crystal. This almost never happened when cadmium was used.

For .0050 per cent iron in zinc, the growth conditions were narrower (10° to 35° above the melting point for 0° to 10° orientation) but still retained a reasonably wide range at low and high orientations.

For .0075 per cent iron in zinc, the growth conditions narrow down considerably and not enough crystals were obtained between 10° and 70° to make a definite statement.

For .01 per cent iron in zinc, the conditions are extremely narrow and many mosaics were obtained.

General Discussion

As the iron goes into the solid solution of zinc in the lattice of the single crystal, it might go in two ways. First, the crystal might throw out pure zinc until the concentration of the iron became sufficiently great to throw in a layer of pure iron, or second, the iron

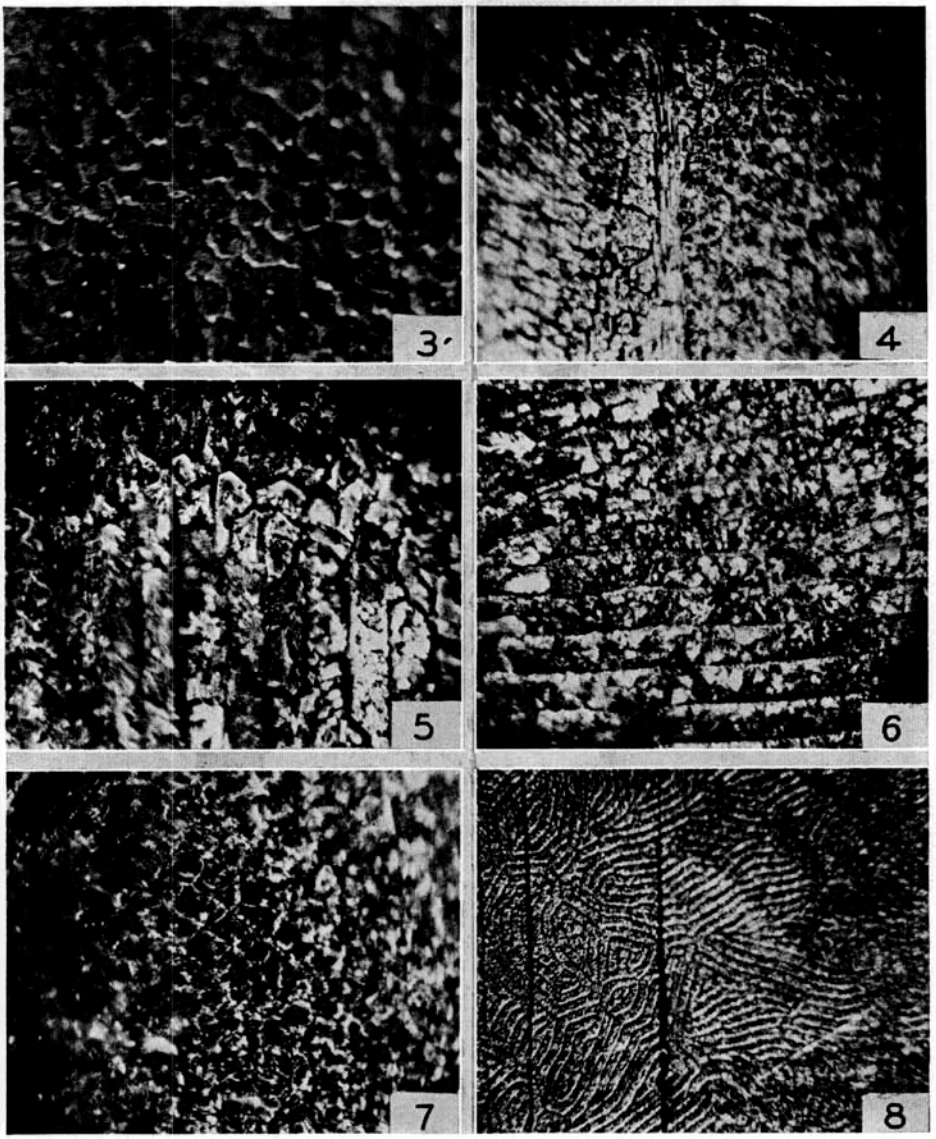


Fig. 3 shows a cross section of a single zinc crystal containing .0010 per cent iron in zinc. This microphotograph shows a hexagonal structure that is very definite.

Fig. 4 shows a cross section of a single zinc crystal containing .0075 per cent iron in zinc. While the hexagonal is observable in scattered places, it is not nearly so distinct as Fig. 3.

Fig. 5 shows a cross section of a single zinc crystal containing .0100 per cent. The hexagonal structure is definitely beginning to break down.

Fig. 6 also contains .0100 per cent iron, but is probably a mosaic instead of a single crystal.

Fig. 7 also contains .0100 per cent iron, but little or no definite structure is observable.

Fig. 8 also contains .0100 per cent iron, but is definitely not a single crystal.

might replace the zinc atoms in the lattice. Normally, the zinc crystal is of the close packed hexagonal type while the iron is the body centered cubic. If the iron tended to throw in a layer of different crystalline structure the crystal would probably not continue as a pure single beyond that point. This would explain why a higher concentration of iron makes it difficult to grow single crystals. It does not, however, explain why the presence of a small amount seems to be necessary for a single to start. It seems more reasonable to believe that up to a certain concentration (probably not more than .005 per cent) an iron atom replaces an occasional zinc atom in the lattice and the resultant crystal is of the close packed hexagonal type with some distortion.

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