Micro-photographs of Single Crystals of Dilute Solid Solutions in Zinc*

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The perfect or ideal single crystal is an orderly arrangement of the atoms so located as to form some type of geometric model. If the material of which the single crystal is composed is perfectly pure, the atoms are so located as to form a perfect lattice regardless of the plane considered. In the case of pure zinc, the "building blocks" are of the hexagonal close packed variety. Such crystals have the usual single crystal properties of being easily bent or strained. They also cleave quite easily along the most densely populated plane which is at right angles to the principal axis. The atoms are so located as to make their total energy a minimum giving them a rather stable equilibrium as shown by the fact that their lattice pattern is apparently unaltered by various annealings and quenchings from near the melting point.

In order to get zinc to crystallize in the single crystal state Hoyem and Tyndall[1] have found that there are, generally speaking, two factors which enter the "building up" or "growing" of the crystal. These two factors are rate of growth and temperature gradient, and they have worked out, experimentally, a necessary ratio between these two variables for successful growth.

Single crystals of other elements have been grown successfully. All of them have their characteristic "model". In the case of copper, like many others, this model is cubic.

It is practically impossible to obtain a sample of zinc which is perfectly pure. The purest zinc[2] obtainable which is exceedingly pure will contain amounts of impurity of the order of Fe 0.002 per cent, Cd 0.0008 per cent, Pb 0.0047 per cent, Cu 0.0002 per cent, Co, Ni, Al, 0.000 per cent. Thus from a practical point of view, we are dealing in the study of single crystals of the so-called pure zinc with zinc atoms occasionally replaced in the lattice by some foreign atom. There has been considerable discussion as to how such an impurity will replace the zinc atoms in the lattice.

The problem has previously been approached from many angles.[3] This paper presents an attempt to throw some light upon this question by a micro-photographic analysis of single crystals of zinc containing known small amounts of various impurities.

Inclusion of impurities in the perfect zinc lattice might be a perfectly random replacement of the zinc atoms by the foreign atom. This could happen if the concentration of one in the other was very small. The two elements crystallize in different forms in their own pure state, as in the case of copper (cubic) and zinc (hexagonal close packed).

The impurities might also go into the lattice in the form of layers. That is, during the growth of the crystal, the one having far greater concentration might go into the lattice until the concentration of the more

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dilute one has reached a point where it will "throw" a layer into the crystal. In such a case, one would expect this layer to take the crystalline form of the pure element. This would mean that at the line of demarcation, a new type of crystal would come into existence having a different form entirely. One might also find eutectics within this layer. Or, the layers formed might be more or less regular in the form of dendrites. Such a crystal could not properly be called a pure single crystal, although it would take high magnification to show it.

A set of micro-photographs has been prepared. This set made from single crystals of Bunker Hill (B. H.) zinc to which had been added small percentages (.5 per cent or less by wt.) of Cu, Au, Ag, and Fe. The crystals to be photographed were carefully cleaved and then etched from 1 to 3 min. in a 5 normal solution of HCl. They were then placed under a Zeiss micrograph with their cleavage planes held horizontally and illuminated by a single source of light at an angle of about 25 degrees with the horizontal. The microscope used was a Spencer No. 3 with an apochromatic objective giving a magnification of x38. The film found to be most satisfactory was the super sensitive panchromatic type.

DESCRIPTION OF FIGURES

Figure 1 shows a cross section of the polycrystalline pure B. H. zinc. The single crystals tend to form along the temperature gradient, that is from the outside toward the inside.

Figure 2 shows the cross section of a polycrystalline sample of the B. H. zinc containing .125 per cent Cu by weight. The small single crystals forming this polycrystalline slab are smaller indicating growth conditions were not so good for the mixture as for the pure zinc.

Figure 3 shows the unetched cleavage plane of the pure zinc crystal. The lines crossing at an angle of 60° to each other are probably strain lines along the minor axis.

Figure 4. Photographed perpendicular to the cleavage plane. It shows the junction of two single crystals coming together. The grooves so formed indicate a "structural line" growth. Such a formation has been previously shown but has not to date been satisfactorily accounted for.

Figure 5. Photographed perpendicular to the cleavage plane. It contains .125 per cent gold and shows a general scattering of gold through zinc with slight tendency to collect along an axis. This may well be a slip in the plane caused by the gold.

Figure 6. Same with .25 per cent gold. Shows same as 5 only more pronounced. They appear as indentations, but are most likely the same as the preceding one.

Figure 7. .5 per cent gold. Same as the two preceding ones only containing .5 per cent gold. This shows a tendency to form a pattern which might be interpreted as meaning that as the concentration reaches a definite point, there is no longer a random displacement but rather a tendency to go into certain favored spots in the lattice.

Figure 8. Photographed perpendicular to the cleavage plane. The zinc crystal contained .125 per cent silver. It shows a general tendency to form along one minor axis with slight amount along the other. The grain of the crystal is quite fine. If these are crystals of pure silver, certainly silver does not readily form single crystals in the range of conditions of this experiment. This is easily understood for experimentally zinc containing silver was difficult to "grow" into single crystals. So far it has been impossible to grow such a crystal of low orientation.

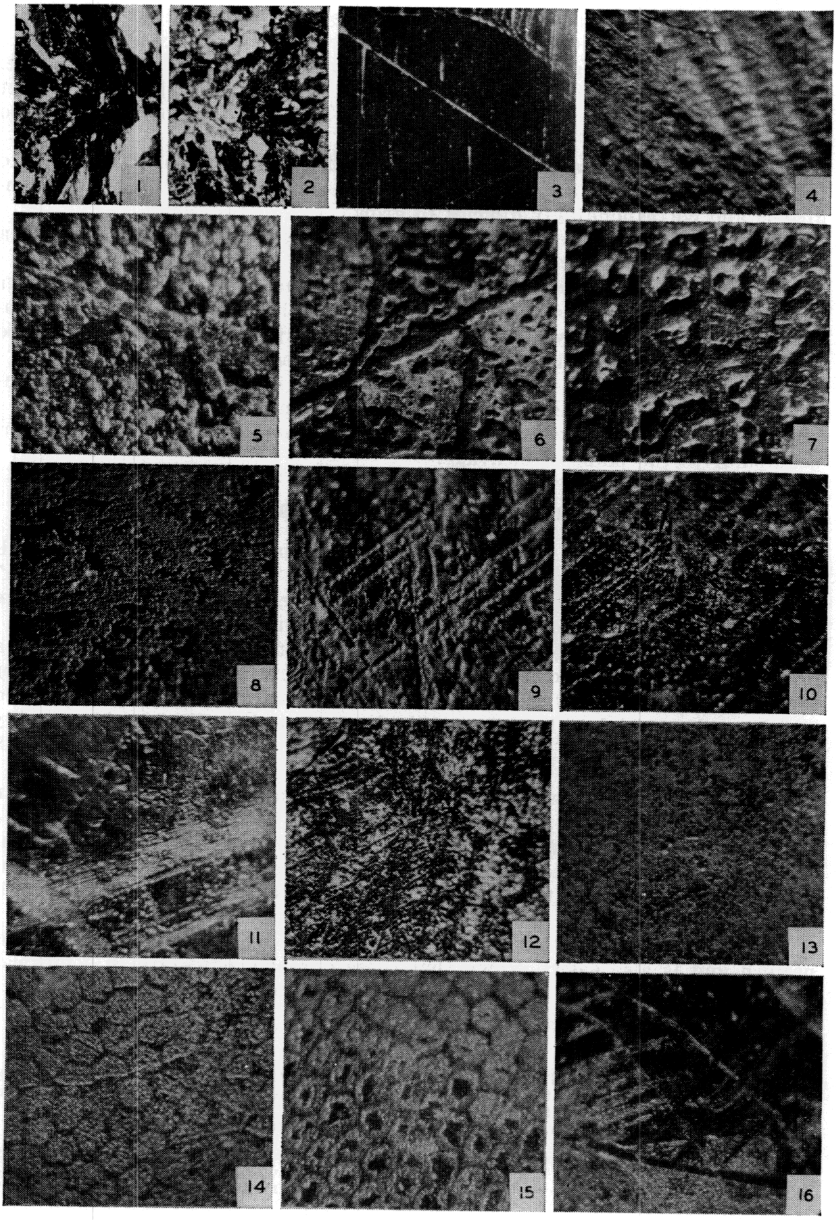

Plate I.—MICRO-PHOTOGRAPHS OF SINGLE CRYSTALS OF DILUTE SOLID SOLUTIONS IN ZINC.

Figure 9. The same as 8 except .25 per cent Ag. Tendency to go along the minor axis more pronounced and lines much finer.

Figure 10. Same as 8 and 9 except .5 per cent Ag. Finer lines yet—more breaking up. Not so symmetrically placed along the axis.

Figure 11. This figure was taken at right angles to the cleavage plane. It contains .125 per cent Cu. There is a very definite tendency to collect along an axis. The crystals containing this amount of copper were not so hard to grow.

Figure 12. Same as 11 but containing .25 per cent Cu. Tendency to collect along axis not so noticeable. Crystals more critical of growth conditions and correspondingly difficult to grow.

Figure 13. Same as 11 and 12 but containing .5 per cent Cu. Nearly a random distribution—Extremely difficult to grow.

Figure 14. This crystal contains .005 per cent Fe. Has many peculiar properties. The iron has an abnormal effect on the resistivity and temperature coefficient of the crystal. It is extremely easy to grow. It gives a nice pattern indicating a tendency to take a favored spot in the lattice.

Figure 15. Same as 14 but has .01 per cent iron. Shows effect of continued etching. Part has been etched longer than other part.

Figure 16 shows a crystal containing 0.005 per cent nickel viewed perpendicular to the plane of cleavage.

DISCUSSION AND CONCLUSIONS

There seems to be very close correlation between range of "growth conditions" and pattern of the photo-micrographs. Where a definite "pattern" appeared on the photograph, the crystal was easy to grow in that the temperature gradient and rate of growth had a comparatively wide range.

This can be accounted for on the theory that the foreign atom takes a preferred position in the lattice. If the concentration is of just the order that the right number of foreign atoms are present to fill in these preferred positions, the crystal will grow as a single very nicely. This would probably give some distortion to the space lattice which might be detectable with X-rays.

If the concentration exceeds this critical value, the impurity will in some cases build up the necessary concentration to throw into the lattice a layer of its own thus breaking up the single crystal. Undoubtedly the various impurities do not go into the lattice the same way and it is certainly true that they do not have the same growth range even for the same atomic concentration.

It seems probable that in the case of iron which gives such a good pattern and is also easily grown that these characteristics are in some way related to the abnormal resistivity[4] and temperature coefficient.

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