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# PHYSICAL CHEMISTRY

M. Valouch and I. B. Borovskii

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**Abstract**

**Full Text**

## **PHYSICAL CHEMISTRY**

**M. Valouch and I. B. Borovskii**

### **DISTRIBUTION OF AN IMPURITY IN A SINGLE CRYSTAL OF METALLIC ZINC WITH A CELLULAR SUBSTRUCTURE**

*(Presented by Academician I. P. Bardin, 10 VII 1958)*

As a number of studies have shown <sup>(1)</sup>, many metal single crystals obtained by crystallization from the melt are characterized by various forms of substructure. One of the common forms of substructure in metallic single crystals, arising at intermediate growth rates and temperature gradients, is prismatic. In cross section, the prismatic fibers of the substructure, which penetrate the single crystal in the direction of growth, have the appearance of a honeycomb.

A qualitative theoretical explanation of the formation of substructure was given in work <sup>(2)</sup>, in which the formation of substructure is associated with the presence of impurities in metals. In the nonequilibrium process of crystallization, impurities cause the formation of a zone of constitutional supercooling in the melt layer adjoining the boundary between the two phases (liquid–solid). In this zone, spontaneous crystallization of the metal readily arises in the form of microscopic nuclei, distributed statistically, without any preferred orientation on the interface plane. Owing to the concentration gradient near the microscopic nuclei, diffusion of impurity atoms occurs, leading to a nonuniform distribution of these impurity atoms in the substructure being formed. From a general consideration of the phase diagram of the base metal–impurity metal, it follows directly that, when the impurity raises the melting point of the metal, the impurity concentration should increase at the center of the substructure fibers. In the case when the impurity lowers the melting point, the impurity content should increase at the boundaries of the substructure fibers. The dimensions of the substructure “cells” are determined by the “sphere of action” of the original microscopic nuclei. The latter, in turn, depends on the rate of growth of the single crystal, the temperature gradient, the relative diffusion rate, and solution exchange.

For the first time, an increase in the content of impurity atoms along the boundaries of substructure fibers was established by means of the radiographic method in studying the substructure of lead single crystals with an antimony impurity (using the active isotope  $\text{Sb}^{124}$ ). The decrease in impurity concentration along the boundaries of substructure fibers predicted from general theoretical consid-

Fig. 1. Microstructure of a zinc single crystal + 5% copper after etching

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Fig. 2. Distribution of copper over a polished section of a zinc single crystal +0.5% copper

Figure 2: Fig. 2. Distribution of copper over a polished section of a zinc single crystal +0.5% copper

erations was not experimentally detected. The purpose of the present work was to investigate the distribution of an impurity (copper) over the elements of the substructure of a zinc single crystal.

By the Czochralski method, a zinc single crystal with an admixture of 0.7% copper\* was obtained. The rate of pulling of the single crystal from the melt was 10 mm/min, and the temperature gradient about 20°/cm. The amount of impurities of other elements was less than 0.01%. The resulting cylindrical single crystal was ground perpendicular to the axis. The pattern of the fibrous cellular substructure was revealed after chemical polishing (Fig. 1).

\* The single crystal was obtained at the Institute of Physics of Charles University in Prague.

**Fig. 1.** Microstructure of a zinc single crystal +5% copper after etching

The distribution of copper over the elements of the substructure of a zinc single crystal was studied by the X-ray spectral method for investigating the chemical composition in microvolumes of alloys ( $\sim 3$ ) on a PCASH-2 apparatus ( $\sim 4$ ).

Figure 2 presents concentration curves for the distribution of copper over the elements of the substructure. The figure shows a sharp increase in the copper content on going from the boundary to the center of the fiber (cell). Quantitative analysis showed that the copper content at the center is 0.7%, and at the boundary 0.4%.

Fig. 2. Distribution of copper over a polished section of a zinc single crystal +0.5% copper

The results obtained convincingly confirm the general theory that an impurity which raises the melting point of a metal is concentrated at the center of the substructure cells, and that the X-ray spectral method for investigating the chemical composition of a substance in a microvolume can be used to study this interesting phenomenon.

In conclusion, the authors express their gratitude to L. E. Loseva for studying the distribution of copper on the PCASH-2 apparatus and to M. Bochak and P. Krakhotvil for preparing the zinc single crystals.

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*Note: Figure translations are in progress. See original paper for figures.*

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