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The Macromosaic Structure of Lead Single Crystals

Eldon J. Nicholson

THE MACROMOSAIC STRUCTURE
OF
LEAD SINGLE CRYSTALS

A Thesis

Presented to

the Faculty of the Department of Metallurgy

Montana School of Mines

In Partial Fulfillment

of the Requirements for the Degree

Bachelor of Science in Metallurgical Engineering

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PURPOSE

In the last half century, great strides have been made in every branch of the sciences. Tantamount with this advancement has been the development of new research tools and the formulation of completely new or improved theories, particularly in solid state studies. One of these new tools is the single crystal.

Single crystals are essentially a true geometric configuration of atoms with physical-mechanical properties unlike their counterpart in the polycrystalline form. However, an understanding of the characteristics of single crystals gives us great insight into the basic mechanisms and properties associated with the polycrystalline materials. Aside from this, these single crystals have unusual properties of their own that make them valuable.

The characteristic grain structure of crystalline materials, and usually that which is associated with the metals, is generally mosaic in nature. Mosaic structures are broadly divided into the micromosaic and macromosaic classes. A micromosaic structure is in the range of magnitude of 10^{-6} cm., while macromosaics are visually observable.

The undertaking herein described is an outgrowth of an initial attempt to grow, and to examine the properties of selectively oriented single crystals of lead. At the outset however, long, banded, macromosaic grain boundaries appeared in the crystals that were grown.

In actuality, no true single crystals were grown. All specimens produced exhibited a longitudinal macromosaic structure (Fig. 4) roughly parallel to the direction of heat flow. Hereafter, in this report, the terms macromosaic structure and striation boundary will be used interchangeably to describe this growth phenomena.

The purpose of this investigation is to examine this structure to determine any properties or characteristics peculiar to it that could shed light on its cause or on the basic mechanism of crystal growth from the melt.

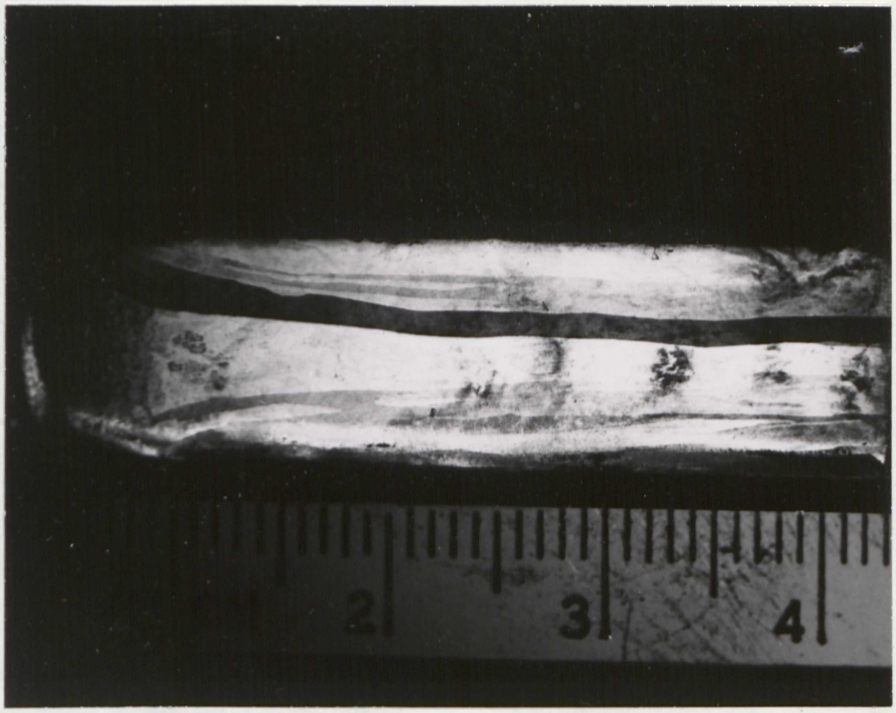

Figure 4

Typical striation boundaries

INTRODUCTION

The existence of a single crystal is verified by the back reflection Laue method. A true single crystal is manifested as an array of separate and distinct spot on a photographic plate. These spots fall on hyperbolic curves and are commonly called patterns (Fig. 1). The spots arrayed on any given curve are reflections from the planes of one zone. By the same token, a polycrystalline specimen would cause these spots to be inseparable from one another, and to arrange in a somewhat circular pattern (Fig. 2).

Single crystal specimen

Figure 1

Polycrystalline specimen

Figure 2

Laue pictures

In the Laue pictures taken of the lead crystals which were grown, there showed a distinct array of spots. The spots were compound in nature. Each spot consisted of from two to six smaller spots (Fig. 3). The individual sub-spots varied in orientation from approximately .5 degree to 5 degrees.

Figure 3

Laue picture of striation boundaries

In 1948, it was suggested by R. D. Heidenreich and W. Shockley[2], that dislocations could cause a crystal to exhibit reflections as though it consisted of independent blocks of a crystal lattice; the difference in orientation could be accounted for in terms of continuous curvature of the crystal or an arrangement of blocks bounded by dislocation walls. This last hypothesis seems to have been born out by the electron micrographs taken by Pfann, Vogel, Thomas and Corey in 1953[14], which show etch pits at the dislocations that constitute a boundary between grains of germanium of about one minute of arc different in orientation.

In 1951, E. Teghtsoonian and B. Chalmers examined the macromosaic structure of tin and found that the structural properties were dependent on the rate of crystal growth and on the crystallographic orientation relative to the flow of heat during growth.[9] Their explanation of the effect submitted that edge-type dislocations, formed from the condensation of vacant lattice sites, were arrayed along the boundaries of the mosaic structure. The hypothesis proposed that vacancies concentrated into disc-shaped arrays that eventually collapsed and caused a resultant pair of edge dislocations.

EXPERIMENTAL PROCEDURE AND RESULTS

A modified Bridgman method was used to grow the lead crystals. A resistance furnace was passed along a Vycor tube which contained the molten lead in a graphite boat. Natural gas, to reduce the effects of oxidation, was passed through the tube and burned at the exhaust end. The temperature was controlled by varying the current to the furnace with a powerstatt. A fairly uniform temperature of approximately 350° C., was maintained in all growth attempts. The furnace was withdrawn by a power-train made up of components listed in Table I. The lead stock used was ordinary testlead (used in gold assaying) produced by The American Smelting and Refining Company, with a specified purity of 99.9%. No chief impurities were listed.

TABLE I

EQUIPMENT

1-Boston Gearworks Ratiomotor (72-1 reduction)

1-Boston Reductor (80-1 reduction)

1-R.C.A. record turntable and gear-train (60-1 reduction)

1-Pulley arrangement (4-1 reduction)

1-General Electric 1/4 hp A.C. motor; (1728 rpm)

1-Hoskins Electric Furnace; (110v. x 4.4 amp)

1-Superior Electric Co. Powerstatt (110v. x 7.5 amp)

1-Standard X-Ray Co. x-ray machine with Laue back-reflection camera; (Cu target operated at 35kv and 15ma)

Striation Width

Variation of the rate of growth of the crystals was found to have an effect on the width of striation boundaries produced. Individual striation boundary width was not constant throughout any given crystal, so in order to obtain a mean width, the number of grain boundaries on the crystal surface was counted and then divided by the width of the crystal. Striation width was found to increase with decreasing growth rates. The results are tabulated in Table II and graphically represented in Figure 5.

TABLE II

Growth Rate (mm/min)	Mean Width (Cm.)
.019	.33
.027	.25
.035	.17
.042	.16
.050	.11

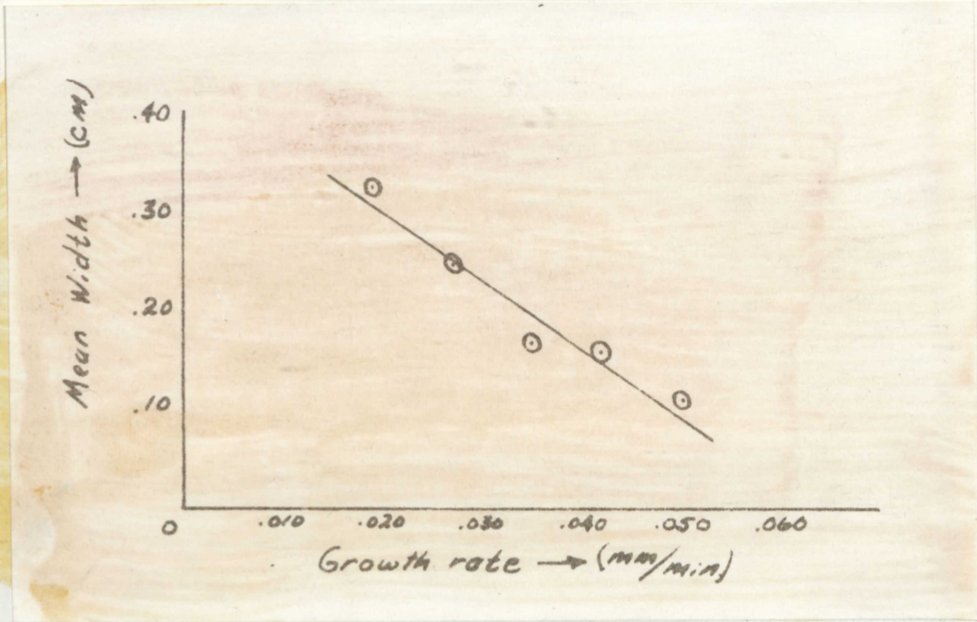

Figure 5

Plot of striation width vs. growth rate

This data cannot be considered conclusive because of the difficulty in carrying out the growth runs without varying anything but the growth rate. Also, since striation boundaries are observed because of the slight differences in the intensity of reflected light from adjoining grains, only those striations that were readily observable were counted. Examination of film sub-spots showed this orientation difference to be about two degrees. It will be shown later that these easily observable striations can be multiple striations of much smaller orientation differences. The data does, however, show a general and regular width preference of the higher order orientation differences.

Striation Distribution

To study the distribution and extent of striations throughout the crystals, the grown specimens were cut transversely with a fine-tooth jeweler's saw and heavily etched to remove the strians introduced during the sawing operation. Great care must be taken during sawing so that the frictional heat generated does not raise the specimen temperature high enough to allow the growth of new grains from the strains introduced by sawing. For the same reason, short etch times or a cooledetch solution should be used so that the heat generated in the chemical reaction does not become too intense.

The following pictures are of one sample, but taken at different angles to show the multiplcity of the striations and their general sectional dimensions. Magnification varies from 10 to 15. The surface striations on the curved face of the crystal shown in Fig. 6 appeared to be as deep as they are broad. The arrows indicate easily observable boundaries on the crystal surface. It can be readily seen that these easily observable striations encompass many finer striations. A back reflection Laue taken between the arrows would exhibit sub-spots much like those shown in Fig. 3. Figures 8 and 9 show the multiplicity and highly irregular shape of the dark interior striation in Fig. 7. Other striations are present throughout the sectional face of the crystal, but because of their orientation differences, they are irresolvable at this particular camera angle.

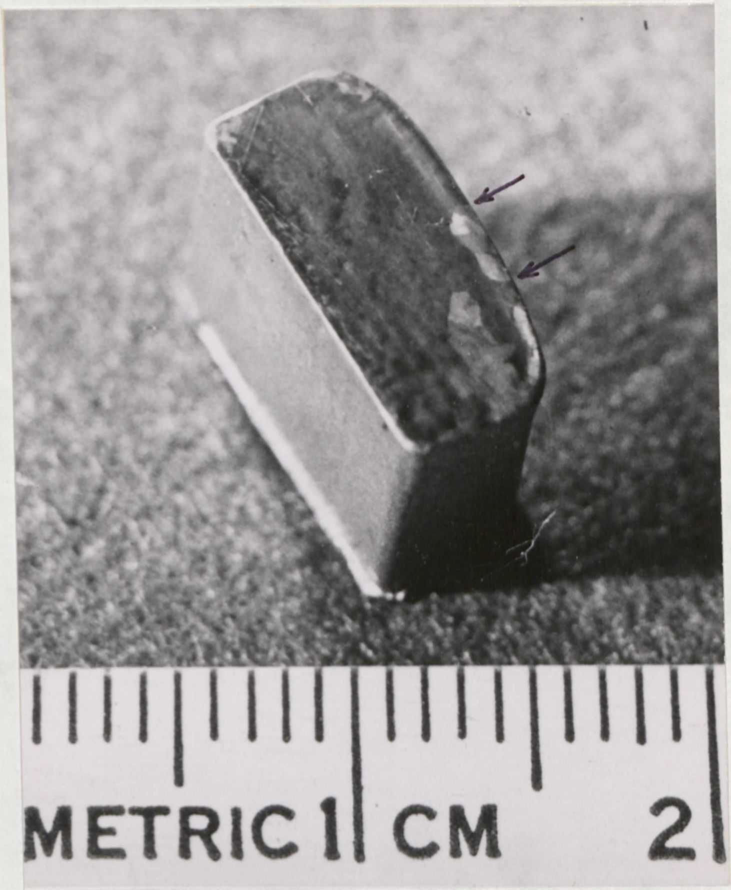

Figure 6

Sectional view of striations

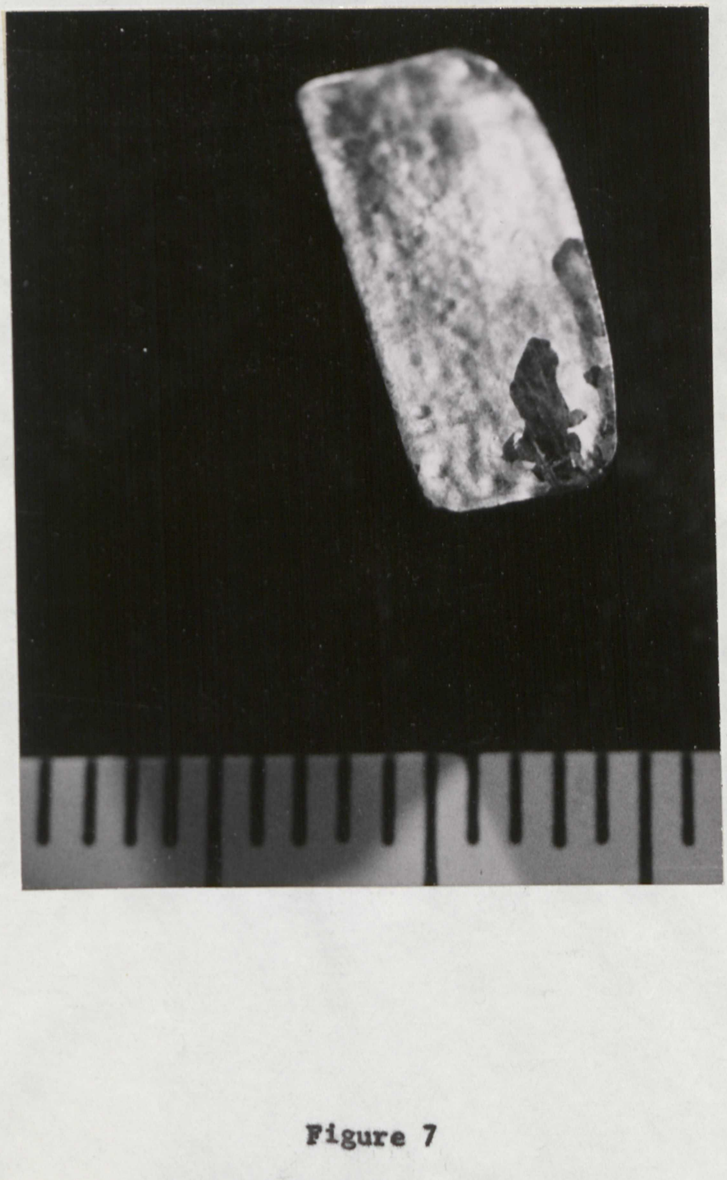

Figure 7

Sectional view of striations

Figure 8

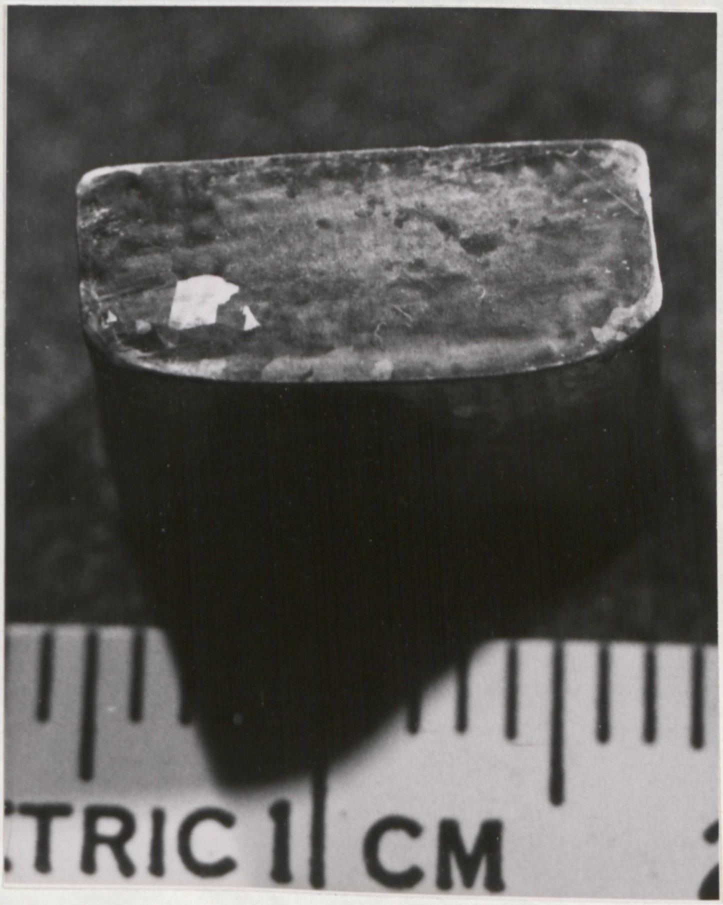

Figure 9

Striation Orientation

Laue pictures taken along a given striation boundary from one end of the crystal to the other showed that the orientation difference increased with increasing distance from its nucleation point. No quantitative correlation of misorientation vs. distance from nucleation point was attempted, but over the crystal length (7 cm.) a variation in the magnitude of 1 to 1.5 degrees was apparent.

Striation Stability

One crystal was annealed for 72 hrs. at 300° C. and subsequently examined. No visible change in the location of the striation boundaries was apparent. These observations indicate that the imperfections causing the boundaries are very stable.

Striation Cause

In an attempt to determine the cause of striations, a lead crystal was innoculated with an impurity. Finely powdered antimony was dispersed on the surface of a lead crystal and the crystal again subjected to the growing process. Figures 10 and 11 show the resultant striations nucleating from the dark inclusions of the powdered antimony. Striation boundaries then, are conclusively nucleated from imperfections caused or associated with impurities present in the crystal melt.

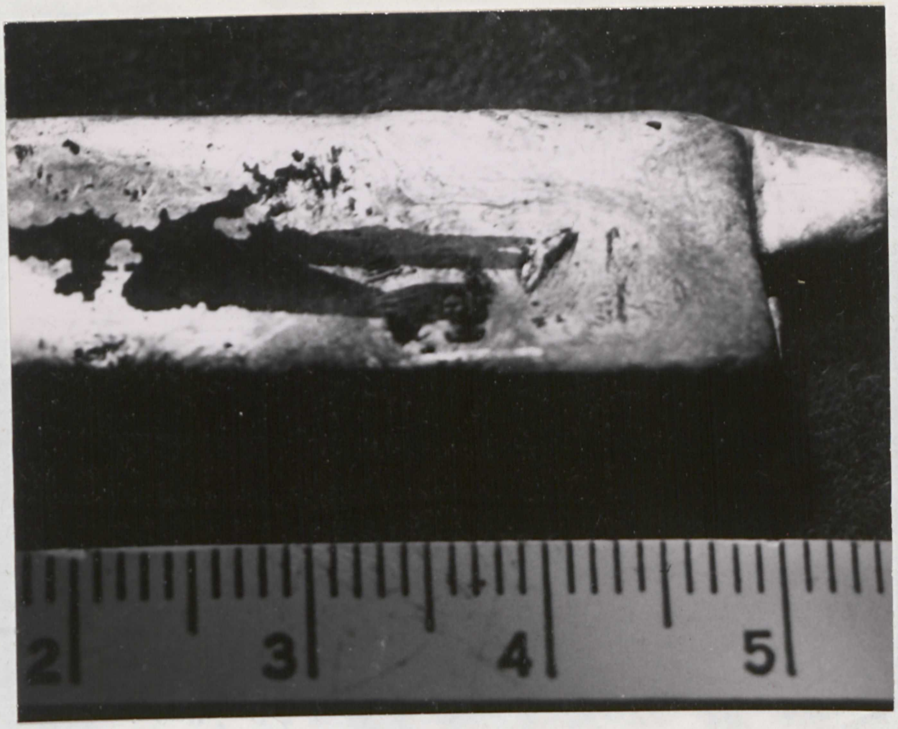

Figure 10

Figure 11

DISCUSSION

Nucleation takes place in a molten metal when the kinetic energy of the atoms becomes low enough to permit the formation of small clusters of atoms with decreased mobility. When the total kinetic energy of the cluster is low enough to absorb the kinetic energy of individual atoms coming in contact with it, without a change in the general make-up of the cluster, then the impingent atoms will join the cluster and growth will take place.

The nucleation taking place during crystal growth is termed heterogenous. Here, the surface of the graphite boat provides low energy sites for the formation or entrapment of the nucleating clusters. In practice, the graphite is at a lower temperature than the melt and a low energy site is merely a point that dissipates kinetic energy to enhance the probability of clusters becoming stable enough to cause nucleation.

Once a growing surface is firmly established at the melting point of a metal, atoms are joining and leaving the surface at equal rates; at temperatures below the melting point, the rate of addition to the surface is greater than the rate leaving and the result is a net transport of atoms to the growing face with subsequent movement and growth of the solid-melt interface. At this temperature, the attractive forces of the atoms are great enough to overcome the translational energy of the atoms and they are forced to arrange themselves in the geometric configuration of the material involved.

Chalmers has shown that the growth of the solid-melt interface must take place by the addition of individual atoms and that dislocations need not be present for this atomic addition to take place.[3] He also has shown that solute atoms of the melt can be rejected by the solid because of energy differences associated with their coordination number and size. In the following discussion, an attempt is made to reconcile these theories to the results of this investigation.

From the antimony-innoculated crystal, it was shown that striation boundaries can be caused by impurity-imperfections; it was also previously established[14] that striation boundaries are composed of dislocations. Hence, the striation boundary effect can be caused by dislocations arising from impurity atoms in the lattice.

From the pictures of the innoculated crystal, it can be seen that the boundaries diverge and lose their unidirectional nature a short distance from the introduced impurities. This appears to be indication that the boundaries are composed of the same type dislocation that caused striation nucleation. If this is the case, striation width should be a function of the amount of impurities present, since it takes a given dislocation density to form a striation boundary.[10] Accordingly, a lower impurity-dislocation density throughout the crystal would limit the amount of dislocations available for boundaries and lessen the number of boundaries present. Fewer striation boundaries necessarily mean wider striations. Therefore, striation boundary width should be a function of impurity concentration.

Striation distribution should be directly proportional to impurity distribution since only individual atoms are the building blocks on the solid-melt interface, i.e., a given array of impurities should cause a corresponding set of striation boundaries.

Striation orientation difference was shown to increase with increasing distance from the nucleation point. This is probably due to a gradually increasing impurity-dislocation density along the striation boundary.

The cause of striations was shown to be impurity-dislocations. It was also postulated that this type of dislocation makes up the striation boundaries. A possible explanation of the boundary effect is that the impurity atoms are rejected from the relatively pure sections of the interface, because of their higher energies, and are only allowed to place themselves on the boundaries where the energy discrepancies are slight enough to permit their attachment.

SUMMARY

Results of this investigation are tabulated below. Any proposed mechanism of striation growth should be coherent with these results.

1) Lead single crystals exhibit a banded macromosaic grain structure, roughly parallel to the direction of growth.

2) A difference of orientation exists between neighboring striations of from about .5 degree to 5 degrees.

3) A rotation of any striation about the parallel axis of its neighbor can cause an orientation common to both striations.

4) Striation width appears to increase with decreasing growth rate.

5) Misorientation of a given striation appears to increase with increasing distance from its nucleation point.

6) Striation structures are very stable, being unaltered by long annealing.

7) Striation boundaries are caused and promoted by impurity-imperfections.

CONCLUSION

Striation boundaries are definitely a phenomena related to the impurity content of the crystal melt. It has been put forth that these impurity atoms cause the dislocation array on striation boundaries with resultant misorientation differences. In any event, the condensation of these dislocations into striation walls is to accommodate the strains introduced during solification. The impurities have been said to cause the striation boundaries, but not necessarily the dislocations arrayed on them.

RECOMMENDATIONS

The analysis of the lead stock used in this investigation was unknown. To greatly simplify any further work on lead crystals, I would suggest procurement of at least 5 lbs. of not less than 99.99% pure lead.

Next in importance, I would suggest that growing boats be of high-purity graphite; take definite precautions that there are no re-entrant faces to cause crystal strain upon removal from the boat. Also, five or six boats should be made so that the growing apparatus can be run continuously, or with two or three samples grown per furnace pass, so that more tests would be possible in the allotted time.

If further work is to be done on lead striations, the following approaches could be made:

1) Correlation between individual presence and concentration of the impurities of Sb, As, Sn, and Ag in the crystal melt.

2) A concrete study of striation width vs. growth rate by counting all of the striations with an X-ray beam of known diameter.

3) A study of the increasing orientation difference vs. distance from the nucleation point, along individual striations, by growing crystals in the magnitude of 20 cm. long.

4) Procurement of an attachment for the X-ray machine that would permit consistent and known crystal orientation with the X-ray beam.

BIBLIOGRAPHY

1. Cullity, B.D., *Elements of X-Ray Diffraction*, Addison-Wesley Publishing Co., Reading, Mass., 1956.

2. Cottrell, A. H., *Dislocations and Plastic Flow in Crystals*, Oxford University Press, London, 1958.

3. Doremus, R. H., Roberts, B. W., Turnbull, D., (editors), *Growth and Perfection of Crystals*, Wiley & Sons, New York, 1958. (Proceedings of an International Conference on Crystal Growth held at Cooperstown, New York, on August 27-29, 1958).

4. Pearson, W. B., *Handbook of Lattice Spacings and Structure of Metals*, Pergamon Press, London, 1958.

5. Lawson, W. D., Nielsen, S., *Preparation of Single Crystals*, Butterworths Publications Ltd., London, 1958.

6. Nye, J. F., *Physical Properties of Crystals*, Oxford University Press, London, 1957.

7. Smithells, C. J., *Metals Reference Book*, Butterworths Publications, London, 1957.

8. The American Society of Metals, *Metals Handbook*, American Society for Metals, Cleveland, 1958.

9. Teghtsoonian, E., Chalmers, B., The Macromosaic Structure of Tin Single Crystals, Canadian Journal of Physics, V. 29, No. 5, pp. 370-381, 1951.

10. Atwater, H. A., Chalmers, B., Influence of Impurities on the Macromosaic Structures of Tin and Lead, Canadian Journal of Physics, V. 35, pp. 208-215, Feb. 1957.

11. Smakula, A., Sils, V., Precision Density Determination of Large Single Crystals by Hydrostatic Weighing, Physical Review, V. 99, No. 6, pp. 1744-1746, Sept. 15, 1955.

12. Smakula, A., Sils, V., Densities and Imperfections of Single Crystals, Physical Review, V. 99, No. 6, pp. 1747-1750, Sept. 5, 1955.

13. Pfann, W. G., *Zone Melting*, Wiley & Sons, New York, 1958.

14. Read, W. T., *Dislocations in Crystals*, McGraw-Hill Co., New York, 1953.

15. Shockley, W., Hollomon, J. H., Maurer, R., Seitz, F., (editors), *Imperfections in Nearly Perfect Crystals*, Wiley & Sons, New York, 1952, (Proceedings of a symposium held at Pocono Manor, Oct. 12-14, 1950).

16. Evans, R. C., Crystal Chemistry, Cambridge University Press, Great Britain, 1946.