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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	3
page range	165-174
year	1951
URL	http://hdl.handle.net/10097/26420

On the Production of Single Crystals of Zinc, Bismuth and Tin by Sucking Up from Their Melts*

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(Received February 8, 1951)

Synopsis

The preparation of single crystals of zinc, bismuth and tin by sucking up from their melts was tried by the use of simple equipment and procedure and the effect of growing conditions upon the percentage of success and orientations of single crystals produced was studied. Single crystals, 5 mm in diameter and 5∼7 cm in length, could be made with 20, 50 and 50 percent success for zinc, bismuth and tin, respectively, and they show a dominant preference of crystal orientations nearly perpendicular to the principal crystallographic axis, namely the hexagonal axis [0001] for zinc, trigonal axis [111] for bismuth, or tetragonal axis [001] for tin.

I. Introduction

Single crystals of pure metals and homogeneous alloys which have no allotropic transformation are primarily produced by slow cooling from the molten state. In this method of slow solidification there have heretofore been the three main types known as (1) the Tammann-Bridgman method, (2) Kapitza method, and (3) Czochralski-Gomperz method (drawing method). The first type of the method, as originated by Tammann[1] and developed by Bridgman[2], consists of displacing the temperature gradient gradually upwards by lowering the temperature of a vertically mounted furnace in which a mold containing metal rests (the lowering-temperature type),[1,3] or alternatively of lowering the mold through the temperature gradient of the furnace (the lowering-mold type).[2] The second type of the method of slow solidification, as originated by Kapitza,[4] employs the principles of the Tammann-Bridgman method except that crystal is grown horizonatally. In this method, molten metal of a rod form (the shape of the rod may be maintained while it is molten by a thin oxide coating), placed directly on a heating metal plate, is cooled slowly from one end (the Kapitza type),[4] or a boat or trough filled with the melt is displaced through a horizontally set furnace (the Goetz-Hasler type),[5] or a horizontal furnace travels over a capillary tube containing a metal wire (the Andrade-Roscoe type).[6] Finally, the third type of the method of slow solidifica-

* The 626 th report of the Research Institute for Iron, Steel and Other Metals.

(1) G. Tammann, *Lehrbuch der Metallographie*, 2 nd edition, Leipzig, (1921), p. 12. See also I. Obreimow and L. Schubinikow, Z. Phys., 25 (1924), 31.

(2) P. W. Bridgman, Proc. Amer. Acad., 60 (1925), 306; 63 (1929), 351.

(3) H. E. Farnsworth, Phys. Rev., 48 (1935), 972; J. G. Walker, H. J. Williams and R. M. Bozorth, Rev. Sci. Instr., 20 (1949), 947.

(4) P. Kapitza, Proc. Roy. Soc. London, A 119 (1928), 358.

(5) A. Goetz and M. F. Hasler, Proc. Nat. Acad. Amer., 15 (1929), 646; Phys. Rev., 35 (1930), 193.

(6) E. N. Andrade and R. Roscoe, Proc. Phys. Soc., 49 (1937), 152.

tion, as originated by Czochralski[7] and elaborated by Gomperz,[8] has an appearance entirely different from the above two methods, and single crystals are grown by drawing a "liquid rod" out of the melt and solidifying continously the rod from its top. So it is frequently called the drawing method.

Now, we may conceive another type of the method of slow solidification, which resembles to the third type of the method or drawing method and in which the melt is sucked up into a tube of suitable material and at the same time cooled slowly from the top. This method may be called the suction method. In order to know whether metallic single crystals may be produced easily by the suction method and further to obtain any knowledge as to the effect of growing conditions upon the degree of success in the preparation of single crystals by this method and upon orientations of single crystals produced, we have carried out some experiments, by the use of simple equipment and procedure, on the preparation of single crystals of hexagonal zinc, trigonal bismuth and tetragonal tin all of which have low melting points.

After we had finished our experiments, we found Sizoo and Zwicker's[9] and Chalmers'[10] papers on the production of metallic single crystals by similar procedure as ours. Sizoo and Zwicker made single crystals 20 cm long from nickel and nickel-iron alloys containing up to 98 per cent nickel by sucking up the melt held at about 50°C above the melting point into a quartz tube of approximately 1 mm in internal diameter. Chalmers obtained single crystals 5 mm in diameter and 6 mm in length by sucking up the melt of 99.987 percent pure tin held at about 300°C into a glass tube drawn out its center to a narrow capillary and by raising the

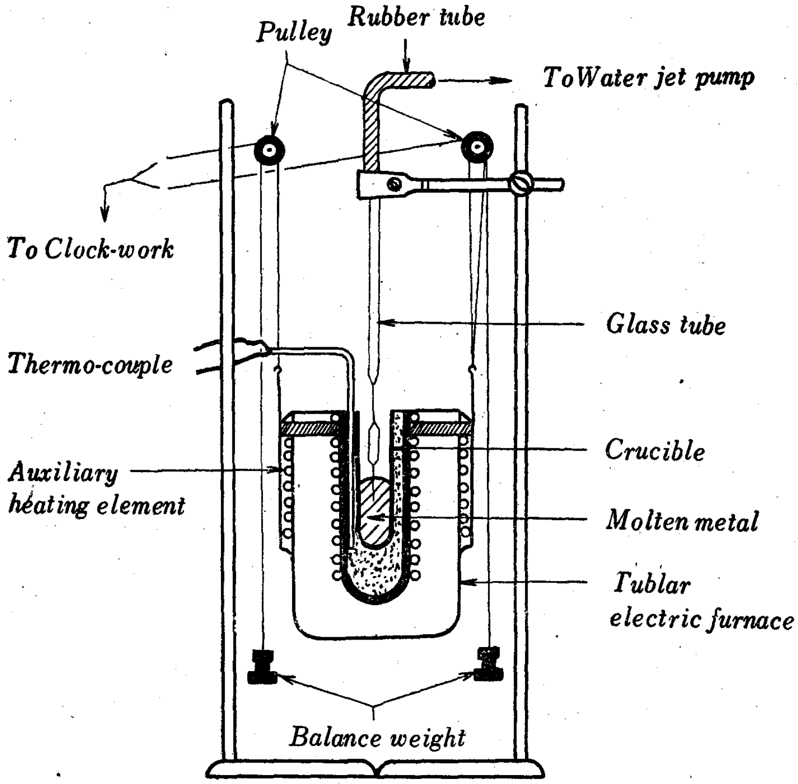

Fig. 1. Arrangement of equipment used for the preparation of metal single crystals by the suction method.

(7) J. Czochralski, Z. phys. Chem., 93 (1918), 219.
(8) E. v. Gomperz, Z. Phys., 8 (1922), 184.
(9) G. J. Sizoo, and C. Zwicker, Z. Metallkde., 21 (1929), 125; G. J. Sizoo, Z. Phys., 57 (1929), 106.
(10) B. Chalmers, Proc. Phys. Soc. 47 (1935), 733.

tube out of the molten tin with the rate of 30 cm per hour. He also found that in the majority of tin single crystals thus prepared [001] axis was nearly normal to the axis of the crystal rod.

II. Materials, Equipment and Procedure for Growing Single Crystals by the Suction Method

Materials used are grobular zinc (comprizing 99.99% Zn), block (SI) and grobular (KI) bismuth (comprizing 99.98 and 99.99 % Bi, respectively), and grobular tin (comprizing 99.89 % Sn), of which the melting points as determined by the thermal analysis are as follows: Zn 419°C, Bi (KI) 267°C, Bi (SI) 266°C, Sn 231°C.

The equipment employed is very simple; the arrangement is as shown in Fig. 1. Main parts are a small, vertically set, electric furance, by which a metal is melted and maintained at constant temperature above its melting point, and a water-jet pump which serves to suck up the molten metal into a mold connected to the pump by a rubber tube. The furance is connected through two pulleys to a clock work, so that it may fall down at an uniform speed. For measuring the temperature of the melt, a chromel-alumel thermocouple is inserted near the bottom of a crucible, in which the metal is melted, through a gap between the crucible and the the inside wall of the furnace, the remaining space of the gap being buried with asbestos powder. It was confirmed that a pyrometer connected to the thermocouple indicated the same temperature as that of the melt by keeping the indication

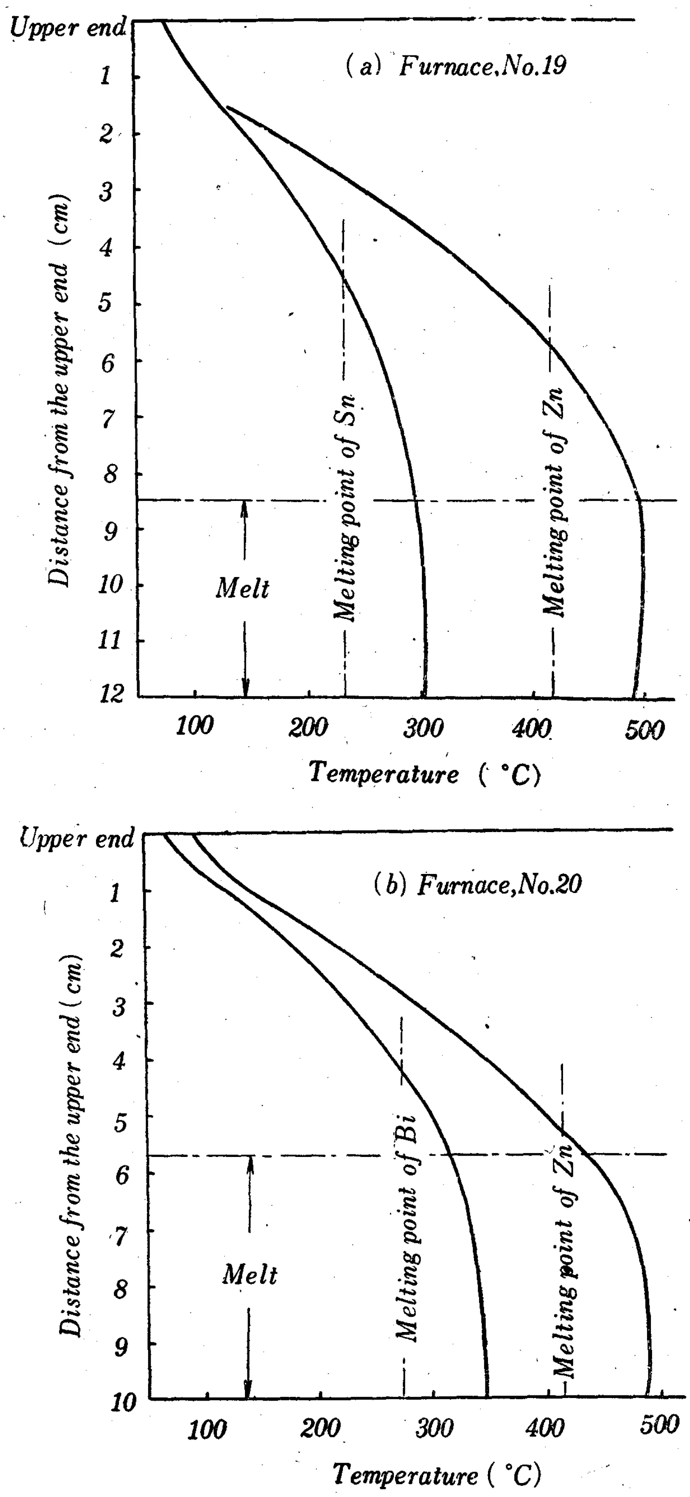

Fig. 2. Temperature distribution in furnaces used.

constant for about half an hour.

We used two electric furnaces, No. 19 and 20; the temperature gradient for the same maximum temperature is lower in the former than in the latter. The temperature distribution in these furnaces for different experimenting maximum temperatures (500°C for zinc, 350°C for bismuth, and 300°C for tin) are shown in Fig. 2.

As molds into which the molten metal is sucked up, soft glass tubes 5 mm in inner diameter and 1 mm in thickness were used for zinc and bismuth, and hard glass tubes of 4.5~5.0 mm in inner diameter and 0.25~0.30 mm in thickness for tin. Two types of the form of molds were tested (Fig. 3); both types (A and B) have capillaries at their lower ends and the B type further has another capillary at its upper portion so that the volume in which crystal nuclei originate may be smallr than in the A type. It was desirable that the lower capillary was possibly narrow so as to avoid sucking up oxides of the metal floating on the surface of the melt together with the melt and to prevent dropping off the sucked-up melt, but its size was restricted by the sucking-power of the water-jet pump used and the specific weight of the molten metal, and so the inner diameter of the lower capillary was 0.03 mm for bismuth and tin and 0.01~0.02 mm for zinc. Glass tubes must be washed enough with cleaning solution (50 percent sulphuric acid saturated with potassium bichromate) and then with running water, in order to remove dirts sticked to their inside wall, and subsequently they must be dried to exclude the moisture. The presence of dirts would give chances to an undesirable formation of crystal nuclei and that of moisture would cause to form blow holes on the surface of the crystal produced.

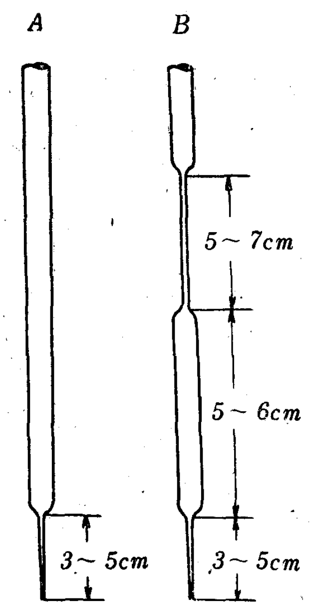

Fig. 3. Form of glass tubes used as molds.

The procedure for growing crystal is as follows. The metal of a proper quantity is melted in an alumina crucible by the electric furnace and kept at a constant temperature 70~80°C above its melting point. Then, oxides floating on the surface of the melt is removed by a small iron spoon, and the surface of the melt is covered by a thin molten paraffin layer so as to restrain the further oxidation of the melt. The glass tube(mold), as connected to the water-jet pump by a rubber tube, is pre-heated sufficiently(11) by a Bunsen burner along the length in which the molten metal is to be filled, and then its lower capillary is immersed into the melt as soon as remaining oxides on the melt are pushed to an inside wall of the tube. The molten metal is sucked up into the tube with an appropriately slow speed by the action of the pump. If this speed is high the melt is sucked up beyond the pre-heated part of the tube, and conversely if this speed is too low the

(11) When this pre-heating is insufficient, pits are produced on the surface of ingots as the sucked-up melt solidifies rapidly.

temperature of the pre-heated part of the tube falls down. In any case the sucked-up melt solidifies quickly, causing the formation of blow-holes. Thus, it is important that above procedure is done in a possibly short-time. Whether a perfect (no-pit) crystal could be obtained or not, depends upon the size of inner diameter of the lower capillary, manner of pre-heating of the mold, temperature of the molten metal, and speed of suction, and therefore it is necessary to control these conditions suitably at each time. The glass tube filled with the molten metal is left for a while, and then it is lifted from the furnace by a hand, or alternatively the furnace is lowered at a constant speed by a clock mechanism (Fig. 1), so that the metal may solidify progressively from its top.

Finally, the glass tube is cut carefully with a file at its upper empty portion and is then etched off with 40 percent hydrofluoric acid. The ingot thus obtained is etched with a reagent appropriate to each metal and the condition of crystal growth is examined. Etching solutions used are concentrated hydrochloric acid for zinc, concentrated nitric acid for bismuth and the mixture of concentrated hydrochloric acid and chromic acid anhydride (95 : 5) for tin. It is hardly needless to say that these metal crystals, especially bismuth ones, must be treated with a gerat care, since a slight stress may produce twin or slip bands easily.

III. Experimental Results

(1) Zinc

As a first step, we tried to produce single caystals of zinc. Experimental results are summarized in Table 1(a). For the first time, molten zinc kept at 500°C in the furance No.20, of which the temperature gradient at a point of the melting point of the metal was 51°C/cm, was sucked up into A-type glass tubes, and then the tubes were cooled slowly by lifting by a hand from the furnace with a mean speed of about 20 cm/hr. Any of ten ingots thus prepared did not become a single crystal, but consisted of several coarse grains which started from the top of ingot and grew parallel downwards. This may be due to the fact that the

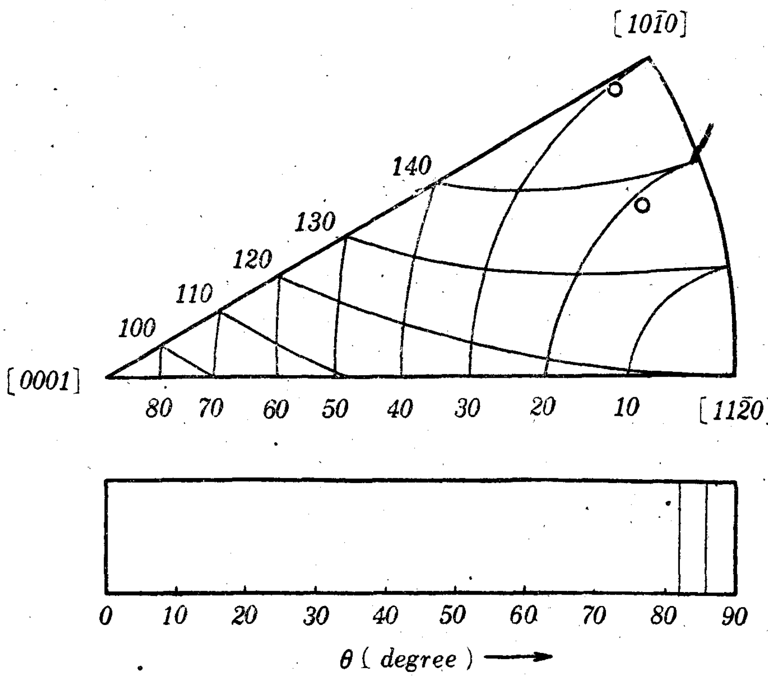

Fig. 4. Distribution of orientations of zinc single crystals prepared by the suction method.

cooling velocity is faster than that of crystal growth. Then, we employed the furnace No. 19, of which the temperature gradient at a point of the meling point of the metal was 47°C/cm, namely slightly lower than that of No. 20, and cooled glass tubes of the A and B types filled with molten zinc by lowering the furnace by a clock work with approximately the same speed as before. A-type tubes failed to make single crystals, but two of ten B-type tubes gave perfect single crystals. Orientations of the single crystals (4 mm in diameter and 5 cm in length) thus made, as determined by the light-figure method developed recently by the present writers,(12) are shown in Fig. 4. It is noteworthy that both orientations are nearly perpendicular to the hexagonal axis [0001].

Table 1. Experimental results on the preparation of single crystals of zinc, bismuth and white tin by the suction method.

(a) Zinc (Diameter 4 mm; length 5 cm). Furnace temperature : 500°C

Form of molds	Furnace No.	Cooling		Number of prepared ingots	Number of single crystals obtained	
		Method	Speed (c m/hr)		Perfect	"Imperfect*"
A	20	by a hand	ca. 20	10	0	0
A	19	by clock-work	18.8	10	0	0
B	〃	〃	〃	10	2	0

(b) Bismuth (Diameter 5 mm; length 5~7 cm). Furnace No. 20.

Material	Form of molds	Furnace temperature (°C)	Cooling		Number of prepared ingots	Number of single crystals obtained	
			Method	Speed (cm/hr)		Perfect	"Imperfect"*
SI	A	400	by a hand	ca. 20	10	4	1
KI	〃	350	〃	〃	15	3	2
KI	B	〃	〃	〃	10	3	1
KI	A	〃	by clock-work	23.8	10	3	5
KI	〃	〃		44.4	10	2	1
KI	B	〃	〃	23.8	20	3	3
KI	〃	〃	〃	44.4	10	3	1

(c) Tin (Diameter 4.5~5.0 mm; length 5~7 cm). Furnace Temperature : 300° C

Form of molds	Furnace No.	Cooling		Number of prepared ingots	Number of single crystals obtained	
		Method	Speed(cm/hr)		Perfect	"Imperfect*"
A	20	by a hand	ca. 20	10	0	0
B	〃	〃	〃	10	1	2
〃	19	by clock-work	5.9	10	4	2
〃	〃	〃	10.1	10	3	2
〃	〃	〃	23.8	10	3	3

* Imperfect single crystals are those which consist mainly of a single grain but contain one or two minute grains.

(2) Bismuth

Molten bismuth (SI) maintained at 400°C by the furnace No. 20 was sucked up into A-type tubes and cooled by lifting tubes by a hand at a mean rate of about

(12) M. Yamamoto and J. Watanabé, Sci. Rep. RITU, A2 (1950), 270.

20 cm/hr. Five of ten ingots became singles crystals, one of these being an "imperfect" single crystal (a crystal consisting mainly of a single grain and containing one or two minute grains). Then, we dropped the furnace temperature down to 350°C for which the temperature gradient at a point of the metal was 34°C/cm, sucked up molten bismuth of the other lot (KI) into glass tubes of both types, and cooled them by lifting by a hand (ca. 20 cm/hr) or by lowering the furnace by a clockwork at the rate of 23.8 to 44.4 cm/hr. It was found that the percentage of of success in the preparation of single crystal was approximately the same as before, as seen from Table 1(b), and that the growth conditions, namely the kind of material, type of glass tubes, furnace temperature, and manner and rate of cooling, have apparently almost no influence on the percentage of success in the scope of this investigation. It is to be noted, however, that the percentage of success is not independent on the growth conditions, but factors other than specified in Table 1b, such as the temperature gradient of the furnace and the manner of pre-heating molds, have greater effects on the preparation of single crystals by the suction method, as described in II. Further, apparently no effect of the cooling rate after suction on the percentage of success indicates that, at the instant just after the completion of suction, the head of sucked-up melt begins to solidify and whether or not a single crystal may be produced has almost been decided. Finally, it may be noted that in cases of A-type tubes it was possible to ensure a single grain when the head of sucked-up melt came to the level of the top-end of the furnace and it solidified in a semi-spherical form.

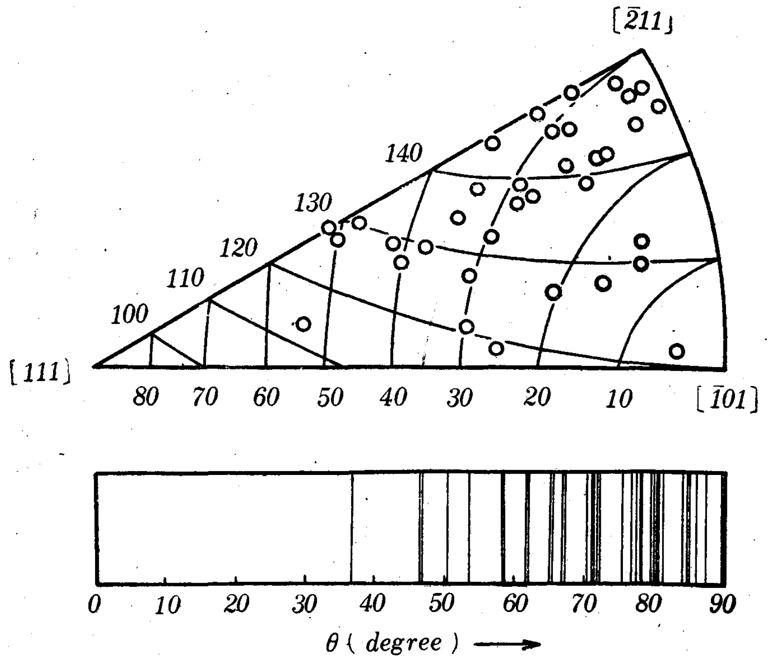

Fig. 5. Distribution of orientations of bismuth single crystals prepared by the suction method.

Orientations of 35 bismuth single crystals (5 mm in diameter and 5~7 cm in length) thus produced were determined by the light-figure method, which will be described shortly in a separate paper. The distribution of orientations is shown in Fig. 5. An angle θ between the rod axis and the trigonal axis [111] ranges from 37° to 89° and orientations close to the [211] axis are most preferred. The influence of specified growth conditions on the distribution of orientations are not distinct because of the shortness of the number of crystals tested.

(3) White tin

The preparation of single crystals of white tin was tried under various conditions except for the fixed furnace temperature of 300°C. Experimental results are summasized in Table 1(c). With the furnace No. 20 and the cooling by a hand with an average speed of 30 cm/hr, A-type glass tubes produced no single crystals, as in the case of zinc, while three of ten B-type tubes made three single crystals, the latter case corresponding to Chalmers'[10] experiments. With the furnace No. 19, of which the temperature gradient at a point of the melting point of the metal is 27°C/cm and B-type tubes, the percentage of success was 50~60 percent regardless of cooling velocity.

Orientations of 20 single crystals of white tin (4.5~5.0 mm in diameter and 5~7 cm in length) thus obtained, as determined by the light-figure method which will be described separately in the near future, are shown in Fig. 6. For very many crystals an angle θ which the rod axis makes with the tetragonal axis [001] is larger than 70° and no crystal has θ smaller than 40°. Such preference of large θ orientations was observed by Chalmers.[10]

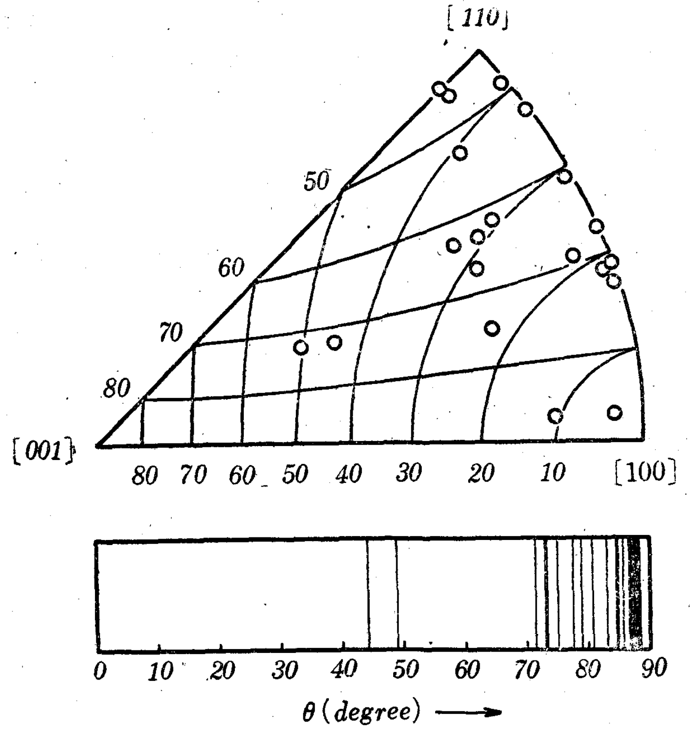

Fig. 6. Distributions of orientations of tin single crystals prepared by the suction method.

As described above, we have succeeded to prepare single crystals of hexagonal zinc, trigonal bismuth and tetragonal tin by the suction method. For zinc and tin, single crystals were not made by the use of the furnace No. 20 of which temperature gradient was higher and A-type glass tubes which had uniform cross-section at their top-end portion, while single crystals could be prepared with the success of 20 and 50 percent, respectively, by the use of the furnace No. 19 which had lower temperature gradient and B-type tubes of which the top-end portions were drawn to a narrow capillary. In the case of bismuth, single crystals could be made with 50 and 40 percent success for A- and B-type tubes, respectively, in spite of the use of the furnace No. 20. From the above results, it may be concluded that, in order to raise the percentage of success in the preparation of metallic single crystals by sucking up from their melt, it is necessary to cool the sucked-up melt more slowly by the use of a furnace of which the temperature gradient is lower and further to minimize the number of originating crystal nuclei by the use of a mold which has a small cross-section at its top-end portion.

The percentage of success for tin was higher than that for zinc, when the same furnace (No. 19) and tubes of the same type (B) were used (cf. Table 1). This may be due to the fact that the melt of tin were cooled more slowly in a temperature gradient lower than in the case of zinc, corresponding to its far lower melting point (see Fig. 2). For bismuth, the percentage of success for A-tpye tubes was rather higher than that for B-type tubes. This may be regarded as concerned with an abnormal volume change, namely expansion of the metal during solidification. It should be noted, further, that the relatively high percentage of success obtained in spite of the use of a furnace with a higher temperature gradient and no effect of temperature rise by 50°C of the melt on the percentage of success in the case of bismuth (Table 1b), may be due to its large velocity of crystal growth.(13)

Single crystals of zinc, bismuth and white tin prepared by the suction method show remarkably preferred orientations. Maxima of density of the distribution of an angle θ, which the rod axis makes with the principal crystallographic axis (the hexagonal axis [0001] for zinc, trigonal axis [111] for bismuth, or tetragonal axis [001] for tin), situate at 80°~90° and there exist no crystals of small θ. It may be expected, however, that the preference of large θ orientations can be remedied to a certain extent by cooling the sucked-up melt more slowly.

Summary

The preparation of single crystals of zinc, bismuth and tin, 5 mm in diameter and 5~7 cm in length, by sucking up from their melts was tried by the use of simple equipment and procedure, and the effect of growing conditions upon the percentage of success and distribution of orientations of crystals produced was studied. Single crystals of zinc and tin were obtained with 20 and 50 percent success, respectively, by the use of a furnace having lower temperature gradient and B-type glass tubes (molds) of which top-end portion was drawn to a narrow capillary. For bismuth, single crystals could be made easily with 50 and 40 percent success for A- and B-types tubes, respectively, in spite of the use of a furnace with a higher temperature gradient (An A-type tube has an uniform cross-section at its top-end portion).

In order to raise the percentage of success, it was found necessary to cool the sucked-up melt slowly by the use of a furnace having low temperature gradient and further to minimize the number of originating crystal nuclei by the use of a mold which has a small cross-section at its top-end portion. In should be noted that in this method the manner of preheating molds and the sucking velocity of the melt both of which are difficult to be controled, have the greatest effect on the percentage of success.

Single crystals of zinc, bismuth and tin produced by this method, as determined by the light-figure method, show the dominant preference of crystal directions

(13) It is well known that bismuth single crystals can be produced far more easily than other metal crystals by the Bridgman method and Kapitza method.

nearly perpendicular to the principal crystallographic axis, namely the hexagonal axis [0001] for zinc, trigonal axis [111] for bismuth. or tetragonal axis [001] for tin; there exists no crystal having an orientation closer to the principal crystallographic axis. It may be expected, however, that the improvement of growth conditions, especially the use of a furnace of lower temperature gradient, would remedy the preference of particular orientation to a certain extent.