JANUARY, 1929 PHYSICAL REVIEW VOLUME 33

AN EXPERIMENTAL STUDY OF THE GROWTH OF ZINC CRYSTALS BY THE CZOCHRALSKI-GOMPERZ METHOD

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Abstract

The conditions necessary to grow zinc single crystals of 2.7 mm diameter and of any desired orientation are determined experimentally. When a constant rate of growth is used and the crystal is initially given the desired orientation by starting it on a suitable nucleus the determining factor for the successful growth of a single crystal rod 10 cm or more in length is found to be the temperature gradient existing in the column of liquid zinc just below the growing crystal. The appropriate temperature gradient is a function of the orientation of the crystal. It is depicted graphically in a figure which shows the upper and lower limiting curves for the region of successful growth when the rate of growth is 1.2 cm/min. The lower curve rises from orientation 0 to 45° and falls from 45 to 90°. The upper curve lies slightly above and parallel to the lower curve from 0 to 50°, but then rises very sharply. The shape of this region does not seem such as to be attributed only to variation in heat conductivity with orientation. Attempts to grow crystals outside of the appropriate region result in sudden or gradual changes to new orientations. In the latter the orientation shifts gradually through a considerable range. Illustrations are given of such changes.

Introduction

Although several investigators have used the Czochralski[1]-Gomperz[2] method for the production of single-crystal rods of zinc, the conditions necessary to obtain a rod of any definite diameter and desired orientation[3] seem to have been largely empirical and suited to the particular form of the apparatus used. The variables on which the diameter of the rod and its orientation must depend are: (1) temperature of the molten zinc; (2) rate at which the crystal is grown; (3) the method used to cool the portion of the crystal already grown; (4) starting conditions, i.e., whether the crystal is started on a nuclear crystal or on a foreign body, such as a glass or copper rod.

Gomperz[2] employed a rate of growth of from 12 to 6 mm per min., and kept the molten zinc at from 25 to 30° above the melting point, in order to obtain ductile (dehnbar) single crystal wires. With the temperature 3° to 5° above the melting point and a corresponding rate of 30 to 60 mm per min., he obtained brittle single crystal wires. The diameters of the crystals ranged from 0.1 to 1.5 mm. They were all started on a glass rod. A stream of N_2 was passed through the apparatus to prevent oxidation of the molten zinc. It undoubtedly also produced a cooling effect, though not a definitely controlled one. He makes no mention of the orientations of the crystals

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[1] Czochralski, Zeits. f. phys. Chem., **92**, 219 (1917–18).

[2] Gomperz, Zeits. f. Physik, **8**, 184 (1922).

[3] The term orientation is used to define the angle between the vertical axis of the crystal and the axis of the rod.

grown, but it may be assumed that the ductile crystals had orientations between 20 and 70°, while the brittle crystals were either nearly 0 or else nearly 90°, since ductility and brittleness generally characterize these particular types of single crystals.

Mark, Polanyi, and Schmid[4] grew ductile crystals using a "high temperature" (not stated specifically) and a rate of 12 to 6 mm per min. Under these circumstances, however, only fifty percent of the trials resulted in successful crystals. They found further that the impurity of the zinc must be less than 0.03 percent to grow these ductile crystals. Using a rate of less than 6 mm per min., they found that brittle crystals could always be grown, signifying by brittle crystals those having an orientation of 90°. They employed a blast of gas directed at the portion of the crystal already grown, for the specific purpose of cooling it. The crystals were started on a foreign body apparently.

Grüneisen and Goens[5] were apparently the first to use a crystal fragment as a nucleus on which to start the new crystal. Their experience of the conditions of growth was at variance with that of others. They were very successful in growing crystals of various orientations and assumed that the blast of cooling gas was an important factor. They stated, further, that with a very slow rate they obtained crystals of 0° (or nearly 0°) orientation, but noted that if the rate was too fast, the crystal would change to approximately 90°.

The Czochralski-Gomperz method was first used in this laboratory by E. G. Linder[6] to grow zinc crystals. Later[7] the apparatus was improved, and a certain empirical procedure was worked out to produce crystals of desired orientations. At first the crystals were started on copper wires and later on nuclear crystals. The method as developed by Linder was, however, still largely a matter of trial and error, and he was not able to produce with certainty a crystal rod of a particular diameter and any specified orientation. During the earlier work, he produced some crystals the orientation of which varied continuously along the lengths of the rods. He states[6] that such crystals were grown at an "excessive rate" (probably more than 10 mm a minute), but no further specifications are given. The air blast which he used was directed towards the surface of the zinc in the crucible and was not used specifically to cool the solid crystal rod.

A mica disk, floating on the surface of the molten zinc and pierced with a circular hole through which the crystal is drawn, has been used by almost all observers and was used throughout in the work described below.

In the fall of 1927, one of the present writers (E.P.T.T.) attempted to place the growth of zinc crystals by this method on a less empirical basis. Linder's second apparatus was used with some slight modifications, which have in the main been adhered to in the work and which will be described

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[4] Mark, Polanyi, Schmid, Zeits. f. Physik, **12**, 58 (1923).

[5] Grüneisen and Goens, Zeits. f. Physik, **26**, 235 (1924).

[6] E. G. Linder, Phys. Rev. **26**, 486 (1925).

[7] Linder, Phys. Rev., **29**, 554 (1927).

below. It was concluded that (1) the rate of growth was not a determining factor in the production of a given orientation; (2) for a given diameter of crystal and given (constant) rate of growth, a crystal of any orientation might be grown if it was started on a nucleus of the desired orientation and was grown with a temperature of the molten zinc appropriate for that orientation; (3) the temperature gradient existing in the column of liquid zinc just below the solidified crystal (see Fig. 1(a)) is the main factor underlying the continued growth of a particular orientation which has been started on a nucleus. This work has been described briefly elsewhere[8] and will not be further elaborated on, as the present paper covers the same ground more fully and is in substantial agreement with the earlier work.

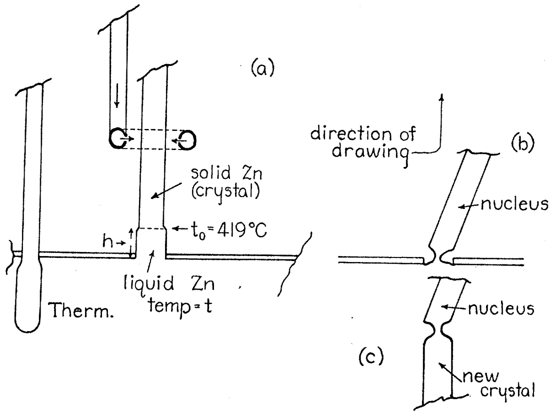

Fig. 1. To illustrate method of growing zinc crystals.

The main object of the present investigation was to obtain more particularly and exactly the relation between this temperature-gradient and the orientation, and, if possible, to shed light on the general problem of the process of crystallization from the liquid state.

APPARATUS

A description of the apparatus has been given by Linder.[9] The tube used for a blast of air by Linder was not so used in this investigation, but a special form of "ring nozzle," placed about 15 mm above the surface of the molten zinc, directed streams of air radially at the crystal. This is shown in detail in Fig. 1(a). A thermometer and a thermocouple were also placed in the molten zinc, the latter being directly below the hole in the mica, through which the crystal is being grown. (It is not shown in the figure.) A stream of CO_2 is admitted through a glass tube (not shown in figure) to keep the surface of the melt free from oxide prior to and during the insertion of the nucleus. No gas passes through this tube during growth of the crystal.

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[8] E. P. T. Tyndall, Phys. Rev., **31**, 313 (1928).

[9] Ref. 7. Fig. 1.

PROCEDURE

The procedure which is used in growing a single crystal rod having a definite diameter and orientation is essentially as follows. A portion of a crystal having the desired orientation is inserted in the drawing apparatus with its length parallel to the direction of drawing or, if a crystal nucleus having the desired orientation is not available, a portion of a crystal of somewhat different orientation is inserted in the holder in such a way that its principal axis makes the desired angle with the direction of drawing. This situation is depicted in Fig. 1(b) and (c). The mica disk previously referred to is now pushed up on the nuclear crystal, so that this nucleus passes through the circular hole in the center of the disk. The diameter of this hole is just about equal to the desired crystal diameter. The zinc in the crucible is then heated until it attains a temperature approximately 50° above the melting point (419°C). A small stream of CO_2 is then passed through the tube previously mentioned. The space above the surface of the molten zinc is thus freed of air. The film of oxide which has previously formed on the surface is skimmed off by means of a glass rod, and the lower end of the nucleus is pushed below the clean surface of the melt. The mica disk is then dropped down and floats on the surface. The stream of CO_2 is now stopped. Fig. 1(b) represents this stage of the process, a well defined "neck," having formed at the junction of the molten zinc and the nucleus. The "ring nozzle" is then adjusted around the nucleus, and the air turned on rather strongly so that the cooling of the molten zinc to the desired temperature of growth is accelerated. When the temperature has become steady at a value within the temperature range in which the crystal is to be grown, the air is adjusted to the right value and the drawing mechanism is started. During the growth of the crystal the temperature is kept as constant as possible. The air blast may be adjusted slightly from time to time, if necessary, in order to keep the crystal diameter equal to that of the hole in the mica disk. A record is kept of the temperature at the start and, as nearly as possible, of every change of temperature, together with the corresponding length of the crystal at the time that the temperature change takes place. It is found that a greater degree of success is attained if the nucleus has the same diameter as the crystal to be grown, since this eliminates the possibility of oxide forming between the mica and the crystal. If such oxide is present, it may adhere to the sides of the crystal and thereby serve as a new nucleus on which another crystal may start. The need of having the surface of the molten zinc entirely free from oxide at the time when the nucleus is inserted can also not be too highly stressed.

THE GROWTH PROCESS

After the crystal has been growing several minutes, it is in the condition shown in Fig. 1(a). The temperature of the liquid zinc just below the hole in the mica is t. Above this point there is a small cylindrical column of liquid zinc the top of which is at temperature t_0 ($=419°C$, the melting point of the zinc). There is probably little lateral loss of heat in this column; thus the temperature gradient is axial (i.e., parallel to the axis of the rod, not crystal axis), and may be considered as proportional to $(t-t_0)$, provided the height, h, of the liquid column is the same for all crystals. It is further assumed that this height is the same for crystals of the *same* diameter being drawn at the *same* rate. The function of the air blast is twofold: (1) to cool the crystal far enough above the plane of solidification so that the heat flow may be normal to this plane, (2) to fix the size of the crystal. Thus, the larger the diameter of crystal for a given temperature of melt, or the higher the temperature for a given diameter, the stronger must be the blast of air.

The conclusion of one of the writers, previously stated, that the determining factor underlying the growth of a particular orientation is the temperature gradient in the liquid column, is of course based on the assumption of proportionality between this temperature gradient and the temperature difference $(t-t_0)$.

In order to obtain the range of this temperature gradient in which a crystal having a definite orientation and diameter should grow, an attempt is made to grow crystals at every few degrees of temperature above the melting point until a temperature is found at which a crystal 10 to 18 cm in length can be obtained. Having found this temperature, the process is continued until both the highest and the lowest temperature at which the crystal can be grown are known. In a similar manner the range for other orientations is obtained, the rate of drawing being kept constant for all orientations.

MATERIALS

Two lots of Reagent Zinc Merck were used in obtaining the data herewith presented. The analyses given on the containers differ slightly. The first lot has as maximum limits of impurities 0.000025 percent of arsenic, 0.0056 percent of matter oxidizable by permanganate (as Fe), and 0.0000 percent of compounds of sulphur and phosphorus. The second, which was used in the latter part of the experiments, contains as maximum limits of impurities 0.000025 percent of arsenic, 0.028 percent of matter oxidizable by permanganate (as Fe), and 0.0020 percent of chlorides. The latter grade proved somewhat easier to handle since it is only slightly subject to oxidization when exposed to air, even at a temperature of 60° above the melting point.

RESULTS AND DISCUSSION

Fig. 2 is a graphical representation of the results which have been obtained for crystals 2.7 mm in diameter drawn at a rate of 1.2 cm per minute. The circles indicate successful crystals grown and are restricted to those which have the same orientation throughout and which are at least 10 cm in length. The crosses signify crystals which were unsuccessful, that is, crystals which grew 1 cm or more with the orientation with which they were started but then changed either gradually or suddenly to a different orientation, the change not being caused by oxide or any other imperfection on the crystal surface or in its interior. The mean of the temperature during the growing of the crystal is used in plotting the successful crystals ,while in the case of the unsuccessful ones the approximate temperature at which the change in orientation took place is plotted. The two smooth curves, drawn so as to lie in the region of uncertainty, therefore represent the extreme limits of temperature at which a crystal can be grown. Hence the region between them is the temperature range in which the particular orientations will grow. Crosses lying far exterior to the limits are not plotted in order that the graph might be clearer; this refers especially to the region of high temperature for crystals below 50° orientation.

The 90° (or nearly 90°) crystals are seldom found to change. They are very readily grown and can be obtained in a very wide range of temperature, which seems evident from the rapid rise of the upper limit curve from 60° to 70°. No attempt was made to grow 80° or 90° crystals with temperatures above the upper limit for the 70° crystals, because the extreme amount of cooling which is necessary at these high temperatures could not be conveniently produced. The lower limits for the 0° (or nearly 0°) and the 90° crystals were not obtained with any degree of definiteness on account of the nearness of approach to the solidification point of the zinc.

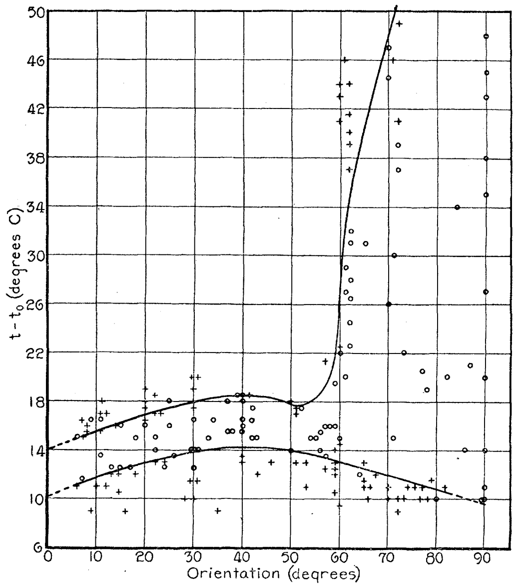

Fig. 2. Graphical representation of the results obtained in growing zinc crystals.

It is to be noted that the crosses and circles overlap slightly. This is due to the fact that successful crystals can occasionally be obtained in the region of uncertainty, provided that the temperature remains very constant, while unsuccessful ones are of course also obtained there. It may be noted here that there are no crosses at 30° orientation higher than $(t-t_0)=11.5°$, and it may be that there is a depression in the lower limit curve in this neighborhood. The writers, however, do not believe this very probable and have not drawn the curve to include this possibility.

Four points which might have been plotted as crosses have been omitted. They are definitely cases of crystals which changed orientation when well within the region in which they should grow. One of these cases was apparently due to the apparatus running somewhat jerkily; a second is of particular interest since it is that of a 90° crystal changing to 73°, the only case of such a change that the writers have ever observed or heard of. There is no obvious explanation for this change, nor for the other two cases.

As already mentioned, crystals started within the appropriate range of temperature and grown at or beyond either limit of this range change orientation either suddenly or gradually. A sudden change in orientation is characterized by a new crystal, which has an orientation different from the original, starting abruptly within the crystal rod without there being any flaw within or on the surface of the rod to which the change might be attributed. These sudden changes occur (1) for the second lot of zinc, when the temperature goes several degrees beyond (i.e., above or below) the limits of the region of successful growth and remains there fairly constant, (2) for the first lot of zinc, as soon as the temperature passes the limits. In these cases of sudden change, the new orientation is usually higher (in 77 cases out of 80 observed) than the original, and the new crystal always crowds out the old after the rod has grown a few centimeters as a double crystal. Temperatures several degrees beyond either limit seem to accelerate this crowding. It is found further that crystals of orientations between 6 and 40°, in changing suddenly, seldom change to crystals having orientations less than 60°. If, however, such a crystal does change to an orientation lower than 60°, a second sudden change usually occurs, giving a final orientation above 70°.

When a crystal changes orientation gradually, the orientation changes continuously along the length of the rod without any evidence of a new crystal entering. Crystals showing this gradual change were, almost without exception, obtained only with the second lot of zinc. A gradual change is caused: (1) by starting a crystal within the range and going below the lower limit, in which case a low orientation (6 to 30°) crystal will shift to a slightly higher one, and a high orientation (50 to 85°) crystal to a lower one; (2) by starting within the range and exceeding the *upper* limit, in which case both the low orientations (6 to 25°) and the high orientations (60 to 70°) shift to slightly higher orientations; (3) by starting and growing the crystal just exterior to the limiting temperatures. It is found difficult, in going below the lower limit, to cause a high orientation crystal (50 to 85°) to shift to below 40°. Usually, if a crystal shifts from 70° down to about 45°, it will change suddenly to a higher orientation if the temperature is kept fairly constant below the range.

Fig. 3 shows the behavior of some of these variable orientation crystals. The "limit" curves are superimposed on the graph in order that the variations in temperature and orientation may be more easily understood. In the lower part of the figure is plotted orientation against temperature above the melting point. Directly above is a graph showing the relation between the orientation and length for each crystal represented. Consider for example curve (a), Fig. 3. A 75° crystal starts at 13° above the melting point,which is well within the range, and the temperature falls until it is 11° above, at which point the orientation begins to shift. By following the arrows on the curve, one sees that the orientation remains constant at the beginning and end of the crystal, when the temperature is within the range, but varies when it is exterior to it. Curve (a′), Fig. 3, shows the relation between the length and orientation for this same crystal. Cases of this kind could be produced at will. In curve (b), Fig. 3, is shown a case in which the orientation begins to shift as soon as the temperature begins to fall. A sudden shift to a higher orientation occurs when the orientation has reached 52°. Had the temperature been increased to within the range at this point (similar to the procedure followed in curve (a)) the crystal would undoubtedly have continued to grow with this orientation. Several such instances of a gradual change followed by a sudden change have been noted, the sudden change always being to a higher orientation. This second change is concordant with the type of sudden change previously discussed. Curves (c), (c′), (d) and (d′) illustrate typical shifts for low orientation crystals.

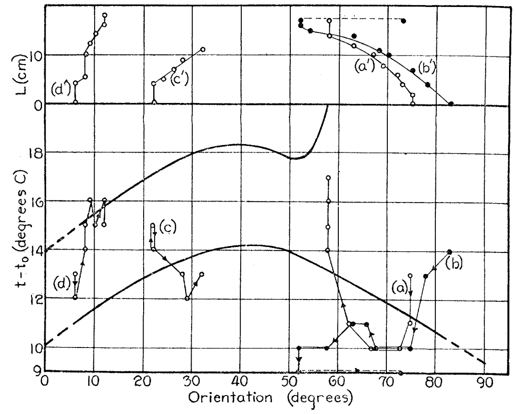

Fig. 3. Showing the behavior of some of crystals of variable orientation.

Besides the variable orientation crystals just discussed, the following peculiar crystals were obtained which are of interest: (1) A 31° crystal which grew uniformly and was straight when the temperature remained within the range, but became slightly crooked and rough when the temperature exceeded the upper limit; perhaps in so doing it was able to retain its original orientation. (2) A 52° crystal which changed suddenly to an orientation of 77° and then this second crystal after a few centimeters of growth changed suddenly to a 65° crystal. This is the only "secondary" sudden change to a lower orientation which has been noted. (3) A 53° crystal which changed suddenly to another 53° crystal when the temperature was below the lower limit. The temperature then entered the range and the crystal continued to grow with the second 53° orientation. The two 53° crystals were so situated in the rod that the axis of the rod and the two vertical crystal axes were in the same plane, that is, the two crystal axes made the largest possible angle with each other.

After the experimental results presented above had been obtained, an effort was made to determine what effect a change in rate of growing the crystals would have on the limit curves. The new rate used was 2.2 cm per minute. Fifteen crystals were grown, the majority of which had orientations of approximately 50°. The results seem to indicate that the lower limit curve for the 50° orientation crystals is raised considerably higher. No definite statement, however, can be made as to the remaining part of the curve. Interesting gradual changes were observed. Two crystals, 82° and 80° orientation, started at a temperature near the lower limit curve for the 1.2 cm per minute rate, were made to shift gradually to orientations of 49° and 44°, respectively, during a crystal length of 15 cm. These shifts are considerably greater than any observed at the rate of 1.2 cm per minute. It is inferred that this is due to two causes: (1) the temperature of growth is probably well below the lower limit for the 2.2 cm per minute rate; (2) the higher rate accelerates the shifting. The explanation for the crystals grown by Linder[6] with orientations varying from approximately 90° to 45° is thus apparent.

Conclusion

The most important result is believed to be the substantiation of the fact that the temperature gradient existing in the liquid zinc just before it solidifies is the main factor determining the continued and successful growth of a particular orientation. Thus there is no particular "crystallization velocity" associated with a certain orientation. The writers do not mean to imply that, for a particular orientation, the permissible value, or range of values, of this gradient is independent of the velocity of growth. Were this so, the region included in the limiting curves of Fig. 2 would always be the region of successful growth, regardless of the velocity of growth.

For crystals of different orientation, but of the same diameter and grown at the same rate, the most obvious factor which varies with the orientation is the thermal conductivity of the crystal. Since, however, the reciprocal of this quantity is a linear function of the square of the cosine of the angle of orientation and thus has no maximum or minimum between 0° and 90°, it is difficult to see how the region of successful growth shown in Fig. 2 can be predicted from considerations of crystal conductivity alone. It seems more likely that the determining gradient in the liquid (or in the solid), in addition to depending on the crystal conductivity, is also an independent function of the orientation.

University of Iowa,
Iowa City, Iowa,
October, 1928.