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著者	YANAGIHARA Tadashi, KAWANISHI Rokuro
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On the Primary Crystallization of the System Sn-Bi*

Tadashi YANAGIHARA and Rokurô KAWANISHI

The Research Institute for Iron, Steel and Other Metals

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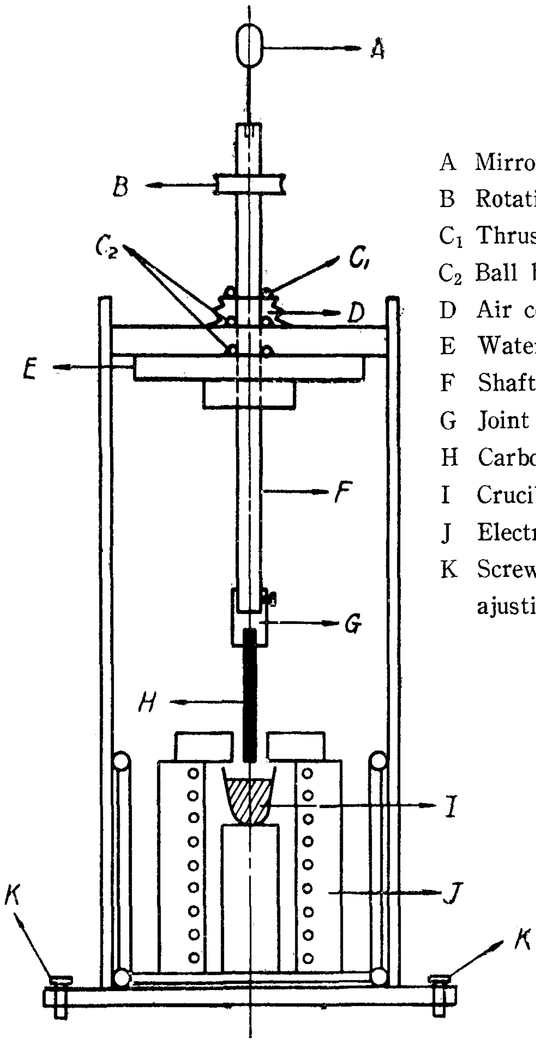
Synopsis

The viscosity change during the solidification of the alloy Sn–Bi was studied with the rotational viscosimeter in place of the capillary method used in the previous work. The size of primary crystal was also microscopically examined. It was found that the primary crystals were apt to solidify in small sizes, as the composition of the alloy approached the eutectic, or when the temperature at which the alloy was kept became low.

I. Introduction

In the previous work(1) the change in viscosity during the solidification of the alloy Sn-Bi containing 10 per cent of tin was studied by the capillary method. The viscosity of the melt kept at high temperatures was somewhat larger than that kept at low temperatures. In spite of large amounts of the primary crystals obtained at low temperatures, the low value of viscosity had been observed. In order to ascertain this peculiarity, a rotational viscosimeter was used in the present work. Further, the influences of the composition and of holding temperature upon the primary crystallization were microscopically examined.



A	Mirror
B	Rotating disc
C_1	Thrust bearing
C_2	Ball bearing
D	Air cooler
E	Water cooler
F	Shaft
G	Joint
H	Carbon rod
I	Crucible
J	Electric furnace
K	Screw for ajusting level

Fig. 1. Viscosimeter.

II. Method of experiment

Samples containing 10～90 per cent of tin were held for a certain period of time at the temperatures lower than the respective liquidus points by 5°C, and then changes in viscosity during the solidifi-

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* The 776th report of the Research Institute for Iron, Steel and Other Metals.

(1) T. Yanagihara, Sci. Rep. RITU, A3 (1951), 657.

cation were measured. The effect of the holding temperature upon the viscosity was studied with the samples containing 10 and 20 per cent of tin.

The rotational viscosimeter is shown in Fig. 1. The carbon rod H immersed in the melt I of 350 g by 30mm is rotated by the difference in weight between M_1 and M_2. The disc B fixed to the shaft F is rotated by the cotton belt connected to the weight system. The carbon rod is connected to the shaft by the joint G. The period of the rotation of carbon rod is measured with a rotating mirror and a stop watch, "Semikrograph", graduated to 1/50 second. In the present work, the period of one revolution was determined from the mean of ten measurements of time between the fourth and the fifth revolutions of the mirror.

The melt in the crucible K is heated in the electric furnace J. C_1 and C_2 are respectively thrust and ball bearings, which are protected from being heated by a water cooler E and an air cooler D. To adjust the carbon rod to be perpendicular, three screws K are used.

III. Experimental results

The equilibrium diagram of the system Sn-Bi is shown in Fig. 2, in which the liquidus points were determined by thermal analyses and the solidus points were taken from Hansen's work(2).

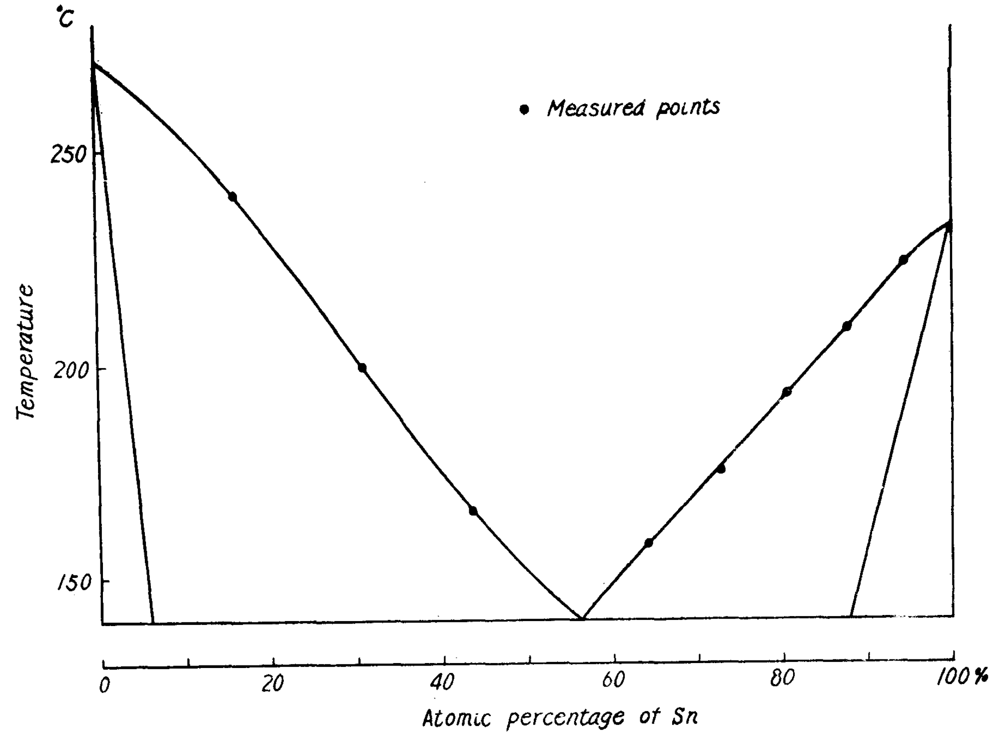

Fig. 2. Equilibrium diagram of Sn-Bi alloy.

The melt of each alloy was superheated higher than the liquidus temperature by 20°C, and when it was cooled to the temperature lower than the liquidus point by about 2°C, the temperature regulating apparatus was made to begin taking the

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(2) M. Hansen, *Aufbau der Zweistofflegierungen*, J. Springer (1936), 334.

subsequent measurement, and then the melt was safely held at the temperature lower than the liquidus point by 5°C. The results are shown in Figs. 3 and 4. Three steps will be recognized in these results, that is, the viscosity of the melt first increases and then decreases and finally is kept at the equilibrium value. As shown in Fig. 3, in the range of the primary crystallization of bismuth, the larger the tin content is, the more viscous the melt becomes both in the maximum and equilibrium states. In the range of the primary crystallization of tin, the same held good with regard to the bismuth content, as shown in Fig. 4.

The liquidus points, the holding temperatures, the time required for the maximum and equilibrium viscosities, and the amounts of primary crystals in the equilibrium

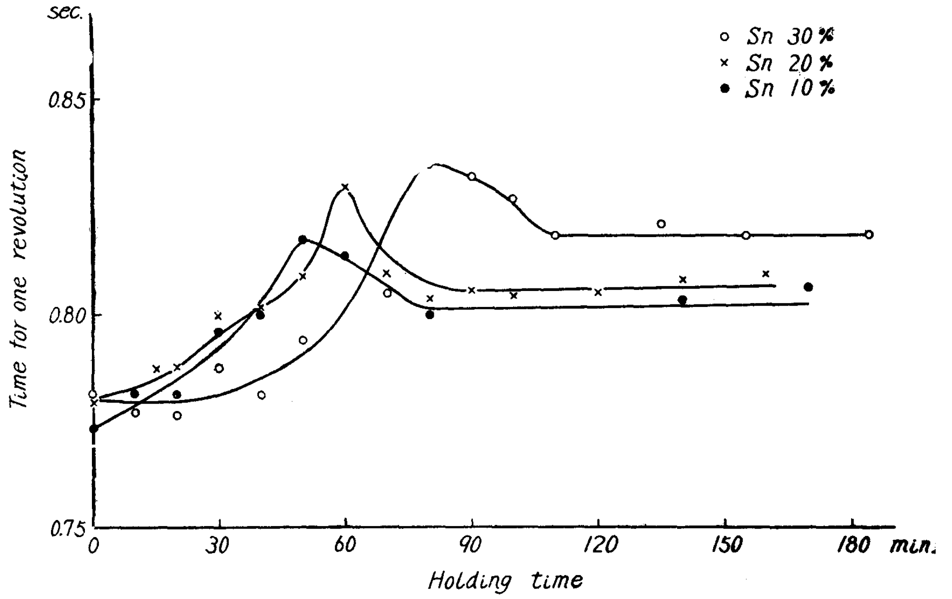

Fig. 3. The relation between the time for one revolution and holding times at the temperature 5°C below the liquidus points of Sn-Bi alloys.

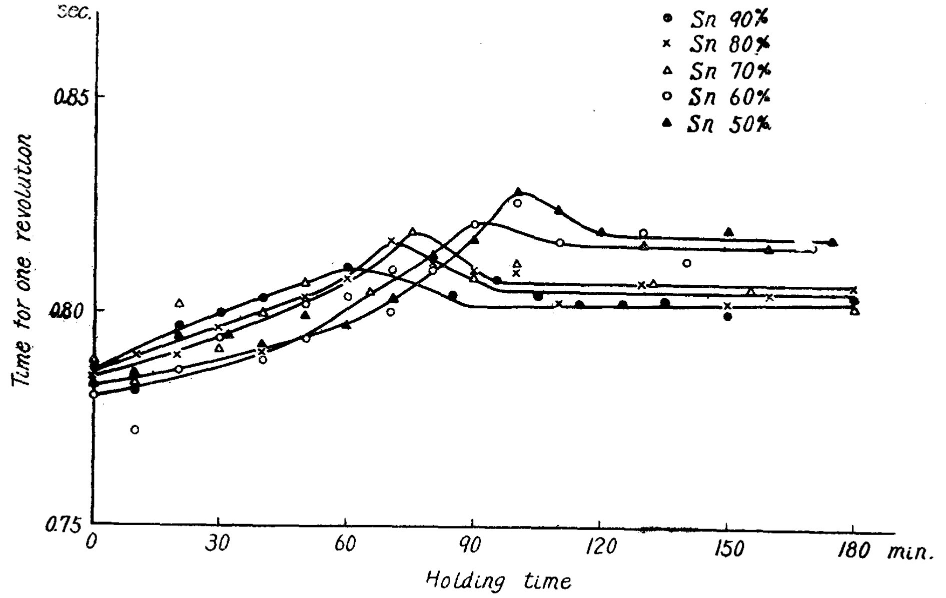

Fig. 4. The relation between the times for one revolution and the holding times at the temperature 5°C below the liquidus points of Sn-Bi alloys.

states at the temperatures lower than the liquidus points by 5°C are shown against the tin contents in Table 1. The amounts of primary crystals in the equilibrium states were determined from Fig. 2 by the lever relation. From Table 1, it will be seen that as the composition of the alloy approaches the eutectic, the viscosity is increased, and that though the amount of the primary crystallization is small, the viscosities both in the maximum and the equilibrium states are high.

Table 1. The liquidus points, the holding temperatures, the times to reach maximum and equilibrium viscosities, the times for one revolution at the maximum and equilibrium and the crystallized amounts of primary crystals in the equilibrium states at the temperatures 5°C below the liquidus points of Sn-Bi system.

Composition of alloy Sn%	Liquidus point °C	Holding temp. °C	The time to reach the maximum min	The time for one revolution at the max. sec	The time to reach the equilibrium min	The time for one revolution at the eq. sec	Crystallized amount at the eq. %
10	240	235	50	0.818	80	0.804	11.7
20	200	195	60	0.830	90	0.808	6.32
30	166	161	80	0.835	110	0.818	6.14
50	158	153	100	0.829	130	0.819	9.26
60	175	170	100	0.827	120	0.817	13.32
70	194	189	75	0.820	100	0.807	16.30
80	209	204	70	0.817	95	0.806	27.27
90	224	219	60	0.811	85	0.804	38.48

Next, the effect of the holding temperature upon the viscosity was examined with the alloys containing 10 and 20 per cent of tin. The primary crystallization occurring between the liquidus point and a definite measuring temperature certainly influences the viscosity in question, which must not be neglected. So the holding time was measured at and after the melt reached the liquidus point. The holding temperatures necessary for the melt of the alloy containing 10 per cent of tin were lower than the liquidus point by 3, 5, 8, 10, 12 and 15°C, and those for the alloy containing 20 per cent of tin were lower than the liquidus by 3, 5, 3, 10 and 13°C. Other conditions were the same as those in the preceding experiments. The results are shown respectively in Figs. 5 and 6. Both at the maximum and in equilibrium states, the viscosity increased with the lowering of the holding temperature. It was conceived that the results of the previous work(1) measured by the capillary method were erroneous. In the specimen with 20 per cent of tin held at the temperature lower than the liquidus by 13°C, the viscosity showed neither the maximum nor the equilibrium point, and the rotation of the viscosimeter stopped when the melt was held for 65 minutes.

The amounts of primary crystals at the equilibrium states against the holding temperature are shown in Table 2, from which it will be seen that with the lowering of the holding temperature, the amount of primary crystal and the viscosity both increase. This increase in the viscosity might be related partly to the increase in the amount of primary crystal in the melt.

Finally, the microscopical observation of the primary crystals in the melts during

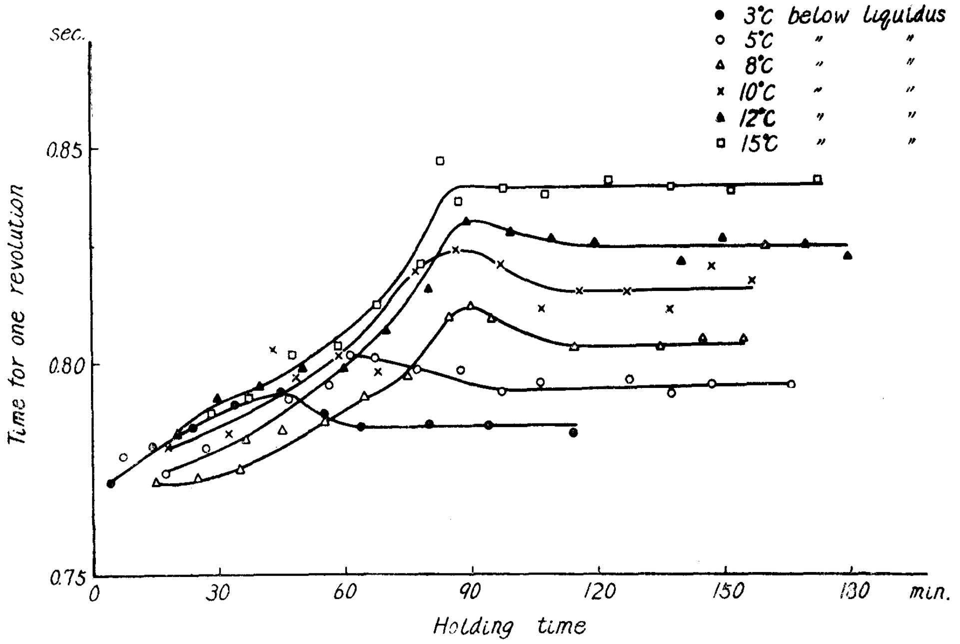

Fig. 5. The relation between the time for one revolution and holding time at various temperatures below the liquidus point of the alloy containing 10% of tin.

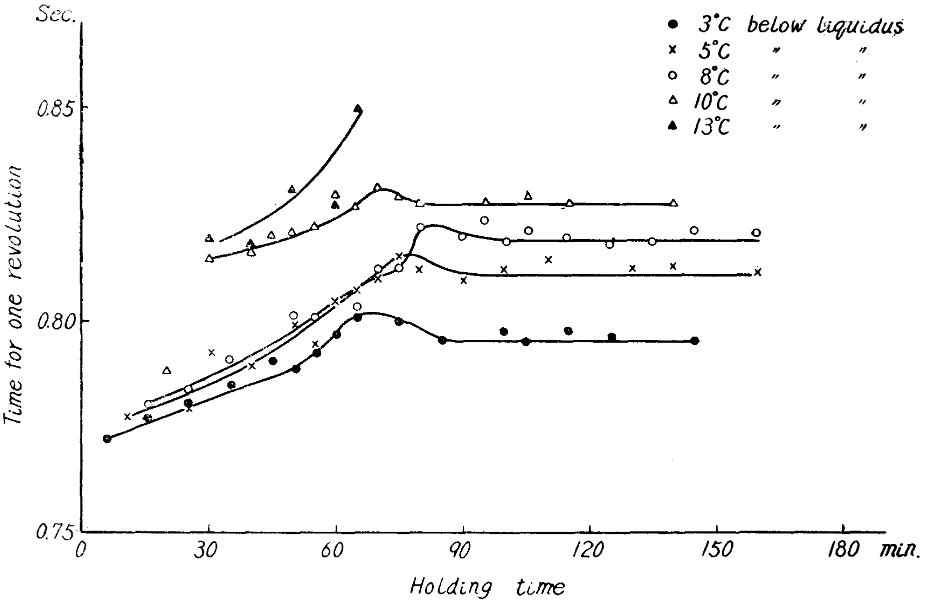

Fig. 6. The relation between the time for one revolution and holding time at various temperatures below the liquidus point of the alloy containing 20% of tin.

Table 2. The crystallized amounts of primary crystals at the equilibrium states of the alloys containing 10% and 20% of tin in related to the holding temperatures.

Holding temps. (°C) \ Compositions of alloy(Sn%)	10%	20%
3°	6.0	3.7
5°	11.7	6.3
8°	17.1	9.9
10°	20.5	12.2
12°	23.7	—
13°	—	14.3
15°	27.8	—

solidification will be mentioned. The samples were rapidly cooled in ice water after definite cooling procedures. The primary crystals in the equilibrium states of the alloys containing 10, 20 and 30 per cent of tin and held at the temperatures lower than the respective liquidus points by 5°C are shown in Photos. 1, 2 and 3, respectively. In accordance with the previous work of one of the present authors(3), the size of the primary crystal became smaller with an increase in the content of tin. This is the reason why the viscosity of the alloy containing less amounts of tin became smaller at the equilibrium in spite of large amounts of primary crystal.

The process of the primary crystallization was observed with the sample containing 10 per cent of tin. The primary crystals obtained after holding for 5 minutes are shown in Photo. 4, and those at the maximum viscosity are shown in Photo. 5. Comparing the Photos. 1, 4 and 5 with one another, a number of small primary crystals will be observable in the maximum state, while in the equilibrium state very large crystals exist, small crystals fading away. It is clearly seen that the small primary crystals begin to grow at the stage showing the maximum viscosity and become very large in the equilibrium state. Most of the primary crystals of large size, however, were also observed in an early stage of crystallization. This is the reason why the viscosity of the melt containing less amounts of tin was small at the maximum point.

The effect of the holding temperature upon the size of the primary crystal in the equilibrium state of the alloy containing 10 per cent of tin is shown in Photos. 6, 7, 8 and 9. Photo. 6 shows the primary crystals when held at the temperature lower than the liquidus by 7°C. Comparing this with Photo. 1, it will be seen that the primary crystals become smaller, and that some fine crystals are observable. At a temperature drop of 8°C, primary crystals became smaller and the number of fine crystals increased as shown in Photo. 7. This tendency was more remarkable at the temperature drop of 10°C, as shown in Photo. 8. In the case of 12° drop no large crystal was observable, as shown in Photo. 9, and most of the fine crystals became too minute to be detected. This behaviour of the primary crystal to become fine with the lowering of the holding temperature shows itself in the form of an increase of the viscosity, together with increasing amounts of the primary crystal.

Some erroneous results in the previous work(1) may arise from the circumstance that the primary crystals of the alloy containing 10 per cent of tin have a strong tendency to become large at high temperatures. The capillary used was too narrow (2 mmϕ) to drain large crystals and closed sooner at high temperatures than at low temperatures.

From the microscopical observation it may safely be said that the size of the primary crystal depends upon both the composition of the alloy and the holding temperature. This coincides with the viscosity change in the melt during solidification; in other words, the conditions for increasing the viscosity coincide with those for obtaining fine primary crystals.

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(3) T. Yanagihara, Sci. Rep. RITU, A2 (1950), 843.

Microphotograph of the primary crystals of bismuth, holding at various temperatures and containing various concentration of tin. (×200)

Photo. 1. 5°C below liquidus, at eq. state, 10% Sn.

Photo. 2. 5°C below liquidus at eq. state, 20% Sn.

Photo. 3. 5°C below liquidus at eq. state, 30% Sn.

Photo. 4. 5°C below liquidus, after 5min., 10% Sn.

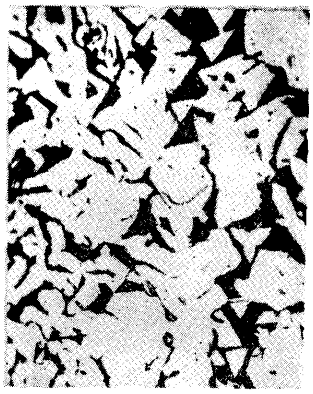

Photo. 5. 5°C below liquidus, at max. state, 10% Sn.

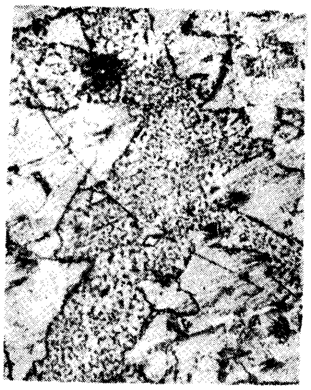

Photo. 6. 7°C below liquidus, at eq. state, 10% Sn.

Photo. 7. 8°C below liquidus, at eq. state, 10% Sn.

Photo 8. 10°C below liquidus, at eq. state, 10% Sn.

Photo. 9. 12°C below liquidus, at eq. state, 10% Sn.

Summary

(1) The process of primary crystallization was investigated with the rotational viscosimeter in place of the capillary method.

(2) The primary crystallization at constant temperature below the liquidus generally proceeded in three steps. In the first step the primary crystallization proceeded to the point where the maximum viscosity would show itself. In the second the growth of the primary crystal took place, giving rise to the lowering of the viscosity. In the last step it reached an equilibrium state.

(3) As the composition of the alloy approached the eutectic, the viscosity was increased during the primary crystallization.

(4) As the composition of the alloy was different from the eutectic, the tendency of growth of the primary crystals became remarkable.

(5) As the holding temperature was lowered, the viscosity increased, and the primary crystals became fine.