Fundamental Research on the Flowabilities of Melts of Metals and Alloys. I : On the Flowabilities of Sn-Bi and Pb-Sn Systems

Fundamental Research on the Flowabilities of Melts of Metals and Alloys. I
On the Flowabilities of Sn-Bi and Pb-Sn Systems[*]

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Synopsis

The reason for the superior flowability of a melt in the neighborhood of the eutectic composition in binary system has been investigated.

The flowability is subjected to two factors, the primary crystallization and the eutectic crystallization. Both increase the viscosity of melt, but the effect of the latter was shown to be less than that of the former.

I. Introduction

The flowability of a melt is not only of the meaning of the reciprocal of the viscosity, but is also accompanied by some complicated factors with casting procedure.

Flowability is generally measured by the filled-up length of melt after solidification which is cast in a mould with the spiral form or straight line. So, it is related not only to the flow of the liquid state, but also to that during the crystallization. The viscosity of a melt increases slowly with temperature drop. But, once the crystallization begins, its viscosity increases rapidly with the increasing amount of crystallized mass, and depends on the form of existing crystals.

Many works on this problem have been carried out, among which the following are the important:

A. Portevin and P. Bastien[1] studied it on Sb-Cd and Sb-Pb systems, and pointed out that the longer the freezing range of alloy is, the better the flowability is. H. Sawamura and S. Morita[2] recognized that Portevin-Bastien's relation may also be applicable to aluminum alloys with some exceptions as in Al-Si system. In the Al-Si system, the maximum flowability did not appear at the eutectic point but at a point with somewhat higher contents of silicon due to supercooling;[3] that is, as the supercooling at the hyper-eutectic point (15.69% Si) is larger than that at the eutectic point, the temperature difference between the casting temperature and supercooled liquidus point becomes greater at the former point than that at the latter, and, accordingly, the flowability becomes better at the former than at the latter. In the Al-Cu system, minimum flowability did not appear at

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* The 607th report of the Research Institute for Iron, Steel and Other Metals.
(1) A. Portevin, P. Bastien Compt. rend. **194** (1932), 850.
(2) H. Sawamura, S. Morita N. K. G. **6** (1942), 28.
(3) H. Sawamura, S. Morita N. K. G. A **14** (1950), No. 6, 4.

the composition having the maximum freezing range, due to supercooling and segregation.[4]

E. Lips and H. Nipper[5] have accomplished a very suggestive research. They suspended flaky graphite or spherical quartz powder of various sizes in the mixed aqueous solution of (HgI_2+KI), and measured the time to drain 50 cc of the solution through a capillary of 2 mm in diameter and 100 mm in length. The relation between the time for draining and the amount of the suspended particles was studied. The viscosity of the suspension was greatly affected by the mass, size and form of suspended particles. It was proved that the flaky graphite is more effective in increasing the viscosity of the suspension than the spherical quartz powder, and that, in both cases, small particles are also more effective than the large ones.

In another experiment, they measured the flow-length and the flowing time of the liquid system of (KNO_3+H_2O) in a transparent spiral glass mould under the condition of superheating by 10°C and found that the nearer the composition of liquid to the eutectic is, the greater the flow-length and the flowing time are. The flowing velocity of the liquid was independent of its composition while the liquid was transparent, but, after crystallization began, it depended upon the composition : the nearer the composition to the eutectic is, the greater the flowing velocity is.

From these results, they suggested that the superior flowability of the eutectic composition would be due to the small effect of the spherical eutectic crystal on the increasing of viscosity. They did not, however, confirm that this idea might also be applicable to alloys.

To interpret these phenomena, the author has carried out the present research.

II. Flowabilities of Pb-Sn and Sn-Bi systems

For the basis of the research, the flowabilities of the Pb-Sn and Sn-Bi systems were first measured.

A. Experimental method

In order to measure the flow-length, the author used aluminum mould as shown in Fig. 1. The melt was poured from the gate A and introduced into the measuring canal C through the down gate B. The measuring canal was of the quadrate section of 4 mm², the length being 170 mm.

100 gr of alloy was melted in a graphite crucible, and, after 10 minutes, was cast in the mould kept at 20°C. From the flowed length vs. casting temperature relation, the flowed length corresponding to the superheating by 100°C was determined*, from which the composition-flowed length relation was obtained.

The liquidus of both systems were determined by thermal analysis.

(4) H. Sawamura, S. Morita N.K.G. B 14 (1950), No. 4, 51.
(5) E. Lips, H. Nipper Die Giesserei. 25 (1938), 369.
 * In casting technics, elevating of a casting-temperature above its liquidus point is usually called superheating.

B. Results

a) Liquidus of Pb-Sn and Sn-Bi systems

They are shown in Figs. 2 and 3, the eutectic temperatures of Pb-Sn and Sn-Bi systems being 183°C and 140 °C, respectively.

b) Flowabilities of Sn, Pb and Bi

The flowed length vs. temperature relations of tin, lead and bismuth are shown in Fig. 4. The relations are linear, and the flowability series are as follows: Sn>

Fig. 1. Apparatus for measuring the flowability.

Bi>Pb. The flowed lengths of tin, bismuth and lead superheated by 100°C are 139, 98 and 88 mm, respectively.

c) Flowability of Pb-Sn system

The flowed length vs. casting temperature relations were investigated with twelve samples of various compositions. Some typical examples are shown in Fig. 5.

The relations are all linear. The relation between the flowed length and the composition are shown in Fig. 6. It is seen from it that the flowability of alloy is inferior to that of each component metal, the difference being remarkable at tin side, and that it has a small maximum at the eutectic composition, minima being at points about 20 and 95% of tin.

d) Flowability of Bi-Sn system

Some flowed length vs. casting temperature relations are shown in Fig. 7. As in the above case it is also linear.

The relation between the flowed length and the composition is shown in Fig. 8, which shows a course similar to that in Pb-Sn system.
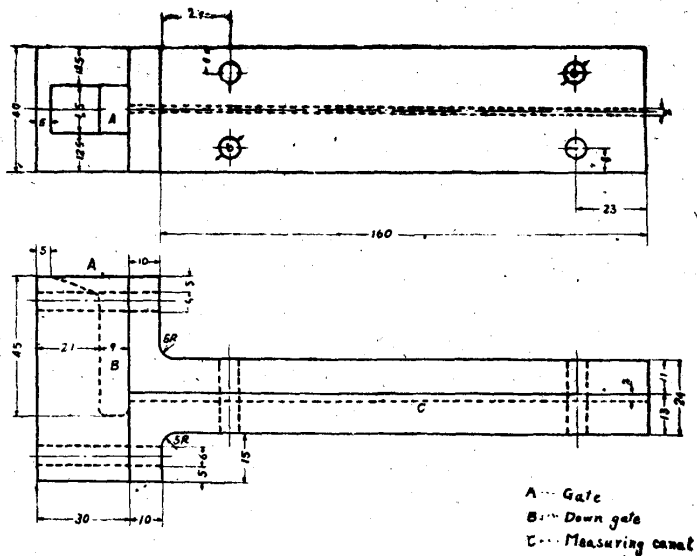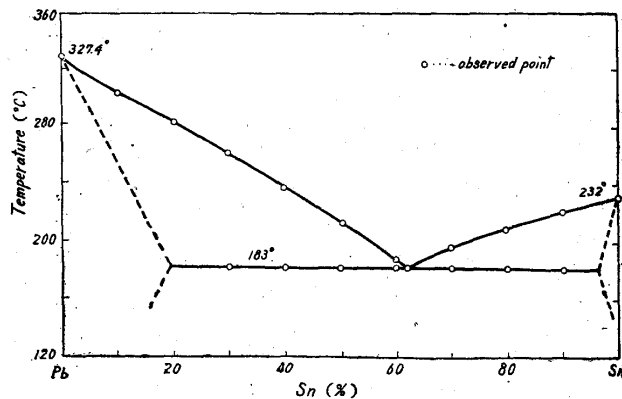

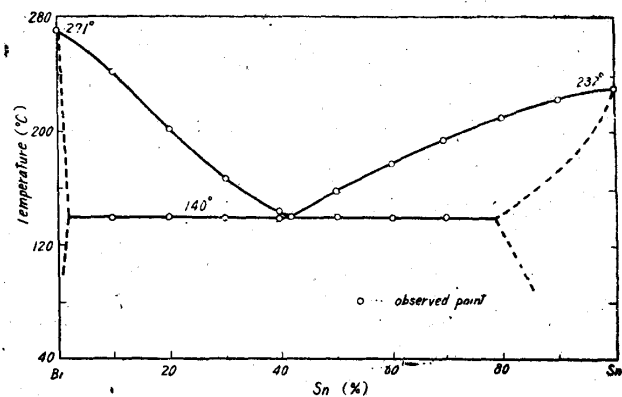Fig. 2. Equilibrium diagram of the Pb-Sn system.

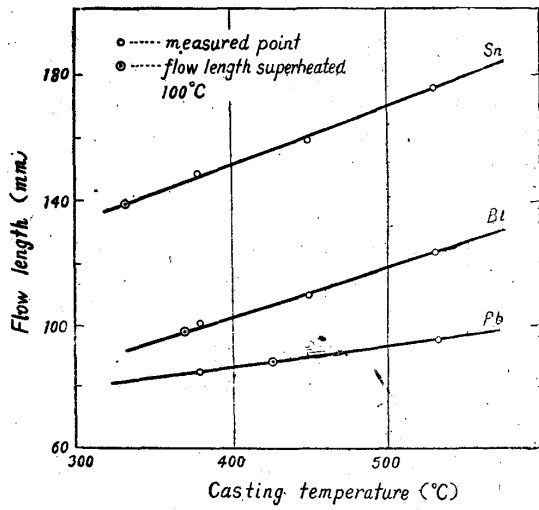Fig. 3. Equilibrium diagram of the Bi-Sn system.

Fig. 4. Flow length-temperature relation
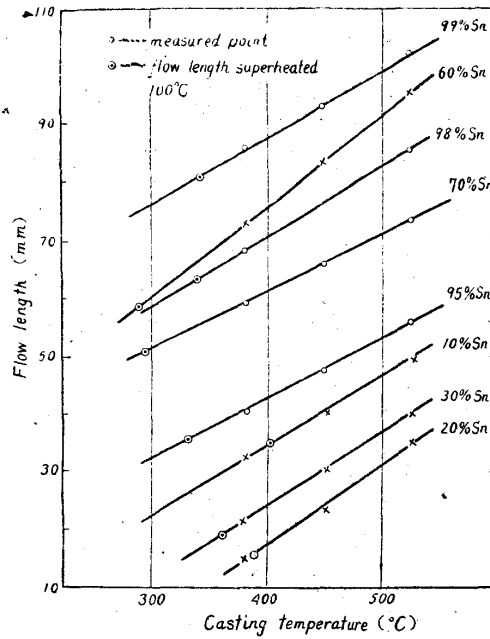of the Sn, Bi and Pb.

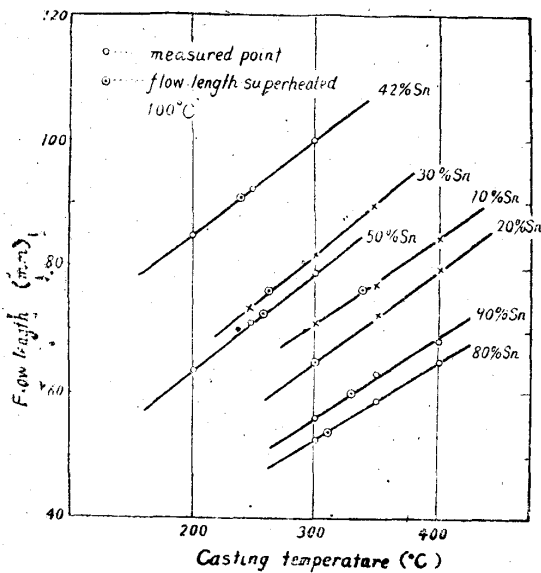Fig. 5. Flow length-temperature relation
of the Pb-Sn system.

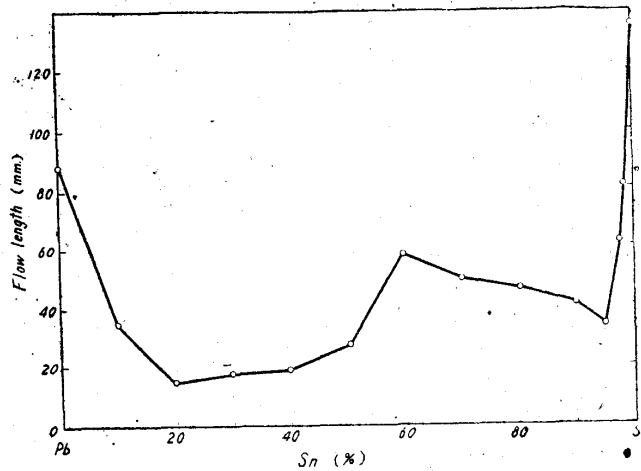Fig. 7. Flow length-temperature relation
of the Bi-Sn system.

Fig. 6. Flowability of the Pb-Sn system,
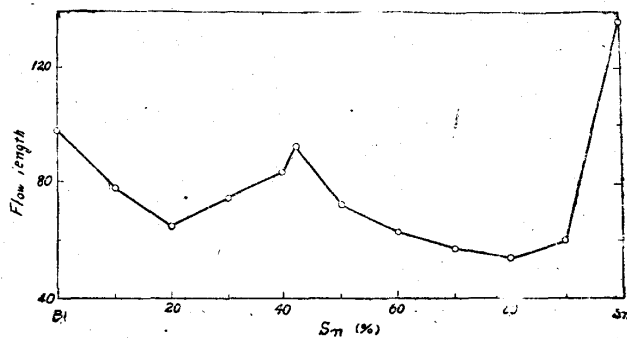superheating by 100°C.

Fig. 8. Flowability of the Bi-Sn system,
superheating by 100°C.

III. Statical stopping temperatures of flow in Bi-Sn system

In the experiments of E. Lips and H. Nipper[4] on KNO_3-H_2O system, the flow of the solution stopped before complete solidification. For instance, the flow of 30% KNO_3 aqueous solution stopped at the temperature at which 15% of the complete crystallization occurred in it.

There is however, no experiment in the cast of metal to confirm how much crystallization occurs untill the flow stops. In order to confirm this point, the author has measured the statical stopping temperatures of the flow of the melt in Bi-Sn system. Here, the statical stopping temperature means the temperature at which the flow of the equilibrially cooling melt stops.

Another purpose of this experiment is to find the effect of the primary crystallization on the flow of melt. The flow of melt is in intimate relation with its viscosity which is much influenced by the mass, shape and volume of primary crystals existing in it.

A. Experimental method

During solidification, the more the primary crystals exist in a melt, the higher its viscosity is, and at a certain temperature the melt ceases to flow. The amount of the primary crystal in the melt can be estimated from the lever relation. By this procedure, the statical stopping temperature was measured. For this purpose, the melts were kept at respective temperatures for 30 minutes in the vessel A shown in Fig. 9. Then the stopper C was raised, allowing the melt to flow out from the capillary B. Drain-

A ‥ Vessel containing the melts
B ‥ Measuring capillary
C ‥ Stopper

Fig. 9. Apparatus for measuring the statical stopping temperature of the melt's flow.

ing the melt for 5 seconds, the flowing was stopped with the stopper. The melt drained was then weighed. The temperature was lowered gradually untill the flowing stopped. The statical stopping temperatures could then be determined by the exterpolation of the relation between the drained mass and the temperature.

B. Results of experiment

The typical examples of the relatians between the temperature and the drained mass are shown in Fig. 10. As shown in Fig. 10, the relation is consisted of two lines intersecting at the liquidus point. For the temperatures higher than the liquidus, the lines are slightly inclined to the temperature axis, whereas they are steeper below the liquidus; that is to say, in liquid state, the amount of the drained melt changes slightly with the temperature, while, below the liquidus, it decreases rapidly. This must be due to the fact that, in liquid state, the viscosity changes slightly with temperature, while, once a primary crystal appears in the
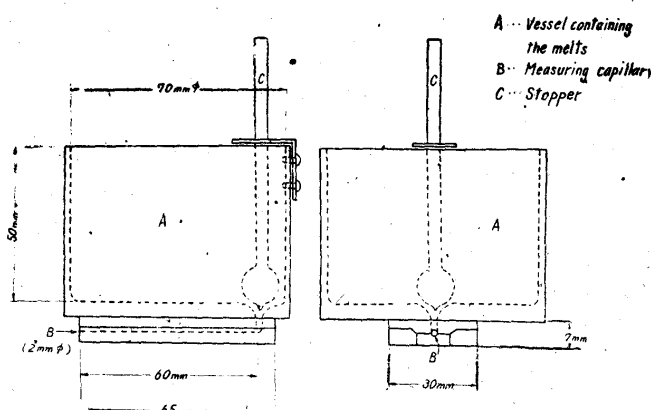
melt, a severe change in viscosity will take place.

In order to confirm the correctness of the statical stopping temperatures determined with the flowing time of 5 seconds, the duration was extended to 30 seconds and the similar relation was examined. The temperatures thus determined were in good agreement with those determined by the former.
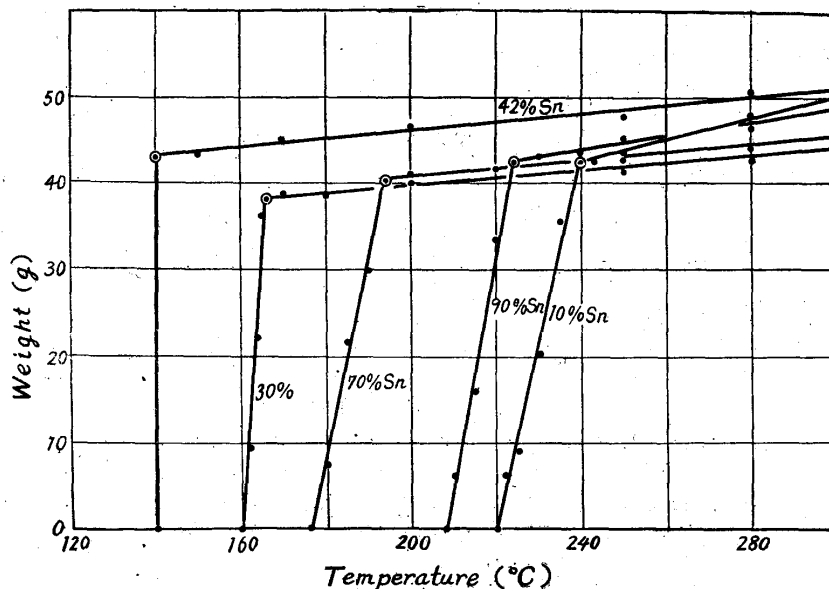

Fig. 10. Drained mass-temperature relation of the Bi-Sn system.

The statical stopping temperatures are shown in Table I. It is seen that the greater the lowering of the statical stopping temperatures from the liquidus is, the farther the composition of the melt goes from the eutectic point. At the eutectic point the flow stopped in 22 seconds without the lowering. The lowering is greater with tin side than with bismuth side.

Table 1. The crystallized primary crystals of the Bi-Sn system in the melts to stop the flow in accordance with the increase of their viscosities.

Composition	Liquidus Temp.	Statical stopping temp. of the flow	Crystallized mass of the primary crystals
Sn %	°C	°C	%
10	240	220	40
20	200	190	12.24
30	166	160	6.45
35	—	148	6.94
40	144	141	4.94
45	—	142	4.16
50	158	150	8.33
55	—	155	17.14
60	175	162	22.95
70	194	176	59.22
80	209	188	57.78
90	224	208	76.67

The amount of primary crystals to stop statically the flow is shown in Table 1. It is seen that the less the crystallized mass is, the nearer the composition to the eutectic is. It may be supposed that the shapes of primary crystals in the neighborhood of the eutectic composition have great effect upon the viscosity, and also that bismuth primary crystals have greater effect than tin crystals.

Hence, the shapes of primary crystals were microscopically examined; that is, the melt was kept at the statical stopping temperature for 30 minutes and then was rapidly cooled in ice-water. The microphotographs are shown in Fig. 11.
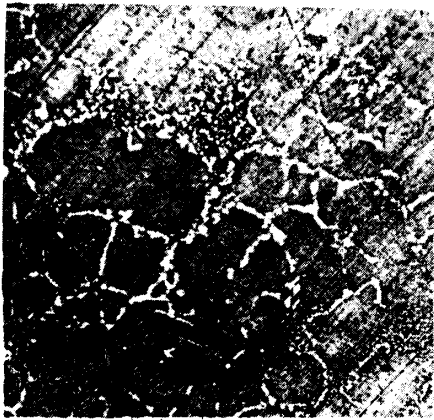
Photo. 1.
80% Sn (×50)

Photo. 2.
55% Sn (×50)

Photo. 3.
10% Sn (×50)
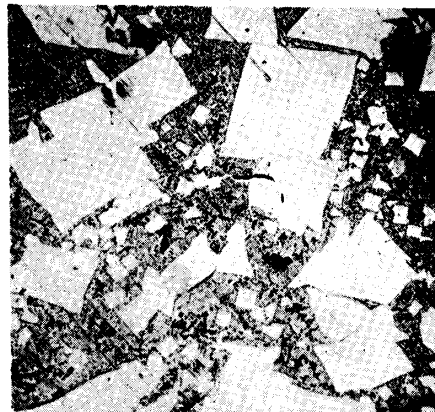
Photo. 4.
20% Sn (×50)

Photo. 5.
30% Sn (×50)

Photo. 6.
40% Sn (×50)

Fig. 11. Microphotographs of the primary crystals of the Bi-Sn system, after holding at the statical stopping temperature for 30 minutes and then cooled in ice-water.

As shown in Photos, the shapes of tin crystals are rather round, whereas the polygonal shape is characteristic of bismuth crystals. It is clear that the effect of polygonal bismuth crystal on increasing viscosity is greater than that of round tin crystal.

Comparing the Photos 1 and 2, it will be seen that the primary crystals of 55% Sn alloy is smaller than that of 80% Sn alloy, and that the shape of the former has a dendritic tendency. Hence, it is clear that the primary tin crystals in the composition nearer to the eutectic have a greater effect on viscosity than that in the other compositions. As seen from photos. 3~6, the same will be said of the alloys in bismuth side.

Judging from these facts alone, the flowability will be inferior in the neighborhood of the eutectic. But it is contrary to the observation on the flowability of Bi-Sn system. This may be due to the circumstance that the melt is practically cooled not equilibrially but rapidly. So the flowability should not be discussed only from the standpoint of the statical stopping temperature. The effect of supercooling must be taken into consideration.

IV. Dynamical stopping temperature of flow in Bi-Sn system

In the case of the measuring of flow-length, the solidification may proceed in a different manner from that when a melt cools equilibrially. Hence, the stopping temperature of the flow of melt during cooling was investigated, which is called here, the "dynamical stopping temperature".

A. Experimental method

In order to measure this temperature, the apparatus shown in Fig. 12 was used
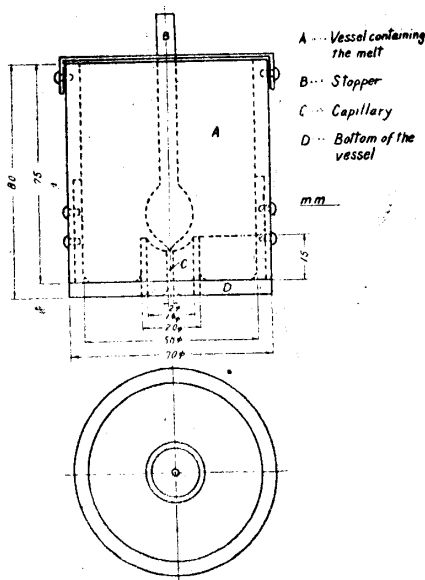

Fig. 12. The apparatus for measuring the dynamical stopping temperature of the melt's flow.

which was made of pure aluminum (99.9%). A measuring capillary C is perforated at the center of melt container A. The flow from A to C is regulated by a stopper B. In order to keep the temperature of the capillary the same as that of melt, its position is adjusted so as to be immersed in the melt. Due to the good thermal conductivity of the apparatus, the neighborhood of the exit of the capillary cools so rapidly that the temperature of the flowing melt becomes lower than that of the inner melt. To prevent this, the paste, made from glass wool and water glass, is baked about 5 mm thick upon the outer surface of the basal part D.

The stopper was raised when the temperature of melt lowered to the statical stopping temperature. The quantity of drained melt, however, was so great that the head of melt was lowered and the hydraulic pressure acting on the flow changed too

much to get the constant dynamical stopping point. To prevent this ambiguity, the dynamical stopping point was measured again, raising the stopper at 3°C above the former stopping point. The head, in this case, scarcely changed.

During the measurement the melt was stirred with porcelain rods to prevent uneven temperature distribution therin. As soon as the flow was stopped it became too viscous to be stirred.

Strictly speaking, the same cooling velocities could not be realized. But, when room temperature does not change greatly, cooling velocities may generally be almost constant. It is about 3°C/min in furnace cool; 10°C/min in air cool; and 20°C/min in air cool with an electric fan.

.B. Experimental results

The dynamical stopping temperatures of the Bi-Sn system containing bismuth from 10% to 90% were measured. The results are shown in Fig. 13, in, which, for comparison, the statical stopping temperatures are also marked.

The lower the dynamical stopping temperature is, the more rapid the cooling velocity is.

Fig. 13. The equilibrium diagram of the Bi-Sn system and the dynamical stopping temperatures of the melt's flow.

As in the case of the statical stopping temperature, the less the lowering of the dynamical stopping temperatures from the liquidus, the nearer the compositions of the melts to the eutectic is. . In the neighborhood of the eutectic, the dynamical stopping temperatures are lowered below the eutectic temperature, the composition range being extended as the cooling rate increases. For example, the range is 40~45% Sn for 3°C/min and 30~55% Sn for 10°C/min. The cooling velocity in usual casting may be more than 100°C/min, and, accordingly, the composition range will be more extended.

This dropping of temperature may be considered to be due to supercooling. In order to confirm whether the supercooling of the eutectic crystallization had occurred or the supercooling of both the primary and the eutectic crystallization had taken place, thermal analyses were accomplished in parallel with the measurements of the dynamical stopping temperatures. The cooling velocity in this case was 10°C/min. At every 5 seconds the temperature was read. The results are shown in Fig. 14.

Every thermal analysis curve shows no supercooling of the liquidus point. In the range of 30~50% Sn, the dynamical stopping points, which are marked with ⊙, appeared on the flat parts of the curves showing the eutectic erystallization. The more the eutectic crystallization occurs before the appearance of the dynamical stopping point, the nearer the composition to the eutectic is, and the dynamical stopping points appear before the eutectic crystallization begins.
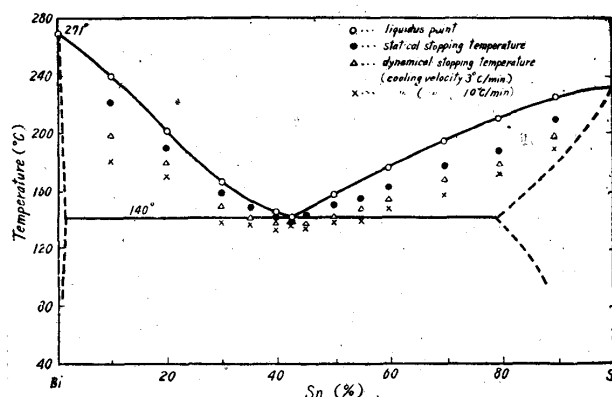
Thus, it is confirmed that there is no supercooling of the liquidus points in Sn‑Bi system, whereas the eutectic crystallization is supercooled in the neighborhood of the eutectic point. In the range in which the dynamical stopping points are below the eutectic point, these points appear after the supercooled eutectic crystallization commences. This range is extended with the increase of cooling velocity.
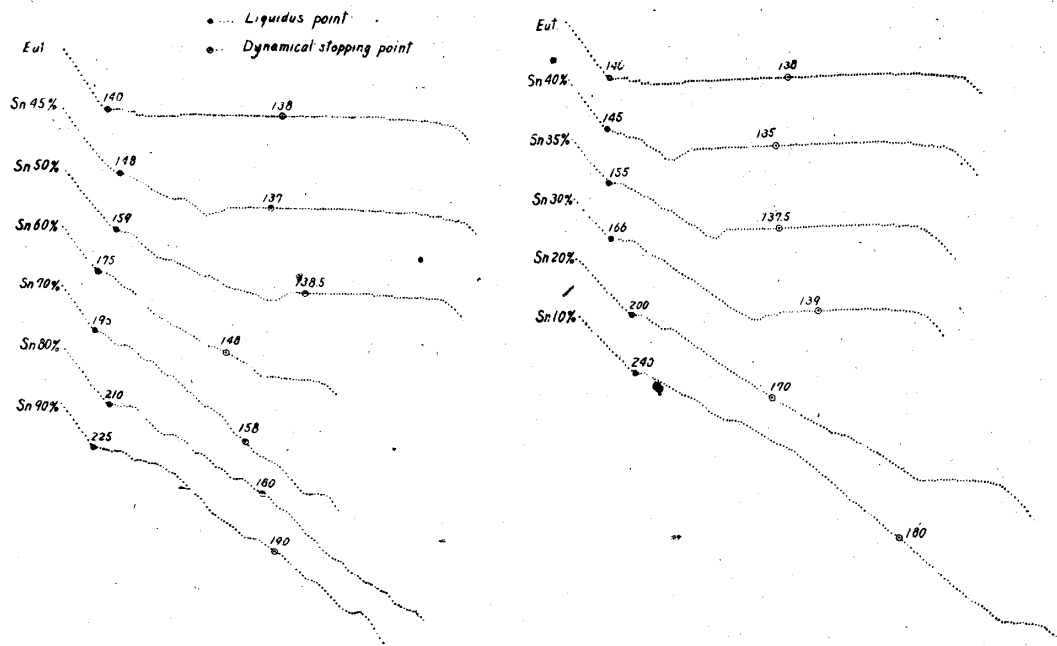

Fig. 14.　Thermal analysis curves of the Bi-Sn system during the measurements of the dynamical stopping temperatures.

V.　Statical and dynamical stopping temperatures in Pb-Sn system

The same observations as that for Sn-Bi system were carried out and the results are shown in Figs. 15~16 and in Table 2, respectively. Comparing the correspond-
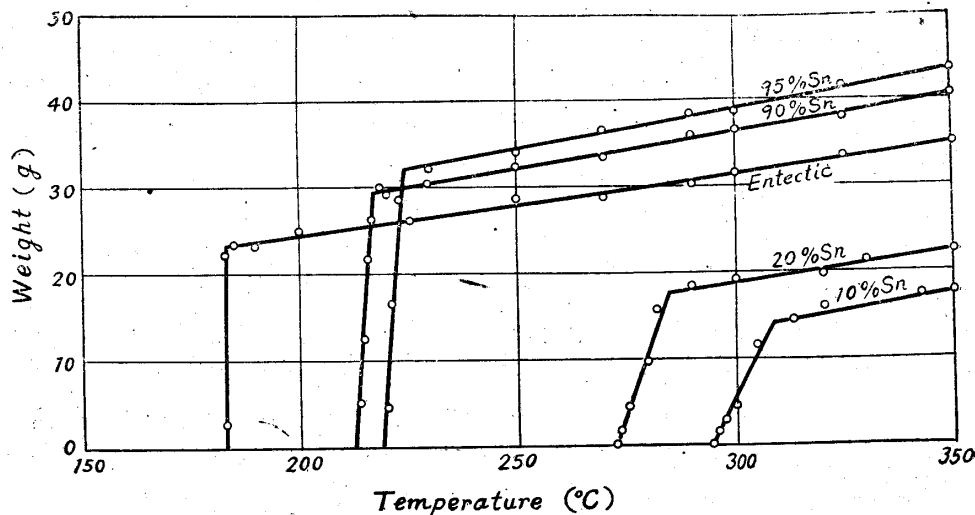

Fig. 15.　Drained mass-temperature relation of the Sn-Pb system.

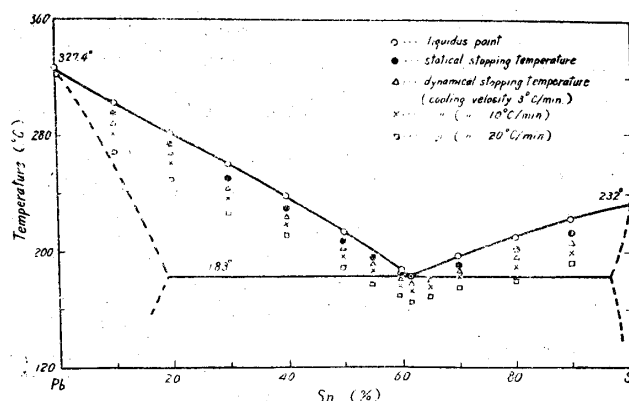ing results in the two cases, it will be seen that the same conclusion as in the above may be drawn out.

Fig. 16. The equilibrium diagram of the Pb-Sn system and the dynamical stopping temperatures of the melt's flow.

Table 2. The crystallized primary crystals of the Pb-Sn system in the melts to stop the flow in accordance with the increase of their viscosities.

Composition	Liquidus temp.	Statical stopp ng temp. of the flow	Crystallized primary crystals in the melts
Sn %	°C	°C	%
10	308	295	41.66
20	282	272	21.62
30	250	243	18.01
40	228	220	13.11
50	208	200	10.67
60	186	184	3.53
70	196	191	12.70
75	204	198	13.21
80	208	204	17.02
90	218	212	36.67
95	225	218	47.06

VI. Discussion

The change of viscosity of melt is the most important factor in the consideration of its flowability which is brought about by two causes: One is the change of liquid state itself with the temperature drop and the other is that due to the crystallization during the course of solidification. The problem is which cause will be more predominating.

From the relation between the temperature and the drained mass determined by the statical stopping temperature, the relation between the composition and the drained mass at a liquidus point can be obtained. The results for two systems are shown in Fig. 17. As seen from Fig. 17 in Bi-Sn system, the drained masses do not so much differ from one another as tin contents. According to the measurement of F. Sauerwald and K. Töpler,[6] the difference in viscosities of melts of various compositions in this system is small. And in Pb-Sn system, the

(6) F. Sauerwald, K. Töpler Z. anorg. Chem. 157 (1926), 17.

drained mass at a liquidus point increases with the increase of tin content. The results of the viscosity measurement of Ragner Arpi[7] also show similar tendeney. These composition vs. drained mass relations at liquidus points are in good agreement with the v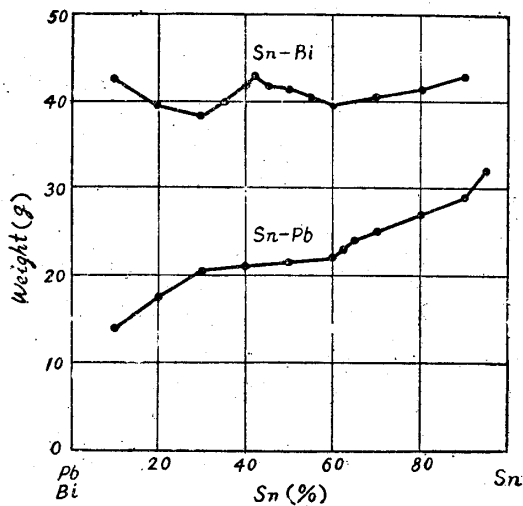iscosity vs. composition relation in liquid state, but not with the flowability vs. composition relation in both systems. Accordingly, the change of viscosity in liquid state itself generally, has, little meaning for the flowability, but the change after crystallization begins will become more important.

According to the measurement on the statical stopping temperature alone, the increasing amount of other metal, in every system, has a tendency to make the flow inferior and in the neighborhood of the eutectic composition it becomes the worst. This is contrary to the fact; that is, only with the effect of primary crystallization on viscosity the flowability vs. composition relation can not be interpreted satisfactorily.

Fig. 17. The composition-flowed out mass relations at the liquidus points in Sn-Bi and Sn-Pb systems.

From the measurements on the dynamical stopping temperature and on the thermal analyses of the Sn-Bi system, it was recognized that, in the neighborhood of the eutectic point, the eutectic crystallization had occurred before the flow of the melt dynamically stopped. The greater the eutectic crystallization, the nearer the composition of the melts to the eutectic. Moreover, the greater the composition range of the eutectic crystallization, the larger the cooling velocity. The crystallite of the eutectic grows radially. In consequence of the spherical form of an eutectic crystal, its effect on the viscosity is less than that of a primary crystal which has the shape of needle, polyhedron, plate, dendrite, etc.

Accordingly, the larger the amount of the eutectic crystal in melt increases, the larger the flow-length is elongated.

In Fig. 11, it is shown that, in Sn-Bi system, the shape of a bismuth primary crystal is of characteristic polygon, and that of a tin primary crystal is somewhat round. The effect of the former on the statical stopping of flow is greater than that of the latter as shown in Table 1. But the flowability curve in Fig. 8 shows better flowability in bismuth side than in tin side. According to the larger quantity of the eutectic crystallization in bismuth side than in tin side as shown in Fig. 14, the former flowability will be better one. Therefore, it follows that the effect of eutectic crystallization on the flowability predominates that of primary crystallization in the case of the dynamical stopping of flow, or, the more preponderating the eutectic crystallization in a melt, the better the flowability.

(7) R. Arpi Internat. Z. Metallograph. 5 (1919), 142.

Thus, it will be concluded that the flowability of the melt of an alloy is mainly determined by the relative amount of crystallization of primary and eutectic crystals in it.

Summary

(1) With the Sn-Bi and Pb-Sn systems, the flowability was studied. The flowability in every case shows the same general tendency as observed in a simple eutectic two-component system.

(2) The results of the measurements on the statical stopping temperature shows a minimum of primary crystallization in the neighborhood of the eutectic. The more the quantity of the primary crystallization, the farther the composition from the eutectic.

(3) The polygonally shaped primary crystal of bismuth had greater effect on increasing viscosity than the round primary crystal of tin, so that the masses of the primary crystals to stop the flow statically were less in the bismuth side than in tin side in the Bi-Sn system.

(4) The lower the dynamical stopping temperature was, the faster the cooling velocity was.

(5) In the neighborhood of the eutectic, the dynamical stopping temperatures were lowered below the eutectic temperature. The composition range which shows this lowering broadened with the increase of cooling velocity.

(6) The thermal analyses, accomplished in parallel with the measurements of the dynamical stopping points in Sn-Bi system, showed the supercooling of eutectic crystallization but none for primary crystallization.

(7) The thermal analyses showed that the dynamical stopping points appeared after the eutectic crystallization had occurred when they were lowered below the eutectic temperature.

(8) The flowability of an alloy was interpreted as the combined effect of primary and eutectic crystallizations.