

## Effect of liquid structural transition on the morphology of solid/liquid interface during the unsteady-state unidirectional solidification

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**Abstract.** The temperature-induced liquid-liquid structural transition has been observed and testified in different kinds of alloys. The effect of liquid-liquid transition on the morphology of solid/liquid interface was investigated by means of the unsteady-state unidirectional solidification. The results showed that the interface instability of Sn-1wt.%Pb was developed after the liquid structural change, which suggested that the solute distribution coefficient decreased due to the structural change of liquid Sn-1wt.%Pb and the solute on the frontier of solid/liquid interface enriched.

### Introduction

It is well accepted that the structure of liquids is playing an increasingly important role in the manufacture of high-quality metallic materials, and the structure of liquids has direct influences on the microstructure and properties of materials[1-6]. However, the exact mechanism of the effect of liquid structure on solidification is still not fully understood.

Over the past two decades, both experimental findings and theoretical predictions have suggested the presence of liquid-liquid structural transitions at constant pressure characterized by significant structural changes[7-12]. Furthermore, the effects of the liquid structural transition on the free solidified structures were investigated for some binary alloys, such as Sn-Pb[13], Bi-Sb[14], Al-Si [2] and Pb-Bi[6]. However, the free solidification method can not be used to study the morphology of solid/liquid interface and the coefficient of solution redistribution. And the existing solidification theories are seldom involved with the effects of the melts' structures.

Most of the unidirectional solidification studies existing in literature have been carried out in steady state heat flow. During unidirectional growth under steady-state conditions the significant controllable variables, the temperature gradient and growth rate, are independently controlled and held constant with time, while in the unsteady-state regime the temperature gradient and growth rate vary freely in time. On the other hand, the analysis of these structures in the unsteady-state regime is very important, since at the beginning of all the steady-state unidirectional solidifications, the solidification of melts must be under the unsteady-state conditions controlled by nucleation. Prior works have suggested that the liquid structural transition improved greatly the nucleation-controlled effect on the solidification process[5,6,15]. Logically, this effect would be imposed on the steady-state growth. In other words, the effect of the liquid structural transition on the morphology of the solid/liquid interface and the coefficient of solution redistribution will take from the unsteady state.

The present article will investigate the change of the morphology of the solid/liquid interface, and preliminary estimate the variation of the coefficient of solution redistribution by some solidification phenomena.

### Experiment

**Experiment Alloy.** In prior works, the structure change of liquid Sn-Pb alloys has been suggested with the internal friction method[11], electrical resistivity [16] and differential thermal analyses [11]. In these experiments, four compositions of Sn-Pb alloy were chosen, that is, Sn-80wt.%Pb,

Sn-60wt.%Pb, Sn-39.1wt.%Pb, and Sn-20wt.%Pb. Considered the aim of the present investigation, experiments in this paper were performed with Sn-1wt.%Pb. However, the turning temperature of the liquid structural change of Sn-1wt.%Pb alloy can not be obtained from the literatures.

The measurement of electrical resistivity is widely applied to explore the property of liquids. Fig.1 showed the resistivity-temperature curve of Sn-1wt.%Pb during heating, the heating rate of which was set as 10°C/min. The experimental procedure was detailed in[16]. In Fig.1, hundreds of degrees far above the liquidus, the obvious turning point can be observed at 810°C on the resistivity-temperature curve. This phenomenon was also observed on the resistivity-temperature curves of some binary alloys, such as Sn-Pb[13], Bi-Sb[14], Bi-In[17], Sn-Sb [18] and Pb-Bi[6]. Since resistivity is one of the physical properties sensitive to structures, it is suggested that there are temperature-induced structure changes in the liquid Sn-1wt.%Pb.

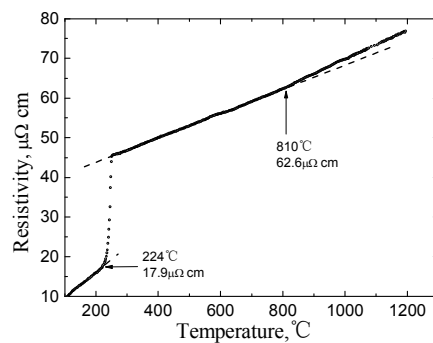


Fig. 1 Resistivity-temperature curve of Sn-1wt.%Pb during heating.

**Unidirectional Solidification Experiment.** Fig.2 shows a schematic of the experimental apparatus. The solidification apparatus was designed in such a way that the heat was extracted only through the water-cooled copper bottom, promoting upward directional solidification. The mold was a cylinder of 6mm inside diameter, 100mm high, and wall thickness 1 mm. The side wall was made of alundum to minimize radial heat losses. During the unidirectional solidification, the sample tube remained stationary and the furnace was moved upward by the drive mechanism at the desired velocity, which aimed to avoid the perturbation of the solid/liquid interface caused by the withdrawal of the sample. At the same time, the level of the cooling water rose at the same velocity to enhance the cooling capacity of the solidified part. During the unidirectional solidification experiments, the temperature gradients were controlled by the temperature of the furnace because the cooling bottom temperature remained relatively constant. Namely, if the temperature of the furnace and pouring temperature of melts were unchanged, the temperature gradients would stay the same.

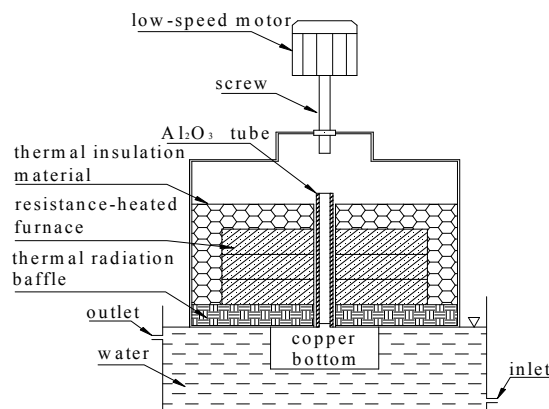


Fig. 2 Sketch map of directional solidification equipment.

All samples were prepared from purity Sn (99.99%) and Pb (99.99%). According to Fig.1, 600°C (below the temperature of liquid structural change) and 1000°C (above the temperature of liquid structural change) were selected as holding temperature. Each sample, weighed 20g, was melted in alundum crucible. All samples were covered with B<sub>2</sub>O<sub>3</sub> slag to prevent them from evaporation and

oxidation during the entire melting process. Table 1 showed the melt preparation procedure. Sample A was heated to 600°C and held for 30min in an electrical resistance furnace. The melt was poured into the mold for the unidirectional solidification experiments. Sample B was heated to 1000°C and held for 30min. And then it was rapidly cooled to 600°C and poured into the the mold for the unidirectional solidification experiments. All the melt would hold at the same temperature of 600°C before solidification in order to eliminate the effects of sensible heat. During the solidification, the temperature of the furnace outside the mold was maintained at 600°C, and it was withdrawn with the rate of 10μm/s. When the furnace was pulled up 20mm, the sample was quenched to preserve the solid/liquid interface structure. Longitudinal sections around the solid/liquid interface and transverse sections (perpendicular to the growth direction) at 15mm from the metal/copper interface were polished and etched with an acid solution (4% Nital) for metallography.

Table 1 Melts preparing procedure for Sn-1wt.%Pb.

| Melting temperature and holding time before solidification |  |
|--|--|
| Sample A   | 600°C, 30min                               |
| Sample B   | 1000°C, 30min <i>rapid cooling</i> → 600°C |

## Results and Discussion

**Change of Morphology of Solid/Liquid Interface.** Under the same conditions, the morphologies of the solid/liquid interface of Sn-1wt.%Pb alloy before and after the liquid structural change were shown in Fig.3. Compare with the interface in Fig.3(a), the interface in Fig.3(b) was not clear and the cellular structure still continued to grow during liquid quenching.

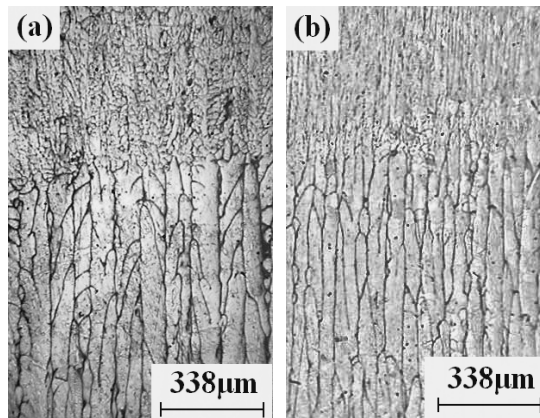


Fig. 3 Morphologies of the solid/liquid interface of Sn-1wt.%Pb before (a) and after (b) liquid structural change.

**Change of Coefficient of Solution Redistribution.** Fig.4 showed the directionally solidified microstructures of Sn-1wt.%Pb alloy in transverse sections before and after the liquid structural change. Two samples solidified under the same conditions; at the same position, however, the morphologies of the Sn-rich solid solution were different, evolved from elongated cells (shown in Fig.4 (a)) to hexagonal cells (shown in Fig.4 (b)) induced by the liquid structural change.

According to the constitutional supercooling (CS) criterion, when  $k_0 < 1$ , the interface will be stable for

$$\frac{G_L}{V} \geq \frac{m_L C_0}{D_L} \frac{1 - k_0}{k_0} \quad (1)$$

With increasing CS, corresponding to a decreased value of  $G_L/V C_0$ , the evolution from nodes or depressions at the interface into a regular or hexagonal substructure is obtained, and the metallographic sectioning is slightly behind the interface[19]. Thus, the comparison between Fig.4 (a) and Fig.4 (b) indicated that the CS in front of the interface increased caused by the liquid

structural change. In present experiments, the temperature gradients in front of the solid/liquid interface were equal at the same position of two samples because the temperature of the furnace and pouring temperature of melts were the same. In other words, in Eq.(1),  $G_L$ ,  $V$ ,  $D_L$  and  $C_0$  are the same for two samples during the unidirectional solidification. Further, the difference between Fig.4 (a) and Fig.4 (b) suggested that the solute distribution coefficient decreased due to the liquid structural change.

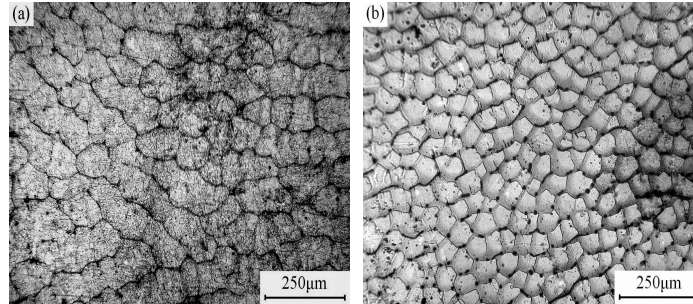


Fig. 4 Microstructures of Sn-1wt.%Pb alloy in transverse sections at 15mm from the metal/copper interface before (a) and after (b) liquid structural change.

Mentioned above, the liquid structural change decreased the solute distribution coefficient. This effect would enrich the solute and increase the liquidus temperature in front of interface. When prepared to quench the melts after the furnace was pulled up 20mm, the actual temperature  $T_q$  in front of interface was greater than the liquidus temperature, shown in Fig.5, and the cellular stopped growing. In Fig.5,  $T_{L1}$  and  $T_{L2}$  is the liquidus temperature in front of interface before and after liquid structural change, respectively. When quenching,  $T_q$  would decrease. Seen from Fig.5,  $T_q$  first intersected with  $T_{L2}$  (e.g.  $T'_q$ , shown in Fig.5). In other words, the cooling rate of water quenching can not prevent the growth of the cellular after the liquid structural change; however, it can do before liquid structural change. This phenomenon illustrated the liquid structural change decreased the solute distribution coefficient once again.

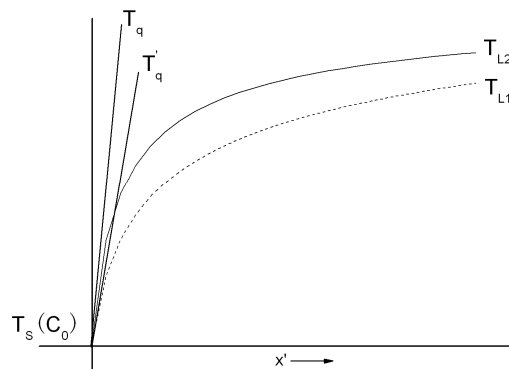


Fig. 5 Effect of actual temperature change on constitutional undercooling before the solid/liquid interface during quenching.

## Conclusions

The unidirectional solidifications of Sn-1wt.%Pb before and after liquid structural change were carried out under unsteady-state heat flow conditions. And the morphology of solid/liquid interface and the change of coefficient of solution redistribution were investigated in detail. The following conclusions can be drawn:

(1) At the cooling rate of water quenching, the tips of cellular of Sn-1wt.%Pb after liquid structural change could keep on growing into component undercooling zone, while the growth of the tips was prevented before liquid structural change and the solid/liquid interfaces in good condition were preserved, which revealed that the interface instability of Sn-1wt.%Pb was developed after the liquid structural change.

(2) Under the same conditions of solidification, the morphology of the Sn-rich solid solution evolved from elongated cells to hexagonal cells at the same position, which indicated that the solute distribution coefficient decreased due to the structural change of liquid Sn-1wt.%Pb and the solute on the frontier of solid/liquid interface enriched.

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