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ARTICLE

# Formation of Anomalous CuSn-shell/Pb-core Macrostructure in Cu-Sn-Pb Hypermonotectic Alloys

**Li Jianqiang[1,2], Sun Hong[1,2], Ma Bingqian[1]**

*[1] National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, CAS Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China; [2] University of Chinese Academy of Sciences, Beijing 100049, China*

**Abstract:** For the core-shell structured immiscible alloys within the immiscible gap, whether the shell is composed of a phase with lower or higher melting point, has no exact answer yet. Based on the Cu-Sn-Pb calculated phase diagram given by reference, the phase separation of 14Sn-73.1Cu-12.9Pb, 14Sn-64.5Cu-21.5Pb, Cu-65Pb and Cu-75Pb alloys have been experimentally investigated by casting method. An anomalous core-shell structure with a CuSn-rich shell and a Pb-rich core forms in 14Sn-64.5Cu-21.5Pb alloy, which differs from the viewpoint that a lower melting point phase generally forms the shell as Cu-75Pb alloy shows. This anomalous phenomenon may be explained by the fact that the liquid separation reaction is suppressed due to undercooling generated during casting process and the monotectic reaction takes place before the liquid separation reaction. This work may provide a method to modify the structure of immiscible alloys through controlling the solidification path.

**Key words:** solidification; metals and alloys; core-shell structure

Immiscible alloys have attracted much attention due to their liquid-liquid phase separation characteristic[1-6]. During the liquid-liquid phase separation process, the high-temperature homogenous melt decomposes into two liquid phases $L_1$ and $L_2$, and then the minor liquid forms as droplets in the matrix of the major liquid due to Ostwald ripening and Brownian movement, and almost at the same time droplets migrate under the combined effects of Marangoni movement, Stokes movements[7-9], and so on. The phase separation mechanism of immiscible alloys has been extensively studied since the 1960s[10-13]. Nevertheless, there are still some questions to be clarified. Particularly, in terms of core-shell structured immiscible alloys, one of remaining problems is that which liquid phase ($L_1$ or $L_2$) forms the outermost shell.

One common viewpoint is that the shell always consists of a phase with a lower melting point (termed LMP phase) for immiscible alloys with composition within the immiscible gap, for example, Al-Bi particles covered by more or less a layer of Bi[14], Cu-Sn-Bi columns with Bi shells[15], Cu-Fe particles with Cu shells[16] and Fe-Sn particles with Sn shells[17]. The reasonable explanation is that the LMP liquid phase generally has lower surface tension[16,18]. Yet there are exceptional cases. 46Cu46Cr8Si (wt%) alloy with Cu-rich core/Cr-rich shell morphology was cooled during the conventional casting process[19]. 48Cu48Fe4V (wt%) alloy with Cu-rich core/Fe-rich shell was obtained by casting method too[20]. It is noticeable that the exceptional cases disagree with the above-mentioned common viewpoint. Until now, the exact reason is not given by further evidence yet.

However, when the alloy compositions are outside of the immiscible gap, a shell of a phase with a higher melting point (termed HMP phase) is possible to form. The solidified structures of 40Sn60Cu-20.0wt%Bi hypomonotectic and 40Sn60Cu-32.5wt%Bi monotectic alloys are CuSn-rich

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Corresponding author: Li Jianqiang, Ph. D., Professor, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, P. R. China, Tel: 0086-10-82544953, E-mail: jqli@ipe.ac.cn

shell/Bi-rich core after casting[15]. For the hypomonotectic alloy, liquid-solid reaction and monotectic reaction had happened, when the CuSn-rich phase continued to crystallize and Bi-rich phase remained liquid and kept being pushed towards the center. For the monotectic alloy, the first reaction was monotectic reaction and the solidification path was similar. This phenomenon enlightened us that if the monotectic reaction occurred first for the alloys in the immiscible gap through adjusting solidification process, a HMP shell would probably appear. Furthermore, a detailed phase diagram is needed for solidification analysis. Miettinen[21] calculated the Cu-Sn-Pb phase diagram at 14 wt% Sn, as shown in Fig.1. An ternary phase region "fcc(copper-rich phase)+$L_1$+$L_2$" emerges under the liquid miscibility gap "$L_1$+$L_2$", which does not exist in the phase diagram of binary immiscible alloys. If a sufficient undercooling degree was achieved, the alloy melt might directly enter the "fcc(copper-rich phase)+$L_1$+$L_2$" phase region and skip the first "$L_1$+$L_2$" phase region, which means that the monotectic reaction would occur first. In order to verify this hypothesis, according to Fig.1, the 14wt%Sn-86wt%(85Cu-15Pb) (termed 14Sn-73.1Cu-12.9Pb) monotectic alloy and 14wt%Sn-86wt%(75Cu-25Pb) (termed 14Sn-64.5Cu-21.5Pb) immiscible alloy were solidified by casting method. Cu-65wt%Pb immiscible alloy was solidified by casting method as a comparison.

## 1 Experiment

High purity elements of Cu, Sn and Pb (99.99 wt%) were mixed in the compositions of 14Sn-73.1Cu-12.9Pb, 14Sn-64.5Cu-21.5Pb, Cu-65Pb and Cu-75Pb (wt%, all the same for such formula in the later text). The mixed powers were tableted and overheated to ~1473 K in a high-frequency induction furnace under argon atmosphere, which is about 200 K above the critical temperatures of alloys. The alloy melts were cast into a cylindrical copper mold with a diameter of 2.5 and 5 mm. The alloy rods were cut at the same horizontal position to show the cross sections. 14Sn-64.5Cu-21.5Pb was also cast into a copper mold with a diameter of 10 mm and cut into two halves along the vertical direction to show its vertical cross section. The cut samples were mounted into epoxy resin and then polished mechanically.

The morphologies of samples were examined by a digital camera (for over-size samples) and scanning electron microscopy (SEM, SSX-550, Shimadzu, Japan) with energy dispersive X-ray spectroscopy (EDS). X-ray diffraction (XRD, D/MAX-RB, Rigaku, Japan) tests were used to identify the phase compositions on the cross sections of the samples.

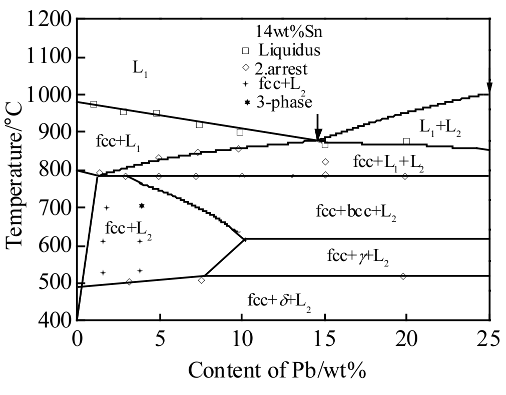


Fig.1 Calculated isopleth at 14 wt% Sn in the copper-rich part of the Cu-Sn-Pb system[21]

## 2 Results and Discussion

### 2.1 Cross-sectional morphologies of alloy

The cross-sectional morphologies of as-cast 14Sn-73.1Cu-12.9Pb, 14Sn-64.5Cu-21.5Pb, Cu-65Pb and Cu-75Pb alloys are shown in Fig.2. As indicated by EDS analysis, the chemical compositions of all the dark grey parts in Fig.2a~2c are identified as Cu and Sn while the white part is almost pure Pb. Fig.2a presents a homogenous structure of 14Sn-73.1Cu-12.9Pb monotectic alloy that consists of CuSn-rich dendrites with Pb well-dispersed between them, as seen in Fig.2b resulting from monotectic reaction. A core-shell morphology with CuSn-rich shell/Pb-rich core is formed in 14Sn-64.5Cu-21.5Pb hypermonotectic alloy, as shown in Fig.2c. It should be noted that the 14Sn-64.5Cu-21.5Pb melt has been cast into copper molds with diameters of 2.5, 5 and 10 mm. Obtained morphologies are all the same as Fig.2c. The Pb-rich droplets migrating toward the core are trapped in the CuSn-rich shell. Fig.2d shows the morphology of a axial direction section of 14Sn-64.5Cu-21.5Pb alloy rod with a diameter of 10 mm. The bottom and the shell of the alloy rod are composed of CuSn-rich phases and discontinuous Pb-rich blocks located in the center. Because of the large density difference between CuSn-rich liquid and Pb-rich liquid, Pb-rich liquid tends to segregate towards the bottom. At the same time, CuSn-rich liquid fills the space where Pb-rich liquid leaves and solidifies quickly, resulting in the discontinuous Pb-rich blocks along the vertical axis. Shrinkage cavities formed in the center due to the solidification of Pb-rich liquid since CuSn-rich liquid solidified firstly at the outside. Fig.2e shows a "network" distribution of the two immiscible liquids in Cu-65Pb alloy after liquid-liquid phase separation process. The core-shell structured Cu-75Pb alloy is given in Fig.2g. The shells of Cu-65Pb and Cu-75Pb alloy consist of mostly Pb-rich phase.

### 2.2 Solidification of 14Sn-73.1Cu-12.9Pb monotectic alloy

The monotectic reaction L→$S_1$ (CuSn-rich) + $L_2$ (Pb-rich) takes place during cooling down from high temperature of 14Sn-73.1Cu-12.9Pb alloy. In high thermal conductivity copper mould, the CuSn-rich liquid phase with high volume fraction quickly cools down. Meanwhile, LMP Pb-rich liquid phase is precipitated on the grain boundary of the CuSn-rich phase. The similar dispersed structures could also be found in

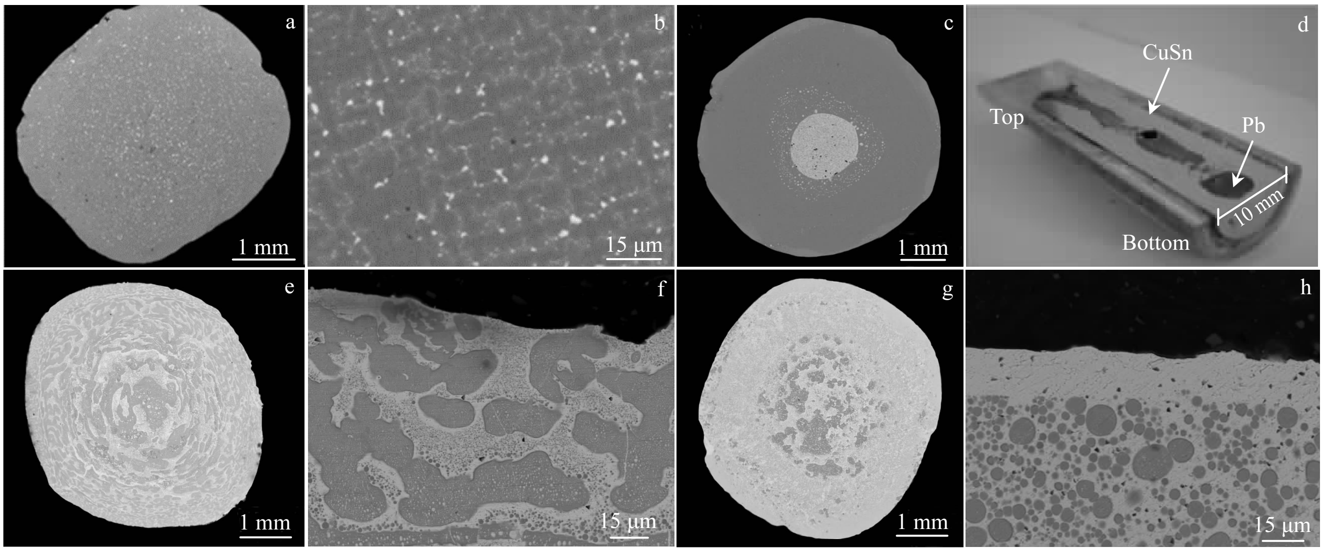


Fig.2 Cross-sectional morphologies of as-cast 14Sn-73.1Cu-12.9Pb alloy (a) and its partial enlarged detail (b); 14Sn-64.5Cu-21.5Pb alloy (c) and its axial direction cross-sectional morphology (d); Cu-65Pb alloy (e) and its enlarged boundary (f); Cu-75Pb alloy (g) and its enlarged boundary (h)

Cu-37.4Pb alloy in Ref.[22].

### 2.3 Difference among 14Sn-64.5Cu-21.5Pb, Cu-65Pb and Cu-75Pb alloys

Fig.3 is the phase diagram of Cu-Pb monotectic alloy[23]. As can be seen from Fig.1 and Fig.3, all three alloys are within the immiscible region. For the hypermonotectic alloys, the high-temperature homogeneous liquid phase is decomposed into two liquids during cooling. And the minor liquid droplets migrate into the center under Marangoni movements.

The shell of 14Sn-64.5Cu-21.5Pb alloy consists of a HMP phase, while the Cu-65Pb and Cu-75Pb alloys are covered by a shell of Pb. With the increase of Pb content, the two-phase network distribution in Cu-65Pb gradually transforms into the core-shell structured Cu-75Pb with Pb core. For network structured Cu-65Pb alloy, the two liquid phases are cooled without sufficient Marangoni movement due to both the slightly low content of Pb liquid phase and rapid cooling speed caused by copper mould with high thermal conductivity. There are many examples of shell with LMP phase[14-18]. After two-phase separation, the LMP liquid phase with lower surface tension has a disposition to spread outer layer, forming the shell layer.

### 2.4 Solidification of 14Sn-64.5Cu-21.5Pb alloy

Phase characterization of 14Sn-64.5Cu-21.5Pb alloy was performed by X-ray diffraction (XRD), and $Cu_{13.7}Sn$, $Cu_{10}Sn_3$ and Pb phases are identified, as shown in Fig.4. The crystal plane index of $Cu_{13.7}Sn$ phase is marked, which indicates that it is face-centered cubic structure. Therefore, the XRD result agrees well with the calculated phase compositions in Ref.[21].

It is commonly considered that after the liquid separation reaction, the liquid with a lower surface tension would form the shell, as shown in Fig.2e~2h. According to the phase diagram in Fig.1, on cooling of alloy melt, the liquid separation reaction $L \rightarrow L_1+L_2$ would take place. Immediately after that, the monotectic reaction $L_1 \rightarrow$fcc (Cu-rich)$+L_2$ would occur

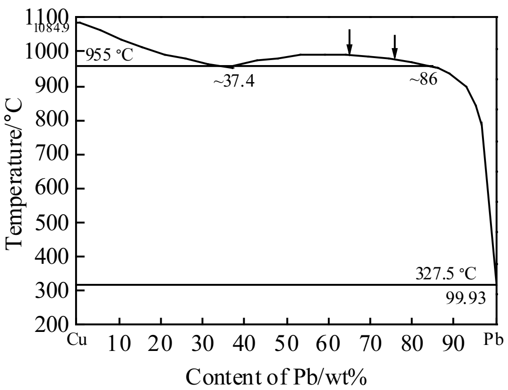


Fig.3 Phase diagram of Cu-Pb monotectic alloy[23]

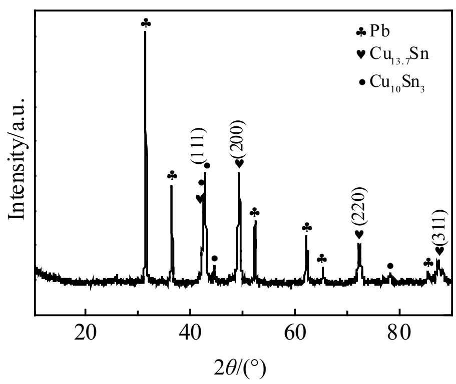


Fig.4 XRD pattern of as-cast 14Sn-64.5Cu-21.5Pb (wt %) alloy

within the temperature range of the ternary phase region "fcc + $L_1$ + $L_2$". However, in the case of 14Sn-64.5Cu-21.5Pb alloy, CuSn-rich phases forms the shell. It may be inferred that the liquid separation reaction is suppressed and the monotectic reaction takes place before the liquid-liquid phase separation reaction. This situation could happen when the alloy melt is undercooled directly into "fcc+ $L_1$+ $L_2$" phase region instead of "$L_1$+$L_2$" phase region during casting process. This deduction will be verified in detail in our further work through decreasing the undercooling degree, such as increasing the melt initial temperature and increasing the temperature of copper mold in order to lower the cooling rate.

## 3 Conclusion

1) Phase separations of 14Sn-73.1Cu-12.9Pb, 14Sn-64.5Cu-21.5Pb, Cu-65Pb and Cu-75Pb alloys have been experimentally investigated and discussed based on the calculated phase diagram.

2) An anomalous core-shell structure with a CuSn-rich shell and a Pb-rich core forms in 14Sn-64.5Cu-21.5Pb alloy. This anomalous phenomenon may be explained by the monotectic reaction which takes place before the liquid separation reaction due to undercooling.

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# Cu-Sn-Pb 过偏晶合金中异常 Cu-Sn 壳/Pb 核宏观结构的形成


李建强[1,2]，孙　虹[1,2]，马炳倩[1]

(1. 中国科学院过程工程研究所 湿法冶金清洁生产技术国家工程实验室 中国科学院绿色过程与工程重点实验室，北京 100190)

(2. 中国科学院大学，北京 100049)



**摘　要**：目前核/壳结构难混熔合金的壳是由低熔点相组成还是高熔点相组成，尚无确切答案。根据文献中 Cu-Sn-Pb 合金的计算相图，通过铸造法研究 14Sn-73.1Cu-12.9Pb、14Sn-64.5Cu-21.5Pb、Cu-65Pb 和 Cu-75Pb 合金的相分离过程。结果表明，14Sn-64.5Cu-21.5Pb 合金具有富 Cu-Sn 相包裹富 Pb 相核/壳结构组织；这一结果与低熔点相（如 Cu-75Pb 合金）形成核的观点不一致，这种异常现象可以解释为：在铸造过程中，由于过冷度的影响，偏晶反应发生在液相分离反应前。这为通过控制凝固路径改变难混熔合金的结构提供了一种可能的方法。



**关键词**：凝固；金属和合金；核/壳结构



作者简介：李建强，男，1975 年生，博士，研究员，中国科学院过程工程研究所，北京 100190，电话：010-82544953，E-mail: jqli@ipe.ac.cn