Research Progresses on the Modification of Solidification Structure of Au-Sn Eutectic Alloy

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Abstract: Au-20Sn eutectic alloy solder is extensively used in high power electronics and optoelectronics packaging. The heterogeneous distribution of primary phase and coarse structure are contributed to the difficulty of the process. Therefore, refining the solidification structure becomes extremely important. The research progresses on the refinement of Au-Sn eutectic alloy solidification structure, such as the effects of composition micro-adjustment and melt temperature treatment on the solidification microstructure, effects of incubated nucleation treatment on the refinement of solidification structure, modification of the solidification microstructure by melt mixing are summarized.

Key words: Au-Sn eutectic alloy; rapid solidification; melt temperature treatment; incubated nucleation; melt mixing.
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金锡共晶合金凝固研究进展

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摘　要：金锡二元共晶合金钎料是一种广泛应用于高可靠微电子与光电子器件封装中的连接材料，目前我国对该类高性能钎料的凝固与成形控制缺乏深入系统地研究。合金铸态组织粗大和硬脆性金属间化合物的不均匀分布是导致合金加工成形困难的根本原因，铸态组织细化将显著提高合金的加工成形性能。综述了合金的快速凝固、熔体温度处理、孕育形核处理和熔体混合处理等对金锡共晶合金凝固组织细化及组织演变规律影响等方面的研究进展。

关键词：金锡共晶合金；快速凝固；熔体温度处理；自孕育形核；熔体混合处理

Au-20Sn eutectic alloy solder is extensively used in high power electronics and optoelectronics packaging due to its high-temperature performance, high mechanical strength, high electrical and thermal conductivity[1]. Au-20Sn eutectic alloy is consisted of ζ′-Au_5Sn phase and δ-AuSn phase [2]. Both ζ′ and δ are intermetallics with very hard and brittle nature, which makes the processing difficulties in the manufacture of the Au-20Sn solder strips or foils. In practice, the nonequilibrium solidification usually results in forming primary ζ′-Au_5Sn phase dendrites. The heterogeneous distribution of primary phase ζ′-Au_5Sn and coarse eutectic microstructures are contributed to the difficulty of the process for this alloy. And the processing performance of Au-Sn alloy can be improved by refinement of the solidification structure. Up till now, the research about the refinement of as-cast structure for Au-Sn eutectic alloy is very

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limited[3-5].

In this paper, the recent research developments on the modification of solidification structure of Au-Sn eutectic alloy are summarized. The advanced solidification technologies, such as, rapid solidification, melt temperature treatment, incubated nucleation, and melt mixing were applied to refine the solidification structure of Au-Sn eutectic alloy.

1 The refinement of as-cast structure by rapid solidification

The rapid solidification is one of the effective methods of refining alloy solidification structure[6]. Deng[7] and Tan[8] have studied the Au-Sn solidification structure, especially the formation of primary phase and evolution under rapid solidification. The injection casting (IC) and suction casting (SC) with changing cast mould were adopted to increase the cooling rate of Au-Sn alloy solidification. Fig.1 illustrated the as-cast microstructures of Au-20Sn alloy under different solidification pathways. At lower cooling rate in the conventional casting (CC, 2.4×10 K/min) and injection casting with graphite mold (IC, 4.2×10^2 K/min) solidification condition, the large coarse dendrites of primary phase ζ′-Au_5Sn were existed in the as-cast structure (showed in Fig.1a and Fig.1b). At higher cooling rate in the injection casting with cooper mold (ICC, 9.0×10^3 K/min), the size of primary phase ζ′-Au_5Sn dendrites were much refined obviously (Fig.1c). And the morphologies of dendrites become to “rosette-like”. At the highest cooling rate in the suction casting cooper mold with water cooling (SC, 3.5×10^4 K/min), the primary phase changed to δ-AuSn phase with very small grain in as-cast microstructure (Fig.1d).

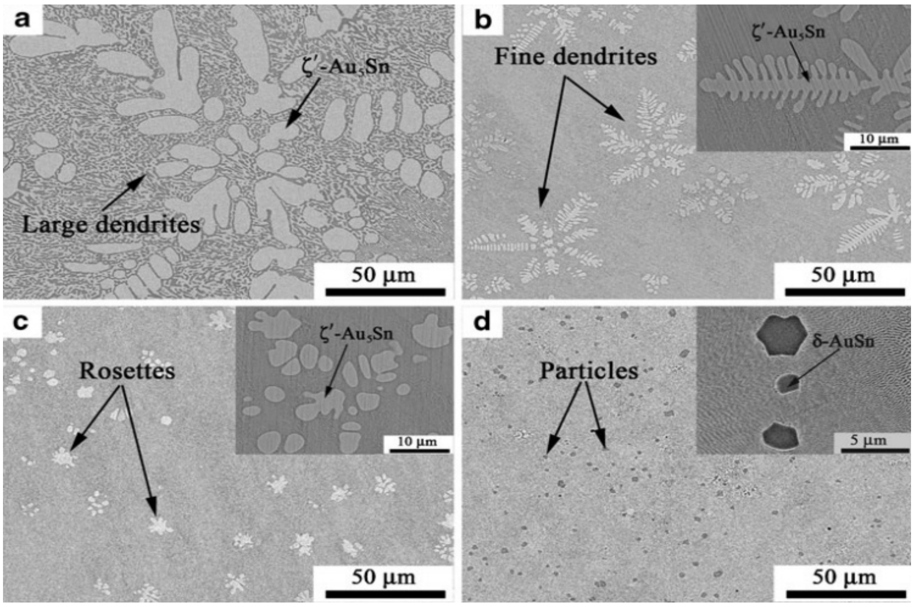

Fig.1 As-cast microstructures of the Au-20Sn alloy showing different primary phases under different solidification pathways

(a. CC; b. IC; c. ICC; d. SC)

图 1 不同凝固条件下的初生相和 Au-20Sn 合金凝固组织

The results indicated that the as-cast microstructure of the Au-20Sn alloy was refined effectively, and the morphology and the kind of primary phase was also changed with the increase of solidification cooling rate. The refining mechanism of solidification structure can be explained as following. Based on the alloy solidification principles, supercooling degree is highly sensitive to the cooling rate, and it increases with increasing the cooling rate. In undercooling melt, the nucleation rate and growth rate is controlled by thermodynamics and kinetics conditions[9]. For Au-Sn eutectic alloy, under small supercooling (conventional casting, e.g. CC and IC in this study), the dendrite growth of ζ′-Au_5Sn phase controlled by diffusion is determined by cooling rate. The size of ζ′-Au_5Sn decreases with increasing the cooling rate because the dynamic condition of dendrite growing up is inhibited. But under large supercooling (rapid solidification, e.g., ICC and SC in this study), alloy solidifies at a very low temperature. Then the nucleation rate has increased dramatically, but the growing up rate has been hindered due to the limited atomic diffusion. When the cooling rate reaches to 3.5×10^4 K/min, there is the process of competitive nucleation between the ζ'-Au_5Sn phase and the δ-AuSn phase. According to the calculation by thermodynamics analysis and Kinetics analysis of phase, the δ-AuSn phase is priority to nucleation. Therefore, in the rapid solidification, ζ′-Au_5Sn primary phase and the basic lamellar eutectic microstructure is refined obviously.

Besides the size, the morphology of the primary phase is also sensitive to the cooling rate. The developed first arms of the dendrites will become short and tend to evolve into the ripened equiaxed dendrites, i.e., rosette, as the cooling rate increases from about 4.2×10^2 (IC) to 9×10^3 K/min (ICC). Based on these observations, a distinct tendency can be depicted that as the cooling rate increases the primary phase size and its volume fraction decrease, and the developed dendrites become small dendrites and even small rosettes. A critical cooling rate must exist under which the primary phase disappears. This critical cooling rate can be estimated between 9.0×10^3 K/min (corresponding to ICC pathway) and 3.5×10^4 K/min (corresponding to SC pathway) as illustrated with a dashed arrow in Fig.1 according to this study. These phenomena have also been observed in other eutectic or hypereutectic alloys [10-11].

In summary, the rapid solidification can effectively refine the Au-Sn alloy as-cast microstructure. The higher cooling rate is and the better the refining effect is. And the precipitation of primary phase in the casting microstructure is obviously inhibited. The average size of the primary phase decreases below 5 μm which is uniform distribution and no macro segregation. The morphologies of primary phase have changed from dendrites to rosette-like. The basic eutectic lamellar microstructure is refined and no obvious intergranular segregation.

2 Effects of composition micro-adjustment and melt temperature treatment on the solidification microstructure

Under the nonequilibrium solidification of Au-Sn eutectic alloy, ζ′-Au_5Sn primary phase usually precipitates firstly and then precipitates ζ + δ eutectic phase at the same time. Based on the alloy solidification theories, under the certain solidification condition, deviating from the eutectic composition of the alloy can be occurred in the eutectic solidification reaction. Then the eutectic structure can be obtained. Melt temperature treatment is also a method of refining as-cast structure of the hypoeutectic and hypereutectic alloy [12].

Recently, Song and Mao[13-15] reported the solidification microstructure with fine full lamellar structure of Au-Sn eutectic alloy, which was obtained by the composition micro-adjustment and melt temperature overheating treatment.

Fig.2 illustrated the solidification microstructure of Au-Sn eutectic alloy by the composition micro-adjustment of increasing Sn addition and different melt temperature treatments. It is seen from Fig.2 that the primary phase ζ′-Au_5Sn with rosette-like exist in the solidification microstructure of Au-Sn eutectic alloy without composition adjustment (as showed in Fig.2a). The average size of the primary phase is 20 μm. But the solidified structure with composition micro-adjustment become to the fine full lamellar structure. The primary phase ζ′-Au_5Sn disappears (as showed in Fig.2b~d).

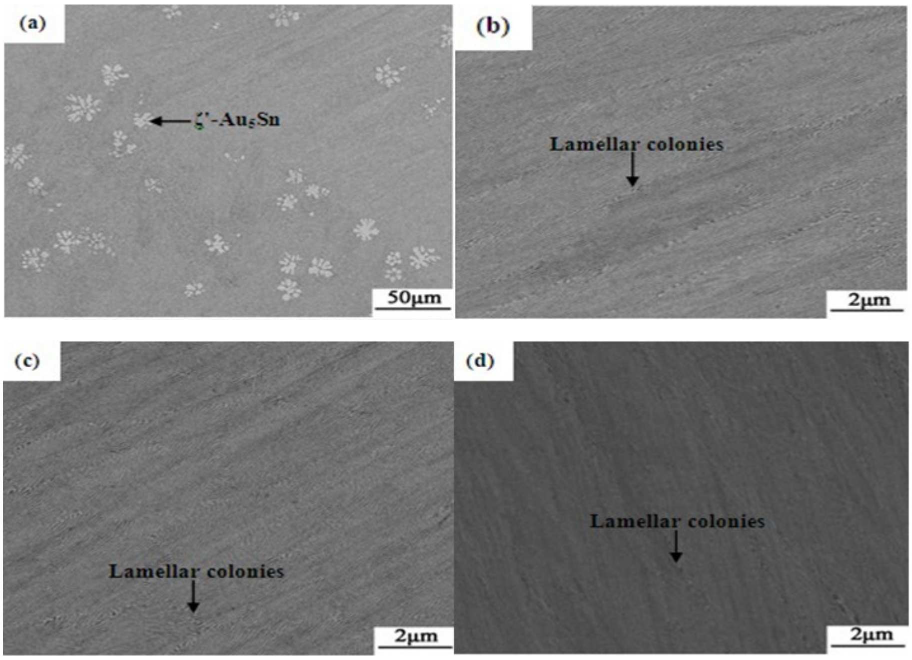

Fig.2 The solidification structure of Au-Sn eutectic alloy without composition adjustment (a) and by composition micro-adjustment and different melt temperature treatment at 300℃ (b), 380℃ (c) and 420℃ (d)

图 2 成分微调(a)及不同熔体温度[(b). 300℃, (c). 380℃ (d). 420℃]处理后的 Au-20Sn 合金凝固组织

From Fig.2b to Fig.2d, it can be further found that the fine full lamellar eutectic structure without primary phase is obtained by melt temperature treatment at different overheating temperatures from 300℃ to 420℃. The spacing of eutectic lamellae is about 0.07μm. But the average size of eutectic lamellar colonies is decrease from 16 μm to 8 μm with increasing the overheating temperature of melt temperature treatment.

Thus, the solidification microstructure of Au-Sn eutectic alloy can be modified effectively by the appropriate combination of composition microadjustment and melt temperature overheating treatment. Especially, the precipitation of primary phase is suppressed completely and the fine full lamellar eutectic structure is obtained by this new advanced solidification method.

3 Effect of incubated nucleation treatment on the solidification microstructure

The incubated nucleation treatment is an effective method to refine and improve the solidified structure in many metal alloys. Usually the incubating agent is added to alloy melt, which can increase a large number of homogeneous nucleation in the metal melting and then refine the grain size of alloy [6]. Chidambaram [16-17] has reported that adding Ag or Cu to Au-Sn alloy can inhibit the formation of brittle ζ′-Au_5Sn phase and promote the formation of relatively toughness Au-Ag phase or Au-Cu phase, which result in improving the processing performance of the alloy.

In recent years, Deng and Song [7, 14, 18] have deeply studied the effects of self-incubated nucleation treatment with adding trace Au or Sn on the solidification microstructure of Au-Sn eutectic alloy.

Fig.3 showed the SEM micrograph of solidification microstructure of Au-Sn eutectic alloy with Au or Sn incubated nucleation treatment, comparing with that of without incubated nucleation treatment. It is seen that there are many large coarse primary phases ζ′-Au_5Sn in the as-cast structure (Fig.3a). The average size and volume fraction of primary phase dendrites is about 200 μm and 20%, respectively. The solidification microstructure of Au-Sn eutectic alloy with self-incubated nucleation treatment has been modified greatly by adding trace Au or Sn. For Au incubated nucleation treatment, the primary phase changed to δ-AuSn phase (Fig.3b). The morphology and average size of primary phase is decreased obviously. For Sn incubated nucleation treatment, the primary phase also changed to δ-AuSn phase (Fig.3c). Comparing Fig.3b and Fig.3c more carefully, it can be found that the average size of primary phase δ-AuSn is decreased from about 120 μm to 80μm, and the morphology and dispensability of δ-AuSn phase particle is much fined and uniformed.

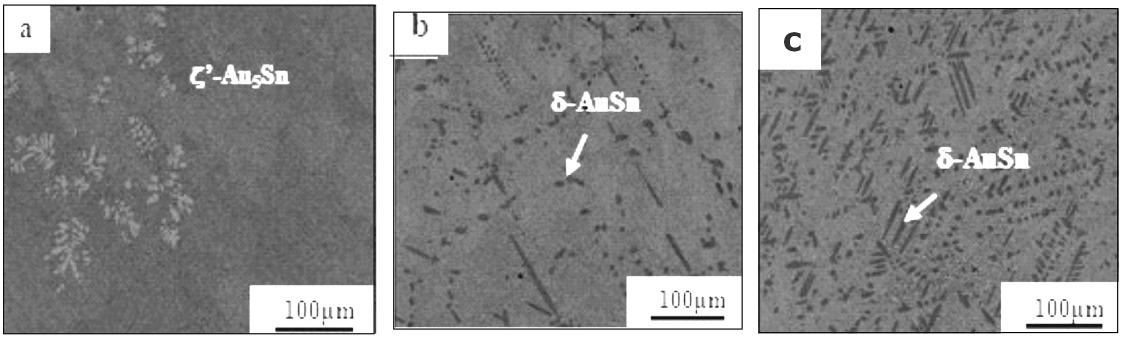

Fig.3 Solidification microstructures of Au-Sn eutectic alloy without incubated nucleation treatment (a) and with incubated nucleation treatment by Au (b) or Sn (c)

图 3 添加不同形核剂孕育形核处理的 Au-20Sn 合金凝固组织

The research results indicated that compared with no incubated nucleation treatment, the solidification microstructure of Au-Sn eutectic alloy are modified greatly by incubated nucleation treatment with Au or Sn. The crystal structure, morphology and the size of primary phase is all changed. The primary phase transforms into fine δ-AuSn phase with uniform distribution from the conventional ζ′-Au_5Sn phase coarse dendrite with non-uniform distribution. Meanwhile, the eutectic structure matrix is also refined. Furthermore, the incubated nucleation effect of Sn is better than that of Au.

4 Modification of the solidification microstructure by melt mixing

Melt mixing is another melt temperature treatment to improve effectively the alloy solidification microstructure[19]. Quite recently, Guo[20-22] have studied the modification of the solidification of Au-Sn eutectic alloy and the formation of anomalous eutectic microstructure by melt mixing with high-temperature and low-temperature melts. The solidification microstructure evolutions of Au-20Sn eutectic alloy by the temperatures of high-temperature melt were investigated.

The research results shows that melt mixing with high-temperature and low-temperature melts can effectively improve the solidification microstructure of Au-20Sn eutectic alloy. Adopting an appropriate melt mixing condition, which is high-temperature melt with 350℃ and low-temperature melt with 283℃, the precipitation of primary phase ζ′-Au_5Sn will be inhibited during solidification procession, and the full lamellar eutectic microstructure was obtained. When the temperature of high-temperature melt is higher (360℃) or lower (340℃), the primary phase ζ′-Au5Sn will also existed in the solidification microstructure. Melt mixing with high-temperature and low-temperature melts can effectively decrease the Au atom segregation and modify the precipitation behavior of primary phase ζ′-Au_5Sn. The compressive behavior at 220℃ exhibits a low yielding stress and a low stress platform for the alloy with full lamellar eutectic microstructure prepared by melt mixing, which indicates that the hot-workability of Au-Sn eutectic alloy can be improved by melt mixing.

Fig.4 illustrated the solidification microstructure of Au-Sn eutectic alloy by melt mixing with high-temperature and low-temperature melts. The effect of different temperatures of the high temperature melt, which were 380, 390 and 400℃ respectively (the temperature of the low temperature melt was all 274℃), on solidification microstructure were showed. It can be seen that compared with the lamellar eutectic prepared by air cooling conventional solidification (Fig.4a), the morphology of solidification microstructure of Au-Sn eutectic alloy could be changed effectively through melt mixing, the conventional lamellar eutectic microstructure transformed into the anomalous eutectic microstructure under suitable melt mixing condition. (Fig.4b~d). When the high-temperature melt is 380℃, the morphology of eutectic microstructure is closed to the grid and honeycomb morphology (Fig.4b), which is named as the Cellular Eutectic by Zhao[23]. It is a transition eutectic solidification structure transformed from the lamellar eutectic to the anomalous eutectic. When the high-temperature melt is increased to 390℃ and 400℃, the eutectic solidification structure transforms to the anomalous eutectic completely. The size of equiaxed grain of anomalous eutectic is increased with increasing the temperature of high-temperature melt in melt mixing from 390℃ to 400℃. The morphology of anomalous eutectic is showed as in Fig.4c and Fig.4d, respectively. The anomalous eutectic formation by melt mixing in the Au-Sn eutectic alloy is explained by dendrite fusing and remelting mechanism.

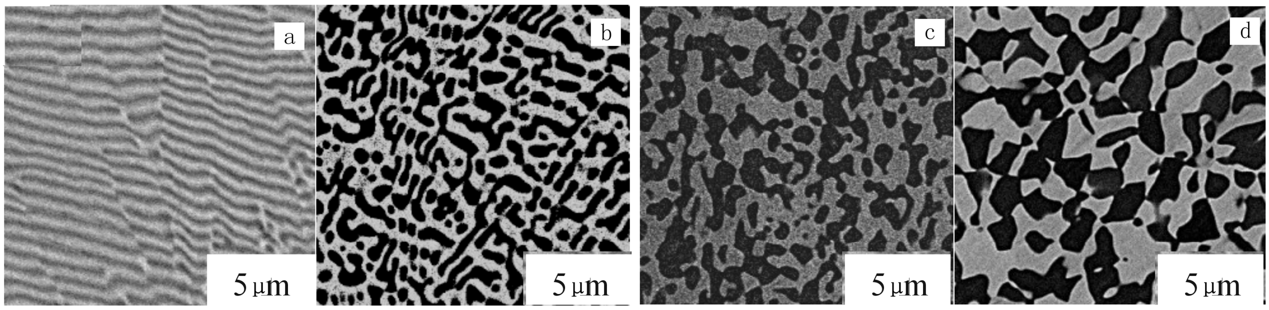

Fig.4 Solidification structures of Au-Sn eutectic alloy

(a. lamellar eutectic by air cooling from 400℃; b. cellular eutectic by melt mixing under 380℃;

c. anomalous eutectic by melt mixing under 390℃; d. anomalous eutectic by melt mixing under 400℃)

图 4 不同熔体温度混合下的 Au-20Sn 合金凝固组织

5 Conclusion

This paper has summarized the research progresses on the modification of solidification structure of Au-Sn eutectic alloy. The Au-Sn alloy solidification microstructure can be greatly refined by rapid solidification, melt temperature treatment and self-incubated nucleation treatment. The effect way to refine the alloy as-cast structure is the appropriate combination of composition micro-adjustment with melt temperature treatment method, which obtains the fine full lamellar eutectic structure. The anomalous eutectic structure can be obtained by melt mixing method. In the future, the formation mechanism of the fine full lamellar eutectic structure and the micro-structure evolution during working process of Au-Sn eutectic alloy should be further studied.

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