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Solidification process and microstructure evolution of bulk undercooled Co−Sn alloys

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Abstract: A series of Co−Sn alloys with Sn content ranging from 12% to 32% (mole fraction) were undercooled to different degrees below the equilibrium liquidus temperature and the solidification behaviors were investigated by monitoring the temperature recalescence and examing the solidification microstructures. A boundary clearly exists, which separates the coupled growth zone from the decoupled growth zone of eutectic phases for the alloys with Sn content ranging from 14% to 31% (mole fraction). The other Co−Sn alloys out of this content range are hard to be undercooled into the coupled growth zone in the experiment. It is found that the so-called non-reciprocal nucleation phenomenon does not happen in the solidification of undercooled Co−Sn off-eutectic alloys.

Key words: Co−Sn alloy; undercooling; recalescence; coupled growth zone; solidification; microstructure evolution

1 Introduction

Rapid solidification of deeply undercooled alloy melts is far from equilibrium. As a result, competitions between various phases or different growth modes exist in the rapid solidification [1−7]. One of them is the selection between single-phase growth and eutectic coupled growth in the rapid solidification of the undercooled alloys around eutectic points. It was revealed that there is a coupled growth zone of eutectic alloys below the eutectic line. When the eutectic alloys are undercooled into the zone prior to nucleation, regular eutectic microstructure forms as the primary phase. Such a finding considerably improved the understanding of the solidification microstructure formation [8,9]. Co−Sn eutectic alloy is often used for studying the solidification behavior of undercooled eutectic alloys [10−12]. Up to now, however, the coupled eutectic zone in the alloy system is not still established. One purpose of this work is to determine the undercooling at which the primary eutectic will form in the solidification of Co−Sn alloys.

During investigating the solidification microstructure of off-eutectic alloys, it was also found that the primary phase was surrounded by a Halo of another phase but the opposite is not true. Such a phenomenon is usually called non-reciprocal nucleation [13−15], meaning that one eutectic phase can trigger the nucleation of the other phase, but not vise versa. If we note that heterogeneous nucleation is realized through crystal lattice matching between the substrates and the crystal to nucleate, the viewpoint of non-reciprocal nucleation is doubtful.

2 Experimental

Co−Sn alloys with compositions ranging from 12%−32% Sn (mole fraction, the same below if not mentioned), including the Co−24%Sn eutectic alloy, were chosen. The raw materials are pure Co and Sn with 99.999% and 99.99% purities (mass fraction), respectively. Undercooling experiment was carried out in a vacuum chamber back-filled with ultra pure argon. The raw materials placed in a quartz glass crucible was induction melted, and then cyclically superheated and cooled under the protection of a molten flux until the

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desired undercooling was achieved. The superheating of melt was controlled to be about 300 K by adjusting the input power of the induction coil. A two-color infrared pyrometer with an accuracy of 1 K and a response time of 1 ms was utilized to monitor the thermal history of the sample during the entire experimental cycle. The temperature data were recorded in computer, from which the cooling curves can be redrawn.

The surface of the as-cast sample was observed without any etching by a JSM7600F field emission gun scanning electron microscope (SEM). Then the sample was cross-sectioned, polished and etched for structural observation under an optical microscope (OM). The etching agent was a mixed solution of $CuSO_4$, HCl and ethanol. Compositions of various phases were analyzed by OXFORD INCA EDX apparatus equipped on the JSM7600F SEM.

3 Results

3.1 Cooling curves

During the rapid solidification of undercooled melts, the growing solid releases latent heat rapidly towards the remaining melt while little heat is transferred into the surrounding, leading to a fast temperature rise of the system, i.e., recalescence. Recalescence behavior therefore reflects the feature of rapid solidification. Co−18%Sn hypo-eutectic alloy, Co−24%Sn eutectic alloy and Co−30%Sn hyper-eutectic alloy were taken as examples, and the corresponding experimental results were described. Defining undercooling as the difference between the equilibrium liquidus temperature T_L and the on-set temperature of solidification, Fig. 1 shows the typical cooling curves as a function of undercooling for the alloys. It can be seen clearly that Co−24%Sn eutectic alloy always shows one recalescence in the whole undercooling range studied in this work. In contrast, the cooling curves of Co−18%Sn hypo-eutectic alloy and Co−30%Sn hyper-eutectic alloy exhibit two temperature recalescences when the undercooling is below a critical value ΔT_c, but only one temperature recalescence at larger undercoolings. The ΔT_c for the two alloys are 170 K and 108 K, respectively.

Recalescence features of all the investigated alloys at different undercoolings are depicted in the Co−Sn equilibrium phase diagram shown in Fig. 2, where the blank circles represent that the alloy melt undercooled to the temperature pointed solidifies with double recalescences, while the solid circles represent the solidification with single recalescence. Clearly, the value of ΔT_c increases gradually as the alloy composition deviates from the eutectic point of Co−24%Sn. As shown in Fig. 2, there is no ΔT_c to be detected for Co−12%Sn, Co−13%Sn and Co−32%Sn alloys. Double recalescence constantly happens in the whole undercooling range studied. It is uncertain at present whether ΔT_c exists in the alloys out of the composition range 14%−31% Sn due to the undercooling limits achieved.

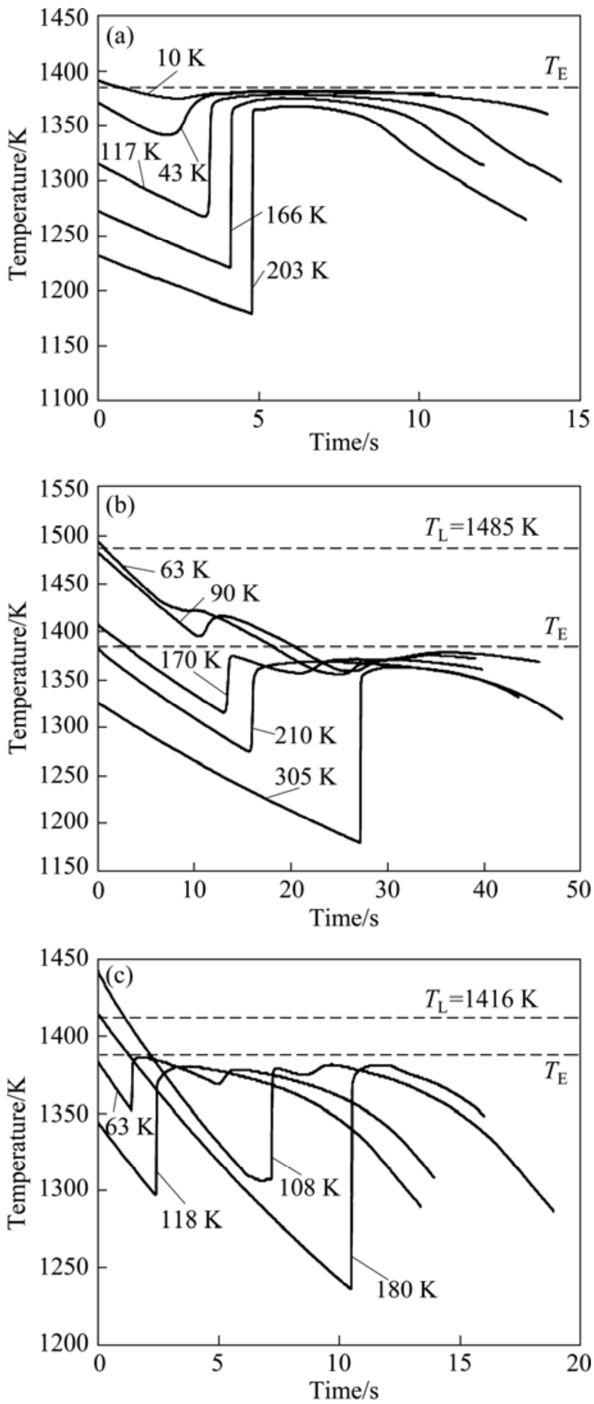

Fig. 1 Cooling curves at different undercoolings: (a) Co−24%Sn eutectic alloy; (b) Co−18%Sn hypo-eutectic alloy; (c) Co−30%Sn hyper-eutectic alloy

3.2 Solidification structure

Figures 3−5 show the cross-sectional micro-structures of Co−24%Sn, Co−18%Sn and Co−30%Sn alloys solidified at different undercoolings, respectively.

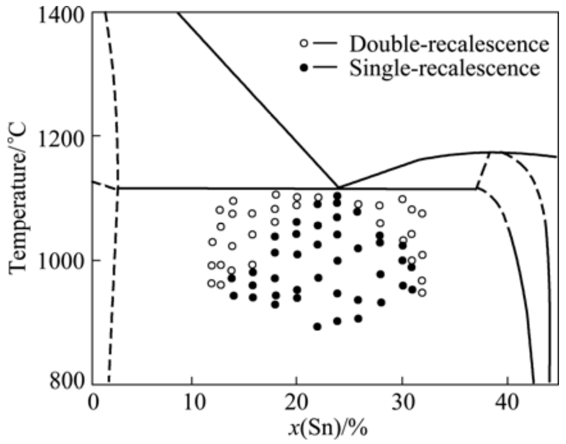

Fig. 2 Recalescence type of cooling curve for different alloys with various undercoolings

As shown in Fig. 3(a), the solidification structure of Co−24%Sn eutectic alloy is composed of regular lamellar eutectic completely at a very low undercooling. When the undercooling increases up to 21 K or higher, anomalous eutectic structures start to form in the center of the eutectic colony, and regular lamellar eutectic grows outwards radically from the edge of anomalous eutectic region (Figs. 3(b) and (c)).

Compared with the Co−24%Sn eutectic alloy, more complex solidification microstructures were observed in the Co−Sn off-eutectic alloys as the undercooling increases. At undercooling below ΔT_c where double recalescence takes place, the primary solid formed in rapid solidification is α-Co single phase dendrite for Co−18%Sn hypo-eutectic alloy. Its branches are surrounded by β-Co_3Sn_2 halos. Lamellar eutectics distribute in the interdendritic regions. As the undercooling increases, more and more α-Co dendrite branches are broken, and anomalous eutectic forms (Fig. 4(b)). At undercooling larger than ΔT_c, similar anomalous eutectics to largely undercooled Co−24%Sn eutectic alloy form (Fig. 4(c)). Outside the anomalous eutectics are residual branches of α-Co and lamellar eutectics.

The microstructure evolution of the Co−30%Sn hyper-eutectic alloy is similar to the Co−18%Sn hypo-eutectic alloy except that the primary β-Co_3Sn_2 instead of α-Co forms at undercooling below ΔT_c (Figs. 5(a) and (b)), and branches of β-Co_3Sn_2 encircle the

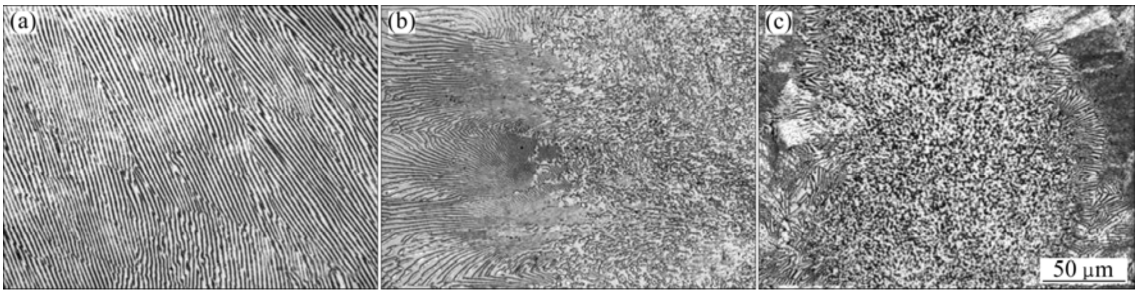

Fig. 3 Cross-sectional microstructures of Co−24%Sn eutectic alloy undercooled at 15 K (a), 43 K (b) and 110 K (c)

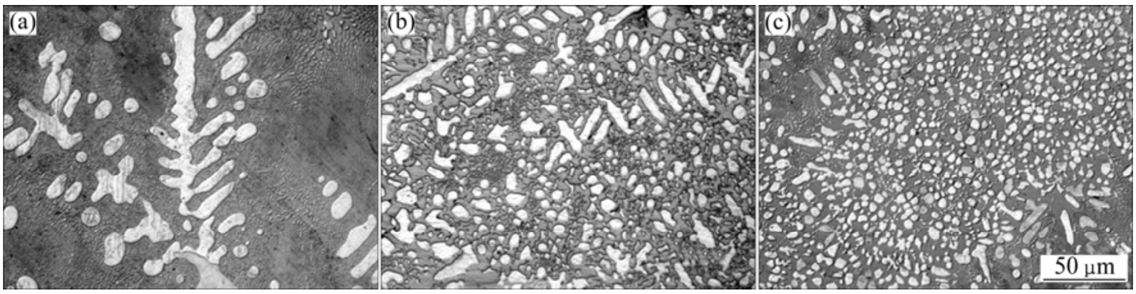

Fig. 4 Cross-sectional microstructures of Co−18%Sn hypo-eutectic alloy undercooled at 63 K (a), 170 K (b) and 210 K (c)

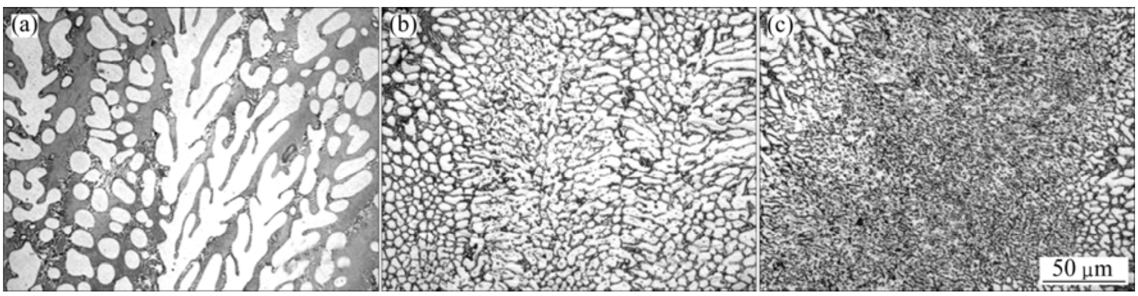

Fig. 5 Cross-sectional microstructures of Co−30%Sn hyper-eutectic alloy undercooled at 20 K (a), 108 K (b) and 118 K (c)

anomalous eutectics at a large undercooling (Fig. 5(c)). Figure 6 shows the surface morphology of the Co−18%Sn hypo-eutectic alloy and Co−30%Sn hyper-eutectic alloy. For both alloys, the coarse primary phase is surrounded by a halo of the other phase.

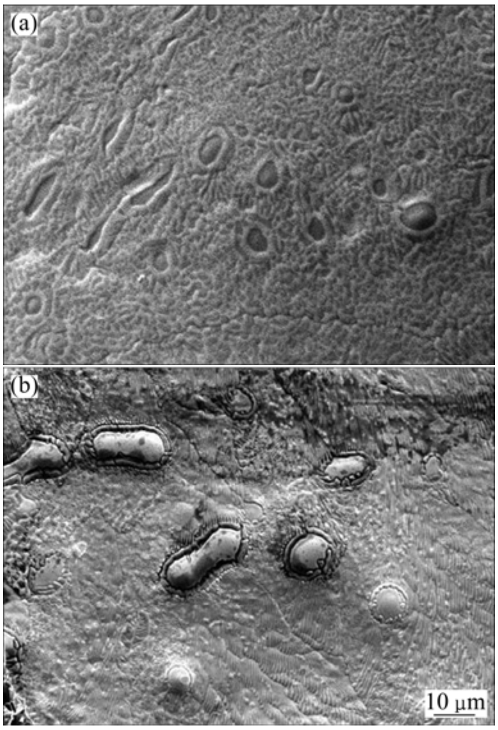

Fig. 6 SEM images of alloy sample surface: (a) Co−18%Sn eutectic alloy undercooled at 63 K; (b) Co−30%Sn hypo-eutectic alloy undercooled at 20 K

4 Discussion

4.1 Eutectic coupled zone

When the undercooling is lower than ΔT_c, the microstructures of off-eutectic alloys consist of coarse single-phase branches and lamellar eutectics surrounding them. Obviously, the primary solid is the single phase, i.e., α-Co for hypo-eutectic alloy and β-Co_3Sn_2 for hyper-eutectic alloy. The solidification results in two temperature recalescences. In our previous work, it had already been confirmed that regular lamellar eutectic forms as the primary solid in the rapid solidification of Co−24%Sn eutectic alloy is in the whole undercooling range investigated (0−203 K) [12]. Correspondingly, only one recalescence occurs during solidification. In the solidification structures of the Co−18%Sn hypo-eutectic alloy and Co−30%Sn hyper-eutectic alloy undercooled above ΔT_c, anomalous eutectics are located at the center of the eutectic colony, and their morphologies are similar to the anomalous eutectics in the Co−24%Sn eutectic alloy. At the meantime, single recalescence rather than double recalescence occurs in the corresponding cooling curve. Thus, it is clear that the off-eutectic alloys first solidify into one of the eutectic phase when undercooling is less than ΔT_c, resulting in the first temperature recalescence. As the primary phase grows, a solute-enriched layer is established around it till the temperature falls to a relatively low value at which the other eutectic phase nucleates in the remaining liquid and subsequently growths with the first phase in a coupled way (i.e. lamellar eutectic growth), triggering the second temperature recalescence. Due to the solute enrichment around the primary phase, a halo of the other phase forms surrounding it (Figs. 6(a) and (b)). The fact that the primary phase is always surrounded by a halo of the other phase and double recalescence constantly occurs at undercooling below ΔT_c whether the alloy is hypo-eutectic or hyper-eutectic indicate that the so-called non-reciprocal nucleation phenomenon does not happen in the solidification of undercooled Co−Sn off-eutectic alloys.

At undercooling above ΔT_c, lamellar α-Co/β-Co_3Sn_2 eutectic solidifies from the undercooled melt as the primary phase. In this case, although one phase is needed to grow in the remaining liquid once coupled eutectic growth stops, fresh nucleation is unnecessary since both phases have been present. Therefore, there is only one recalescence to be observed. In the phase diagram ΔT_c constitutes the upper boundary of the eutectic coupled zone. Limited by the maximum undercooling obtained in this experiment, the lower boundary was not determined. For the alloys with Sn content less than 14% or more than 31%, coupled eutectic as the primary phase was not discovered in the experiment.

4.2 Formation of anomalous eutectic

For the Co−24%Sn eutectic alloy regular lamellar eutectic is the primary solid in the rapid solidification. When undercooling is very low, the recalescence is too weak to break the initial lamellar eutectic morphology under the action of superheating and remelting. When the undercooling exceeds 21 K, the recalescence becomes strong enough to remelt part of the primary lamellar eutectic, leading to the formation of anomalous eutectic. As undercooling increases, more and more primary lamellar eutectics solidify in the rapid solidification, and the volume fraction of anomalous eutectics enlarges gradually.

Due to complex solidification mode, the formation of anomalous eutectic in off-eutectic Co−Sn alloys is more complicated than that in the Co−24%Sn eutectic alloy. When undercooling is high enough but still lower than ΔT_c, both the primary single phase solid formed in the first recalescence and the regular lamellar eutectic formed in the second recalescence will be disintegrated into anomalous eutectics owing to superheating and remelting. When the undercooling exceeds ΔT_c, coupled eutectic growth first happens in the undercooled melt as done in the Co−24%Sn eutectic alloy. In this case, anomalous eutectics only result from the partial remelting of the primary lamellar eutectics.

5 Conclusions

1) The upper boundary of coupled growth zone of eutectic phases is determined for the Co−Sn alloys whose Sn content ranges from 14% to 31%. For the alloy in the composition range, lamellar eutectic instead of single phase primarily forms during solidification once the alloy melt is undercooled below the boundary accompanied by a single recalescence.

2) The simultaneous presence of double recalescences and halo-like structure surrounding the primary phase in the hypo-eutectic and hyper-eutectic Co−Sn alloys indicates that the so-called non-reciprocal nucleation phenomenon does not happen in the solidification.

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大体积深过冷 Co−Sn 合金的凝固过程与组织演化

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摘 要：将含 12%−32%Sn(摩尔分数)的系列 Co−Sn 合金熔体过冷至平衡液相线以下不同温度进行凝固实验，通过监测快速凝固过程中的温度再辉与凝固组织分析不同过冷度下各合金的凝固行为进行研究。确定了 Sn 含量从14%到 31%范围内 Co−Sn 合金凝固时共晶两相进行耦合生长和非耦合生长的分界线，在此成分范围之外的 Co−Sn 合金则很难被过冷至共晶共生区。在非共晶成分 Co−Sn 合金的深过冷凝固过程中不存在非互惠形核现象。

关键词：Co−Sn 合金；过冷度；再辉；共晶共生区；凝固；组织演化

(Edited by Xiang-qun LI)