Metastable Phase Separation and Concomitant Solute Redistribution of Liquid Fe-Cu-Sn Ternary Alloy *

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Liquid Fe-Cu-Sn ternary alloys with lower Sn contents are usually assumed to display a peritectic-type solidification process under equilibrium condition. Here we show that liquid $Fe_{47.5}Cu_{47.5}Sn_5$ ternary alloy exhibits a metastable immiscibility gap in the undercooling range of 51–329 K (0.19T_L). Macroscopic phase separation occurs once undercooling exceeds 196 K and causes the formation of a floating Fe-rich zone and a descending Cu-rich zone. Solute redistribution induces the depletion of Sn concentration in the Fe-rich zone and its enrichment in the Cu-rich zone. The primary Fe phase grows dendritically and its growth velocity increases with undercooling until the appearance of notable macrosegregation, but will decrease if undercooling further increases beyond 236 K. The microsegregation degrees of both solutes in Fe and Cu phases vary only slightly with undercooling.

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Liquid phase separation has aroused great research interest in the field of condensed matter and materials physics for many years,[1–9] and can occur in various systems including metallic alloys,[10–12] polymers,[13] and liquid crystals.[14] In metallic systems, although this kind of liquid-liquid phase transformation is usually characteristic of stable monotectic alloys, some peritectic alloys with large positive mixing enthalpy also display immisciblility gaps in the metastable undercooled state, such as Fe-Cu[15] and Co-Cu[16] alloys. So far, there have been extensive investigations on metastable phase separation of binary alloys.[10–12,15] In contrast, much work remains to be performed on the solidification mechanism and solute distribution of metastably separated ternary alloys.

Fe-Cu-Sn ternary alloys form a peritectic-type system. Previous research on this ternary system mainly focused on alloy thermodynamics, reporting several isothermal sections of its phase diagram.[17–19] It is highly desirable to investigate the metastable liquid phase separation of a Fe-Cu-Sn ternary peritectic alloy system. In this Letter, the substantial undercooling of $Fe_{47.5}Cu_{47.5}Sn_5$ ternary alloy is realized by the glass fluxing method, which is formed by adding 5 at%Sn into $Fe_{50}Cu_{50}$ binary alloy. The objective of this work is to explore the metastable phase separation and the solute redistribution characteristics of undercooled ternary $Fe_{47.5}Cu_{47.5}Sn_5$ alloy. In addition, the dendrite growth feature of the primary Fe phase is also studied experimentally.

$Fe_{47.5}Cu_{47.5}Sn_5$ ternary alloy was prepared from high purity Fe(99.99%), Cu(99.99%), and Sn(99.99%). When the experiment was performed, the 1 g sample was contained in an alumina crucible together with a suitable amount of fluxing agent. Under the protection of argon gas, the sample was melted by radio frequency induction heating and then overheated to 200 K above its liquidus temperature for several minutes. Afterwards, it was cooled naturally by switching off the power. Each sample experienced the heating-cooling cycle for 2 to 5 times. Its temperature was measured by a Yunan–Land NQO8/15C infrared pyrometer, while the crystal growth velocity was measured with an infrared photodiode device. The finally solidified samples were sectioned, polished and etched with 200 g CrO_3+17 ml HCl+20 g $Na_2S_2O_3$+1000 ml H_2O. The thermodynamic properties and phase constitutions were determined with a Netzsch DSC 404C differential scanning calorimeter (DSC) and a Rigaku D/max 2500 x-ray diffractometer (XRD), respectively. The solidification microstructures were analyzed by an FEI Sirion electron microscope, whereas solute distribution profiles were investigated with an INCA Energy 300 energy dispersive spectrometer (EDS).

Figure 1(a) shows the isothermal section at 1523 K of the Fe-Cu-Sn ternary alloy phase diagram.[17] The composition of $Fe_{47.5}Cu_{47.5}Sn_5$ alloy (marked as point C_0) lies in the liquid immiscibility gap. According to the isothermal section at 298 K of this ternary alloy phase diagram,[18,19] if equilibrium solidification happens, its microstructures at ambient temperature should be composed of αFe solid solution, (Cu) solid solution and Cu_3Sn intermetallic compound.

In order to determine the liquidus temperature and investigate the phase transition process of $Fe_{47.5}Cu_{47.5}Sn_5$ ternary alloy, DSC thermal analysis was carried out with a scan rate of 10 K/min. The DSC heating and cooling curves are illustrated in Fig. 2(a). The liquidus temperature T_L is obtained to be 1722 K from the heating curve. During cooling, the homogeneous alloy melt separated into two liquid phases at 1671 K: one is a Fe-rich liquid and the other is a Cu-rich liquid. This phase separation is identified by a baseline fluctuation in exothermic direction on the cooling curve. Therefore, for $Fe_{47.5}Cu_{47.5}Sn_5$ ternary alloy, the critical undercooling of liquid phase separation is 51 K, which is larger

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than the 28 K value of binary $Fe_{50}Cu_{50}$ alloy.[15] This indicates that the introduction of the Sn element has raised the critical undercooling for metastable phase separation. With the decrease of temperature, the Fe-rich liquid phase begins to crystallize at 1611 K, and the corresponding exothermal peak is very sharp. In the subsequent cooling process, there exist four phase transitions, which are $\gamma Fe \rightarrow \alpha Fe$ at 1201 K, $L + \gamma Fe \rightarrow (Cu)$ at 1068 K, $L + (Cu) \rightarrow Cu_{5.6}Sn$ at 1013 K, and $Cu_{5.6}Sn \rightarrow (Cu) + Cu_{41}Sn_{11}$ at 778 K.

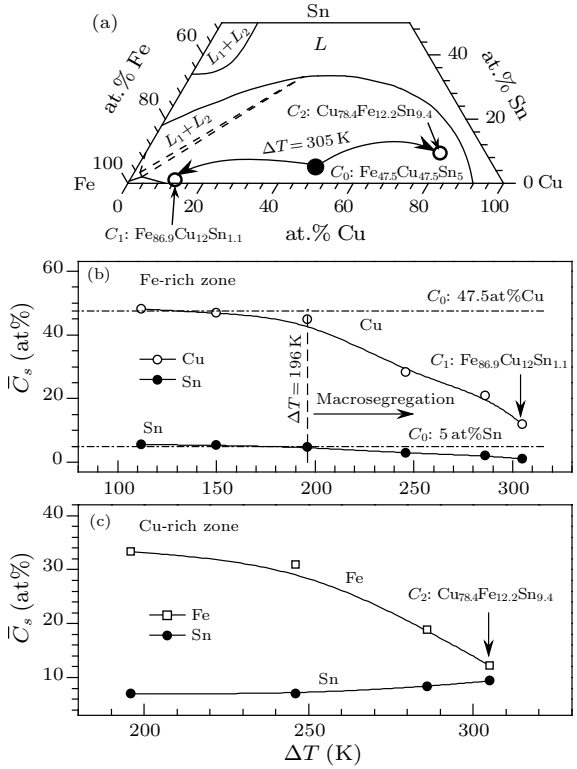


Fig. 1. Selection of alloy composition and EDS analyses of phase separated zones: (a) $Fe_{47.5}Cu_{47.5}Sn_5$ ternary alloy located on the isothermal section at 1523 K of the Fe-Cu-Sn ternary alloy phase diagram,[17] (b) average composition of the Fe-rich zone versus undercooling, and (c) average composition of the Cu-rich zone versus undercooling.

The bulk undercooling is defined as the temperature difference between the liquidus temperature and the nucleation temperature of primary solid phase. By this definition, the maximum undercooling achieved in this work was 329 K($0.19T_L$). XRD analysis was performed to verify the phase constitution of $Fe_{47.5}Cu_{47.5}Sn_5$ ternary alloy, and the results are shown in Fig. 2(b). The samples of different undercooling levels were composed of αFe solid solution, (Cu) solid solution and $Cu_{5.6}Sn$ intermetallic compound, which differs slightly from the equilibrium phase constitution.

According to the microstructural observation, liquid phase separation occurred in all the samples undercooled by more than 51 K and the extent of phase separation is strongly dependent on the undercooling level. If a sample is undercooled by less than 196 K, liquid phase separation takes place only in a microscopic scale and the solidification microstructure is characterized by coarse and well-developed αFe dendrites with interdendritic Cu-rich phase. For instance, Fig. 2(c) presents the sample morphology without the occurrence of macrosegregation, which corresponds to a moderate undercooling of 112 K. Once alloy undercooling exceeds 196 K, conspicuous phase separation has taken place and caused the formation of two segregated zones, where the Cu-rich zone only occupies about 7% of the sample volume. When undercooling increases to 305 K, the Fe-rich zone floats up to the sample top completely, while the Cu-rich zone with a volume fraction of 47% settles down, as seen in Fig. 2(d).

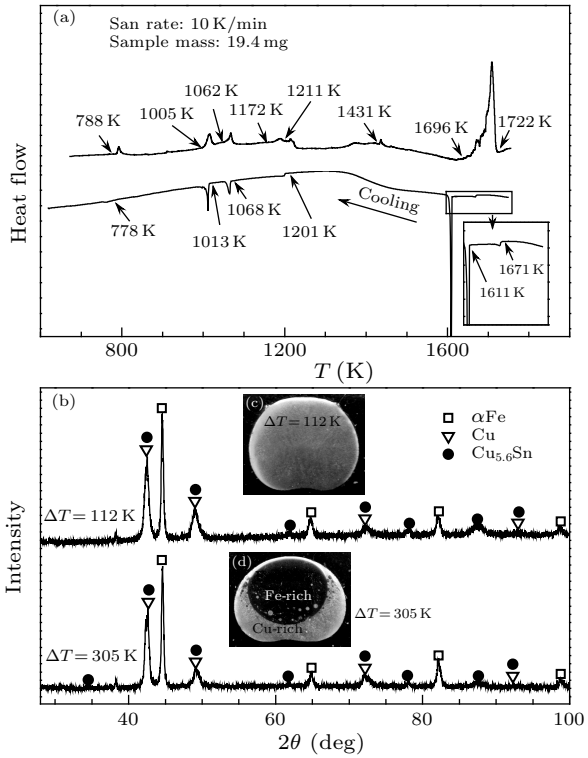


Fig. 2. Thermal analysis and x-ray diffraction of ternary $Fe_{47.5}Cu_{47.5}Sn_5$ alloy: (a) DSC thermogram, (b) XRD patterns, (c) sample morphology at 112 K undercooling, and (d) sample morphology at 305 K undercooling.

In fact, after the phase separation of homogeneous Fe-Cu-Sn ternary alloy melt at 1671 K, the compositions of two separated liquids would tend to follow the boundary of immiscibility gap continuously until rapid solidification of Fe-rich liquid occurs. In order to explore the concomitant solute redistribution characteristics, the average compositions of the Fe-rich and Cu-rich zones were measured by using the EDS method, and the average solute concentrations of macrosegregated zones at various undercoolings are shown in Figs. 1(b) and 1(c). In the undercooling range of 112–196 K, only slight microscopic liquid phase separation takes place. In this case, the average Cu and Sn contents are close to their initial compositions, maintaining only a weakly declining value of 48–44.8 at%Cu

and 5.1–4.8 at%Sn, respectively, as seen in Fig. 1(b). With the continuous increase of bulk undercooling, the average Cu content of the Fe-rich zone reduces dramatically from 44.8 to 12.1 at%Cu, and the corresponding Sn content shows a similar variation tendency of 4.8–1.1 at%Sn. For the Cu-rich zone, the average Fe content decreases from 46.9 to 12.2 at%Fe with the increase of undercooling from 196 to 305 K, while the solute Sn content increases from 5.1 to 9.4 at%Sn. The EDS analysis results indicate that the solutes Cu and Sn are rejected from the Fe-rich liquid zone, whereas the solute Fe is rejected from the Cu-rich liquid zone with the increase of undercooling. In addition, the macroscopic solute redistribution induces the depletion of Sn concentration in the Fe-rich zone and its enrichment in the Cu-rich zone. As illustrated in Fig. 1(a), at the bulk undercooling of 305 K, $Fe_{47.5}Cu_{47.5}Sn_5$ alloy is separated into a Fe-rich zone with the average composition of $Fe_{86.9}Cu_{12}Sn_{1.1}$ (marked as point C_1) and a Cu-rich zone with the average composition of $Cu_{78.4}Fe_{12.2}Sn_{9.4}$ (marked as point C_2). Therefore, the solidification process of undercooled $Fe_{47.5}Cu_{47.5}Sn_5$ ternary alloy involves two stages: the prior solidification of the Fe-rich zone and the subsequent solidification of the Cu-rich zone.

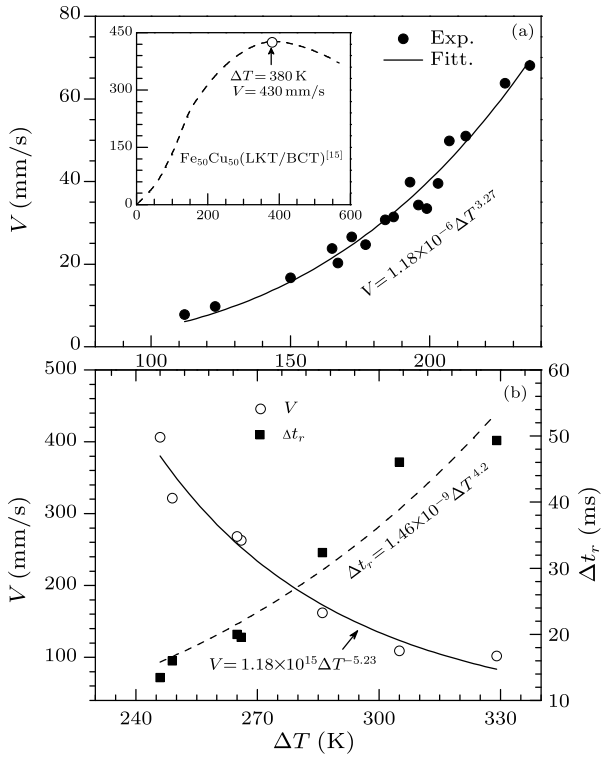


Fig. 3. Dendrite growth velocity of primary Fe phase versus undercooling: (a) dendritic growth without notable macrosegregation, and (b) dendritic growth after remarkable macrosegregation.

The growth velocity of the primary Fe phase was measured to reveal the dendrite growth characteristics of $Fe_{47.5}Cu_{47.5}Sn_5$ ternary alloy, and the result is illustrated in Fig. 3. It can be seen that the dendrite growth velocity does not increase monotonically with undercooling. Within the smaller undercooling range of 112–236 K, because microscopic phase separation cannot produce notable macrosegregation, primary Fe phase grows dendritically without interruption and its growth velocity increases with undercooling. As shown in Fig. 3(a), dendrite growth velocity V increases from 7.8 to 68.3 mm/s with the increase of undercooling ΔT, and their relationship satisfies the following power law:

$$V = 1.18 \times 10^{-6} \Delta T^{3.27}. \quad (1)$$

In comparison, the calculated dendrite growth velocity on the basis of the LKT/BCT dendritic growth model in binary $Fe_{50}Cu_{50}$ alloy[15] is also presented at the top left corner of Fig. 3(a). At the same undercooling level, the growth velocity of primary Fe dendrite in ternary $Fe_{47.5}Cu_{47.5}Sn_5$ alloy is much smaller than that in binary $Fe_{50}Cu_{50}$ alloy. This indicates that the introduction of the Sn element has reduced the dendrite growth velocity of primary Fe phase.

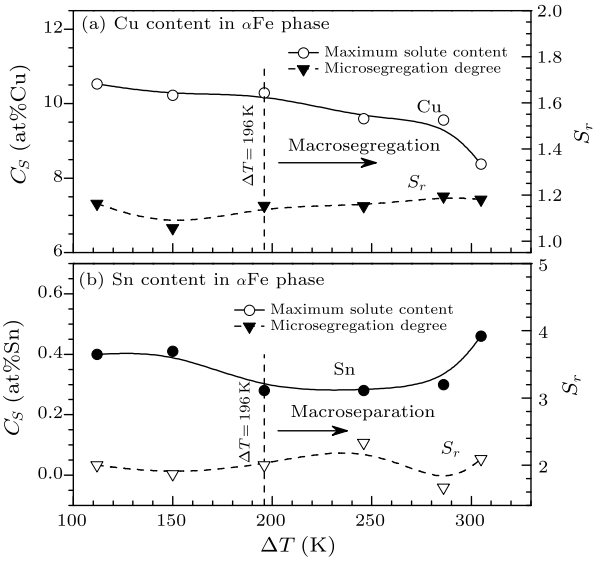


Fig. 4. Maximum solute content and microsegregation degree of αFe phase in the Fe-rich zone: (a) solute Cu, and (b) solute Sn.

However, if the undercooling further increases beyond 236 K, the dendrite growth kinetics of primary Fe phase in the Fe-rich zone changes drastically due to remarkable macrosegregation, as shown in Fig. 3(b). The nominal growth velocity V decreases and the recalescence time Δt_r increases with the rise of undercooling ΔT, which are caused by the interruption of Cu-rich droplets during phase separation and the reduced atomic diffusion speed. The decreasing tendency of dendritic growth velocity is expressed according to the function:

$$V = 1.18 \times 10^{15} \Delta T^{-5.23}. \quad (2)$$

Nevertheless, the absolute value of dendrite growth velocity within the high undercooling regime beyond 236 K increases by roughly an order of magnitude, as

compared with that within the smaller undercooling range. This is because the dendrite growth in concentrated liquid alloys is mainly controlled by solute diffusion and consequently a more dilute alloy melt facilitates a more rapid dendritic growth process. With the proceeding of macrosegregation, the composition of the Fe-rich zone is diluted from point C_0 into point C_1, as illustrated in Fig. 1, which results in the enhancement of dendritic growth velocity accordingly.

The actual solute distributions of αFe phase in the Fe-rich zone and (Cu) phase in the Cu-rich zone were measured and the results are shown in Figs. 4 and 5. Although a significant solute trapping effect may have occurred to the primary Fe phase during its dendritic growth, the coupled influences of retrograde solubility and phase separation make its solute redistribution become a very complicated kinetic process. As seen in Fig. 4(a), the maximum solubility of Cu in the αFe phase decreases from 10.53 to 8.38 at%Cu within the undercooling range of 112–305 K. For the solute content of Fe in the (Cu) phase, a similar declining tendency from 5.82 to 3.44 at%Fe is shown in Fig. 5(a). It should be noticed that the initial solute contents of the primary Fe phase and (Cu) phase may be significantly different from those detected inside ambient temperature microstructures, because some solid state transformations have proceeded to a certain extent.

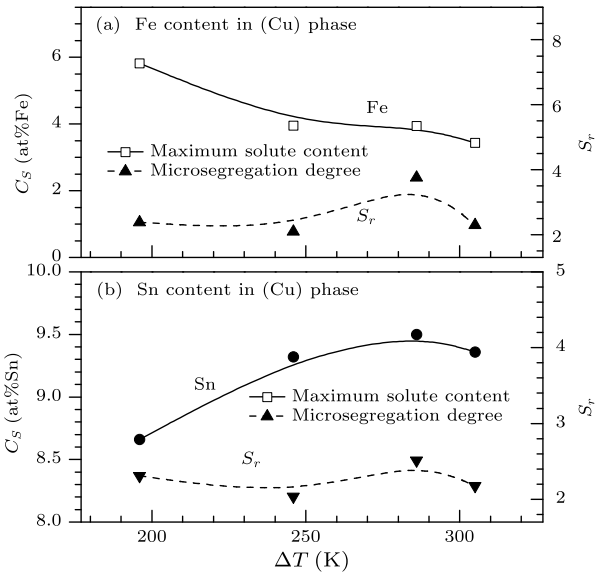


Fig. 5. Maximum solute content and microsegregation degree of (Cu) phase in the Cu-rich zone: (a) solute Fe, and (b) solute Sn.

The Sn content in the (Cu) phase is much larger than that in the αFe phase, suggesting that the (Cu) phase has a stronger affinity for the solute Sn, as shown in Figs. 4(b) and 5(b). In the αFe phase, the maximum content of Sn exhibits a negligible rise from 0.28 to 0.46 at%Sn in the experimentally achieved undercooling range, which is far smaller than the initial concentration of 5 at%Sn. In the (Cu) phase, the maximum content of Sn shows an increasing tendency with the increase of undercooling and exceeds the initial concentration of the Sn element even at the moderate undercooling of 196 K. When undercooling increases to 305 K, the solubility of Sn rises to 9.36 at%Sn, which is beyond the maximum equilibrium solubility of 9.1 at%Sn. It is apparent that the solubility of Sn in the (Cu) phase is effectively extended under high undercooling conditions.

The microsegregation degree S_r is defined as the ratio of the maximum solute content $C_{\max}$ to the minimum solute content $C_{\min}$,[20] and the corresponding solute segregation degree is also presented in Figs. 4 and 5. In the αFe phase, the solute distribution of Cu is relatively uniform, and the solute segregation degrees of Cu and Sn display rather small variation ranges in the vicinity of 1.15 and 1.99, respectively. As compared with those in the αFe phase, the solute segregation degrees in the (Cu) phase are relatively larger. In the undercooling range of 196–305 K, the solute segregation degrees of Fe and Sn maintain the average values of 2.63 and 2.26 with only little fluctuations.

In summary, metastable phase separation has been observed for liquid $Fe_{47.5}Cu_{47.5}Sn_5$ ternary alloy in the undercooling range of 51–329 K($0.19T_L$). Within the smaller undercooling regime below 196 K, liquid phase separation took place only in the microscopic scale and shows little influence on the dendritic growth of the primary Fe phase. A macrosegregation pattern consisting of an upper Fe-rich zone and a lower Cu-rich zone is formed by macroscopic phase separation once undercooling exceeds the critical value of about 196 K, which leads to a drastic change of the dendritic growth kinetics of the primary Fe phase. The macroscopic solute redistribution brings about the depletion of Sn concentration in the Fe-rich zone and the corresponding enrichment in the Cu-rich zone. On the other hand, the microsegregation degrees of both solutes in the Fe and Cu phases demonstrate only slight variations with undercooling because of the complex coupled effects of retrograde solubility, phase separation and solute trapping.

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