Solidification microstructure evolution and its corresponding mechanism of metastable immiscible Cu₈₀Fe₂₀ alloy with different cooling conditions

Shichao Liu, Jinchuan Jie*, Zhongkai Guo, Guomao Yin, Tongmin Wang, Tingju Li

Key Laboratory of Solidification Control and Digital Preparation Technology (Liaoning Province), School of Material Science and Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China

1. Introduction

Immiscible alloys characterized with a miscibility gap in the liquid state exhibit an obvious liquid-liquid phase separation during solidification [1,2]. Namely, if a homogeneous liquid enters the miscibility gap, it will inevitably decompose into two liquids that are generally immiscible with each other. Thus these alloys show serious phase separation and segregation during ordinary solidification, even under microgravity or gravity-free condition. Among them, Cu-Fe is a typical peritectic immiscible system possessing a nearly flat liquidus line and a retrograde solidus line; therefore it exhibits a metastable miscibility gap in the liquid state. In addition, Cu-Fe alloys have a good combination of high electrical conductivity and good mechanical strength, and can be used as materials for magnetic recording, optical devices, electrical contact materials, and sensors [3–8]. Compared with other similar FCC-BCC type alloys such as Cu-Nb [9–11] Cu-Ag [12–14], etc., Fe is a common and cheap metal, widely used in daily life and industry, and is abundant on earth. The application of Cu-Fe alloy has, nevertheless, been limited because, generally, serious segregation of components and phase separation take place during conventional solidification. Thus extensive investigations have been conducted on the metastable immiscible Cu-Fe alloy in order to address the grand challenge in recent years.

Understanding the solidification characteristics, especially the degree of undercooling, is crucial to control the solidification process and obtain an anticipated solidification microstructure, especially for the binary Cu-Fe system. Nakagawa et al. [15] for the first time confirmed the existence of liquid–liquid separation in an undercooled binary Cu-Fe alloy system, where the authors measured the change of magnetic susceptibility as a function of demixing and examined the microstructure of quenched specimens. Ever since then, many studies have been carried out to gain insight into the solidification behavior, microstructure evolution, minority phase motion, and size distribution of the undercooled Cu-Fe alloy and significant progress has been made [16–25]. However, the previous extensive efforts mainly focused on the undercooled state of the alloy via the high-pressure gas...
atomization [16–21] or cyclical superheating [22–26] techniques. Both such above-mentioned strategies are aimed at achieving undercooling of the entire sample. In fact, the entire undercooling of the alloy can barely take place in practical solidification processes. Instead, the constitutional undercooling phenomenon can easily occur during solidification, which has great influence on the resultant solidification microstructure and properties. We shall see that, based both on experiment and theory, very few studies have been performed to study the effect of constitutional undercooling on the microstructure evolution of Cu-Fe alloy during solidification. It is, therefore, of great interest to fundamentally understand its effect on microstructure evolution. However, it is worth pointing out that the constitutional undercooling is complex and dominated by many factors, among which the cooling condition and the corresponding crystal growth play important roles [27]. Thus, a strong interest in the systematic examination of the effects of cooling condition on microstructure evolution has developed to clarify the effect of constitutional undercooling on metastable immiscible Cu-Fe alloy.

In this work, microstructure evolution in the metastable immiscible Cu80Fe20 alloy under different cooling conditions was studied using different molds. Then the microstructure was characterized with an optical microscope and scanning electron microscope. The corresponding microstructure evolution mechanisms in terms of constitutional undercooling, as well as the segregation and immiscibility behavior of alloy, were analyzed.

2. Experimental

2.1. Preparation of the Cu80Fe20 alloy

The experimental Cu80Fe20 alloy was prepared from pure Cu (99.95 wt%) and Fe (99.99 wt%). The Cu80Fe20 alloy was pre-alloyed in an arc-melting furnace, evacuating and purging the chamber several times with high purity Ar. To guarantee the homogenization of the alloy, samples were repeatedly melted several times. Then the alloys were remelted by induction melting in a ceramic crucible and poured into different prepared molds.

2.2. Solidification at different cooling rates

To obtain different cooling rates, two kinds of self-designed molds were used in the present experiment. After induction melting and holding for 10 min, the alloy was cast into the two molds at 1873 K (schematic illustration of the used molds is shown in Fig. 1). The experimental details are as follows: (a) the melting alloy was cast into a graphite mold with a length of 105 mm, an upper inner diameter of 16 mm, and a bottom inner diameter of 13 mm. According to measurements, the cooling rate of an experimental graphite mold is about 50–100 K/s; (b) the melt was quickly poured into the copper plate mold and simultaneously another copper plate without the rectangular groove immediately covered it. Eventually three different cooling rates were obtained by means of different depths of a rectangular groove in copper molds, i.e., 1.5 mm, 2 mm, and 3 mm. For this condition, the cooling rate $T$ was calculated using an empirical equation as follows [28]:

$$T = KZ^n$$  \hspace{1cm} (1)

where $K$ and $n$ are constants dependent on the material and the geometry of the mold, $Z$ is the depth of the mold (in mm). In our experiment, the parameters are estimated: $K = 715$ and $n = -0.619$. Although practically, there are differences in the cooling rate at different positions of the same sample, according to Eq. (1), the cooling rates $T$ are about 362 K/s, 465 K/s, and 556 K/s in the copper plate molds with depths of 1.5, 2, and 3 mm, respectively.

2.3. Microstructures and phase identification

To investigate the solidification behavior of metastable immiscible Cu80Fe20 alloy at different cooling rates, the as-obtained samples were polished and etched by a solution consisting of 95 ml C2H5OH + 5 ml HCl + 5 g FeCl3 for morphology observation and phase composition analysis. Microstructures were observed using an Olympus GX51 optical microscope and a scanning electron microscope (SEM, Zeiss supra 55) equipped with an energy dispersive spectrometer (EDS) operated in secondary electron mode and with an accelerating voltage of 15 kV. The chemical compositions of Fe-rich phase and the Cu-rich matrix were reproducibly analyzed by EDS.

3. Results

3.1. Microstructure of Cu80Fe20 alloy solidified in graphite mold

Fig. 2a shows the microstructure of Cu80Fe20 alloy solidified in the graphite mold. The dark region in the image corresponds to the Fe-rich phase, and the bright region corresponds to the Cu matrix. In addition, the Fe-rich phase reveals two different morphologies, i.e., the dendritic Fe-rich phase, which uniformly and arbitrarily distributes in the copper matrix (shown in Fig. 2b) and apparently results from the normal liquid-solid phase transformation [21,24]; and the approximately spheroidal Fe-rich phase (afterwards denoted as Fe-rich spherulites), which is the typical characteristic shape of the separated minority phase often observed in the immiscible alloys. Most of the Fe-rich spherulites distribute and segregate together in certain areas in a range of about 300–500 μm (as shown by the dotted frame in Fig. 2a), while a minority of the Fe-rich spherulites are entrapped in the interdendritic region of about 10–20 μm (shown in Fig. 2c). Fig. 2d shows the phase composition of selected spherulites measured by EDS. In order to reduce the error of the data, the measurements were carried out only on spherulites larger than 5 μm. The result shows that the composition of Fe-rich spherulites is Fe70.92Cu29.08, further indicating that the Fe-rich spherulites are the result of liquid-liquid phase separation of Cu80Fe20 alloy.

Fig. 3 shows the magnified SEM image of the region circled by the dashed frame in Fig. 2a. It can be seen that some of the Fe-rich spherulites connect with each other (Fig. 3a), which indicates a tendency of collision and coalescence of the Fe-rich phase after liquid-liquid separation. Fig. 3b illustrates the substructure of the Fe-rich spherulites. Especially notable, many white nano-sized Cu-rich dots are dispersed in the core region of Fe-rich spherulites, which can be ascribed to the occurrence of a second liquid-liquid phase separation. Meanwhile, the Fe-rich rims are also found in the periphery of Fe-rich spherulites. As temperature decreases, the high Cu concentration of phase-separated Fe-rich spherulites needs to decrease in order to maintain the balance with the matrix. There are two mechanisms for this. One is by a second liquid-liquid phase separation in an “in situ” process, eventually forming the dispersed nano-sized Cu-rich dots. Another mechanism is the ejection of excess Cu atoms to the matrix. The two mechanisms are suggested by the substructures of Fe-rich spherulites. As seen in Fig. 3b, the Fe-rich rims of the substructure correspond to the ejection of the supersaturated Cu atom, whereas the dispersed nano-sized Cu-rich dots in the core relate to a second liquid-liquid phase separation.
Al-Bi, Cu-Co-Ni, and Cu-Co alloys [29,30]. It has been recognized that the first peak is governed by the diffusive growth, while the second peak is related to the collision and coagulation of the phase-separated spherulites under the action of various types of mechanisms such as forced convection, Brownian motion, Ostwald ripening phenomenon etc. [16,20,23]. However, the size distribution in the interdendritic region shows a unimodal distribution and fits well with the normal distribution, indicating the collision and coagulation processes of the region are greatly suppressed during solidification.

3.2. Microstructure of Cu80Fe20 alloy solidified in copper plate molds

Fig. 5 shows the microstructures of Cu80Fe20 alloy solidified in the copper plate molds with different thicknesses. Apparently the cooling condition in all samples changes remarkably, since Fig. 5 taken from the vertical-section shows a clear microstructure transition. All samples have microstructures of similar morphology, exhibiting a dispersion of cellular and developed Fe-rich dendrites in a Cu-rich matrix. The cellular Fe-rich dendrites, with
homogeneous size, distribute at the edge of the samples that possess a higher cooling rate, while the developed Fe-rich dendrites, similar to that observed in graphite mold as shown in Fig. 2b, have a well-defined dendritic array and distribute at the center of samples. A quantitative analysis reveals that there are differences in size and corresponding occupied region of Fe-rich dendrites between the three samples. Fig. 5a presents the microstructure of the obtained 1.5 mm sample. The region occupied by cellular dendrites takes up about 69 vol% of the sample, with size ranging from 500 nm to 1 mm (Fig. 5b). When the thickness increases to 2 mm (Fig. 5d), the region occupied by cellular Fe-rich dendrites decreases to 41 vol%, where the size of the cellular Fe-rich dendrite phase is about 1e3 mm larger than that of 1.5 mm sample. However, with further increase of thickness up to 3 mm (Fig. 5g), only small regions at the edge of the mold present the cellular Fe-rich dendrites and their size barely changes. The corresponding distribution area of the cellular Fe-rich dendrites dramatically decreases, only accounting for about 7 vol%. In general, the results show that the overall changing trend of microstructure evolution in all as-quenched samples is that the morphology of the Fe-rich particles remarkably changes from cellular (Fig. 5b, e and h) to developed dendrites (Fig. 5c, f and i) along the vertical direction with decreasing cooling rate.

It is noted that a gradient of cooling rates exists due to the shape of the mold. Thus melt quenching of the same Cu_{80}Fe_{20} alloy exhibits the varied microstructures. Among them, ScC(0) is the long wavelength limit (q→0) of the composition—composition structure factors ScC(q), which is usually known as concentration fluctuations and very useful for ascertaining the immiscibility and the degree of segregation, and understanding the mixing behavior in binary liquid alloys. In addition, it can be directly obtained either from the thermodynamic functions or from the small-angle scattering experiments, and can be expressed as follows [32]:

Above all, the solidification microstructure evolution of metastable immiscible Cu_{80}Fe_{20} alloy with different cooling rates is summarized in Table 1 and Fig. 6. When the cooling rate is 50–100 K/s, primarily the liquid-solid transformation takes place, and the liquid-liquid phase separation only exists in a small region or in the interdendritic region of about several tens to hundreds microns. With further increase of the cooling rate (350–560 K/s), only liquid-solid transformation takes place. It has been demonstrated that for a given alloy the solidification microstructure strongly depends on the cooling rate. Thus the change of cooling rate will result in a different solidification behavior. Due to the existence of the cooling rate gradient of the molds, the as-quenched samples exhibit varied microstructures and a clear Fe-rich morphology transition. The change in morphology of the Fe-rich phase might be attributed to the stability of the solid–liquid interface.

4. Discussion

4.1. Segregation and immiscibility behavior of Cu_{80}Fe_{20} alloy

Empirical criteria as well as microscopic parameters either based on the structural data or on the available thermodynamic function and thermophysical data can be used to identify segregated alloys [31]. Among them, ScC(0) is the long wavelength limit (q→0) of the composition—composition structure factors ScC(q), which is usually known as concentration fluctuations and very useful for ascertaining the immiscibility and the degree of segregation, and understanding the mixing behavior in binary liquid alloys. In addition, it can be directly obtained either from the thermodynamic functions or from the small-angle scattering experiments, and can be expressed as follows [32]:

Fig. 3. (a) SEM image of the Fe-rich spherulites that underwent liquid-liquid phase separation in Cu_{80}Fe_{20} alloy solidified in a graphite mold, (b) enlarged image of (a).

Fig. 4. Distribution of the radius of Fe-rich spherulites for Cu_{80}Fe_{20} samples solidified in the graphite mold; (a) measured from the small regions with a range of about 300–500 μm, (b) measured from the interdendritic regions.
and (f) are enlarged images of (d), (g) 3 mm, (h) and (i) are enlarged images of (g).

Copper plate molds; (a) 1.5 mm, (b) and (c) are enlarged images of (a), (d) 2 mm, (e)

Microstructures of obtained Cu₈₀Fe₂₀ alloy with different thickness solidi

\[ S_{cc}(0) = \frac{RT}{\alpha^2 \Delta G_M} \left( \frac{\partial \Delta G_M}{\partial c^2} \right)^{-1} = c_A \hat{\sigma}_A \left( \frac{\partial \sigma_A}{\partial c_A} \right)^{-1} = c_B \hat{\sigma}_B \left( \frac{\partial \sigma_B}{\partial c_B} \right)^{-1} \]

where \( R \) is the ideal gas constant, \( c_A \) and \( c_B \) are the molar fractions of the components A and B, and \( \hat{\sigma}_A \) and \( \hat{\sigma}_B \) are the activities of components A and B, respectively. It is pointed out that \( (\hat{\sigma} \Delta G_M/\hat{\sigma}^2) \) is also known as the stability function for the solution.

It is clear that according to Eq. (2) \( S_{cc}(0) \) can be calculated directly from the activity data or from the Gibbs energy of mixing. For an ideal mixing alloy, \( S_{ccid}(0) = c_A c_B, \Delta S_{cc}(0) = S_{cc}(0) - S_{ccid}(0) \) is the deviation of \( S_{cc}(0) \) from \( S_{ccid}(0) \); thus the correlation between thermodynamic properties and structure of the liquid alloy is established through this relationship. The deviation of \( S_{cc}(0) \) from the ideal value \( S_{ccid}(0) \) is an important factor in order to visualize the nature of atomic interactions in the mixture. If, at a given composition \( \Delta S_{cc}(0) > 0 \), which means like-atom pairs are energetically preferred as nearest neighbor (homo-coordination), then there is a tendency for segregation and demixing. Vice versa for \( \Delta S_{cc}(0) < 0 \), which means that unlike-atom pairs are energetically preferred as nearest neighbor (hetero-coordination), and the alloy liquid then exhibits a homogeneous state [33,34].

The calculated \( \Delta S_{cc}(0) \) of liquid binary Cu-Fe alloy at different temperatures are depicted in Fig. 7. The prominent feature is that the alloy exhibits a positive \( \Delta S_{cc}(0) \) value over the whole Fe concentration, and \( \Delta S_{cc}(0) \) increases sharply with the decrease in temperature as it approaches the critical concentration point. Thus according to the calculated \( \Delta S_{cc}(0) \), the binary Cu–Fe system belongs to the homo-coordination type and exhibits a phase separation tendency, which agrees well with previous molecular dynamics simulations [35,36]. Meanwhile, for a given composition, the degree of the segregation and immiscibility behavior becomes more pronounced with the decrease in temperature.

4.2. Constitutional undercooling driven liquid-liquid phase separation during solidification

The currently accepted phase diagram of the Cu-Fe system including the metastable miscibility gap is shown in Fig. 8 [37,38]. Due to the existence of the miscibility gap, the liquid–liquid phase separation can take place during solidification of Cu-Fe alloys. In this paper, the interval between liquidus and the metastable liquid gap is defined as the critical undercooling \( \Delta T_C \). If the actual undercooling of liquid alloy \( \Delta T \) is less than \( \Delta T_C \), the solidification of the alloy occurs above the miscibility gap boundary, and then the liquid–solid transformation occurs; otherwise, the liquid–liquid phase separation takes place, i.e., \( Z \rightarrow L_1(\text{Fe-rich}) + L_2(\text{Cu-rich}) \).

For samples solidified in a graphite mold, it is noteworthy that the cooling rate is about 50–100 K/s, which is impossible that the liquid alloy can achieve an actual entire undercooling larger than \( \Delta T_C \) (about 50 K for Cu₈₀Fe₂₀) [21]. In fact, although the actual entire undercooling of the sample is not sufficient to result in the liquid–liquid phase separation, it indeed comes into being either in a small region or in the interdendritic region in our experiment. Previous studies suggested that the occurrence of liquid-liquid phase separation is prior to that of the liquid-solid transformation for undercooled Cu-Fe alloy. In addition, it is also found that liquid-liquid phase separation is an asynchronous solidification behavior and randomly takes place in the entire sample [23,26]. However, instead of being randomly distributed in the entire sample, the

<table>
<thead>
<tr>
<th>Mold type</th>
<th>Cooling rate</th>
<th>Microstructure type</th>
<th>Transformation type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>50–100 K/s</td>
<td>Fe-rich sphericity</td>
<td>liquid-liquid, liquid-solid</td>
</tr>
<tr>
<td>Copper plate</td>
<td>350 K–560 K/s</td>
<td>Fe-rich dendrites</td>
<td>liquid-solid</td>
</tr>
</tbody>
</table>

Fig. 5. Microstructures of obtained Cu₈₀Fe₂₀ alloy with different thickness solidified in copper plate molds; (a) 1.5 mm, (b) and (c) are enlarged images of (a), (d) 2 mm, (e) and (f) are enlarged images of (d), (g) 3 mm, (h) and (i) are enlarged images of (g).
liquid-liquid phase separation in the present study only takes place within a small region of about 300–500 μm or the interdendritic region of 10–20 μm. Furthermore, those corresponding regions are mainly located away from the surface of the sample. As we know, the degree of undercooling greatly influences the resultant solidification microstructure of the alloy. The occurrence of liquid-liquid phase separation in a small region or the interdendritic region can be elucidated by the undercooled zone obtained ahead of the solid-liquid interface during solidification. It can be concluded that the occurrence of the liquid-solid transformation is prior to that of liquid-liquid phase separation in our study, which is different from those observed in previous studies.

Following onset of the liquid-solid transformation, the γ-Fe dendrite solidifies as the leading phase according to the equilibrium phase diagram. During the growth of γ-Fe dendrite, the total undercooling \( \Delta T \) of the melt ahead of solid-liquid interface is given by the sum of thermal undercooling \( \Delta T_T \), constitutional undercooling \( \Delta T_C \), curvature undercooling \( \Delta T_K \), and kinetic undercooling \( \Delta T_K \):

\[
\Delta T = \Delta T_S + \Delta T_R + \Delta T_T + \Delta T_K
\]

(3)

Constitutional undercooling is due to compositional changes in the liquid at interfaces, and results in the liquid temperature change ahead of the solid-liquid interface, which is given by:

\[
\Delta T_S = m_L C_0 \frac{(1 - k_0)\nu_{v0}(P_{EC})}{1 - (1 - k_0)\nu_{v0}(P_{EC})}
\]

(4)

where \( m_L \) is the liquidus slope given by the phase diagram, \( C_0 \) is the initial alloy concentration, \( k_0 \) is the actual solute partition coefficient, \( \nu_{v0}(P_{EC}) \) is the Ivantsov function of solute Peclet number and given by:

\[
\nu_{v0}(P_{EC}) = \frac{C^*_t - C_0}{C_t(1 - k_0)}
\]

(5)

where \( C^*_t \) is the concentration of the dendrite tips.

Curvature undercooling \( \Delta T_K \), which represents the effect of the solid-liquid interface curvature on the equilibrium temperature (decrease in melting point), is expressed as:

\[
\Delta T_K = \frac{2\gamma_{SL}}{r}
\]

(6)

where \( r \) is the dendrite tip radius, and \( \gamma_{SL} \) is the Gibbs–Thomson coefficient. \( \Delta T_K \) is estimated to be about 0.2 K. It should be noted that \( \Delta T_K \) plays a negative effect on the total undercooling of the solid-liquid interface.

Kinetic undercooling \( \Delta T_K \), which provides the driving force for the atoms at the interface to transform from liquid into solid, is expressed as follows:
\[ \Delta T_T = \frac{V}{\mu} \]

where \( \mu \) is the kinetic coefficient of the \( \gamma \)-Fe phase and \( V \) is the growth speed of the crystal. Kinetic undercooling is generally negligible in comparison with the other contributions in most metals where the kinetic coefficients are greater than \( 1 \text{ m/s K} \).

Thermal undercooling \( \Delta T_T \) occurs in bulk undercooled melt where the released latent heat of fusion is dissipated into the undercooled liquid. As the thermal diffusivity in both liquid and solid is typically four orders of magnitude larger than the solute diffusion in the liquid, \( \Delta T_T \) can also be neglected. Therefore, constitutional undercooling \( \Delta T_C \) plays a dominant role in the total undercooling ahead of the solid–liquid interface.

Assuming that the solidification process is near-equilibrium, \( k_0 \) is taken from Ref. [25]. According to above Eqs. (4) and (5), \( \Delta T_C \) of the undercooled zone can be estimated at about 42.6 K, and mainly determines the total undercooling of the solid–liquid interface. On the other hand, as shown in Fig. 8, \( \Delta T_T \) is decreased with increase of Fe concentration on the Cu-rich side. Thus, although the calculated constitutional undercooling is less than the \( \Delta T_C \) of Cu_{90}Fe_{20}, the enrichment of Fe in the local region would result in the decrease of \( \Delta T_C \), which can be less than 50 K. In addition, it is worth mentioning that the segregation and immiscibility behavior of Cu-Fe alloy becomes more pronounced with the decrease of temperature (see Fig. 7), which may also enhance the constitutional undercooling ahead of the solid–liquid interface and result in the decrease of \( \Delta T_C \). As a result, the constitutional undercooling can be high enough to trigger the liquid–liquid phase separation of the local region. This can properly account for the occurrence of liquid–liquid phase separation within a small region or the interdendritic region for samples solidified in a graphite mold. It should be noted that both the Marangoni migration and the Stokes motion are greatly inhibited after the liquid–liquid phase separation, because the temperature gradient and density difference of where the liquid–liquid phase separation occurs can be neglected.

For the case of solidification in the copper plate molds, only Fe-rich dendrites exist and no evidence of phase separated microstructure is observed. It is indicated that only liquid–solid transformation takes place. There is a growing awareness of the role of undercooling in rapid solidification processing. Usually at cooling rates exceeding \( 10^4 \text{ K/s} \), the melt may be undercooled prior to nucleation [39]. Although the cooling rate is not high enough to obtain large undercooling of the entire sample, it is still higher than that of the graphite mold and so is the corresponding growing velocity. The velocity dependence of the actual solute partition coefficient \( K_\text{s} \) developed by Aziz is given by Ref. [40]:

\[ K_\text{s} = \frac{K_\text{e} + V \alpha_0/D_1}{1 + V \alpha_0/D_1} \]

where \( \alpha_0 \) is the interatomic spacing. If the cooling rate is high enough, \( K_\text{s} \approx 1 \), namely the solutes will be trapped in the solid phase without diffusion into the liquid phase. According to calculation, the experiment solidified in the copper plate molds is associated with relatively high cooling rate of about 350–560 K/s. In such a case, it would be difficult to achieve the necessary solute diffusion because of the extremely short time for massive solidification. This will suppress the solute redistribution and improve the solid solubility. As a result, the constitutional undercooled zone ahead of the solid–liquid interface cannot be generated and only the liquid–solid transformation takes place.

The present study clarifies that the cooling rate plays a crucial role in the solidification of the metastable immiscible Cu_{90}Fe_{20} alloy. Specifically, the solidification behavior of the alloy is greatly affected by the solute redistribution and corresponding constitutional undercooling ahead of the solid–liquid interface. Therefore the solidification microstructure of the Cu-Fe alloy can be tailored by changing the cooling conditions. Moreover, the study also demonstrates that the anticipated microstructure without the phase separation for industrial application can be obtained by controlling the appropriate cooling rate. Thus the study has provided guidance in the manufacture of this kind of alloy with expected microstructure.

5. Conclusions

The metastable immiscible Cu_{90}Fe_{20} alloy solidified under different cooling rates using two kinds of molds. The independent effect of phase transformation type and microstructure evolution on the alloy was studied. It was found that the cooling rate had a pronounced effect on solidification microstructure of the alloy. For samples solidified in a graphite mold with a cooling rate of about 50–100 K/s, the liquid–solid transformation primarily takes place, and the liquid–liquid phase separation only exists in a small region or the interdendritic region of about several tens to hundreds microns. The liquid–liquid phase separation is ascribed to the large constitutional undercooling ahead of the solid–liquid interface according to the calculations and occurs behind the liquid–solid transformation. However, for the sample solidified in a copper plate mold with a greater achievable cooling rate of 350–560 K/s, there is no evidence of the occurrence of liquid–liquid phase separation. Meanwhile, due to the apparently different cooling conditions of copper plate molds, the samples show two different microstructures, namely irregular cellular and well-developed Fe-rich dendrites. In general, the morphology of the Fe-rich phase remarkably changes from developed dendrite to cellular with increase of cooling rate. Besides, due to the segregation and immiscibility behavior of the alloy in liquid state, all as-quenched samples show the existence of Cu clustering and Fe aggregation.

Acknowledgements

The authors gratefully acknowledge the support of National Natural Science Foundation of China (Nos. 51501028, 51690163, 51471042, 51525401).

References
