Solidification microstructure evolution and grain refinement mechanism under high undercooling of undercooled Ni$_{90}$Cu$_{10}$ alloys

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Abstract

The maximum undercooling of about 240 K of Ni$_{90}$Cu$_{10}$ alloys was achieved by using molten glass purification and cyclic superheating methods. The solidification structure of the undercooled Ni$_{90}$Cu$_{10}$ alloy under different undercooling was observed by optical microscope. The microstructure evolution of the undercooled Ni$_{90}$Cu$_{10}$ alloy under different undercooling was systematically studied, and the grain refinement structure was obtained under low undercooling and high undercooling, respectively. High-speed camera was used to capture the solidification changes of the solid-liquid interface, and it can be seen that the morphology of the solidification front was also different in different undercooling intervals. Moreover, with the difference of initial undercooling, the starting position of solidification nucleation point in the whole undercooled melt is also different. The driving force of recrystallization mainly comes from the deformation energy accumulated during the recalescence of undercooled melt. It was confirmed by optical microscopy and electron back scattering diffraction analysis that recrystallization under high undercooling is the main mechanism of grain refinement.

1. Introduction

Non-equilibrium phenomenon is the basic physical process in materials science [1–10]. Grain refinement plays an important role in improving the properties of microstructure [11–22]. Since Walker [23] first found grain refinement in undercooled pure Ni, the phenomenon of obtaining fine grains in undercooled metals or alloys has attracted more and more attention [11–22]. In previous studies, it was found that there were two grain refinement phenomena at low undercooling and high undercooling, respectively. So far, a generally accepted mechanism for grain refinement is dendrite remelting at low undercooling. However, the mechanism of grain refinement at high undercooling is still controversial. Many mechanisms have been proposed to explain grain refinement under high undercooling conditions, such as dendrite remelting [24, 25], recrystallization [26, 27], critical speed mechanism [28–30], and the fluid flow effects [31] etc.

Under low undercooling, it is generally believed that the first type of grain refinement of supercooled binary single-phase alloys is conducted by dendrite remelting in the later stage of recalescence. The effects of dendritic remelting include dendritic remelting fracture driven by solid/liquid interfacial tension proposed by Karma [25] and dendritic remelting fracture caused by chemical overheating proposed by Li [32]. However, under high undercooling conditions, it can be seen from the microstructure that the proportion of dendritic remelting is small, so dendrite remelting mechanism cannot explain grain refinement under high undercooling conditions. Under high undercooling conditions, the recrystallization mechanism caused by stress accumulation is widely considered to be the main cause of grain refinement [1–10]. Recrystallization was conducted by the driving of the deformation and stress, with gradually increasing of the degree of undercooling, the primary dendritic stress broken off and plastic deformation has happened due to the sharp recalescence process solid fluid volume contraction which has provides more sufficient thermodynamic driving force that has been called the plastic strain energy for the subsequent rapid solidification of solid reply and recrystallization process, the more
deformation energy stored in intracrystalline, the more driving force will be provided in the late recrystallization recrystallization process. At the same time, dendrites gradually become equiaxial crystals and get finer grain structure.

In our work, the maximum undercooling of about 240 K of Ni_{90}Cu_{10} binary single-phase alloys was obtained by means of molten glass purification and cyclic superheating methods. At the same time, the relationship between solidification front morphology and solidification structure in different undercooling is described in detail.

2. Experimental procedure

Ni_{90}Cu_{10} alloys were prepared by melting pure Ni pieces (99.99%) and pure Cu pieces (99.99%) in suit under the protection of argon atom-sphere. To ensure the uniformity of the alloy composition, the alloy was remelted at least 3 times. Approximately 4 g samples were cut from the alloy block for deep undercooling experimental. The quartz tube and the alloy sample are preliminarily cleaned in an ultrasonic cleaner that has been poured into alcohol for at least 6 min to ensure the removal of surface impurities. Then put the sample in a quartz test tube and add B_{2}O_{3}. Put the tube in high frequency induction heating, heating coils are first heated to a temperature is not higher than the temperature of the alloy melting point melted the B_{2}O_{3} and coated around the alloy, and then gradually heating temperature is higher than the melting point alloy 150 K to 200 K and insulation about 20 min, the purpose is to enable the scavenger to fully adsorb impurities in the alloy and reduce the heterogeneous nucleation point to obtain a large degree of undercooling. The melting and preparation of the whole undercooling sample was carried out under vacuum conditions, the vacuum pressure was 10^{-4} pa, and the temperature variation rule during the whole process was recorded by the infrared thermometer with reaction time of 1 ms. The recrystallization phenomenon of the rapid solidification of the alloy sample was recorded by a high-speed camera (ix camera 221). The maximum frame rate of the high-speed camera is set to 43 000 fps to achieve the best results.

The undercooled sample is cut, mounted, polished, and etched. Corrosion was performed using 50% HCl and 50% HNO_{3} configured etching solution, and then microstructure analysis of the supercooled sample was performed using an optical microscope (OM, Leica DM2500M). The samples were subjected to vibration polishing using an Al_{2}O_{3} colloidal polishing solution, and the samples were subjected to electron back scattering diffraction (EBSD) to observe grain orientation and texture.

3. Results and discussions

The maximum undercooling of about 240 K of Ni_{90}Cu_{10} alloys was achieved by using molten glass purification and cyclic superheating methods. According to the solidification structure, there are two grain refinement phenomena in the whole solidification process. One occurs in the range of small undercooling, and one occurs when the undercooling ΔT is greater than a certain critical undercooling ΔT\*.

Figure 1 shows the temperature curve of undercooled Ni_{90}Cu_{10} alloy at 240 K, and figure 2 shows the corresponding microstructure. It can be seen that the grains are very fine and have a very straight boundaries, and there are also annealed twins are presence in the grains, which is an important evidence of recrystallization.

3.1. The recrystallization process

Figure 3 shows the undercooling-recrystallization curve of the undercooled Ni_{90}Cu_{10} alloy. It can be clearly seen that with the increase of the undercooling, the recrystallization point temperature will also decrease. The time of recrystallization process will also decrease, which means that the solidification time will become shorter with the increase of undercooling, and the solidification rate of the alloy will increase. The recrystallization process is a typical exothermic stage of solid-liquid transformation, in which heat energy is converted into light, so that the solidification process can be captured by high-speed camera. Figure 4 is respectively the solidification-recrystallization image of 37 K, 105 K and 280 K. The dark areas in the picture represent undercooled melts and the bright areas represent condensed solids. It can be seen that the recrystallization process is a continuous process, and the recrystallization front moves from one side to the other side, so the solidification velocity can be quantitatively expressed according to the moving speed. The morphology of solidification front is also different under different undercooling. The solidification front is a plane with a small angle at a small undercooling. Under the condition of moderate undercooling, the characteristic of the front edge is angular front. Under higher undercooling, the solidification front is smooth plane. It can be seen from figure 4 that, under medium and small undercooling conditions, solidification nucleation always starts at the interface, which is due to the early nucleation caused by impurities in contact with the purifier. But at high undercooling conditions, nucleation starts inside the undercooled melt because the impurities have been absorbed by the purifier.
Figure 1. The cooling curve of undercooled Ni$_{90}$Cu$_{10}$ alloy at undercooling $\Delta T = 240$ K.

Figure 2. The microstructure of undercooled Ni$_{90}$Cu$_{10}$ alloy at undercooling $\Delta T = 240$ K.

Figure 3. Recalssence process of Ni$_{90}$Cu$_{10}$ alloy at different undercooling degrees ($a = 50$ K; $b = 100$ K; $c = 200$ K; $d = 240$ K).
3.2. Stress accumulation during solidification

It is known that recrystallization occurs due to deformation causing deformation storage energy inside the crystal grains, the system is in an unstable state of high-energy, therefore in the subsequent isothermal process, the deformation storage energy is used as the driving force, and the new crystal structure is regenerated by recrystallization nucleation and growth by the thermal activation process. The stress-induced recrystallization mechanism proposed by Liu [27] has been widely accepted to confirm the grain refinement phenomenon of binary single-phase alloys under high undercooling conditions. The accumulation of stress increases with the increase of undercooling. In general, there are two stages in the solidification process of undercooled melt: one is the rapid recalescence process of undercooled melt, and the other is the process equilibrium solidification in the later recalescence stage. The difference of solidification velocity between the two processes is very large. Therefore, we can approximate the assumption that the stress of the dendritic skeleton during the whole solidification process is all derived from the fast recalescence process. At the same time, with the increase of the initial subcooling, the recalescence process begins to shorten, and the number of integral crystals formed in the

**Figure 4.** High-speed camera pictures of the undercooled Ni$_{90}$Cu$_{10}$ alloys (a 37 k; b 105 k; c 280 k).
whole period will increase continuously. A continuous dendritic network is formed in the remelting melt, and the dendrite skeleton is formed. It also begins to have a certain strength and exhibits a certain resistance. As the cumulative stress increases continuously, when the stress is greater than the strength of the dendritic framework, the precipitated dendrites will undergo stress fragmentation and plastic deformation. Therefore, a large amount of deformation energy will be stored throughout the dendrite fragmentation segment, which provides a driving force for subsequent recrystallization. Models of stress accumulation have been developed [19].

### 3.3. Microstructural analysis

Solidification structures at different undercooling were observed, which can be divided into the following areas:

1. $23 \text{ K} < \Delta T < 50 \text{ K}$ figure 5(a) shows the microstructure in a sample undercooled by 30 K. It can be seen that the whole picture is occupied by dendrite trunks, which are thick and surrounded by many secondary dendrite arms of remelting. The formation of such dendrites is due to the rapid occupation of the whole melt volume during nucleation, and the heat energy released by nucleation inhibits the formation of other crystal nuclei. In this undercooled range, the dendrite granularity of the whole microstructure is large.

![Figure 5](image-url)
Figure 6. (a) and (b) respectively represent grain boundary orientations of undercooled Ni$_{90}$Cu$_{10}$ alloy at 58 K and 240 K; (c) grain boundaries of (a), (d) grain boundaries of (b); (e) the inverse pole figure of (b) showing a nearly random texture; (f) represents the recrystallization fraction of supercooled Ni$_{90}$Cu$_{10}$ alloy at 240 K.
With the increase of undercooling, dendrite structure morphology changes, the dendrites are fragmented, dendrite structure is gradually replaced by equiaxial crystals, that is, the first type of grain refinement. This can be confirmed by optical microscopy figure 5(b). Moreover, it can be seen that the grain has a curved grain boundary. By referring to the above figure 5(a), the grain coarsening phenomenon occurred in the whole process.

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3.4. EBSD and TEM analysis

Figures 6(a) and (b) shows EBSD grain orientation of undercooled Ni_{90}Cu_{10} alloy at 58 K and 240 K, respectively. Different colors indicate different grain orientation, and the same or similar color indicates the same grain orientation [16]. It can be seen that the whole grain orientation is disordered, and the grain orientation is the same or similar in some areas. By comparing figures 6(a) and (b), it can be clearly seen that the grain boundary changes from a small-angle boundary to a large-angle boundary, and the grain boundary becomes straighter, which indicates that grain boundary migration occurs under the condition of large undercooling. At the same time, the corresponding grain boundary diagrams, figures 6(c) and (d), it can be observed to show obvious changes in the grain boundary, and the presence of twins can be seen at 240 K. Based on the above observations, these structures have typical characteristics of recrystallization, indicating that recrystallization occurs under large undercooling, which proves that the mechanism of grain refinement at large undercooling is recrystallization. Also we can observe the inverse pole figure figure 6(e) under 240 K, the microstructure of the inverse pole figure show a random distribution, the reason is that during the period of rapid solidification stress of the primary dendritic network segment and recalescence dendrite remelting of the break period caused by rapid solidification alloy organization are randomly distributed, then the deformation of dendrite recrystallization and grain growth process does not make the final microstructure appears the new texture, this also confirms the occurrence of recrystallization under high undercooling. Figure 6(f) shows the recrystallization fraction of undercooled Ni_{90}Cu_{10} at 220 K, the blue, red and yellow represent recrystallization, deformation and substructural region respectively. It is obvious that recrystallization certainly exist in the case of undercooled Ni_{90}Cu_{10}.
Within the statistical analysis, the Σ3 boundaries were defined as the interfaces with a misorientation of 60° (with 8.71 as the maximum angular deviation) about a 111 60° crystal axis. Figure 7 is a transmission electron map (TEM) of undercooled Ni$_{90}$Cu$_{10}$ alloy at 240 K. As can be seen from the figure 7(a), there are annealed twins in the alloy, figure 7(d) shows the electron diffraction points of the annealing twin. Electron diffraction spot is a typical twin diffraction spot in FCC alloy.

4. Conclusion

The maximum undercooling of about 240 K of Ni$_{90}$Cu$_{10}$ alloys was achieved by using molten glass purification and cyclic superheating methods. The solidification process and microstructure under different undercooling were systematically studied. According to this experiment, the conclusions are as follows:

(1) During the whole solidification process, there are two grain refinement phenomena with the increase of undercooling. It occurs under the condition of lower undercooling and higher undercooling.

(2) According to the experimental results in this paper, the grain refinement mechanism under large undercooling degree can be attributed to the recrystallization in the later stage of recalescence. The driving force for recrystallization mainly comes from the rapid recalescence of supercooled melt. As the recalescence process continues, the accumulated stress gradually exceeds the deformation resistance of the dendrite framework, and the dendrite fragments occur, storing a large amount of deformation energy in the dendrite fragments, providing the driving force for the recrystallization in the later stage of recalescence.

(3) By observing the solidification structure under high undercooling and comparing EBSD images under low undercooling and high undercooling, it can be clearly seen that the grain boundary has migrated, and a large number of annealing twins exist in the grains, which is an important evidence for the occurrence of recrystallization, and indirectly confirms the occurrence of recrystallization under high undercooling.

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