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Microstructure and microtexture evolution of undercooled Ni−15%Cu alloy

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Abstract: Rapid solidification of undercooled Ni−15%Cu (mole fraction) alloy was studied using glass fluxing and cyclic superheating. To show the effect of cooling history on the microstructure and microtexture evolution, the as-solidified samples were either cooled naturally or quenched into water after recalescence. At low undercooling, grain-refined microstructure has a random texture and a highly oriented texture without annealing twins for the case of naturally cooling and quenching, respectively. At high undercooling, a fully random texture as well as a number of annealing twins are observed, and recrystallization and grain growth independently happen on the cooling history. Fluid flow and recrystallization play an important role in the microtexture formation for grain refinement at both low and high undercooling.

Key words: solidification; undercooling; grain refinement; microtexture; Ni−Cu alloy

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1 Introduction

Rapid solidification of bulk undercooled melts has been extensively studied since it is a good method for the preparation of metals in metastable states, such as grain-refined materials [1]. Compared with the fine equiaxed grains produced by the conventional solidification (e.g. magnetic and mechanical stirring, copious nucleation induced by grain refiner), grain refinement upon rapid solidification of undercooled melts spontaneously occurs. To date, a number of mechanisms have been proposed to account for the origin of grain refinement, e.g., copious nucleation due to cavity collapse, development of growth instabilities, dendrite remelting, recrystallization upon or after solidification, dynamic nucleation. A detailed description of the mechanisms is available in the review of LIU and YANG [2].

To show the actual mechanism for gain refinement, different kinds of undercooling experiments (e.g., electromagnetic levitation (EML), electrostatic levitation (ESL), glass fluxing and drop tube) and microstructure analysis methods (SEM, TEM, X-ray and EBSD) were adopted. For example, a comparative study between EML and ESL was carried out for undercooled $Ni_{99}B_1$ [3]. At low undercooling, grain refinement happens in EML but not in ESL, whereas at high undercooling, grain refinement occurs for both cases. This difference is ascribed to the fluid flow effect. Nowadays, texture analysis, macrotexture by X-ray [4,5] or microtexture by EBSD [3], seems to be the best choice for the microstructure analysis due to the ability to show the orientation relationship between different grains. The evolution of microstructure and microtexture of undercooled Ni−15%Cu alloy was studied, and the direct evidences for the origin of grain refinement (i.e. dendrite remelting) were given by WANG et al [6]. The investigation of the microtexture instead of the macrotexture was performed, since by this way not only the orientations but also their direct link to the microstructure can be obtained. To minimize the grain growth and hold the primarily solidified structure, the sample was quenched into water after recalescence. Different to the previous work [4,5], a highly oriented texture rather than a random texture was found when grain refinement occurred at low undercooling. This implies that microstructure and texture for undercooled

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melts are influenced by not only the undercooling method but also the cooling history.

In this work, a comparative study between samples with and without quenching after recalescence was carried out for undercooled Ni−15%Cu alloy. It was found that the cooling history has a significant effect on not only the critical undercooling for grain refinement but also the texture. These results are quite helpful for the microstructure control which is one of the important research goals of material science.

2 Experimental

Experiments were performed in a high-frequency induction facility. The sample of Ni−15%Cu alloy of 5 g was prepared by pure Ni (99.98%) and Cu (99.99%). Before the experiment, the surfaces of Cu and Ni were mechanically polished and then cleaned in an ultrasonic bath of 10% (volume fraction) hydrochloric acid and 90% ethanol. Fluxing technique was applied to denucleate the alloy by reaction, adsorption, and passivation of the foreign catalytic sites.

Before heating, the sample together with some pieces of B_2O_3 glass was put into a clean quartz-glass crucible. Then the sample was cyclically superheated and cooled until a desired undercooling was achieved. After the high frequency power source was turned off, solidification begun spontaneously. After recalescence, the sample was naturally cooled or immediately quenched into water (about 25 °C). Upon solidification, the thermal behavior of the sample was monitored by an infrared pyrometer with absolute accuracy, relative accuracy, and response time of less than 10 K, 3 K, and 5 ms, respectively. The cooling curve was calibrated with a standard PtRh30-PtRh6 thermal couple, which was encapsulated in a silica tube and then immersed into the melt in an identical condition. From the cooling curves, the melting temperature and the undercooling could be read as compared to the absolute temperature recorded by the standard thermal couple.

The sample was cut, mounted, ground, and finally polished with SiO_2 colloidal suspension in a vibratory polisher. The crystallographic orientations were measured with a step size of 2 μm using a JSM-6490LV SEM equipped with a fully automated EBSD analysis system. In all the EBSD orientation maps presented in this work, the black and blue lines represent the high-angle grain boundaries (GBs) (>10°) and the low-angle GBs (2°−10°), respectively. The red lines stand for the $\sum 3$ boundaries (60°⟨111⟩) defined with a tolerance of 1° on the rotation angle and 5° on the rotation axis. In the misorientation distribution maps, only the misorientation angle (>2°) was considered.

3 Results and discussion

3.1 Microstructure and microtexture

3.1.1 Grain refinement at low undercooling

For the case without quenching, complete grain refinement happens at ΔT=40 K. The corresponding EBSD orientation map, boundary misorientations, misorientation distribution and {100} pole figure are shown in Figs. 1(a)−(d), respectively. The microstructure is composed of the fine equiaxed grains and the large-strip grains (Fig. 1(a)). The orientation difference between different grains is normally very large and almost no annealing twins are found (Fig. 1(b)). The texture appears quite random (Fig. 1(d)) and the high-angle grain boundary (GB) prevails. A random texture without anneal twins is found. Note that the frequency at a given range of misorientation angle in the misorientation distribution map actually denotes the fraction of the boundary length relative to the total length of all the GBs.

For the case with quenching, complete grain refinement happens at a little bit larger undercooling, i.e. at ΔT=47 K. The microstructure is also composed of the fine equiaxed grains and the large-strip grains. But some neighboring equiaxed grains almost possess the same orientations. The grain size is much smaller than that without quenching. The reason is that the grains have enough time to grow with the GB energy as the driving force for the case without quenching. Compared with Figs. 1(b) and (c), there are much more low GBs in Figs. 2(b) and (c), but also without annealing twins. Moreover, a highly oriented texture with only one primary orientation is found (Fig. 2(d)).

3.1.2 Grain refinement at high undercooling

For the case without quenching, complete grain refinement happens at ΔT=164 K. The grains are much smaller than the grain at small undercooling and the grain size distribution is almost homogeneous (Fig. 3(a)). A completely random texture is found (Fig. 3(d)). The fraction of the misorientation angle near 60° (i.e. annealing twin) as well as the fraction of the $\sum 3$ boundary is substantially increased (Figs. 3(b) and (c)). The fraction of the low-angle GBs is very small. This means that recrystallization occurs. As the increase of undercooling (e.g. ΔT=253 K), the grains become larger and some are much larger than others, as shown in Fig. 4. But the annealing twins and the random textures remain. This means that grain growth or even abnormal grain growth happens after recrystallization. For the case with quenching, the microstructure and microtexture evolution are similar except that complete grain refinement happens at a relatively larger undercooling, ΔT=174 K; the detailed microstructure and microtexture information is not repeated here.

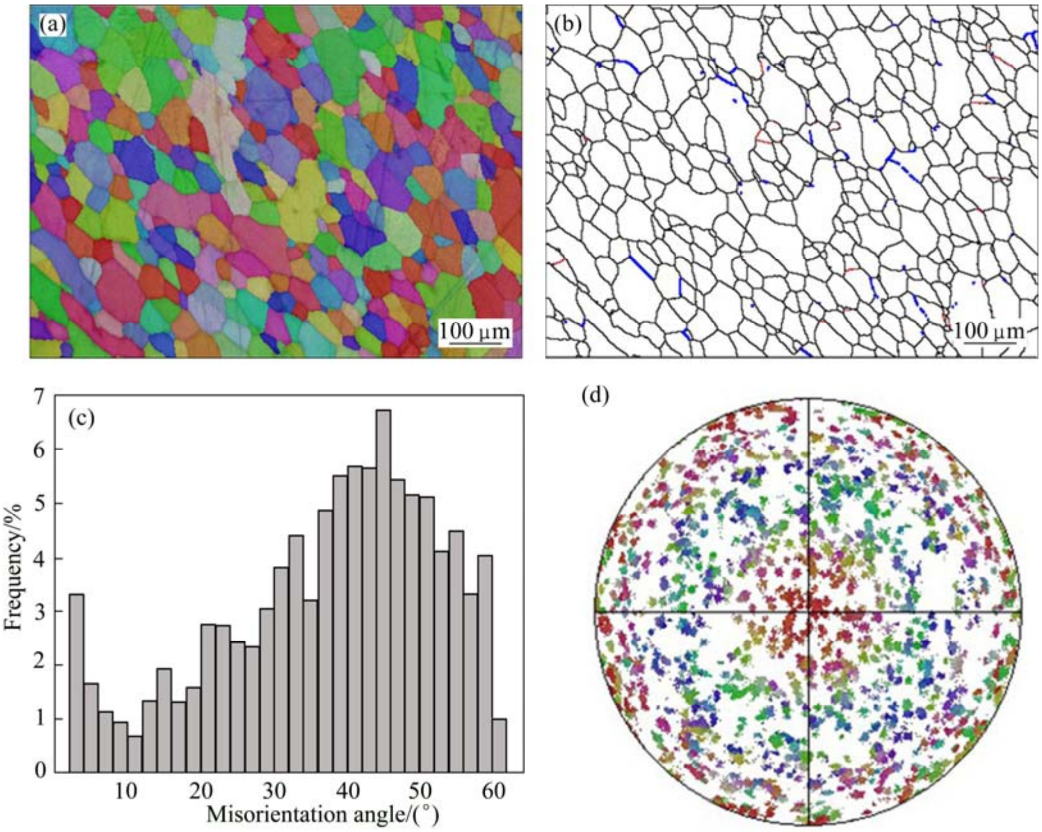

Fig. 1 EBSD orientation map (a), boundary misorientation (b), misorientation distribution (c) and {100} pole figure (d) of Ni−15%Cu alloy solidified at Δ*T*=40 K without quenching

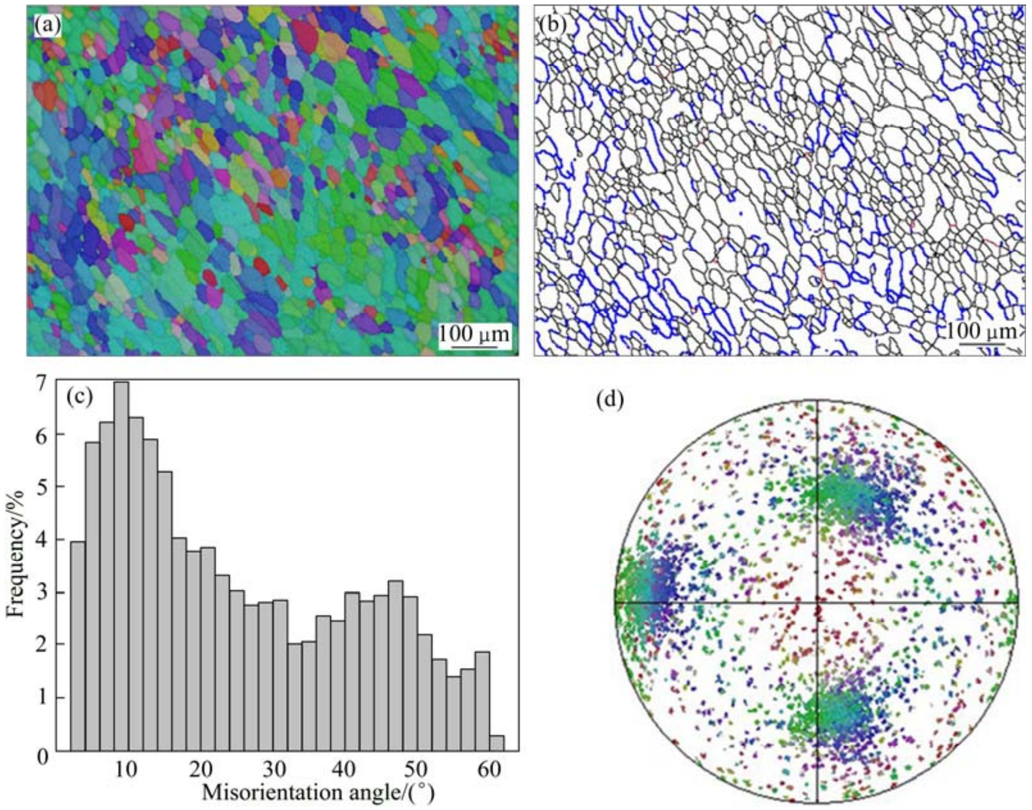

Fig. 2 EBSD orientation map (a), boundary misorientations (b), misorientation distribution (c) and {100} pole figure (d) of Ni−15%Cu alloy solidified at Δ*T*=47 K with quenching

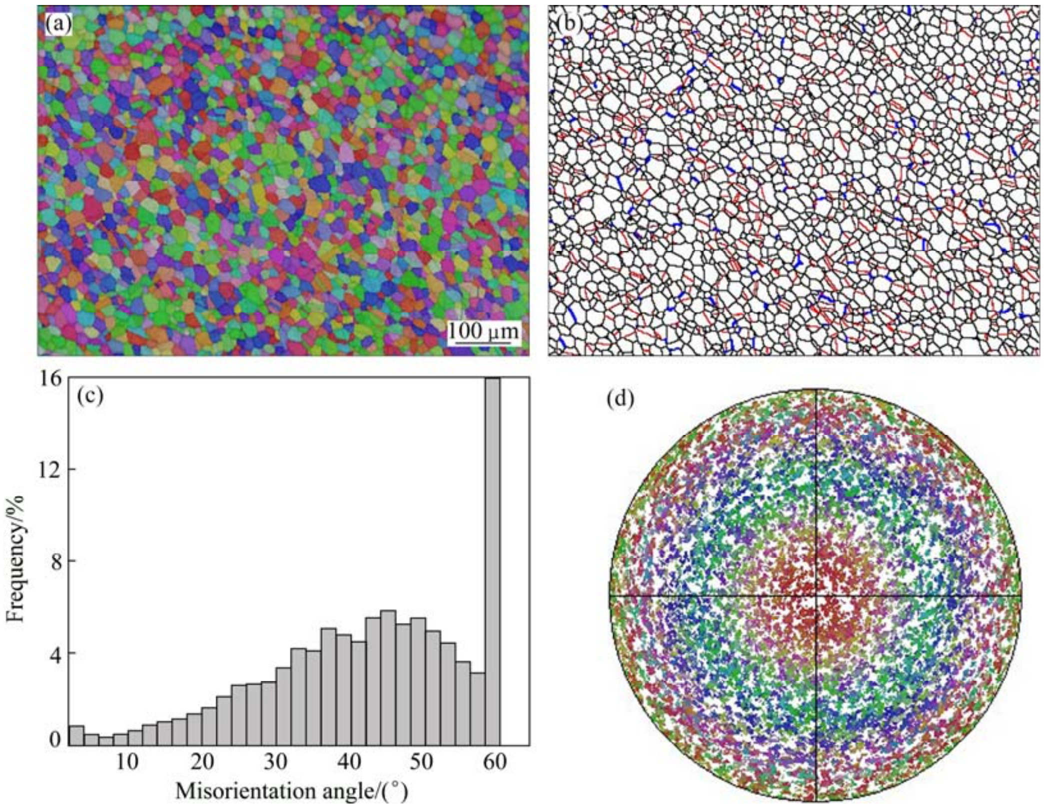

Fig. 3 EBSD orientation map (a), boundary misorientations (b), misorientation distribution (c) and {100} pole figure (d) of Ni−15%Cu alloy solidified at Δ*T*=164 K without quenching

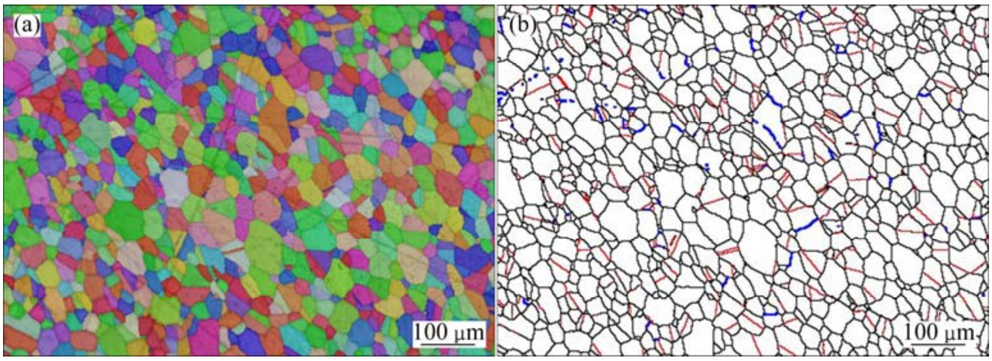

Fig. 4 EBSD orientation map (a) and boundary misorientations (b) of Ni−15%Cu alloy solidified at Δ*T*=253 K without quenching

3.2 Formation of grain refinement microtexture

If the critical Δ*T* for complete grain refinement isn't considered, the only difference between the samples with and without quenching is the microtexture difference at low undercooling, i.e. a random texture for the case without quenching and a highly oriented one for that with quenching. This difference and the microtexture formation at high undercooling can be described by the effect of fluid flow and recrystallization.

Generally, the fluid flow upon solidification can be induced externally (e.g. stirred by electromagnetic or mechanical approaches) or internally (e.g. Maranogoni thermal convection, natural solutal convection, shrinkage induced fluid flow). On one hand, the fluid flow during solidification can collide with and wash the dendrite arms, the arms may shrink due to mechanical collision or fluid erosion. So, the fluid flow can be a driving force for dendrite fragmentation. This effect has an advantage over other driving forces at low Δ*T* where the growth velocity is small, and it is weakened as Δ*T* increases [3]. At low Δ*T*, the fluid flow and also remelting (Section 3.3) have enough time in the case of without quenching to fragment the dendrite, so that critical Δ*T* for grain refinement is 7 K smaller than that with quenching. On the other hand, the fluid flow can penetrate into the mushy zone and transport the dendrite fragments out to the open liquid. This transport can be very soon even without imposed stirring [7]. After that, the fragments float subject to the fluid flow, some may survive while the others are remelted depending on their local environments. If the flow fluid has enough time (e.g. without quenching), the fragments can then be moved far away from their origins (i.e. the matrix dendrite) and be rotated with large angles, resulting in a random texture (Fig. 1). Whereas if the fragments do not have enough time (e.g. with quenching) to travel with the fluid flow, they will be rotated insufficiently and then a highly oriented texture is found (Fig. 2).

At high undercooling, recrystallization happens and dendrite deformation provides the driving force. Dendrite can be deformed through mechanical interactions with the parent melt, i.e. by the fluid flow. Based on the model of DAHLE et al [8], the stress developed by the shrinkage induced fluid flow was modeled by LIU et al [9] for rapid solidification. This model indicates that, once the dendrite coherency is formed, the strength starts to develop and is exchanged between the as-formed dendrite skeletons. Accordingly, the stress increases gradually with the undercooling. DRAGNEVSKI et al [10] proposed another model by considering the external fluid flow. Accordingly, the predicted stress is related to the value of dendrite tip radius, where the smaller dendrite tip radius corresponds to the larger stress and vice versa. However, in this work, there is no external fluid flow because the power is shut off during solidification. In this case, recrystallization has no influence on small undercooling and no annealing twins are found. At high undercooling, however, dendrite deformation is so severe that recrystallization can not be suppressed any more. On one hand, new grains with new orientations are formed during recrystallization. On the other hand, the non-uniform dendrite deformation upon solidification may lead to the non-uniform distribution of annealing twins, as shown in Figs. 3(b) and 4(b). This is the reason that a completely random texture is found at high undercooling. Moreover, as the increase of undercooling and hence dendrite deformation, recrystallization happens much fast and after that grain growth or even abnormal grain growth can happen (Fig. 4).

3.3 On critical undercooling for grain refinement

The current results are consistent with our former work [6], in which dendrite remelting was concluded to be the origination of grain refinement. Actually, the difference between the critical undercooling for grain refinement at both low and high ΔT could be also described qualitatively by this mechanism.

In the classical model of KARMA [11], microstructure transition is determined by comparing the dendrite breakup time Δt_{bu} with the plateau duration Δt_{pl}: if $\Delta t_{\mathrm{bu}}>\Delta t_{\mathrm{pl}}$, a coarse dendritic microstructure forms, whereas, if $\Delta t_{\mathrm{bu}}<\Delta t_{\mathrm{pl}}$, a refined equiaxed microstructure forms. However, this classical model suffers several limitations: 1) The inter-dendritic liquid is believed to be solidified completely at the plateau stage, which is inconsistent with the actual solidification process, e.g. the prediction of overall solidification model with back diffusion effect [12]; 2) The model itself can not predict ΔT_{pl} and it is obtained from experimental measurement. In a thorough modeling, the model itself should have the capability to predict the microstructure transition. Regarding this, a modified grain refinement model [13] have been proposed recently based on the overall solidification model. The prediction of this model is shown in Fig. 5. The physical parameters used are available in Ref. [13]. For the case of quenching, the cooling history can not be measured, so that the cooling rate ϕ (174.5 K/s) is chosen as a fitting parameter. Accordingly, complete grain refinement occurs for 24.1 K$\le\Delta T\le$36.5K and $\Delta T\ge$174.1 K. Thus, a good agreement between the model prediction and the experimental result is obtained, especially at high ΔT. The prediction for low ΔT is within measurement error. For the case without quenching, the averaged cooling rate according to the measurement is ϕ=25 K/s, which results in a large deviation between the experimental result and prediction. If ϕ is considered as a fitting parameters, ϕ=154.9 K/s can give a good model predication, i.e. complete grain refinement occurs for 22.1 K$\le\Delta T\le$37.9 K and $\Delta T\ge$164.3 K. The difference between the actual cooling rate and that for a good model prediction is quite large. One possible reason for this large deviation is that this model does not include the fluid flow as a driving force (Section 3.2) for dendrite remelting at low ΔT.

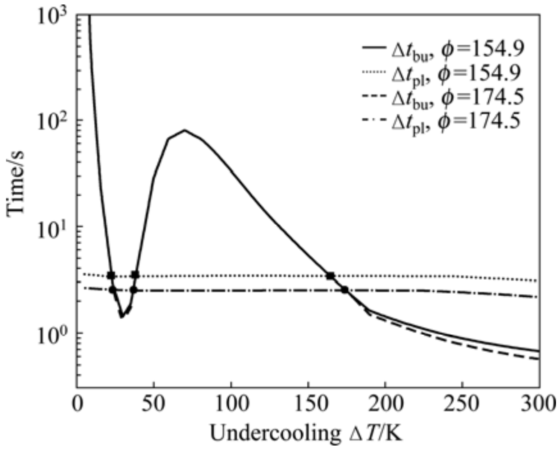

Fig. 5 Predication of dendrite breakup time Δt_{bu} with plateau duration Δt_{pl} as a function of ΔT. The samples denote the critical ΔT for grain refinement

4 Conclusions

A comparative study of microstructure and microtexture evolution between natural cooling and quenching after recalescence was carried out for rapid solidification of undercooled Ni−15%Cu alloy. Fluid flow has a significant effect on the microstructure and microtexture formation because it not only is a driving force for dendrite remelting but also can transport the dendrite fragments out to the open liquid. At low undercooling, fluid flow effect can lead to a random texture while at high undercooling it deforms the dendrite and hence recrystallization and annealing twins result in a random texture. Prediction of the modified grain refinement model shows that the fluid flow effect should be taken into consideration to obtain good model prediction for the microstructure formation and transition.

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过冷 Ni−15%Cu 合金组织与微观织构演化规律

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摘 要：采用熔融玻璃净化和循环过热方法实现 Ni−15%Cu(摩尔分数)合金的深过冷。采用再辉后自然冷却和水淬两种方式研究凝固冷却对凝固组织和微观织构的影响。在小过冷度下，自然冷却条件下晶粒细化组织呈随机位向，而快淬条件下晶粒细化组织呈集中位向，但均无退火孪晶；在大过冷度下，晶粒细化组织呈随机位向，大量退火孪晶出现，再结晶和晶粒长大发生。分析表明：在小过冷度和大过冷度下的晶粒细化组织的微观织构形成过程中，对流和再结晶起重要作用。

关键词：凝固；过冷；晶粒细化；微观织构；Ni−Cu 合金

(Edited by Chao WANG)