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Experimental observation of solidification of undercooled single phase alloys①

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[Abstract] The solidification process of undercooled $Cu_{70}Ni_{30}$ alloy melt in a cylindrical crucible was investigated by high speed cinematography. In the experiment, nucleation location was controlled at one end of the sample by means of artificial triggering. The results show that the equiaxed dendritic crystals obtained at low undercooling form in sequential solidification, rather than simultaneously in the entire sample, and the morphology of the recalescence front frequently changes with time. If increment of undercooling results in that the dendrite growth is controlled by thermal diffusion, the primary dendrite arms propagate parallel to each other in 〈100〉, and eventually directional solidification microstructure is obtained. At higher undercooling, dendrite growth is destabilized due to solidification contraction, and the microstructure develops into fine quasi-spherical grains through recrystallization, however, the massive nucleation is not found.

[Key words] undercooled alloy; solidification; high speed cinematography; microstructure evolution
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1 INTRODUCTION

Relatively large undercooling is gained in bulk alloy melt with moderate cooling rate by eliminating the solid inclusions in the melt and by eliminating the effect of container wall on the triggering of nucleation. The accumulated driving force for crystallization causes rapid crystal growth as soon as nucleation is trigered, which makes temperature rise quickly. In this process, thermal diffusion is limited in a narrow area ahead of the interface, and the shape and moving rate of the recalescence front can be used to represent the status of solidification interface and crystal growth velocity. Although actual metal melts are not transparent, much of crystal growth information can be obtained by observing the recalescence with photosensitive elements or high speed camera.

So far the observation of solidification process of undercooled melts was mainly aimed at measuring the velocity of crystal growth[1~4], and little attention was paid to the relation between recalescence behavior and solidification microstructures. In this article, the solidification process of undercooled $Cu_{70}Ni_{30}$ alloy melt is investigated by high speed cinematography. This work is helpful for the understanding of the microstructure evolution in undercooled melts.

2 EXPERIMENTAL

The experimental material was $Cu_{70}Ni_{30}$ alloy. The preparation of the alloy was conducted in a high frequency induction unit. Firstly, the glass purifier was melted in a fused silica crucible with the inside size of d10 mm × 100 mm, then Cu and Ni with purity > 99.99 % were charged. Under the protection of the melted glass, pure metals were in situ melted into alloy, and subsequently the alloy was cyclically superheated and cooled until large undercooling was present. Single sample weighed 50 g, and was about 65 mm in height. In order to observe the sample, a square hole was made in the side of refractory sheath which was used to support the crucible. During cooling, the sheath as well as crucible was raised from the induction coil, and made the square hole face the camera (NAE-10 type, made in Japan). When the melt was undercooled to the predetermined temperature, the camera was initiated, and one second later nucleation was stimulated by a metal needle at the top of sample so that the location and shape of solidification front at different time were recorded. Two photographing rates, 800 and 1 000 s^{-1} were used. If the photographing rate is too high, it will cause poor photographing quality due to insufficient sensitization. The as-solidified sample was longitudinally sectioned to make metallographic analysis.

3 RESULTS AND DISCUSSION

3.1 Equiaxed dendrite growth at low undercooling

With crystal growing into undercooled melt, the released heat of fusion makes the temperature of the

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solidifying zone higher than that of unsolidified zone. The difference between the two zones is approximately equal to the initial undercooling ΔT, so the contrast of the photograph is very poor at low undercooling. Fig.1 shows two photographs of the sample undercooled by 50 K. The interval between them is 25 ms. It is apparent that the macro solidifying interface is irregular, and it changes with time. The corresponding microstructure is shown in Fig.2. The chemical superheating of the solid in recalescence makes the primary dendrite break into fine granular grains[5-7]. However, there were theoretical analyses to indicate that the crystal growth in the $Cu_{70}Ni_{30}$ alloy melt undercooled below 90 K is mainly controlled by solute diffusion[8], and all the original microstructures consist of equiaxed dendrites[6]. The high speed cinematography clearly indicates that the equiaxed dendrites at low undercooling form at the triggering point firstly, and then extend toward the other end batch by batch, rather than emerge simultaneously in the entire sample. Such forming mechanism of equiaxed dendrites is relative to the dissociation and growth of crystals, because the isolated nucleation of crystals will result in the simultaneous recalescence of the sample.

3.2 Directional dendrite growth at moderate undercooling

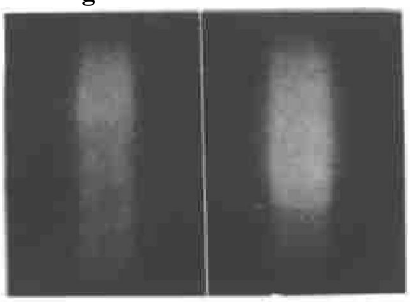

Fig.1 Solidified images at undercooling of 50 K (Interval between two images is 25 ms)

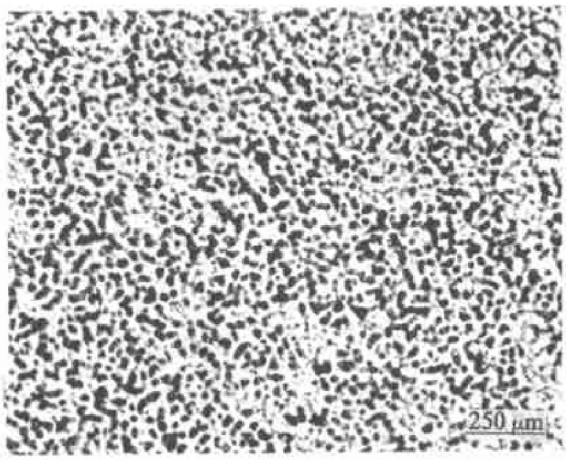

Fig.2 Microstructure of $Cu_{70}Ni_{30}$ alloy at undercooling of 50 K

As undercooling increases higher than 90 K, dendrite growth velocity exceeds 1 m/s. The marked solute trapping makes the enrichment of solute ahead of solid/liquid interface decrease, and the effect of solute diffusion on the crystal growth is weakened. Crystal growth is under the control of thermal diffusion. In this case, the solidification front is flat (as shown in Fig.3) and maintains unchanged during solidification process with the exception of the initial solidification stage in which the solidification boundary appears round. Eventually directional solidification microstructure is gained (as shown in Fig.4), and often there is single crystal in the directional solidification zone. X-ray diffraction of the transverse section at undercooling of 116 K is shown in Fig.5. The section is in the plane of (200), and the direction of dendrite growth is [100]. (111) peak originates from the local remelting of dendrites, which results in the occurrence of a few granular grains. Such a directional solidification can be performed until undercooling reaches 175 K.

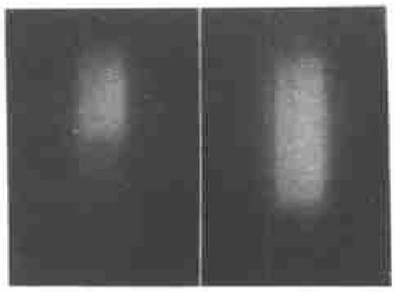

Fig.3 Solidified images at undercooling of 168 K (Interval is 2.5 ms)

Fig.4 Microstructure of $Cu_{70}Ni_{30}$ alloy at undercooling of 160 K

3.3 Destabilization of dendrite growth and secondary grain refinement at large undercooling

If $Cu_{70}Ni_{30}$ alloy melt is undercooled higher than 175 K, primary dendrite arms are no longer parallel to each other (as shown in Fig.6). The primary dendrite arms frequently adjust their growth direction

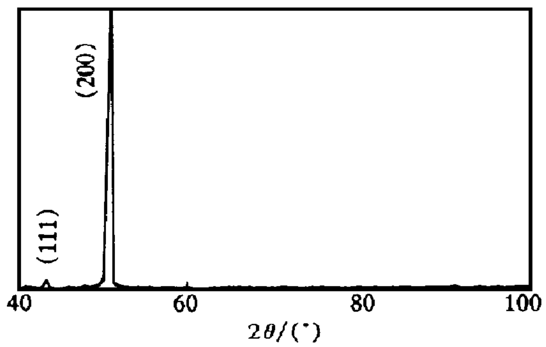

Fig.5 X-ray diffraction of transverse section of directional solidification microstructure at undercooling of 116 K

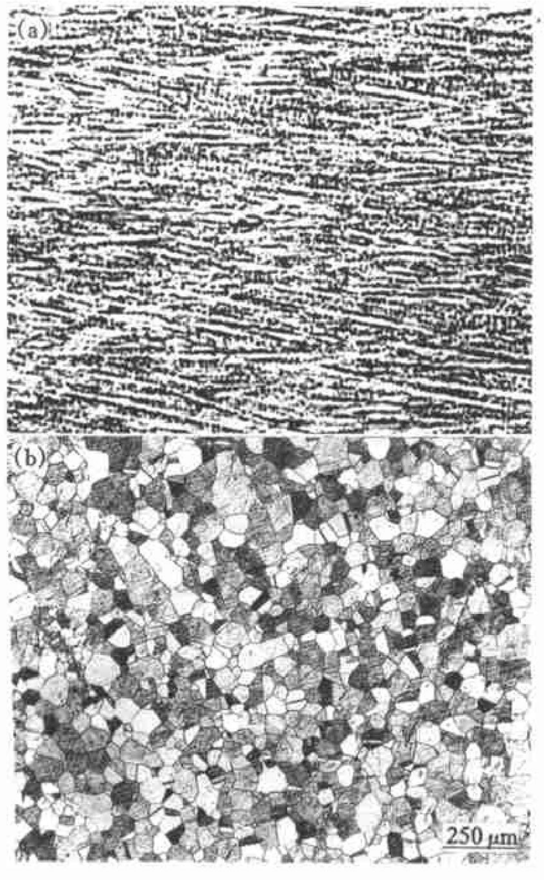

Fig.6 Microstructures of $Cu_{70}Ni_{30}$ at different undercoolings
(a) —182 K; (b) —221 K

during solidification process and the change becomes quicker and quicker as undercooling increases, whereas secondary dendrite arms are degenerated meantime. Recrystallization occurs when undercooling reaches 185 K. The quasi globular microstructures with the grain size of several micron are gained above the critical undercooling of 210 K (as shown in Fig.6 (b)) in addition to annealing twins. Deep etching also reveals the existence of dendritic submicrostructure in refined grains[9]. Chemical composition analysis by electroprobe shows that the components with low melting point are found rich on the boundaries of dendrite submicrostructures, rather than on the boundaries of the quasi-spherical grains. Also the macro solidification front still propagates from the top of specimen to the bottom above the undercooling of 175 K (as shown in Fig.7) although the micro dendrite growth is destabilized. This implies that grain boundaries form due to recrystallization.

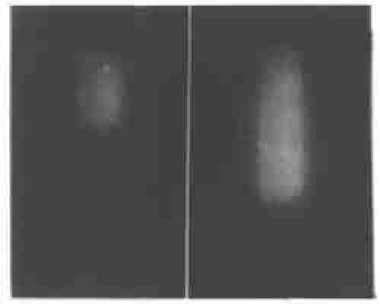

Fig.7 Solidified images at undercooling of 221 K
(Interval is 1 ms)

The direction adjustment of dendrite growth and the occurrence of the recrystallization at high undercoolings originate from the solidification contraction. When paraboloid of revolution propagates in undercooled melt, the normal crystal growth velocity on the solid/liquid interface possesses the maximum value at the dendrite tip. If dendrite growth velocity is too high, and the solidification contraction can not be supplied in good time, a tensile stress (i.e. negative pressure) will occur in the tip area, which even cause the cavity sometimes. In this case, the dendrite growing in the original direction is difficult. Meanwhile the secondary dentrite arm branched on the side of the primary dendrite tip quickly protrudes into the melt at a certain angle in the original direction, and develops into a new primary dendrite arm, so that the rapid solidification can be maintained. The repetition of the foregoing course results in the microstructure as shown in Fig.6(a). The tensile stress and the pulse pressure accompanied by the collapsing of the cavities make dendrite skeleton deform and recrystallize in the following stage, so the microstructure is gained, as shown in Fig.6(b). It is demonstrated by both microstructures and high speed cinematography that the solidification above the critical undercooling performs still by epitaxial crystal growth. No renucleation ahead of solidification front is found.

The increment of dendrite growth velocity with undercooling slows down above the critical undercooling was certified by many researchers[10,11]. This work demonstrates that it originates from the breakdown of continuous dendrite growth.

4 CONCLUSIONS

1) When a single phase alloy melt solidifies at low undercooling, the macro solidification interface is irregular, and varies with time continuously. Eventually equiaxed crystals form.

2) By controlling the nucleation point at one end of a cylindrical sample, $Cu_{70}Ni_{30}$ melt undercooled in the range of 90 ~ 175 K directionally solidifies in the crystal orientation [100]. In this case, the solidifying front maintains an invariable flat.

3) As undercooling increases up to 175 K, the dendrite growth destabilizes due to rapid solidification contraction, leading to the frequent adjustment of the primary dendrite growth direction. At higher undercooling, the contraction stress even causes the deformation of solid skeleton, and the subsequent recrystallization makes grain size decrease abruptly. However, it is observed that the macro solidifying interface is still flat.

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