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Microstructure Transition and Grain Refinement Mechanism of Undercooled Alloys

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Abstract: The solidification microstructures of undercooled Ni90Cu10 alloys under different undercoolings were studied systematically by means of melt coating and cyclic superheating. In the obtained undercooling range, the solidification structures of the two undercooled alloys have similar transformation processes, and there are two kinds of grain refinement structures under the conditions of low undercooling and high undercooling, respectively. The microstructures of the two grain refinement processes were analyzed in more detail by electronic backscattering diffraction technique. Under the condition of small undercooling, dendrite remelting is considered to be the main reason of grain refinement. However, under the condition of high undercooling, the existence of annealing twins and obvious migration of grain boundary are important evidences for the occurrence of recrystallization process.

Key words: microstructure transition; grain refinement; undercooled alloys; Ni-Cu alloys

1 Introduction

In recent years, researchers have been committed to the research and preparation of alloy materials with excellent properties[1-6]. The solidification of metals and alloys requires a certain degree of undercooling. However, with the difference of initial undercooling of metals or alloys, the solidification appearance will change greatly. A large number of studies[7-10] have shown that the refined microstructure can be obtained by deep undercooling and rapid solidification of highly undercooled metals or alloys. Different from the traditional refined grain structure, under the condition of deep undercooling, the alloys or metals have not been plasticaly processed or annealed, so the method of deep undercooling to obtain refined grain structure has attracted much attention.

In previous studies, it has been noted that there are generally two kinds of grain refinement structures in the whole undercooling range[11,12]. One occurs in the range of low undercoolings and the other exists in the condition of high undercoolings. There is also controversy about the mechanism of the two grain refinements. For small undercoolings, dendrite remelting[11] driven by solid/liquid interfacial tension and dendrite remelting caused by chemical overheating are widely considered as the main mechanisms of grain refinement. However, under the condition of high undercoolings, many physical mechanisms have been proposed to explain the grain refinement, *eg,* critical growth velocity[13], kinetics induced growth instabilities[14], recrystallization[15], dendrite remelting and dendrite fragmentation[16]. First of all, the deformation energy stored in the deformed metal and alloy is the driving force for the recrystallization transformation[17]. Therefore, we predict the relationship between the initial undercooling of the undercooled metal and the deformation energy stored in the dendrite, and draws the conclusion that the deformation energy stored in the dendrite will increase with the increase of the undercooling. EBSD was used to detect the refined grain structures under high undercoolings and it was found that there were annealing twins in the grains, which also confirmed the occurrence of

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recrystallization under high undercoolings.

In this experiment, we systematically studied the solidification structure evolution process of undercooled Ni90Cu10 alloys under different undercoolings, and predicted the relationship between the dendrite remelting and the initial undercooling of undercooled Ni90Cu10 alloy, and calculated the change of the accumulated stress in the dendrite with the initial undercooling. EBSD technology was used to detect the microstructure of typical grain refinement.

2 Experimental

The mater alloys were prepared by melting pure nickel (99.99%) and copper (99.99%) particles. Before melting, the pure nickel (99.99%) and copper (99.99%) were pre-polished with sandpaper to remove surface oxidants and etched with HCI solution. In order to ensure the chemical homogeneity of mater alloy, the mater alloys should be remelted at least 3 times under the protection of argon gas. Then about 3 g samples were cut from the mater alloys for undercooling experiments. Before the undercooling test, the quartz glass test tube and the sample are pre-cleaned in the alcohol ultrasonic cleaner for at least 6 minutes. Before the undercooling experimental, the quartz glass test tubes and sample should be cleaned in an ultrasonic cleaner with alcohol for at least 6 minutes. Then put the sample and purified agent B_3O_2 into the glass tube, and fix them in the high frequency induction heating coil. Turn on the heating switch for heating. First, it is heated until the purifying agent B_3O_2 becomes a molten state, and keep it for 10 minutes, in order to fully absorb the impurities on the surface. Then gradually increase the temperature to about 150-200 K higher than the melting point of the metal, keep it for 15 minutes, then turn off the heating power, and the undercooled alloy melt begins to cool spontaneously, this is repeated until the required undercooling is obtained, the whole temperature change process is collected by an infrared thermometer with an accuracy of ± 5 K and a response time of 10 ms, and transmitted to a computer in real time. At the same time, a high-speed camera (olympusi-speed3) is used to record the solidification changes. In order to achieve better shooting results, the shooting frequency of the high-speed camera is set at 43000fps. In order to obtain more detailed solidification evolution regular, the undercooling interval of each undercooled sample is about 10 K.

The obtained sample is subjected to a series of processes such as cutting, setting, and grinding. The polished samples were corroded by nitric acid solution (100 mL HNO_3 + 100 mL H_2O), and the solidified microstructure was obtained by observation with PMG3 Olympus optical microscope. The electron backscatter diffraction (EBSD) sample was subjected to vibration polishing, and the EBSD pattern of the typical solidified structure was observed by the electron back scattering diffraction detection system.

3 Results and discussion

3.1 Solidification structure of undercooled Ni90Cu10 alloy

The undercooling of Ni90Cu10 alloy with a maximum of 270 K was obtained using the method of melt coating and cycle superheating, and the typical solidification structure was obtained in the range of undercoolings (Fig.1). At the same time, the evolution of solidification structure was systematically studied.

a) 20 K<ΔT < 45 K, Fig.1(a) shows the microstructure at an undercooling of 35 K. It can be seen that the solidification structure with a small undercooling has a very large dendrite size, and the whole structure shows a very coarse dendrite structure. It is obvious that the whole microstructure has a very large grain size in the range of undercooling.

b) 20 K<ΔT<100 K, with the increase of undercooling, the solidification structure also changed obviously. It can be seen from Fig.1(b) that the coarse dendrites are replaced by the refined equiaxed crystals, and the grain size decreases sharply, this is the phenomenon of grain refinement that occurs at small undercoolings. It can be seen that the whole grain structure presents a spheroidized structure, which indicates that dendrite remelting occurs in the later stage of recalescence.

c) 100 K<ΔT<180 K, when the undercooling increases to the range of 100-180 K, the solidification structure changed obviously again. The refined equiaxed crystal structure is replaced by dendrite again, but it is obviously different from the dendrite structure under small undercoolings. The dendrite under this undercooling has a dense dendrite network and smaller dendrite pitches (Fig.1(c)).

d) ΔT >180 K, when the undercooling is over 180 K, the dense dendrite is replaced by the fine equiaxed structure. Fig.1(d) shows the solidification structure when the undercooling is 180 K. It can be seen that the whole grain structure has a very straight grain boundary, which is completely different from that under low undercooling, and there are annealing twins in the grain, which is an important evidence of recrystallization (Fig.1(e)).

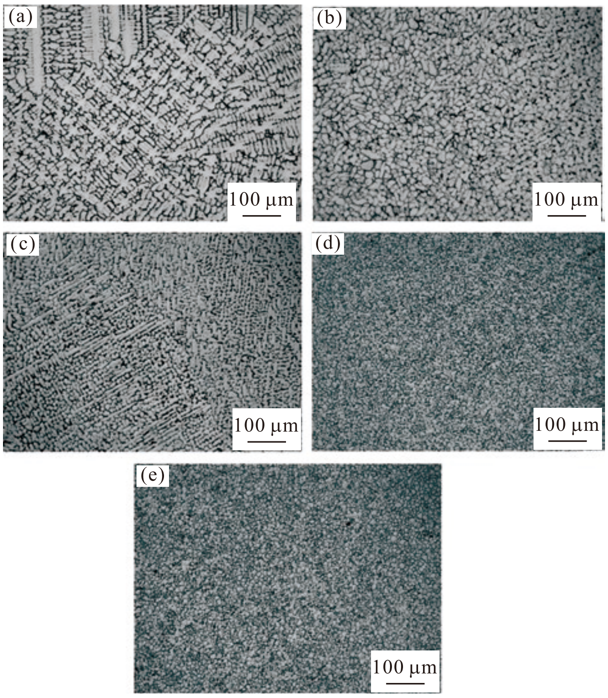

Fig.1 Typical microstructure images of $Ni_{90}Cu_{10}$ under different undercooling degrees: (a) 30 K; (b) 47 K; (c) 150 K; (d) 185 K; (e) 270 K

Different from near-equilibrium solidification under normal conditions, the morphology of primary dendrites formed under rapid solidification conditions is often changed by the subsequent release of crystallization latent heat, and the effect of crystallization latent heat on primary dendrites increases with the increase of solidification speed. In the range of 45 K <ΔT <100 K undercooling, the solidification structure has smooth grains and wide boundaries (Fig.1(b)), and the grain size of the refined structure is similar to that of dendrite secondary arms under the same undercooling .When the initial undercooling of the melt is greater than the critical undercooling degree ΔT^* (about 180 K), the solidified structure is transformed into completely equiaxed grains with relatively uniform grain size (Fig.1(d)), accompanied by the presence of annealing twins. Obviously, the grain refining structures under the conditions of 100 K<ΔT<180 K and $\Delta T > \Delta T^*$ undercooling conditions respectively represent the two kinds of different refinement mechanisms. It is generally believed that dendrite remelting caused by release of latent heat of crystallization during solidification is the main reason for grain refinement under low undercoolings. During the solidification process, the release of latent heat of crystallization will cause the primary dendrites to undergo remelting, resulting in the change or disappearance of the original dendrites. The chemical superheating action proposed by Li[26] plays an important role in the grain refinement process of the solidification structure of undercooled alloys. According to Li's model, the chemical overheat remelting fraction of dendrites can be calculated by the following equation:

$$f_L = \frac{k_0(T_R - T_S)/\Delta T_0}{1-(1-k_0)(T_R-T_S)/\Delta T_0} \tag{1}$$

where, T_R is the maximum recalescence temperature, T_S is the equilibrium solidus temperature corresponding to the compositions C_S of the central part in the dendrite trunks and ΔT_0 is the equilibrium crystallization temperature interval of the alloy with compositions C_S. Assuming that the solidification in recalescenceis an adiabatic process T_R can be calculated from the law of conservation of mass and energy. It is obvious that with the increase of the initial undercooling, the remelting fraction increases to the maximum value and then decreases. When the undercooling is ΔT (40 K <ΔT < 50 K), the dendrite remelting fraction reaches the maximum value. This indicates that in the range of 40 K <ΔT < 50 K, primary dendrites have the greatest remelting tendency, so for the first grain refinement of undercooled Ni90Cu10 alloy, the dendrite skeleton breakage driven by solid-liquid interfacial tension and chemical overheating caused by dendrite remelting play an important role in grain refinement. With the increase of undercooling, the dendrite remelting fraction decreases gradually, and the effect of dendrite remelting on primary dendrites also decreases gradually.

The model theory of liquid phase flow induced by solidification shrinkage proposed by Liu has been widely accepted to explain the grain refinement under high undercooling. With the increase of initial undercooling, the solidification rate will gradually increase.Therefore, the primary dendrite network formed during the recalescence process will continue to increase, gradually forming a continuous dendrite network in the alloy liquid, and at the same time, the dendrite network begins to have strength and exhibits deformation resistance. It can be clearly seen that the stress in the dendrite skeleton increases with the increase of undercooling. When the accumulated stress in the dendrite is greater than the strength of the dendrite skeleton at the corresponding temperature, the

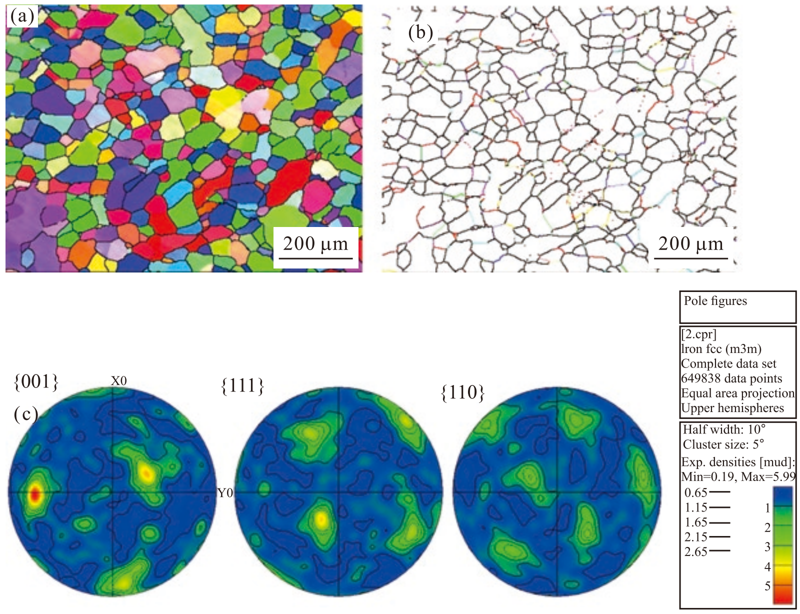

Fig.2 (a) Represent grain boundary orientations of undercooled Ni90Cu10 alloy at 47K; (b) Grain boundaries of (a); (c) The pole figure of (a)

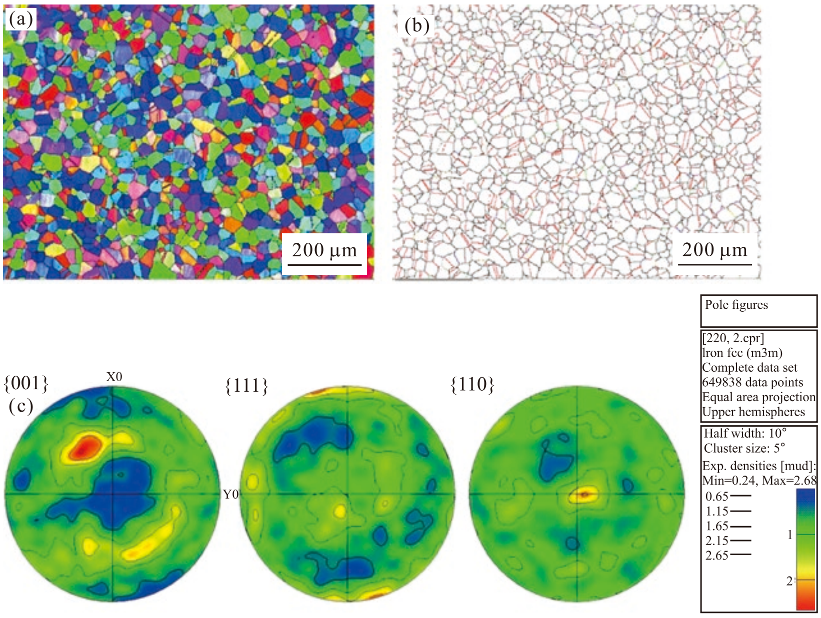

Fig.3 (a) Represent grain boundary orientations of undercooled Ni90Cu10 alloy at 270 K; (b) Grain boundaries of (a); (c) The pole figure of (a) showing a nearly random texture

precipitated dendrite will have stress fragments and plastic deformation, and a large amount of strain energy will be stored in the deformable dendrite fragments, thus making the dendrite fragments in a metastable state, which provides a driving force for the subsequent recovery and recrystallization.

3.2 EBSD characterization of grain refinement structure

In order to better study the mechanism of fine grain refinement under low and high undercooling conditions, the solidification microstructure has been investigated in detail. Therefore, we used EBSD technology to characterize the microstructure of refined grains in more detail. Fig.2 shows EBSD pictures of Ni90Cu10 alloy undercooled by 47 K. It can be clearly seen that the grain structure has smooth grain boundary and wide grain boundary, which indicates that obvious grain coarsening has occurred. We can observe the pole figure Fig.2(b) under 47 K, the microstructure of the inverse pole figure show a random distribution. Fig.3 shows EBSD pictures of a Ni90Cu10 alloy undercooled by 270 K. By comparing

Fig.2(a) and Fig.3(a), it can be clearly seen that under the condition of high undercooling, the grain has a more straight grain boundary, and the grain boundary changes from a small angle boundary to a large angle boundary, which indicate that obvious grain boundary migration has occured during the grain growth process. At the same time, the existence of annealing twins can be seen obviously in the grains, which indicates that recrystallization occurs under the condition of high undercooling.

4 Conclusions

In this paper, the solidification structure of binary single-phase Ni90Cu10 under different undercooling was systematically studied. Through the EBSD test of refined grain structure, there is evidence that recrystallization occurs under the condition of high undercooling, but there is no recrystallization under the condition of small undercooling. The main conclusions of this paper are as follows:

a)Through the analysis of all undercooled samples of Ni90Cu10 alloy, it is found that the microstructure of the alloy has undergone the evolution process of "coarse dendrite - equiaxed crystal - directional fine dendrite - equiaxed crystal", and there are two grain refinement phenomena with significantly smaller grain size.

b)The internal causes of the two grain refinement phenomena are different. The grain refinement under high undercooling is caused by recrystallization, while the grain refinement under small undercooling is caused by dendrite overheating remelting.

c)The average size of grain refinement caused by recrystallization is smaller than that caused by dendrite remelting.

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