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Rapid dendrite growth subjected to multi-solute trapping in an undercooled Fe-based quaternary alloy

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ABSTRACT

The influence of multi-solute trapping on dendrite growth remains unclear yet. In this paper, rapid solidification of Fe-5Ni-5Mo-5Ge (wt.%) alloy was accomplished to investigate (αFe) dendrite growth involving three solutes. The dendrite growth velocity increases sluggishly and then rapidly with the rise of undercooling. Compared with Ni and Mo solutes, Ge solute plays the dominant role on the sluggish dendrite growth within a wide moderate undercooling range. All the solutes promote the rapid dendrite growth at a higher undercooling. The segregationless dendrite growth was achieved due to multi-solute trapping effect at the maximum experimental undercooling.

1. Introduction

Dendrites are the frequently observed structural morphology when the solidification of an alloy is investigated. The free growth of a dendrite from an undercooled melt is one of the most fundamental topics in the field of solidification science [1–4]. In the case of a deeply undercooled alloy melt, rapid dendrite growth is driven by the great difference of the Gibbs free energy between liquid and solid phase. As a result, the dendrite growth velocity is commonly within the range of about 1–100 ms^{-1} [5–8], which gives rise to far deviation from the assumption of local equilibrium. The solute diffusion changes correspondingly. If the solid/liquid interface advances so rapidly that solute partitioning cannot follow, the solute concentration of the growing dendrite is close to that of liquid phase and then solute trapping [9–12] occurs. Therefore, the investigation on rapid dendrite growth under far-from-equilibrium solidification condition should take into account the solute trapping effect.

The research work on rapid dendrite growth has mainly focused on pure metal (or semiconductor), binary alloys and transparent solution in recent decades, i.e. pure Ni, pure Si, Ni–Cu alloy and succinonitrile [13–19]. The dendrite growth velocity is obtained as a function of undercooling by means of experimental measurement or theoretical calculation. Only one or two elements participate solute diffusion during rapid dendrite growth in these materials. However, as for multi-component alloys, the investigation on rapid dendrite growth involving multi-solute trapping is particularly limited so far. Whether multi-solute trapping takes place under extreme non-equilbrium condition is unclear, so does the influence of solute element type and number on dendrite growth. These situations exist especially for Fe-based alloys which are of crucial importance for industrial applications.

In light of this, the objective of our work is to investigate the rapid growth of (αFe) dendrite involving three solutes in undercooled Fe-5Ni-5Mo-5Ge quaternary alloy, in which metallic and semiconducting elements are concerned. For this purpose, the phase constitution and microstructural morphology of the undercooled alloy and dendrite growth in related undercooled binary alloys are also analyzed.

2. Experimental

Fe-5Ni-5Mo-5Ge (wt.%) alloy samples were prepared from pure Fe (99.99%), pure Ni (99.999%), pure Mo (99.99%) and pure Ge (99.999%) in an arc melting furnace. Throughout this paper all compositions are given in wt.%. Each sample had a mass of 1 g.

The alloy was highly undercooled by the glass fluxing method. In this experiment, the alloy melt was solidified rapidly with a slow

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cooling rate [20]. The sample covered with 70%B_2O_3 + 20% $Na_2B_4O_7$ + 10%CaF_2 denucleating agent was placed in an alumina crucible in the vacuum chamber. The vacuum chamber was evacuated to 2×10^{-5} Pa and then backfilled with argon gas. Then the sample was superheated by RF induction heating and cooled by switching off the heating power. During this experiment, the temperature was continuously monitored by a Yunnan-Land NQO8/15C infrared pyrometer and the dendrite growth velocity was measured by an infrared photodiode device.

In comparison, the sample with a low undercooling value of 60 K was achieved in the electromagnetic levitation experiment by triggered nucleation. The sample was containerlessly melted by RF induction heating in the vacuum chamber of an electromagnetic levitation facility, which was evacuated to 10^{-5} Pa and then backfilled with a mixture of He and Ar gases. The solidification of sample was triggered by an outside force from its bottom as soon as the heating power was switched.

After the two experiments, the samples were cross-sectioned, mounted in epoxy, polished and etched. The thermodynamic properties, phase constitution and microstructures of the samples were analyzed by a Netzsch DSC 404C differential scanning calorimeter (DSC), a Rigaku D/max 2500V X-ray diffractometer (XRD), an FEI Sirion 200 scanning electron microscope (SEM), an Oxford INCA 300 electron dispersive spectrometer (EDS) an Oxford electron back-scattered diffraction (EBSD) system, respectively.

3. Results and discussion

3.1. Microstructural characteristics

Liquidus temperature of Fe-5Ni-5Mo-5Ge alloy was determined by DSC analysis due to the lack of thermodynamic parameters for quaternary alloy. Fig. 1(a) is the DSC curve of the alloy, in which the heating-cooling rate remains 10 $Kmin^{-1}$ unchangeably. The liquidus temperature is 1731 K and fusion enthalpy is 116 Jg^{-1}. The occurrence of endothermic peaks and corresponding exothermic peaks on the DSC curve hint that two phase transitions take place and at least two phases form in the process of solidification.

The alloy is undercooled up to 131 K in the DSC experiment. Glass fluxing method is applied in order to obtain higher undercooling, as a result, the undercooling range of 165–433 K ($0.25T_L$) is achieved. A low undercooling of 60 K is obtained in the electromagnetic levitation experiment by triggered nucleation for comparison.

XRD analysis was employed to determine the phase constitution of the undercooled alloys and the result is illustrated in Fig. 1(b). The strongest diffraction peak of the alloy at different undercoolings is identified as the strongest diffraction peak of both (110) αFe and (125) Fe_7Mo_3 phases according to X-ray diffraction powder data files. Because the relative content of αFe phase is remarkably higher than that of Fe_7Mo_3 phase by the following microstructural analysis, the strongest diffraction peak on the XRD pattern mainly reflects the relative content of (αFe) phase. When undercooling increases, only some weak diffraction peaks change, nevertheless, all the diffraction peaks belong to (αFe) and Fe_7Mo_3 phases.

The microstructural morphologies of the alloy at different undercoolings are illustrated in Fig. 2. The solidification of the undercooled alloy melt is a two-staged process. Two phase transitions of L → (αFe) and L → Fe_7Mo_3 take place in succession during the solidification of Fe-5Ni-5Mo-5Ge alloy according to the solidified morphologies, the DSC curve and XRD pattern. At a low undercooling of 60 K, the morphology is characterized by well-branched coarse (αFe) dendrites and interdendritic Fe_7Mo_3 phase (Fig. 2(a) and (b)). As far as (αFe) phase is concerned, a remarkable morphological transition of "coarse dendrite → anomalous grain → fine equiaxed grain" occurs with the increase of undercooling, which is accompanied by a grain refinement effect. A small amount of Fe_7Mo_3 phase distributes at (αFe) grain boundaries within the undercooling range of 60–433 K. The occurrence of the holes and cracks at grain boundaries in the sample undercooled by 433 K (Fig. 2(d)) is due to etching.

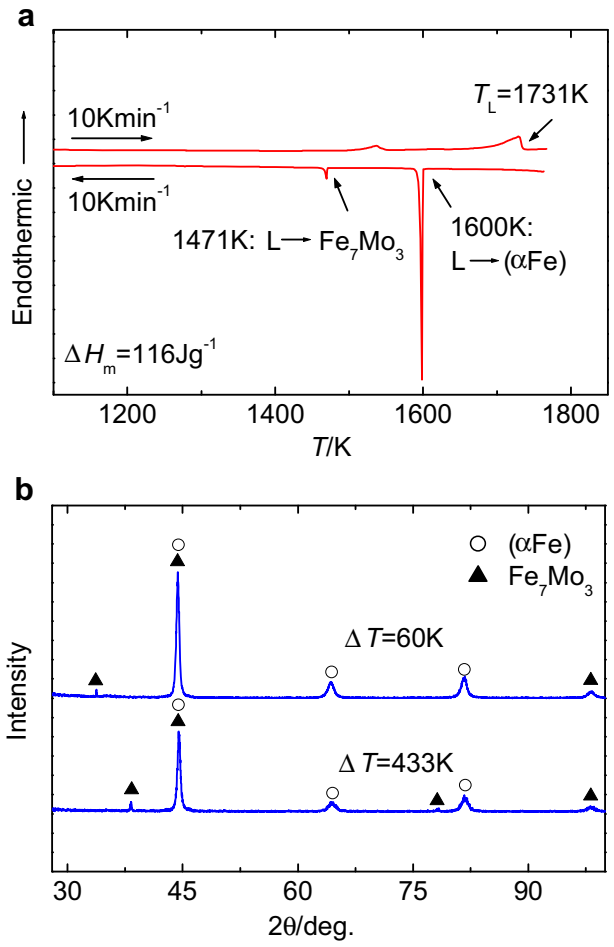

Fig. 1. DSC and XRD analyses for Fe-5Ni-5Mo-5Ge alloy: (a) DSC curve; (b) XRD patterns at different undercoolings.

The microstructural transition from coarse dendrite to fine equiaxed grain in highly undercooled Fe-5Ni-5Mo-5Ge alloy is preferably ascribed to dendrite fragmentation. Different mechanisms have been proposed controversially to explain the transition from coarse dendrite to fine equiaxed grain. An earlier explanation is copious nucleation ahead of the solidification front induced by a pressure pulse due to the collapse of shrinkage cavities [21,22]. In recent decades, prevailing propositions are recrystallization initiated by the stored deformation energy [23–25] and dendrite fragmentation mechanism based on Karma's model [26–29]. In our experiment, the EBSD analysis of equiaxed (αFe) grains in the sample undercooled to 433 K demonstrates that dendrite fragmentation is the main cause for the transition to fine equiaxed grain, the results are shown in Fig. 3. The equiaxed (αFe) grains are oriented to only several scattered poles. The misorientation angle distribution is within a wide range comprised of both low and high misorientation angles. It should be noted that the misorientation angles exhibit sharp peaks at nearly 0° and 5°, indicating the very low misorientation among the remelted dendrite arms. Capillary effect, back-diffusion and fluid flow are considered as the driving force for dendrite fragmentation [28,29].