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Concentration and fluid flow effects on kinetics, dendrite remelting and stress accumulation upon rapid solidification of deeply undercooled alloys

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ABSTRACT

Upon free solidification of a deeply undercooled melt, the solute diffusion in both the interface and the bulk liquid is far from equilibrium, and the concentration and the fluid flow may also play an important role in the solidification. Thus, under such conditions, assumptions about local equilibrium, ideal dilute solution solidification and solidification free of fluid flow can no longer be valid. In the present work, first, in order to reveal the concentration effect, we compared the results of the non-equilibrium dendrite growth models describing the solidification of dilute and non-dilute undercooled melts. It was found that under local non-equilibrium conditions, the predicted results of the non-dilute solution model and the dilute solution model are to a certain extent different from each other at the intermediate undercooling range. It was also found that the concentration effect could substantially decrease the relaxation effect. Second, we considered the effect of fluid flow on the rapid solidification of an undercooled melt. It was found that the fluid flow would affect not only the size of the dendrite tip radius, mainly at the small undercooling range, but also the dendrite growth velocity at the intermediate undercooling range. In particular, fluid flow makes the sizes of the dendrite tip radius at high undercooling close to those predicted by the dilute model. Thus, fluid flow could make the non-dilute solution exhibit dilute solution solidification behaviors. It was also found that fluid flow reduces the relaxation effect to some extent. Considering the fluid flow effect, we used an extended chemical superheating model to predict the dendrite remelting phenomenon of the non-dilute melt. The model predicted that the dendrite remelting phenomenon would abruptly disappear once the dendrite growth velocity exceeded the solute diffusion velocity in a bulk undercooled melt. Third, considering the fluid flow effect, we used the concept of equivalent undercooling and a recently developed physical model to calculate the stress accumulation during rapid solidification. The results of this new model could explain well the stress-induced dendrite breakup mechanism of grain refinement at high undercooling.

1. Introduction

Rapid solidification has been a key subject in the solidification field [1–44]. In the theoretical rapid solidification research, the modeling of dendrite growth has been mainly based on the local equilibrium assumption at the interface and in the bulk liquid phase. Considering local non-equilibrium effects, the authors of reference [44] introduced a relaxation effect and hyperbolic transport into the solute diffusion profile in the bulk undercooled liquid phase. However, this treatment was based on an assumption of an ideal dilute solution (**IDS**), which is obviously not the case for the concentrated solution, i.e., non-ideal non-dilute solution. For example, for the rapid solidification of undercooled concentrated alloys, the ideal dilute solution assumption cannot be valid, and the assumption of a non-ideal non-dilute solution should be applied. Galenko [2] introduced the concentration effect in the solute trapping model. Moreover, fluid flow, which may also play an important role, should also be considered deliberately. Here, we should note that the dilute and non-dilute solution models that used local non-equilibrium conditions are described in the work of

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Sobolev [Sobolev SL. 1995 Phys. Lett. A 199, 383 - solute trapping within the dilute solution model] and Galenko [Galenko PK. 2007 Phys. Rev. E 76, 031606 - solute trapping within the non-dilute solution model], respectively.

An interesting phenomenon (i.e., grain refinement) has been extensively investigated [3–24,36,37] in the rapid solidification of bulk deeply undercooled alloy melts. To elucidate the grain refinement mechanisms, a number of studies have been carried out, and many different grain refinement mechanisms have been suggested such as dynamic nucleation [3], critical growth velocity [7,8], growth instabilities [4–6], dendrite fragmentation [9,11], dendrite remelting and [10,11] recrystallization [9]. Walker [3] was the first to investigate the grain refinement in a rapidly solidified undercooled nickel melt. He observed that the grain size would abruptly refine when the initial bulk undercooling ΔT exceeded a critical value. Thereafter, Powell [7] discovered the existence of a critical undercooling in his investigations of the microstructural evolution of the undercooled Ni-, Cu- and Ag-based alloys. Powell suggested that the recrystallization process during the recalescence and post-recalescence periods should be the origin of the grain refinement at the high undercooling range [7]. A pronounced effect of stress on the grain refinement is a known effect that was discovered and first described by Ovsiyenko [41,42] 60 years ago.

In the present study, we chose a Ni-20 at.%Cu alloy system, which is a nickel-based alloy that has been widely used in industry. The main subject of the present work is the investigation of the effects of the concentration and fluid flow on the kinetics, dendrite remelting and stress accumulation upon rapid solidification of deeply undercooled alloys. First, we experimentally investigated the microstructural evolution of undercooled concentrated Ni-20 at.%Cu alloys as a function of initial undercooling. Second, considering the local non-equilibrium as well as the concentration and fluid flow effects, dendrite growth behaviors were analyzed using a current dendrite growth model. Third, dendrite remelting and solidification stress were explained by an extended chemical superheating model and an extended stress accumulation model, respectively.

2. Materials and methods

Ni-20 at.%Cu (atomic percent) alloy samples each weighing approximately 3 g were prepared by *in situ* by melting pure Ni pieces (99.9% purity) and pure Cu pieces (99.9 wt% purity) under the protection of an argon (Ar) atmosphere in a vacuum chamber. Prior to melting, the surfaces of the metals were cleaned and ground off mechanically to remove the surface oxide layer and then etched chemically in an HCl solution diluted by alcohol. A high-purity quartz crucible containing the Ni-20 at.%Cu alloy specimen was placed in the center of an induction coil. The melting process was conducted in the vacuum chamber. The undercooling experiment was executed by using a fluxing liquid and high-frequency induction heating and thermal cycling under the protection of an argon atmosphere. The vacuum chamber was evacuated and subsequently back-filled with 99.99% argon gas. Each sample was melted, superheated, solidified and subsequently remelted in superheating–cooling cycles to obtain various undercoolings. For each of the alloys, 20–30 undercoolings were made, and the natural cooling rate of 20 K/s is applied in the experiments. After the high-frequency power source was turned off, the alloy sample was spontaneously cooled to room temperature, while the cooling curve of the specimen was monitored by an infrared pyrometer with an accuracy of 5 K and response time of 10 ms. The infrared pyrometer for the described temperature ranges was calibrated using a standard thermocouple. The quenching experiments were well designed such that the Ga-In liquid alloy in the injection apparatus was directly injected onto the highly undercooled melts before rapid solidification. High cooling rates applied in the liquid metal quenching experiment may produce additional stresses in crystallized dendrites. We executed a quenching experiment on the melt with no undercooling and found that there were few dislocations in the as-formed microstructures. Thus, the additional stresses induced by the high cooling rate can be ignored compared to the rapid solidification (of deeply undercooled melt)-induced stress. After the experiment, the solidified specimens were sectioned longitudinally and processed according to standard metallographic procedures. The microstructure observations were performed using a PMG3 Olympus optical microscope, and the average grain sizes of the dendrite length and spherical grain diameter were determined by the linear intercept method. Various microstructures were further intensively studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM, Technai F30 G2 300 kV) to reveal the dense dislocation networks. The TEM specimens were prepared by standard procedures, which will not be given here for brevity.

3. Theory

Due to the progress in experimental methods and theoretical models, the understanding of dendrite growth has been greatly improved recently. It has been found that not only the growth velocity but also the morphology and the size of dendrites are basically influenced by the fluid flow, strongly affecting the heat and mass transfer processes during the solidification [32]. It has been shown that the fluid flow can play a very important and dominant role in the heat and solute transport processes near the migrating interface by altering the local temperature and concentration gradients and thus changing the variation of the solidification front [22,23]. Fluid flow can be produced by different methods, e.g., by a buoyancy force due to thermal and solute gradients (i.e., natural convection), specifically by surface tension gradient (i.e., Marangoni convection) and by external force (i.e., forced convection). Under microgravity, natural convection is weakened to zero gravity and should disappear entirely. However, because surface tension acts at the liquid interface, it causes a surface tension gradient, and the surface tension gradient exceeds the viscous force, causing the liquid to flow, and capillary convection occurs. This phenomenon was discovered by Marangoni in 1865 and is called Marangoni convection. Heat convection capillary convection is a gravity independent natural convection in the liquid with a free surface for which the surface tension gradient is present along the surface of the liquid, ensuring the appearance of the Marangoni convection, which does not need to overcome an activation barrier. The temperature gradient is sufficiently small to begin to flow. The temperature Marangoni convection is caused by a temperature gradient that can be easily controlled to maintain the flow of the liquid; nevertheless, the solute Marangoni convection is often erratic.

The equilibrium phase diagram shows that the molten fraction of a solid alloy that has been heated into the solid-liquid binary phase regime is related to the chemical superheating [11]. Here, due to the non-equilibrium effect involved in the rapid solidification of undercooled melts, it is reasonable to speculate that the non-equilibrium kinetic phase diagram can treat the molten fraction of the solid phase more realistically and practically. Then, an extension of Li's model [11] will give the non-equilibrium chemical superheating model, which can predict the molten fraction of a solid alloy by the following equation:

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