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Influence of solutal convection on solute distribution of melt during preparation of directionally solidified Sn–36 at.%Ni peritectic alloy

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ABSTRACT

Experiments consisting of melting followed by thermal stabilization on Sn–36 at.%Ni peritectic alloy have been carried out in a Bridgman-type furnace. Due to imposed temperature gradient, a mushy zone is created between the complete liquid zone and the non-molten zone. Microstructure evolution and solute distribution in the melt during thermal stabilization have been characterized. As thermal stabilization time increases, the volume fraction of liquid in the mushy zone decreases. A Sn boundary layer which results from evacuation of liquid in the mushy zone is built up at the solid/liquid interface at the initial of thermal stabilization then gradually disappears. A model is proposed to describe this boundary layer which is influenced by solutal convection during thermal stabilization. It is found that solute segregation in the complete liquid zone can be destroyed by solutal convection. This solute boundary layer can lead to further downward migration of the solid/liquid interface during thermal stabilization.

1. Introduction

Preparation of the initial conditions on which the growth of crystals starts, i.e. solid/liquid interface morphology and solute distribution in the melt, is a critical step in directional solidification process. In theory [1], the initial solid/liquid interface is regarded as flat, and the solute concentration in the melt is homogeneous and equals to the initial composition of the sample. In experiments, the initial conditions result from a thermal stabilization stage following the melting under a temperature gradient. Researches on preparation of the initial solid/liquid interface and melt during directional solidification [2–7] show that the condition is quite different from the theoretical model. On the one hand, a mushy zone forms between the non-molten solid zone and the complete liquid zone, resulting in a corrugated initial solid/liquid interface when the thermal stabilization duration is not long enough. On the other hand, solute exchange between the mushy zone and the complete liquid zone takes place during thermal stabilization, resulting in deviation of the composition in the melt from the initial value of the sample. The aforementioned two aspects depend on the resolidification of the liquid in the mushy zone during thermal stabilization, which is governed by melting/resolidification processes by temperature gradient zone melting (TGZM) [2–7] or their interactions.

Solute exchange between the mushy zone and the complete liquid zone changes the solute distribution in the samples. The rejected solute in the liquid at the solid/liquid interface is proposed to lead to back-melting of this interface and build-up of a solute boundary layer which in practice leads to melt segregation in the complete liquid zone [2,3]. It has also been shown that duration of this boundary layer is determined by both evacuation of liquid in the mushy zone and the solutal convection in the complete liquid zone. If the rejected solute is denser than the solvent, as in Al–1.5 wt.%Ni alloy [2,3], the solutal convection cannot be induced. Conversely, as in Al–3.5 wt.%Li alloy [2], fluid flow induced by solutal convection will mix the bulk liquid on ground, resulting in homogeneous solute concentration in the complete liquid zone. Hence, the knowledge of the effect of solutal convection on this solute boundary layer which has been investigated in the regime of both pure diffusion [2] and solutal convection [2,3] is critical to understand preparation of the initial conditions. However, this effect has not been discussed when the difference in density between the solute and solvent is not so significant, such as Sn–Ni peritectic alloy. Thus, precise description of this solute boundary layer and its influence on solid/liquid interface is necessary.

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In the present work, experiments consisting of melting and thermal stabilization ranging from 0 to 6 h under a constant temperature gradient have been performed on Sn–36 at.%Ni peritectic alloy. First, microstructure evolution in the mushy zone and the solute concentration in the melt have been characterized. Second, the description of the solute boundary layer and influence of solutal convection on it during thermal stabilization in Sn–Ni peritectic alloys has been carried out using a boundary-layer model. Finally, effect of this solute boundary layer on migration of the initial solid/liquid interface during thermal stabilization has been discussed.

2. Experiments

Sn–36 at.%Ni alloy was induction melted from pure Ni and Sn (99.9%). As-cast rods of 3 mm in diameter and 110 mm in length were cut from the ingot. Experiments consisting of melting followed by thermal stabilization for different periods of time ranging from 0 to 6 h were carried out in a Bridgman-type furnace. As-cast rod was placed into a high purity Al_2O_3 tube, and 10 mm of the rod was immersed into liquid Ga–In–Sn to preserve its original microstructure. For each experiment, after the temperature of the furnace was raised to 1230 °C, the rod was submitted to thermal stabilization with different time (0–6 h). Subsequently, the tube was quickly dropped into liquid Ga–In–Sn alloy to preserve its microstructure. Temperature profiles were measured using R-type thermocouples inserted within a fine alumina tube (0.6 mm in inner diameter) near the outside surface of the Al_2O_3 tube, and the temperature gradient was deduced from the temperature profiles. The average temperature gradient in the mushy zone is 40 °C /mm.

The microstructure of the longitudinal section of rods was analyzed by optical microscopy (OM) and scanning electron microscopy (SEM (Quanta-200)). Energy dispersive X-ray spectrometers (EDS) was applied to determine composition of phases in the Sn–36 at.%Ni peritectic alloy. In addition, energy dispersive spectrometer (EDS) was also employed to analyze the concentration distribution in the samples. The points were measured with a distance of 52 μm between two adjacent points, each point was measured for 2000 ms to achieve an acceptable statistics.

3. Results and discussion

3.1. As-cast microstructure of Sn–36 at.%Ni alloy

The relevant part of Sn–Ni phase diagram published by Schmetterer et al. [8] is shown in Fig. 1(a). It is originated from the phase diagram obtained by Nash and Nash [9] but modified in some respects according to many experimental studies and thermodynamic calculations on Sn–Ni alloys in the past two decades. The initial alloy concentration in the present study is shown as the solid line. Under equilibrium solidification, the Sn–36 at.%Ni alloy undergoes three reactions as follows:

(1) $T_L = 1040$ °C: $L \rightarrow Ni_3Sn_2$;
(2) $T_P = 798$ °C: $L + Ni_3Sn_2 \rightarrow Ni_3Sn_4$;
(3) $T_E = 231.15$ °C, $L \rightarrow Ni_3Sn_4 + Sn$.

Where T_L, T_P, T_E correspond to the liquidus, the peritectic and the eutectic temperatures. It can be observed from Fig. 1(b) that as-cast microstructure of Sn–36 at.%Ni alloy is composed of three phases. The composition of three different phases A, B and C determined through EDS are 45.22, 56.73 and 99.02 at.%Sn, respectively. Fig. 2 illustrates the optical morphology of as-cast microstructure of Sn–36 at.%Ni alloy. Thus it can be concluded that the black phase in Fig. 1(b) (dark gray phase in Fig. 2) represents the primary Ni_3Sn_2 phase, the gray phase in Fig. 1(b) (white phase in Fig. 2) represents the peritectic Ni_3Sn_4 phase and the white phase in Fig. 1(b) (light gray phase in Fig. 2) represents the eutectic (Ni_3Sn_4 + Sn).

3.2. Formation of the mushy zone and its microstructure evolution during thermal stabilization

When Sn–36 at.%Ni alloy rod is melted in a Bridgman-type furnace, a vertical temperature gradient is imposed on the rod. According to the equilibrium phase diagram (shown in Fig. 1), four different zones corresponding to different temperature ranges are created due to this vertical temperature gradient. As shown in Fig. 3, a mushy zone consisting of two sections is observed between the complete liquid zone and the non-molten solid zone. Three interfaces are observed and they correspond to T_E, T_P and T_L from the bottom to the top of the mushy zone. As the thermal stabilization time increases, the microstructure of the mushy zone changes in several respects. The initial solid/liquid interface changes from corrugated to flat and moves downward to lower positions while the peritectic interface and eutectic interface remain invariant. The volume fraction of liquid in the mushy zone decreases. In parallel, orientation arrangement of Ni_3Sn_2/Ni_3Sn_4 grains along the direction of vertical temperature gradient can also be observed.

The microstructure evolution of the mushy zone during thermal stabilization can be explained by the TGZM theory [10] which has been applied to describe a migration phenomenon of liquid droplet or channel through the solid in researches [11–16]. When a

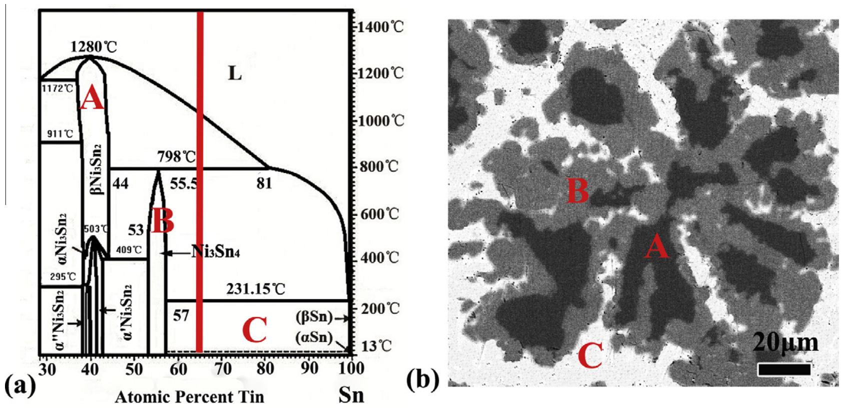

Fig. 1. The solidification path and microstructure of Sn–36 at.%Ni peritectic alloy: (a) the relevant part of Sn–Ni binary phase diagram [8], and (b) the BSE image of the phases of the microstructure: A. primary Ni_3Sn_2 phase, B. peritectic Ni_3Sn_4 phase, C. eutectic (Ni_3Sn_4 + Sn).