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Grain refinement and coarsening in hypercooled solidification of eutectic alloy

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ABSTRACT

Applying glass fluxing combined with thermal cycle, hypercooled solidification was achieved for $Ni_{78.6}Si_{21.4}$ and $Fe_{83}B_{17}$ eutectic alloys, thus giving grain refinement and coarsening, respectively, in the as-solidified morphologies. Based on the theoretical analysis in terms of classical nucleation theory (CNT), the above phenomenon can be ascribed to the effect of increased or decreased nucleation rate under hypercooled condition.

1. Introduction

For a liquid metal or alloy subjected to sufficiently high undercooling (ΔT), the enthalpy of the liquid is reduced to a level equivalent to that of the solid phase at the melting temperature, and a hypercooled solidification results. The isenthalpic temperature marks an upper limit of hypercooling, i.e., the temperature after recalescence cannot reach the solidus and the entire liquid can be solidified rapidly within the adiabatic recalescence. Theoretically, the hypercooling for pure metal and alloy can be given as $\Delta T_{hyp} = \Delta H_m/C_p + (T_L - T_S)$ [1], with ΔH_m as the enthalpy of fusion, C_p the specific heat of liquid, T_L and T_S the equilibrium liquidus and solidus, respectively. So far, hypercooled solidification has been achieved for pure metals such as Ni [2], Fe [3] and Mo [4] and some alloys such as Ti–Al [1], Co–Pd [5], etc. Recently, Willnecker et al. [5] observed hypercooled solidification in a completely miscible Co–Pd alloy which has concavous liquidus and solidus lines due to their reduced melting enthalpies. It was found that, subjected to ΔT_{hyp}, a dendritic morphology was obtained and grain refinement due to fragmentation vanished. In the hypercooled Ti–Al alloy samples, Liu et al. [1] observed a fine microstructure with improved strength and hardness. However, the forming mechanism for the hypercooled microstructure was not thoroughly interpreted. In the present letter, grain refinement and coarsening, in $Ni_{78.6}Si_{21.4}$ and $Fe_{83}B_{17}$ eutectic melt after ΔT_{hyp}, will be described and interpreted, using calculations of the classical nucleation theory (CNT).

2. Experimental procedure

The experiment was conducted in a high-frequency induction facility, where high-purity elements of Ni (Fe) and Si (B) were alloyed in situ to form 5 g eutectic $Ni_{78.6}Si_{21.4}$ ($Fe_{83}B_{17}$) samples. Glass fluxing was adopted to purify the alloy melt. Once a desired ΔT was achieved by cyclic superheating, primary solidification was initiated by manual triggering, and then the remaining melt cooled down naturally. The cooling curve was recorded using a two-color infrared pyrometer and calibrated with a standard $PtRh_{30}$–$PtRh_6$ thermal couple, which was encapsulated in a silica tube and then immersed into the melt in the identical condition. PMG3 Olympus optical microscope, JSM-6460 (SEM) techniques were adopted to investigate the microstructure.

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3. Results and discussion

3.1. Microstructure evolution with undercooling

The as-solidified morphology of $Ni_{78.6}Si_{21.4}$ alloy melt with $\Delta T = 9$ K is shown in Fig. 1a, where a lamellar eutectic prevails. With increasing ΔT, a complicated structure evolution was observed [6], where a fine dendritic colony (Fig. 1b) changes into a fine anomalous eutectic (Fig. 1c), and then a superfine anomalous eutectic (Fig. 1d), which is formed due to a substantial grain refinement. Analogously, a lamellar eutectic prevails in the as-solidified morphology of $Fe_{83}B_{17}$ alloy with $\Delta T = 5$ K (Fig. 2a). Both Figs. 1a and 2a can be ascribed to a coupled growth of eutectic phases, i.e. Ni_3Si and α-Ni [6], Fe_2B and Fe [7]. With increasing ΔT, the coupled growth is broken, and the above lamellar eutectic is substituted by a typical hypereutectic, i.e., a primary phase Fe_2B and a eutectic Fe_2B/Fe (Fig. 2b). For a sufficiently high ΔT, the above hypereutectic is replaced by an anomalous eutectic, where Fe_2B solidifies as the leading phase, and then α-Fe forms within the as-formed Fe_2B skeleton (Fig. 2c). As ΔT increases further to above ΔT_{hyp} ($\Delta H_f(Fe_3B)/C_p = 356.8$ K), a transition from Fe_2B/Fe eutectic to Fe_3B/Fe eutectic (Fig. 2d and e) takes place. This is consistent with the theoretical calculation for phase competition between the metastable Fe_3B and the stable Fe_2B [7]. In contrast to Fig. 1d, however, an obvious grain coarsening is observed, accompanied with the occurrence of Fe_3B (Fig. 2d and e).

Fig. 3 illustrates the corresponding recalescence curves for $Fe_{83}B_{17}$ alloy, which is compatible with the above microstructure evolution. Particularly, for $\Delta T > \Delta T_{hyp}$, the temperature after recalescence is much lower than the solidus and the entire liquid transforms into solid within recalescence, i.e., the original microstructure formed adiabatically during recalescence can be retained due to the disappearance of remelting after recalescence, as compatible with Ref. [5]. In combination with the forming mechanism for anomalous eutectic, the final grain size is determined by the nucleation rate of Fe_3B in the hypercooled solidification.

3.2. Nucleation kinetic in hypercooled melt

The following equation gives a description for heterogeneous nucleation rate [8]:

$$I = \frac{k_B T N_n}{3\eta(T) a_0^3} \exp\left[-\frac{\Delta G^* f(\theta)}{k_B T}\right] \quad (1)$$

where k_B is the Boltzmann constant, a_0 the interatomic spacing, $f(\theta)$ the catalytic factor, $\eta(T)$ the temperature-dependent viscosity of the undercooled melt ($\eta(T) = 10^{-3.3}\exp[3.34T_e/(T-T_g)]$ with $T_g = 0.25 \times [(1-C_0)T_{Am} + C_0 T_{Bm}]$ as the glass transformation temperature), T the nucleation temperature, ΔG^* ($= 16\pi\sigma^3 \Delta H_f T_L^2 / 3(T_L - T)^2$) the critical nucleation work, and σ ($= \alpha \Delta S_f T/(N_A V_m^2)^{1/3}$) the interfacial free energy, which can be given by the negentropic model developed by Spaepen and Meyer [9]. In the case of heterogeneous nucleation, the potential nucleation sites N_n, should decrease with progressing purification [6], but the effect of N_n on the nucleation rate is negligible as compared with that of ΔG^* at sufficiently high ΔT. Here, N_n is reasonably assumed as equal to $10^{-10} N_A$ (N_A is Avogadro's constant) [10].

Using Eq. (1) and the physical parameters listed in Table 1, the heterogeneous nucleation rate as a function of ΔT for $Ni_{78.6}Si_{21.4}$ and $Fe_{83}B_{17}$ eutectic alloys was calculated (Fig. 4a). For $Fe_{83}B_{17}$ alloy, the maximal nucleation rate is achieved at $\Delta T = 327$ K, which corresponds to an experimental observation where the minimal grain size occurs at $\Delta T \approx 341$ K (Fig. 2c). With increasing ΔT, the nucleation rate descends substantially. This, in combination with Fig. 3, explains why the grain size (after ΔT_{hyp}) increases with ΔT (Fig. 2c–e). As for $Ni_{78.6}Si_{21.4}$ alloy, the maximal nucleation rate occurs at $\Delta T = 608$ K, which is larger than ΔT_{hyp} ($\Delta H_f(\alpha\text{-Ni})/C_p = 513.8$ K). Accordingly, the nucleation rate at $\Delta T \approx 550$ K (Fig. 1d) is not equal to, but very close to, its maximal value (Fig. 4a). As compared to grain coarsening in

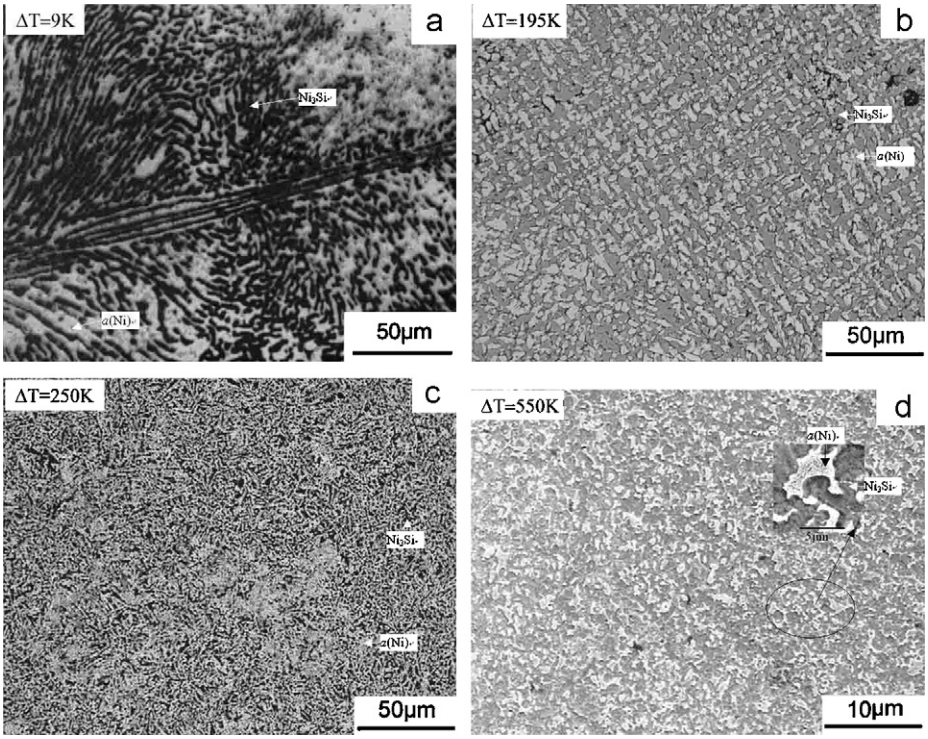

Fig. 1. Microstructural evolution of $Ni_{78.6}Si_{21.4}$ eutectic alloy solidified at different undercoolings: (a) $\Delta T = 9$ K, (b) $\Delta T = 195$ K, (c) $\Delta T = 250$ K, (d) $\Delta T = 550$ K.