Article

Primary dendrite growth of Ni$_3$Sn intermetallic compound during rapid solidification of undercooled Ni-Sn-Ge alloy

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Liquid Ni-31.7%Sn-2.5%Ge alloy was highly undercooled by up to 238 K (0.17T_L) with glass fluxing and drop tube techniques. The dendritic growth velocity of primary Ni$_3$Sn compound shows a power-law relation to undercooling and achieves a maximum velocity of 380 mm/s. The addition of Ge reduces its growth velocity as compared with the binary Ni$_{75}$Sn$_{25}$ alloy. A structural transition from coarse dendrites into equiaxed grains occurs once undercooling exceeds a critical value of about 125 K, which is accompanied by both grain refinement and solute trapping. The Ni$_3$Sn intermetallic compound behaves like a normal solid solution phase showing nonfaceted growth during rapid solidification.

Intermetallic compounds have developed into an important category of structural materials with potential high temperature applications. Since their microstructural morphology and solute distribution are intrinsically correlated with mechanical properties, extensive work has been done on the directional and rapid solidification processes of intermetallic alloy [1–6]. However, most previous investigations were concentrated on the microstructural evolution at small undercooling condition. If an intermetallic compound nucleates and grows from a highly undercooled alloy melt, its formation mechanism will display novel kinetic characteristics because of the extremely nonequilibrium thermodynamic state. During conventional solidification, the heterogeneous nucleation caused by the crucible or mold walls prevents liquid alloys from achieving large undercoolings. Fortunately, glass fluxing [5] method and drop tube processing [1] provide an effective way to eliminate heterogeneous nuclei and subsequently undercool liquid alloys to a great extent.

The Ni$_3$Sn intermetallic compound has attracted much attention in research because it shows an anomalous increase in yield stress with rising temperature like the Ni$_3$Al alloy [2,7–9]. The Ni$_3$Sn intermetallic compound has a cubic BiF$_3$-type(DO$_3$) crystalline structure above 1193.5 K and transforms into an ordered hexagonal Mg$_3$Cd-type (DO$_{19}$) structure at lower temperatures. Meanwhile, Ni$_3$Sn-based alloys usually exhibit satisfactory undercoolability to realize bulk rapid solidification. The objective of this paper is to investigate the dendritic growth mechanism and solute trapping effect of the Ni$_3$Sn intermetallic compound during the rapid solidification of the highly undercooled ternary Ni-Sn-Ge alloy. Both glass fluxing and drop tube techniques have been applied to achieve high undercoolings.

1   Experimental procedure

The Ni-31.7%Sn-2.5%Ge alloy was prepared from high purity elements of 99.99%Ni, 99.999%Sn and 99.99%Ge by an in situ alloying procedure. The sample had a mass of 1 g and was contained in an alumina crucible with a size of 8 mm ID×10 mm OD×12 mm together with a suitable amount of 70%B$_2$O$_3$+20%Na$_2$B$_4$O$_7$ +10%CaF$_2$ fluxing agent. The vacuum chamber was evacuated to 2×10^{-4} Pa and then

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backfilled with Argon gas to a pressure of 10^5 Pa. The sample was melted by radio frequency induction heating and was superheated to 200–400 K above its liquidus temperature for several minutes. Afterwards, the sample was cooled naturally by switching off the heating power. The heating and cooling processes were monitored by an infrared pyrometer, while the dendrite growth velocity was measured by an infrared photodiode device [5].

As an alternative approach to achieve rapid solidification, the bulk alloy melt was atomized into a series of tiny droplets with diameters from 81 to 1290 μm. These alloy droplets fell freely inside a 3 m drop tube [1] and were solidified in a container-less state. After the experiments, the solidified samples were sectioned, polished, and then etched with a solution of 1 g $CuSO_4$+40 mL HNO_3+75 mL H_2O for 5 s. Their solidification microstructures were analyzed by an FEI Sirion 200 Scanning Electron Microscope, a Rigaku D/max 2500 X-ray Diffractometer, and an INCA Energy 300 Energy Dispersive Spectrometer. In addition, the liquidus temperature and latent heat were measured with a TA SDT-Q600 differential scanning calorimeter.

2   Results and discussion

2.1   Rapid growth of Ni_3Sn compound within bulk undercooled alloy

The differential scanning calorimetry heating and cooling curves of ternary Ni-31.7%Sn-2.5%Ge alloy are shown in Figure 1(a). The liquidus temperature T_L of the Ni-31.7% Sn-2.5%Ge alloy was determined to be 1429 K, while its melting enthalpy was measured as 100.56 J/g. The first phase transition during solidification corresponds to the formation of the primary phase, L→Ni_3Sn (HT) at 1396 K. This is immediately followed by the eutectic transition, L→ (Ni)+ Ni_3Sn, which takes place at 1389 K. When the temperature further decreases to 1062 K, the eutectoid transition occurs, i.e., Ni_3Sn (HT)→(Ni)+ Ni_3Sn (LT). The X-ray diffraction results are illustrated in Figure 1(b). The samples of small and large undercoolings are all composed of the

Ni_3Sn intermetallic compound and the (Ni) solid solution phase.

The microstructures and grain size of the primary Ni_3Sn compound at different undercoolings are presented in Figures 2 and 3(a), respectively. At the small undercooling of 76 K, the primary Ni_3Sn compound grew into very coarse and well-developed dendrites. Its grain size was found to be as long as 1.91 mm. When the alloy undercooling attains a critical value of about ΔT^*=125 K, the thermal recalescence effect brings about a structural transition from coarse dendrites into equiaxed grains, so that the grain size decreases to 0.42 mm. At the largest undercooling of 190 K, the grain size is reduced to only 41 μm, which is about 46.6 times finer than the case of 76 K undercooling. Figure 3(b) demonstrates the relationship between the volume fraction of the primary Ni_3Sn phase and undercoolings. It indicates that the volume fraction of the primary Ni_3Sn phase decreases firstly and then increases with undercooling. The primary Ni_3Sn phase occupies 67% volume in the solidified structures when undercooling is 76 K. With the increase of undercooling, the volume fraction of the primary Ni_3Sn phase reduces to 60% at the critical undercooling of ΔT^*= 125 K. Subsequently, the volume fraction of the primary Ni_3Sn phase increases slightly and attains 63% at the largest undercooling of 190 K.

The interdendritic spacings are always filled with lamellar (Ni+Ni_3Sn) eutectic structures, which are shown in Figure 4. At 76 K undercooling, the eutectic (Ni+Ni_3Sn) structures display a lamellar spacing range of 1.3–3.3 μm, as shown in Figure 4(a). With the increase of undercooling, the eutectic structures become refined to some extent and their interlamellar spacings vary from 0.9 to 2.5 μm. There are many feather-like (Ni+Ni_3Sn) eutectic structures originating from the primary Ni_3Sn phase at the largest undercooling of 190 K, which is demonstrated in Figure 4(b).

Most intermetallic compounds usually grow in a faceted way, if their Jackson factor [10,11] $\alpha = \Delta S_f/R$ is larger than 2, where ΔS_f and R represent the formation entropy and gas constant, respectively. According to the differential scanning calorimetry results of Figure 1 and the work of
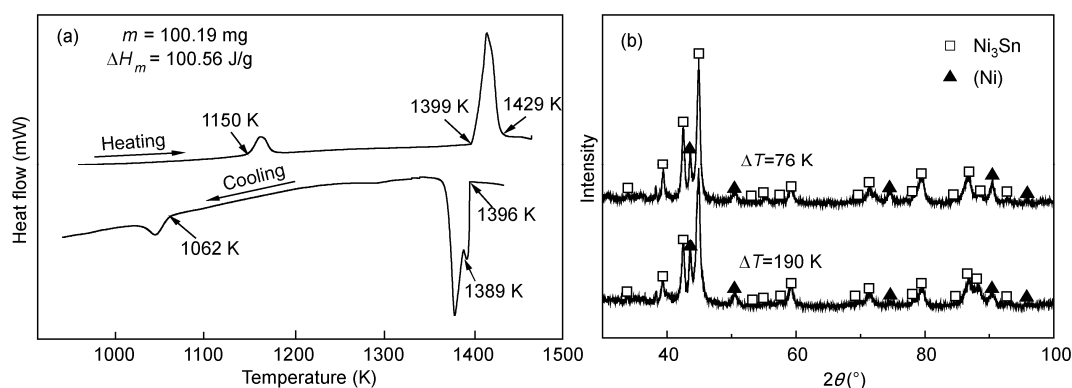

Figure 1   Differential scanning calorimetry thermal analysis (a) and X-ray diffraction spectra (b) of ternary Ni-31.7%Sn-2.5%Ge alloy.
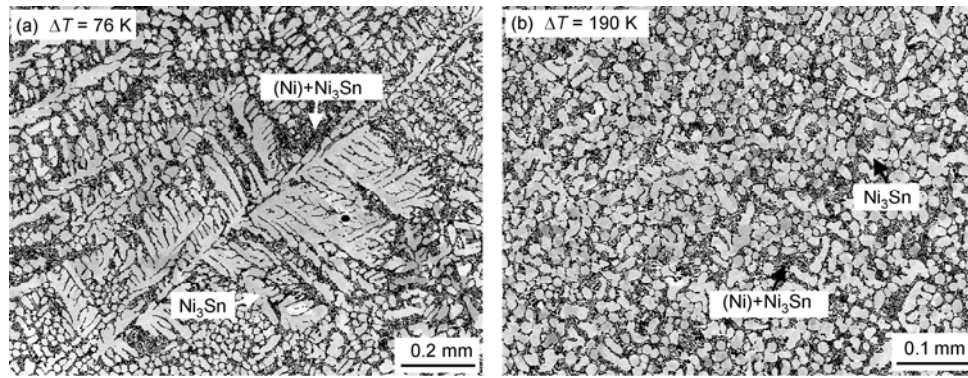
Figure 2   Typical microstructures of the primary Ni$_3$Sn intermetallic compound at different undercoolings (a) ΔT=76 K, (b) ΔT=190 K.
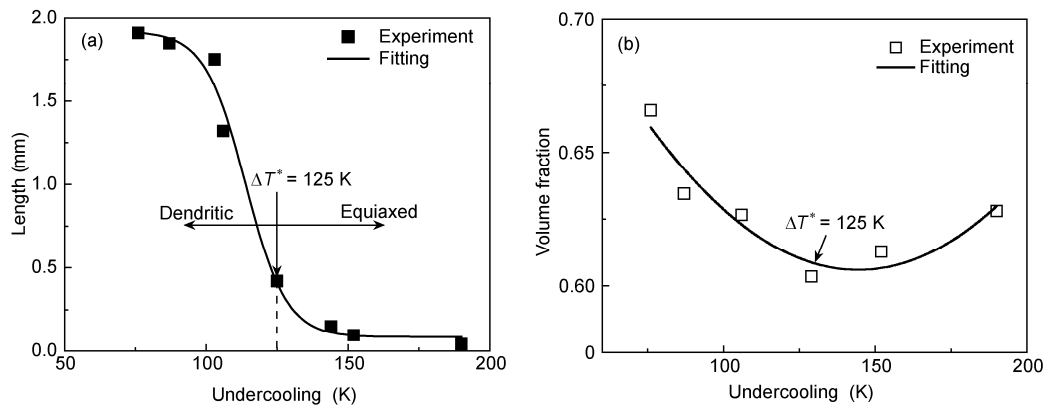

Figure 3   Grain size and volume fraction of the primary Ni$_3$Sn phase versus undercooling. (a) Grain size, and (b) volume fraction.
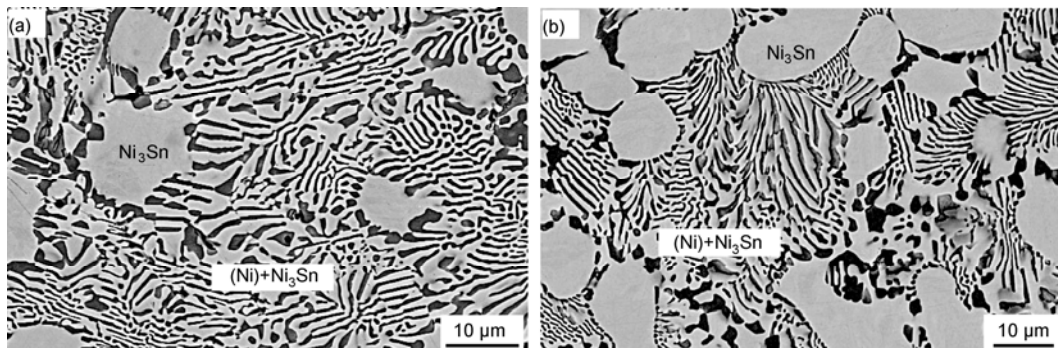

Figure 4   Eutectic microstructures within the interdendritic spacings of the primary Ni$_3$Sn compound at different undercoolings. (a) ΔT=76 K, and (b) ΔT=190 K.

Vassilev et al. [12], the Jackson factor of the primary Ni$_3$Sn phase in the Ni-31.7%Sn-2.5%Ge ternary alloy is estimated to be α = 1.76<2, which predicts nonfaceted growth. This assumption is confirmed by the microstructures of the primary Ni$_3$Sn compound shown in Figure 2. The primary Ni$_3$Sn compound has grown dendritically just as a normal solid solution phase under various undercoolings.

In order to explore the kinetic mechanism of rapid dendritic growth, the growth velocity of the primary Ni$_3$Sn compound was measured as a function of undercooling. The results are presented in Figure 5(a). Clearly, the growth ve-

locity of the primary Ni$_3$Sn compound increases continuously with the rise of undercooling. At the small undercooling of 27 K, the growth velocity is merely 2.5 mm/s. As the alloy undercooling increases to 190 K, the primary Ni$_3$Sn dendrite achieves a velocity of 380 mm/s. A power-law relation is derived from fitting the dendrite growth velocity V versus the bulk undercooling ΔT:

$$V=3.22\times10^{-9}\Delta T^{4.88} . \qquad (1)$$

As a comparison, the dendritic growth velocity of the primary Ni$_3$Sn compound in the undercooled ternary

Ni-31.7%Sn-2.5%Ge alloy is found to be much slower than that in binary Ni$_{75}$Sn$_{25}$ alloy[13] at the same undercooling level. For example, the growth velocity of the Ni$_3$Sn compound in the binary Ni$_{75}$Sn$_{25}$ alloy attained 1.76 m/s at 190 K undercooling, which is 4.6 times faster than in the ternary alloy at the same undercooling. This indicates that the introduction of Ge has obviously reduced the growth velocity of the Ni$_3$Sn compound.

Energy dispersive spectrometry analyses revealed that the actual solute content in the center of the primary Ni$_3$Sn phase is 2.41–2.62 wt% Ge, which displays only a slight increase with the rise of undercooling, as shown in Figure 5(b). At the small undercooling of 76 K, the maximum and minimum Ge contents are 2.41 and 1.89 wt%, respectively. As the undercooling increases to 190 K, the maximum and minimum concentrations of Ge become 2.55 and 2.01 wt%, respectively. Furthermore, the solubility of Ge is just 2.5 wt% at 125 K undercooling, which indicates that this critical undercooling has a significant influence on both the structure morphology and solute distribution.

2.2 Rapid growth of Ni$_3$Sn compound under free fall condition

The advantage of rapid solidification under free fall condition in a drop tube is that it combines high undercooling with rapid cooling and reduced gravity. Figure 6 illustrates the microstructures of the primary Ni$_3$Sn compound formed during the container-less rapid solidification inside a drop tube. When the alloy droplet diameter D is larger than 300 μm, the solidification structure is characterized by coarse and well-developed primary Ni$_3$Sn dendrites. The lamellar (Ni+Ni$_3$Sn) eutectic microstructures grow among the interdendritic spacings of the primary Ni$_3$Sn compound. For those small alloy droplets with diameter $D<300$ μm, the primary Ni$_3$Sn compound is refined significantly, and their microstructures consist of fragmented dendrites and equiaxed grains. Apparently, a conspicuous "coarse dendrite-

equiaxed grain" transition occurs with the decrease of droplet diameter.

Because it is very difficult to measure the actual undercooling and cooling rate of tiny droplets during free fall inside a drop tube, theoretical estimations are performed by the analytical models of Lee et al. [14] and Grant et al. [15]. Figure 6(c) gives the calculated relationship between the undercooling ΔT and cooling rate V_c versus droplet diameter D. Evidently, the undercooling and cooling rate both increase as the size of droplets reduces. For the largest droplet with diameter D=1290 μm, the undercooling ΔT=17 K, and the cooling rate V_c=6.75×10^2 K/s. When the droplet diameter decreases to the minimum D=81 μm, the undercooling increases to ΔT=238 K (0.17T_L), and the cooling rate attains V_c=8.91× 10^4 K/s. In fact, the calculated results of Figure 6 demonstrates that the microstructural transition of the primary Ni$_3$Sn compound in the alloy droplets is essentially consistent with that in the bulk undercooled alloy shown in Figure 2.

Energy dispersive spectrometry analyses are also carried out for various alloy droplets solidified inside the drop tube. As shown in Figure 6(d), the solubility of Ge at the centers of the dendrite trunks and equiaxed grains increases slowly with the reduction of droplet size. However, completely segregation-less dendrite growth of primary Ni$_3$Sn compound has not been achieved even for the smallest alloy droplet. It should also be mentioned that the microgravity effect during free fall has not shown an apparent influence on the dendritic growth process of the primary Ni$_3$Sn intermetallic compound.

4 Conclusions

In summary, bulk samples and small droplets of liquid Ni-31.7%Sn-2.5%Ge ternary alloy are successfully undercooled by up to 190 K(0.13T_L) and 238 K(0.17T_L) respectively. The primary Ni$_3$Sn intermetallic compound behaves
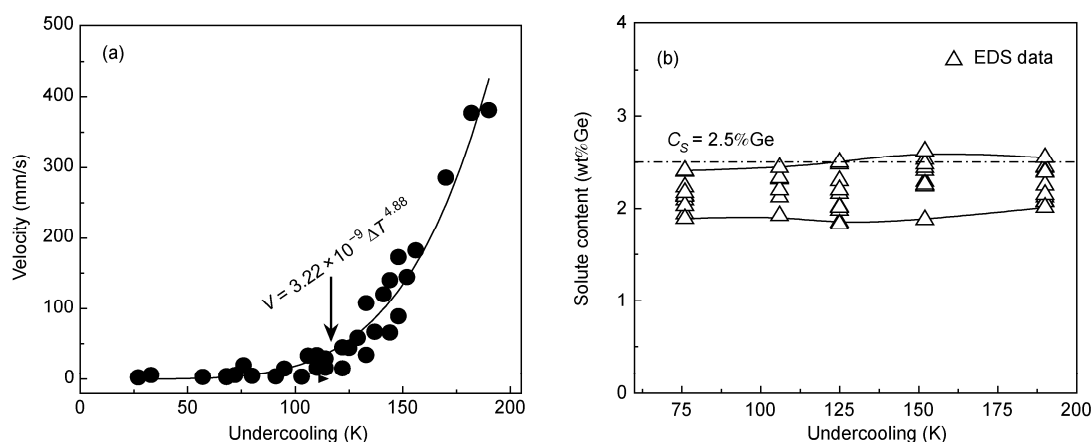

Figure 5 Dendritic growth velocity and solute content of the primary Ni$_3$Sn compound versus undercooling. (a) Dendritic growth velocity, and (b) Ge content in the dendrite.
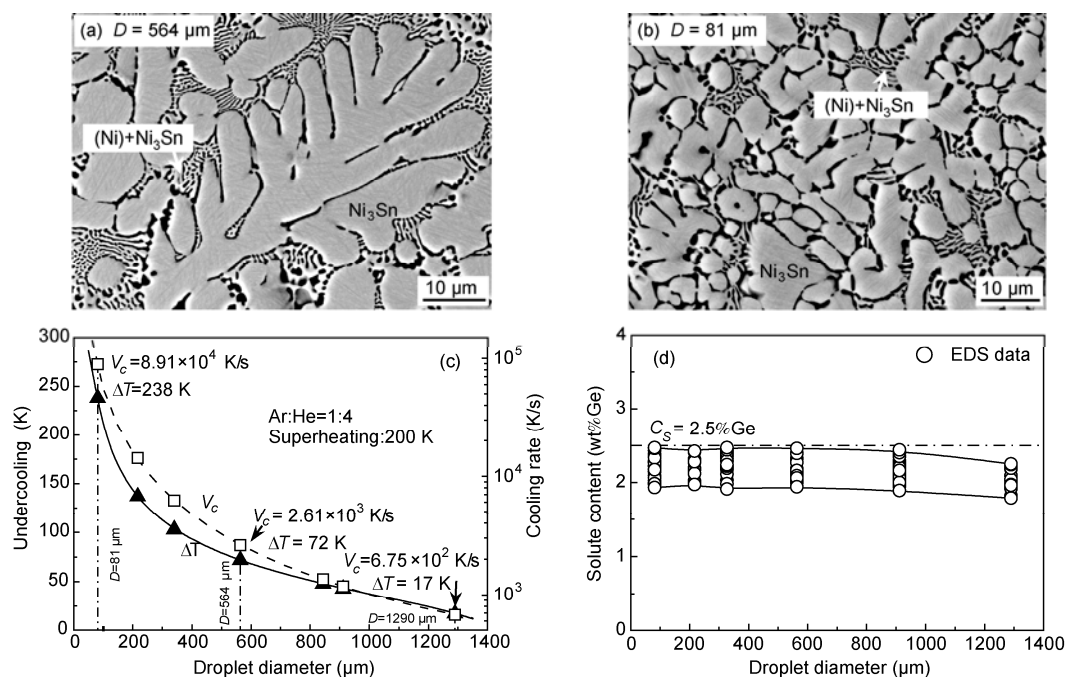
Figure 6   Solidification microstructures and process parameters versus alloy droplet diameter. (a) and (b) microstructures corresponding to *D*=564 μm and *D*=81 μm, (c) calculated undercooling and cooling rate, and (d) Ge content in the dendrite.

just like a normal solid solution phase showing nonfaceted growth. The microstructures of the primary Ni_3Sn intermetallic compound transform from coarse dendrites into equiaxed grains with the rise of undercooling and the decrease of droplet diameter. This is accompanied by a conspicuous grain refinement effect at the critical undercooling of approximately 125 K. The dendritic growth velocity of the primary Ni_3Sn intermetallic compound increases with undercooling by a power-law relation and actually achieves 380 mm/s. As compared with the binary $Ni_{75}Sn_{25}$ alloy, the introduction of Ge has significantly reduced its dendritic growth velocity. The energy dispersive spectrometry analyses of solute distribution reveal that solute trapping of Ge atoms occurs at high undercoolings. Nevertheless, microsegregation still exists even though the droplet undercooling and cooling rate are as high as 238 K and 8.91×10^4 K/s, respectively, under free fall condition.

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