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Directional solidification of Ni–Ni_3Si eutectic *in situ* composites by electron beam floating zone melting

Chunjuan Cui [a,*], Jun Zhang [b], Kun Wu [a], Dening Zou [a], Youping Ma [a], Lin Liu [b], Hengzhi Fu [b]

[a] *School of Metallurgical Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China*
[b] *State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China*

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ABSTRACT

Combining the intermetallic compound with the ductile metal at the eutectic composition is one promising method to improve the ductility of the intermetallic compound. This paper reports the microstructure and the micro-hardness of the Ni–Ni_3Si eutectic *in situ* composites prepared by electron beam floating zone melting technique. Ni–Ni_3Si eutectic *in situ* composites display regular lamellar eutectic structure at the solidification rate $R=0.3$–4.0 mm/min. The lamellar spacing is decreased with the increase of the solidification rate. The phase composition of the Ni–Ni_3Si eutectic *in situ* composites is also determined by X-ray diffraction. Ni–Ni_3Si eutectic *in situ* composites present lower micro-hardness than pure Ni_3Si, although a small quantity of metastable $Ni_{31}Si_{12}$ phase is formed during the directional solidification process.

1. Introduction

Intermetallics possess higher melting temperatures than the superalloys, and with metallic bonding, at least the possibility of better toughness than ceramics. Therefore, intermetallics have been paid more attentions. Ni_3Si-based alloy has been considered to be a candidate material, which can be used as the basis of high-temperature structural materials and chemical parts because Ni_3Si displays an increasing strength with increasing temperatures [1] and also shows excellent oxidation and corrosion resistance over a wide range of temperatures [2–4]. However, the major obstacles for the use of Ni_3Si compound are its poor ductility at ambient temperatures and its bad fabricability at high temperatures [5,6]. Much work has been done to improve the ductility of the Ni_3Si compound, for example, disordering treatment [7], alloying [1,8–10], grain refinement [11], etc.

The incorporation of a ductile phase into the intermetallic materials is an attractive method to improve the ductility of the intermetallic materials. This can be achieved by directional solidification process of eutectic alloys, and eutectic *in situ* composites which are thermodynamically stable, chemically compatible, and well aligned can be obtained. Caram et al. [12,13] produced Ni–Ni_3Si eutectic *in situ* composite with the Bridgman directional solidification technique at solidification rates $R=32$–56 μm/s. Although many significant results have been achieved, there are still a series of unsolved problems such as the microstructure control, crystal growth mechanism, and the phase composition of the Ni–Ni_3Si composites. The preparation technique still needs to be improved as well. Electron beam floating zone melting (EBFZM) technique has many advantages, e.g. high energy density(10 thousand times arc), high vacuum degree ($<10^{-5}$ mbar), high temperature gradient (350–500 K/cm) and no crucible pollution. These advantages can result in the improvement of the final structure, grain size and properties of the alloy. In the present paper, the EBFZM technique is adopted in order to obtain Ni–Ni_3Si eutectic *in situ* composite which has high-aligned and uniformly-distributed Ni_3Si compounds embedded into the Ni matrix. The solidification characteristics and phase composition are studied in detail. In general, the harder the metal material is, the worse its ductility is. Therefore, micro-hardness can be used to represent the ductility of the Ni–Si alloy. Micro-hardness of the Ni–Ni_3Si eutectic composites at the different solidification rates are studied by micro-hardness tester.

2. Experiments

The master alloys are obtained by cutting the middle of the Ni–11.5 wt% Si alloy into $\emptyset 6\times 120$ mm slices, which are produced with vacuum induction melting technique. The Ni–Ni_3Si eutectic *in situ* composites are prepared by EBZM-20 directional solidification equipment at different solidification rates. The schematic diagram of the electron beam gun is shown in Fig. 1. The directionally solidified samples are treated with conventional

* Corresponding author. Tel.: +86 29 82205104; fax: +86 29 82202923.
E-mail address: cuichunjuan@xauat.edu.cn (C. Cui).

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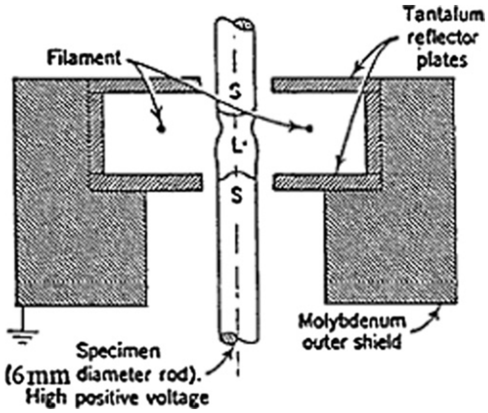

Fig. 1. Schematic diagram of the electron beam gun.

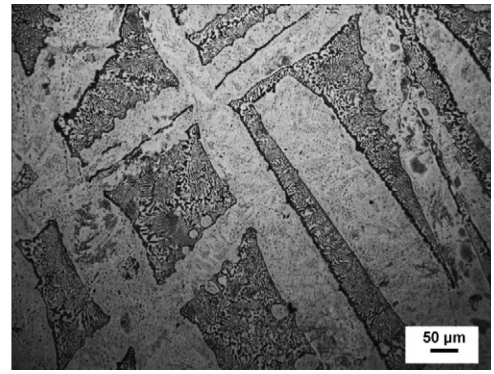

Fig. 2. Microstructure of the Ni–Si alloy produced with vacuum induction melting technique.

metallographic technique and etched by the mixture of 5%HCl+H_2O+Fe_3Cl solution. Microstructure and phase distributions are observed with OLYMPUS GX51 optical microscope. Phase composition of the Ni–Ni_3Si eutectic *in situ* composites are studied by X-ray diffraction (X Pert MPDPRO) technique. Micro-hardness of the Ni–Ni_3Si eutectic composites at different solidification rates are studied by 40MVD micro-hardness tester.

3. Results and discussions

3.1. Microstructure of the Ni–Ni_3Si eutectic in situ composites

The longitudinal microstructure of the Ni–Si alloy prepared by vacuum induction melting technique is shown in Fig. 2. The longitudinal and transverse microstructures of Ni–Ni_3Si eutectic *in situ* composites prepared by the EBFZM technique at the different solidification rates are shown in Figs. 3 and 4, respectively. On the optical micrographs, the dark phase is Ni matrix, and the light one is Ni_3Si compound. It can be seen from Figs. 2 and 3 that the crystal growth direction of the master alloy is random and the crystal grain is coarser, while the directional solidification microstructures are regular lamellar eutectic structures at the solidification rates R=0.3–4.0 mm/min and the crystal grain gets fined obviously. It can be seen from Fig. 4 that the lamellar spacing of the Ni–Ni_3Si eutectic *in situ* composites is decreased with the increase of the solidification rate.

In the process of the crystal growth, both the nucleation rate and the diffusion rate of solute in the liquid are the two important parameters. At low solidification rates, atomic diffusion is efficient enough and eutectic growth happened at near equilibrium conditions. This can result in well-aligned and a large lamellar spacing as shown in Figs. 3a and 4a. According to the theory of constitutional undercooling, an increase in the solidification rate leads to the increase of constitutional undercooling, the nucleation rate of eutectic is increased, whereas the atomic diffusion in the melt is not efficient. If the solidification rate is relatively low, the nucleation rate will play the main role, which can result in the refinement of the solidification microstructure [14]. This is in concordance with the crystal growth theory of the regular eutectic alloys [15], and the lamellar spacing of Ni–Ni_3Si eutectic *in situ* composite is decreased with the increase of the solidification rate as shown in Fig. 4.

As far as Ni–Ni_3Si eutectic is concerned, Ni is a non-faceted phase, while the Ni_3Si compound is a faceted phase. Li and Zhou (LZ) [16] found that the kinetic effect will significantly alter the eutectic growth behaviors, and maintain the coupled eutectic growth to higher undercoolings when crystallization products contain intermetallic compounds or other topologically complex phases. With the increase of the solidification rate, the undercooling is increased, and the kinetic undercooling is increased as well. Therefore the regular lamellar eutectic could be obtained at the solidification rate R=0.3–4.0 mm/min.

3.2. Phase composition of the Ni–Ni_3Si eutectic in situ composites

Fig. 5 shows the X-ray diffraction pattern of Ni–Ni_3Si eutectic *in situ* composite prepared by the EBFZM technique. The XRD pattern clearly indicates that a small amount of metastable $Ni_{31}Si_{12}$ phase is found in the Ni–Ni_3Si eutectic *in situ* composite besides Ni phase and Ni_3Si phase. Formation mechanism metastable $Ni_{31}Si_{12}$ phase is as same as discussed in our former paper [17]. According to Ni–Si phase diagram, at the eutectic composition at 1143 °C, there are three phases: α-Ni, liquid phase and β_3-Ni_3Si phase. With the decrease of the temperature, the β_3-Ni_3Si phase transforms to β_2 phase, and finally transforms to β_1 at 1035 °C. During these process, Silicon-rich β_1-Ni_3Si is also formed through the eutectoid decomposition $\beta_2 \rightarrow \beta_1 + \gamma$, where γ has the formula $Ni_{31}Si_{12}$ and a complex hexagonal crystal structure [18]. Thus the metastable $Ni_{31}Si_{12}$ phase is formed. However, as compared with the X-ray diffraction pattern of Ni–Ni_3Si eutectic *in situ* composite prepared by the Bridgman technique shown in Fig. 6 [17], the X-ray diffraction peak intensity of metastable $Ni_{31}Si_{12}$ phase in the Ni–Ni_3Si eutectic *in situ* composite prepared by the EBFZM technique is greatly decreased. Which means the amount of the metastable $Ni_{31}Si_{12}$ phase is decreased during the EBFZM crystal growth process. The high temperature gradient (350–500 K/cm) and high solidification rates are the main reasons to decrease the amount of the metastable $Ni_{31}Si_{12}$ phase.

3.3. Micro-hardness of the Ni–Ni_3Si eutectic in situ composites

Table 1 shows the micro-hardness of the Ni–Ni_3Si eutectic *in situ* composites prepared by the EBFZM technique at the different solidification rates. The relationship between solidification rate and micro-hardness of the Ni–Ni_3Si eutectic *in situ* composites is shown in Fig. 7, which demonstrates that micro-hardness of the Ni–Ni_3Si eutectic *in situ* composites are decreased as compared with the pure Ni_3Si compound, i.e., the ductility of the composites has been improved when Ni_3Si compound is combined with Ni matrix at the eutectic composition. Micro-hardness of the Ni–Ni_3Si eutectic *in situ* composites is firstly decreased and then increased with the increase of the solidification rate. The minimum micro-hardness of the Ni–Ni_3Si eutectic *in situ* composites is obtained when the solidification rate is R=1.0 mm/min. As compared with our former data [17],