Microstructure and mechanical properties of Ni₃Al intermetallics prepared by directional solidification electromagnetic cold crucible technique

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Abstract: The present work focused on the Ni₃Al-based alloy with a high melting point. The aim of the research is to study the effect of withdrawal rate on the microstructures and mechanical properties of directionally solidified Ni-25Al alloy. Ni₃Al intermetallics were prepared at different withdrawal rates by directional solidification (DS) in an electromagnetic cold crucible directional solidification furnace. The DS samples contain Ni₃Al and NiAl phases. The primary dendritic spacing (λ) decreases with the increasing of withdrawal rate (V), and the volume fraction of NiAl phase increases as the withdrawal rate increases. Results of tensile tests show that ductility of DS samples is enhanced with a decrease in the withdrawal rate.

Key words: intermetallic; directional solidification; microstructure; mechanical property; fracture

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Due to their excellent high-temperature strength, and good oxidation resistance^[1-3], Ni₃Al-based alloys have long attracted considerable interest as a class of high-temperature structural material. These properties, combined with their unique high thermal conductivity, make them ideal for special applications, such as blades in gas turbines and jet engines. However, polycrystalline Ni₃Al alloys show almost no ductility and extremely low fracture resistance at ambient temperatures, which is ascribed to the intrinsic brittleness of their grain boundaries^[4]. It has been found that these grain boundaries are also susceptible to moisture. Thus, Ni₃Al alloys easily suffer from environmental embrittlement^[5].

Recently, Ni₃Al alloys with high ductility at room temperature have been made by directional solidification (DS) without alloying. Binary single-phase Ni₃Al alloys with columnar-grained structure, prepared by a floating zone method, showed about 60% tensile

elongation along the columnar grains direction at room temperature^[6]. The ductility improvement of DS Ni₃Al alloys have been interpreted by transgranular fracture mode, since low angle columnar-grained boundaries are more resistant to fracture^[7]. During directional solidification, the solidification parameters affect the microstructures and mechanical behaviors of the alloys^[8]. Therefore, the effects of solidification parameters on the microstructure and mechanical properties have been investigated widely for different alloys, such as Al-based alloys, TiAl-based alloys^[9], Fe-Ni alloys^[10], and Cu-Sn alloys^[11]. These studies mostly focused on eutectic alloys or peritectic alloys with low melting points. For binary alloys with high melting points, the effects of solidification parameters on the microstructures and mechanical properties have rarely been reported.

Hence, the present work focused on the Ni₃Al-based alloy with a high melting point. The aim of the research is to study the effect of withdrawal rate on the microstructures and mechanical properties of directionally solidified Ni-25Al alloy, and the effect of NiAl phase on strength and ductility is discussed. The results provide a reference for the microstructure control of Ni₃Al-based alloys by directional solidification.

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1 Experimental procedure

A master alloy with a composition of Ni-25Al (mole fraction, %) was prepared by induction melting under Ar atmosphere and dropped into a cylindrical ingot of 80 mm in diameter and 180 mm in length. The purities of raw materials used in this work were Ni 99.99% (mass fraction), and Al 99.9%. DS rods were cut from the master ingot into cylinder bars of $\Phi 15\text{ mm} \times 160\text{ mm}$ by wire electro-discharged machine (EDM) and placed into high purity alumina crucibles of 16 mm inside diameter and 18 mm outside diameter. DS experiments were performed under an argon atmosphere in a set of electromagnetic continuous casting (EMCC) experiment equipment with liquid metal cooling. The EMCC process details concerning the working procedure can be found in previous study by Shen et al^[12]. The equipment for the EMCC process used in the present study is schematically shown in Fig. 1. The alumina crucible with the as-cast rod was positioned in a cyclodial crystallizer with an inner dimension of $\Phi 33.00\text{ mm}$ and a four-turn induction coil arranged outside the crystallizer and heated up to 50 kHz by induction heating and then kept for 10 min. This operation was controlled by a servomotor at various withdrawal rates of 0.5, 1.0, 1.5, 2.0, 2.5 $\text{mm} \cdot \text{min}^{-1}$, respectively. The sample was quenched into liquid Ga-In to cool the heating ingot at the bottom.

The directionally solidified samples were sectioned transversely and longitudinally by EDM for metallographic analysis. The metallographic process involved grinding, mechanical polishing and chemical etching with a solution of 10 g CuSO_4 , 50 ml HCl and 50 ml H_2O . The etched specimens were revealed and analyzed using an Olympus GX71 optical microscopy (OM) and a scanning electron microscopy (SEM) equipped with energy dispersive spectrometry (EDS). The phase

Fig. 1: Schematic of electromagnetic continuous casting process

analysis was conducted by X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM). The tensile tests at room temperature were carried out on a universal electronic material testing machine (INSTRON5569).

2 Results and discussion

2.1 Macrostructure and microstructure of the directionally solidified samples

The macrostructures and microstructures of the DS sample at $V = 1\text{ mm} \cdot \text{min}^{-1}$ are shown in Fig. 2. Three distinguished regions can be observed in the DS sample, which are the initial

Fig. 2: Macrostructure and microstructure of typical directionally solidified Ni_3Al : (a) DS sample at a withdrawal rate of $1.0\text{ mm} \cdot \text{min}^{-1}$; (b) initial solidification region; (c) directional solidification region; (d) final solidification region

solidification region, directional solidification region and final solidification region. The initial interface is the beginning position of directional solidification. It should be noted that the original alloy is unmelted in the bottom of the initial solidification region shown in Fig. 2(b). Grains can attach on the surface of the unmelted alloy to nucleate and to grow during cooling. Subsequently, these grains become coarse, and grow competitively along the withdrawal direction. In the directional solidification region, the columnar grains are relatively fine, continuous and aligned with the withdrawal direction as shown in Fig. 2(c). Figure 2(d) shows the microstructure in the final solidification region, and it was found that columnar grains develop along the surface of the alumina crucible and also

inwards into the material.

Figure 3(a)-(e) show the transverse sections of DS Ni_3Al samples at different withdrawal rates. It can be seen from Fig. 4 that the primary arm spacing (λ) decreases with an increase in the withdrawal rate (V). The number of columnar grains in the DS region depends on the withdrawal rate of ingot and increases with an increase in the withdrawal rate (V). Primary arm spacing is mainly determined by the heat conduction in directional solidification process and decreases with increasing capability of heat conduction. Generally, the capability of heat conduction increases with an increase in the cooling rate. In this study, the cooling rate increases with the increase of withdrawal rate. Thus, the value of λ decreases with the increase of V , according

Fig. 3: Macrostructure of cross-section in directional solidification region at withdrawal rates of: (a) $0.5 \text{ mm} \cdot \text{min}^{-1}$; (b) $1.0 \text{ mm} \cdot \text{min}^{-1}$; (c) $1.5 \text{ mm} \cdot \text{min}^{-1}$; (d) $2.0 \text{ mm} \cdot \text{min}^{-1}$; and (e) $2.5 \text{ mm} \cdot \text{min}^{-1}$

Fig. 4: Variation of primary dendrite arm spacing (PDAS) with different withdrawal rates for directional solidified Ni_3Al alloy

to the relationship:

$$\lambda = kV^{-m} \quad (1)$$

where k is a material constant and m is the rate exponent. Using linear regression analysis, the experimental data can be expressed as:

$$\lambda = 39.6V^{-0.43} \quad (2)$$

The correlation coefficient r^2 of this fit is better than 0.98. The measured value m is closed to a theoretical value of $\lambda \propto V^{-0.43}$ resulting from the models of Hunt^[13] and Kurz and Fisher^[14].

2.2 Phase constitution

Figure 5 shows XRD patterns of the DS region in DS Ni₃Al samples prepared at different withdrawal rates. It can be seen that Ni₃Al phase can be observed in samples at any withdrawal rate. Also NiAl phase patterns appeared in the sample prepared at 2.5 mm·min⁻¹. NiAl phase content might be small and difficult to detect using XRD at low withdrawal rates.

Figure 6 shows the microstructures of samples directionally solidified at different withdrawal rates. The microstructure is a duplex structure consisting of gray Ni₃Al matrix and black NiAl precipitates at all withdrawal rates. Meanwhile, NiAl precipitates with irregular shape and uneven distribution are observed mainly near grain boundaries and a few inside grains. The chemical composition of NiAl phase in the samples is measured using energy dispersive X-ray analysis (EDX).

Fig. 5: XRD of directional solidification region of DS Ni₃Al samples at different withdrawal rates

Fig. 6: Microstructure of directional solidification region at withdrawal velocities of: (a) 0.5 mm·min⁻¹; (b) 1.0 mm·min⁻¹; (c) 1.5 mm·min⁻¹; (d) 2.0 mm·min⁻¹; (e) 2.5 mm·min⁻¹

According to the EDX results, composition deviation from the withdrawal rate is very small, and the chemical composition of NiAl is in the range of 33 to 36at.% Al.

TEM images in Fig. 7 reveal the crystal structure of both matrix Ni_3Al and NiAl phase precipitates. From the diffraction spots of the sample, it can be confirmed that the sample contains Ni_3Al with Ll_2 -type structure and NiAl phase with B2-type structure. The lattice constants are $a=0.356\text{ nm}$, $c=0.356\text{ nm}$ for Ni_3Al phase and $a=0.288\text{ nm}$ for NiAl phase.

Figure 8 shows the statistic result of NiAl phase content, which suggests that the NiAl volume fraction increases with increasing withdrawal rate. Based on the Ni-Al phase diagram, the liquid undergoes a peritectic reaction $\text{liquid}+\text{NiAl}\rightarrow\text{Ni}_3\text{Al}$. The Al-rich NiAl is a primary phase which is not stable below the peritectic temperature. It dissolves into Ni_3Al when cooling below the peritectic temperature. At the lower withdrawal rates, the precipitated NiAl were kept at high temperature for long enough to dissolve completely into the Ni_3Al matrix. As a result, the nearly single phase Ni_3Al was obtained at room temperature, when the withdrawal rate was $0.5\text{ mm}\cdot\text{min}^{-1}$. With increasing the withdrawal rate, it is difficult for the dissolution process to

be completed and some residual NiAl will remain in the matrix, resulting in the increasing of NiAl precipitation.

2.3 Tensile properties

Room temperature tensile properties of DS Ni_3Al were strongly dependent on the withdrawal rate of ingot. Figure 9 shows the stress-strain curves of the samples at different withdrawal rates. In comparison with the as-cast values^[15], the tensile properties are improved by directional solidification. The elongation, tensile strength and yield strength can be related consistently to the withdrawal velocity as shown in Fig. 9, which is also related to the microstructures. Sample at $0.5\text{ mm}\cdot\text{min}^{-1}$ exhibited large tensile elongations of 29%, and a small yield strength of 66 MPa. With an increase in the withdrawal rate, the elongation and tensile strength decreased, but the yield strength increased. Regardless of the withdrawal rates, all the samples were elongated uniformly throughout the gauge section and finally fractured abruptly without necking. For $0.5\text{ mm}\cdot\text{min}^{-1}$ sample, stress drop occurred during the tensile tests before fracture but it recovered soon.

Fig. 7: TEM photographs showing crystal structure of both matrix Ni_3Al and NiAl phase precipitates at a withdrawal rate of $2.5\text{ mm}\cdot\text{min}^{-1}$

Fig. 8: Statistic result of NiAl phase content at different withdrawal velocities

Fig. 9: Stress-strain curves of samples at different withdrawal rates

Figure 10 shows the SEM micrographs of the fractured surfaces of the DS samples. As we know, the fracture mode is the intergranular fracture in the as-cast Ni_3Al [16], which is brittleness of polycrystalline Ni_3Al . The fracture mode in the $0.5 \text{ mm} \cdot \text{min}^{-1}$ sample is transgranular fracture as shown in Fig.10(a). These column grain boundaries parallel to the loading direction could interrupt main crack propagation. Many intergranular cracks are observed, indicating that the main crack releases more energy to generate second crack. The occurrence of slip indicates that dislocation could transfer across grain boundaries and the transgranular fracture occurred after considerable plastic deformation. By contrast, the fracture mode is a mixture of transgranular and interphase fractures in the $2.5 \text{ mm} \cdot \text{min}^{-1}$ sample, as shown in Fig.10 (b). The fracture mode in Ni_3Al matrix is still transgranular fracture, which could be highly resistant to cracking. However, cracking occurs at the $\text{Ni}_3\text{Al}/\text{NiAl}$ phase boundaries and cleavage fracture of NiAl phase deteriorates the ductility. Therefore, the change from transgranular fracture mode to mixture fracture mode is the main result of the decreasing of elongation with increasing the withdrawal rate. The increasing of yield strength is mainly due to the increasing of NiAl phase content, because NiAl phase interfaces could be facilitated in restricting dislocation movement and resisting local plastic deformation,

hence resulting in higher yield strength.

3 Conclusions

The effect of withdrawal rate on the macrostructure, microstructure and the room temperature tensile properties of the directionally solidified Ni_3Al were studied and the following conclusions were drawn:

(1) Macrostructures of DS Ni_3Al depend strongly on the withdrawal rate. Primary arm spacing decreases with an increase in the withdrawal rate according to the relationship: $\lambda \propto V^{-0.43}$.

(2) The microstructures of DS Ni_3Al consist of Ni_3Al with a smaller amount of NiAl . With an increase in the withdrawal rate, the NiAl volume fraction increases. This microstructural change with the withdrawal rate can be qualitatively explained by the cooling process and peritectic reaction in the Ni-Al system.

(3) The mechanical performance of DS Ni_3Al alloy samples is enhanced, which is attributed to their columnar structure, since column grain boundaries could greatly interrupt crack propagation and cause transgranular fracture.

Fig. 10: SEM micrographs of fractured surfaces of DS samples

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