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Effect of withdrawal rate on the microstructure of directionally solidified NiAl–Cr(Mo) hypereutectic alloy

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ABSTRACT

Solidification microstructure and growth interface morphology of directionally solidified Ni–31Al–32Cr–6Mo(at.%) hypereutectic alloy were studied. The experiments were carried out at higher temperature gradient of about 250 K cm^{-1} with different withdrawal rates of 4–500 μm s^{-1}. When the withdrawal rate was less than 50 μm s^{-1}, the primary Cr(Mo) dendrites were gradually eliminated through competitive growth between the primary phase and the eutectic phase. When the withdrawal rate exceeded 100 μm s^{-1}, no primary phase formed, eutectic phase grew directly. Fully eutectic microstructures with lamellar morphology were observed at all withdrawal rates. With increasing withdrawal rate V, the growth interface changed from planar to cellular and then dendritic, the solidification microstructure also transformed from planar eutectic to two-phase cellular eutectic and dendritic eutectic. The microstructure was refined and the eutectic interlamellar spacing λ decreased according to the relationship of $\lambda = 4.82V^{-0.42}$. Compared to the alloy at eutectic composition, the volume fraction of Cr(Mo) strengthening phase was increased obviously.

1. Introduction

Compared to commercial Ni-based superalloys, long-range ordered NiAl intermetallic has higher melting point, Young modulus, thermal conductivity in combination with a lower density and excellent high-temperature oxidation resistance [1–3]. The series of attractive properties make NiAl alloy an ideal candidate material for the next generation of high-temperature structural materials. Unfortunately, along with these positive characteristics, binary NiAl alloy possesses low ductility and fracture toughness at ambient temperatures as well as inadequate strength and creep resistance at elevated temperature, which limit its application in the aviation industry [4,5].

In order to enhance the elevated-temperature creep strength and room-temperature fracture toughness of NiAl alloy, relevant researches have been proceeded for many years, and some strengthening and toughening methods were proposed, such as alloying, second-phase strengthening and single crystal preparation [6–8]. Though these methods had enhanced the properties of NiAl alloy to some extent, it still cannot satisfy practical requirement. With the development of technique of directional solidification, people combined second-phase strengthening with directional solidification by adding refractory metals like Cr, Mo, V, Ta, and paid more attention to directionally solidified eutectic in-situ composites [9–13]. Walter and Cline [14] investigated directionally solidified NiAl–Cr alloy, it consisted of fibrous Cr strengthening phase and NiAl matrix. In contrast to binary NiAl alloy, the toughness and strength of NiAl–Cr alloy were enhanced markedly. What's more, Cline et al. [15,16] found that substitution of Cr with Mo led to a change of microstructure from Cr fibers to Cr(Mo) lamellae when the Mo content exceeded 0.6%(at.%). Directionally solidified NiAl–Cr(Mo) alloy, where the lamellae were ideally parallel to the growth direction, could combine the properties of high room-temperature fracture toughness and elevated-temperature creep strength.

Since the 1970s, many researches on solidification microstructures and mechanical properties of directionally solidified NiAl–Cr(Mo) multicomponent eutectic alloy have been done. However, previous experiments were only carried out at eutectic composition, which was believed to be Ni–33Al–(34 − x) Cr–xMo(at.%, $0 \leq x \leq 6$) [17–20]. To date, studies on hypereutectic alloys have not been reported. At the same time, the temperature gradient they used was low, generally less than 100 K cm^{-1}. So far, few persons have deeply researched the influences of solidification parameters and chemical composition on the phase selection as well as the growth characteristics and variation of solidification

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microstructure during directional solidification process. Because of low temperature gradient, fully eutectic structure can be obtained just at eutectic composition. If the fully eutectic structure is got in hypereutectic alloy, the volume fraction of strengthening phase would be greatly increased, and the melting point of hypereutectic alloy is higher than that of eutectic alloy. So higher temperature gradient and hypereutectic composition were adopted in present study, expecting to get a microstructure with fully eutectic lamellae and large volume fraction of Cr(Mo) strengthening phase, which may greatly improve the room-temperature fracture toughness and elevated-temperature creep strength of NiAl–Cr(Mo) alloy.

Microstructure evolution and solid/liquid interface morphology of directionally solidified Ni–31Al–32Cr–6Mo hypereutectic alloy grown at different withdrawal rate were researched in this paper. In the meanwhile, the effects of withdrawal rate on the microstructures and eutectic interlamellar spacing were investigated.

2. Experiments

Button ingots of Ni–31Al–32Cr–6Mo(at.%) for directional solidification were prepared by the vacuum non-consumable arc melting furnace with starting materials of 99.96%(wt.%) electrolytic nickel, 99.99% aluminum, 99.9% chromium and 99.95% molybdenum. Dry argon was introduced to prevent oxidation during the melting process, each ingot was turned over and remelted 5 times to improve the homogeneity. Chemical analysis was performed by the inductive coupled plasma technique, and the result is consistent with the nominal alloy composition.

The Φ4 mm rods were cut from the button ingots by wire electro-discharged machine and placed in the high purity alumina crucible which is 4 mm in inner diameter and 100 mm in length for directional solidification in Bridgeman apparatus with induction heating, the vacuum level was about 7×10^{-3} Pa before filling with high purity argon. The coolant was Ga–In–Sn liquid metal, and the temperature gradient ahead of the solid/liquid interface was about 250 K cm^{-1}. The samples were pulled down at withdrawal rates of 4, 6, 10, 15, 50, 100, 200 and 500 μm s^{-1}. As the solidification distance reached 50 mm, the samples were rapidly quenched into the liquid metal to retain their solid/liquid interface morphologies. The directionally solidified samples were cut along the longitudinal and transverse directions, the location of the cross sections is 5 mm below the solid/liquid interface. After grinding and polishing, the specimens were etched with a solution of 80% HCl + 20% HNO_3 by volume. The microstructures were observed by scanning electron microscopy (SEM) and optical microscope, the constituent phases were identified by energy dispersive spectroscopy (EDS), the eutectic interlamellar spacing and volume fraction of Cr(Mo) phase were measured by SISCIASV8.0 metallurgical analysis software.

3. Results and discussion

3.1. *Microstructure evolution during the directional solidification process*

3.1.1. *Competitive growth between primary phase and eutectic phase*

The microstructure evolution of directionally solidified hypereutectic Ni–31Al–32Cr–6Mo alloy grown at 4 μm s^{-1} is shown in Fig. 1. Fig. 1(a)–(d) are backscattered electron micrographs of the microstructures of as-cast, initial stage, transition zone and steady-state zone, respectively. The solidification direction is from left to right, as shown by the arrow in Fig. 1(b). The microstructure of as-cast alloy was equiaxed dendrites + eutectic, and the dendrites were identified to be Cr(Mo) phase. Primary Cr(Mo) dendrites appeared in the initial stage of directional solidification, interdendritic region exhibited lamellar eutectic microstructure. The Cr(Mo) primary dendrites and eutectic lamellae were parallel to the growth direction, but the lamellae were not regular. As the directional solidification proceeded, the number of primary dendrites gradually decreased through competitive growth between primary phase and eutectic phase. When directional growth reached steady state, the Cr(Mo) dendrites were eventually eliminated, fully eutectic microstructure was observed, and the arrangement of lamellae became well-aligned. The similar results were obtained at withdrawal rates of 6 and 10 μm s^{-1}. When the withdrawal rate increased to 15 and 50 μm s^{-1}, the two-phase competitive growth was also seen, the only discrepancy was the morphology of eutectic microstructure. At higher withdrawal rates, the eutectic microstructures were cellular.

Eutectic growth conditions have great influence on the properties of in-situ composite, how to get fully eutectic microstructure is key to the non-eutectic composition alloy. From the equilibrium phase diagram, it is apparent that fully eutectic microstructure can be obtained only when the composition is exactly eutectic. The liquidus is always higher than the eutectic temperature in the non-eutectic composition alloy, so primary phase formed in the initial stage. Nevertheless, when the composition does not deviate from the eutectic point far away, due to the different growth characteristics of dendrite and eutectic during the directional solidification, diffusion-coupled eutectic growth is much faster than isolated dendritic growth. Accordingly, even at off-eutectic compositions, the eutectic may outgrow the individual dendrites, resulting in a fully eutectic microstructure [21]. For example, Milenkovic et al. [22] found primary dendrites of W presented in the initial stage in directionally solidified hypereutectic NiAl–W alloy, and observed the fully eutectic microstructure with fibrous morphology in the steady-state region.

Mollard and Flemings [23] analyzed the two-phase growth of directionally solidified hypoeutectic alloy grew from the initial stage to the steady-state zone and found the fully eutectic microstructure was observed in the non-eutectic alloy. Similarly, because the NiAl–32Cr–6Mo alloy is in the rage of hypereutectic composition, primary Cr(Mo) dendrites formed in the initial stage at lower withdrawal rates (Fig. 1(b)). As the solidification proceeded, the compositions of solid phase and liquid phase at solid/liquid interface changed along the solidus and liquidus, respectively. When the temperature at solid/liquid interface reached the eutectic temperature T_E, liquid composition at solid/liquid interface was eutectic composition C_E, eutectic reaction occurred, Cr(Mo) and NiAl phases presented simultaneously. After that, eutectic growth reached steady state, and fully eutectic microstructure was observed.

In 1960s, Hunt and Jackson [24] and Mollard and Flemings [23] found the eutectic coupled zone was expanded with increasing value of G/V, where G is the temperature gradient, and V is the withdrawal rate. This means that the fully eutectic microstructure can be obtained at fast withdrawal rate under high-temperature gradient. Cline and Walter [15] observed Cr(Mo) dendrite in the steady-state zone when the growth rate exceeded 3.53 μm s^{-1}, but planar eutectic without primary phase was observed at 10 μm s^{-1} in the current work. The reason for this discrepancy may be mainly attributed to the difference of temperature gradient. The temperature gradient in their experiments was only 100 K cm^{-1}, which was significantly lower than 250 K cm^{-1} in present study. The increase in temperature gradient led to the eutectic coupled growth at higher withdrawal rate.

3.1.2. *Direct eutectic growth*

When the withdrawal rate increased to 100 μm s^{-1}, many dendrites formed in the initial stage as shown in Fig. 2(a). This kind of dendrite morphology changed greatly compared to the primary