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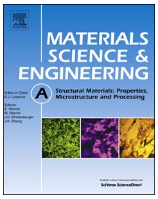

# Investigations on the solidification microstructures and room temperature compression properties of Nb-doped NiAl-32Cr-6Mo hypereutectic alloy

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ABSTRACT

Solidification microstructures and compression properties of NiAl-32Cr-6Mo hypereutectic alloys containing different contents of Nb were investigated. The addition of Nb did not change the basic phase constituents, though a new phase of Laves $Nb(Cr_{1-x-y}Ni_xAl_y)_2$ was observed. However, the primary Cr(Mo) phase no longer showed obvious dendritic morphology, the formation of lamellae was disturbed and the eutectic cellular microstructure degenerated. When the Nb content was 5%, eutectic lamellae coarsened and became spherical and poorly aligned. Fully eutectic microstructures were obtained in the directionally solidified hypereutectic alloys grown at 6 μm/s regardless of the addition amount of Nb. With the increasing content of Nb addition, the volume fraction of Laves phase located at the NiAl/Cr(Mo) boundary became more. The yield strength of directionally solidified NiAl-32Cr-6Mo-3Nb alloy reached to 2072 MPa, which is the highest value in the NiAl-based eutectic alloy at present. Well-aligned microstructure and more strengthening phase are conducive to the improvement of properties. All the alloys exhibited brittle quasi-cleavage fracture mode, cleavage in the NiAl phase and debonding of the NiAl/Cr(Mo) interface accompanied by Cr(Mo) lamellae and $Cr_2Nb$ phase pulled out were observed in the fracture surface.

## 1. Introduction

With the development of aerospace industry, high-temperature and light-weight structural material with high performance are urgently required. Compared to widely used Ni-based superalloys, intermetallic NiAl possesses some attractive advantages, such as higher melting point, Young modulus, thermal conductivity, lower density and excellent high-temperature oxidation resistance. So NiAl alloy could be considered as a potential high-temperature structural material of the turbine blade of aeroengine. Unfortunately, low ductility and fracture toughness at room temperature as well as inadequate creep strength at elevated temperature make it unable to meet the application requirements [1–3]. Previous researches showed that combined second-phase strengthening with directional solidification by adding refractory metals Cr and Mo to prepare directionally solidified NiAl-Cr(Mo) eutectic in-situ composites, where the eutectic lamellae were ideally parallel to the growth direction, could obtain high room-temperature fracture toughness and elevated temperature creep strength simultaneously [4–13]. Furthermore, Z. Shang et al. found the volume fraction of Cr (Mo) strengthening phase greatly increased in directionally solidified NiAl-Cr(Mo) hypereutectic alloy, and the room-temperatue fracture toughness and tensile strength at 1000°C were markdely improved [12,13]. However, greater improvement of high-temperature strength is still necessary.

Refractory elements like Ti, Hf and Nb were the typical strengthening elements in binary NiAl alloy through solid solution strengthening and precipitation strengthening [1–3]. Thus, they were also introduced into the NiAl-Cr(Mo) alloy. However, the additions generally led to increasing strength but decreasing ductility and toughness [14–19]. For example, J.T. Guo et al. found that Hf addition would improve the high-temperature strength by solution strengthening and precipitation strengthening but reduce the room-temperature ductility and toughness due to the existence of the Heusler phase at the NiAl/Cr (Mo) phase interface [15–17]. Nevertheless, K.W. Huai et al. found Nb-doped NiAl-Cr(Mo) alloy could exhibit a reasonable balance of high-temperature strength and room-temperature compression ductility [18]. But the research on the Nb addition was only focused on the as-cast NiAl-Cr(Mo) alloy with eutectic composition. Therefore, to further increase the mechanical properties, Nb is added into the directionally solidified NiAl-Cr(Mo) hypereutectic alloy to get fully eutectic microstructure with large volume fraction of Cr(Mo) strengthening phase. The influences of Nb addition on the phase selection, the growth

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characteristics and evolution of solidification microstructure as well as the room temperature fracture behaviors in directionally solidified NiAl-Cr(Mo) hypereutectic alloy were researched in this work.

## 2. Experiments

The as-cast alloys of NiAl-32Cr-6Mo-xNb ($x = 0$, 1, 3 and 5 at%, respectively, Ni and Al have a 1:1 stoichiometry) were prepared by the vacuum induction melting. During the melting process, high purity argon was imported into the melting furnace to prevent oxidation. The actual compositions analyzed by the inductively coupled plasma technique (ICP) were Ni-30.8Al-32.2Cr-5.9Mo, Ni-30.4Al-32.1Cr-5.9Mo-1.1 Nb, Ni-29.3Al-32.3Cr-5.8Mo-3Nb and Ni-28.4Al-32.1Cr-6.1Mo-4.9Nb (at%), respectively, which were mainly in accordance with the designed compositions. So the nominal compositions were used in this paper. The Φ7 mm rods were cut from the ingots by wire electro-discharged machine (EDM) and placed in the high purity alumina crucible for directional solidification in Bridgeman apparatus with induction heating, the vacuum degree was about $6 \times 10^{-3}$ Pa before filling with high purity argon. The samples were heated to 1600 ± 10 °C by a high purity graphite heater. After thermal equilibrium was reached, all samples were pulled down at a withdrawal rate of 6 μm/s. Previous experiments showed the eutectic growth could reach the steady state when the directional solidification length exceed 35 mm [12]. In this experiment the pulling length was 50 mm to insure steady growth, then the samples were rapidly quenched into the Ga-In-Sn liquid metal to retain their solid/liquid interface morphologies. The temperature gradient ahead of the solid/liquid interface was measured to be about 250 K/cm.

The metallographic samples were cut from the as-cast alloys and the directionally solidified samples along the longitudinal and transverse directions, respectively. The location of the cross sections was 5 mm below the growth interface. After conventional grinding and polishing, the specimens were etched with a solution of 80% HCl + 20% $HNO_3$ by volume. The compression samples with the dimensions of $4 \times 4 \times 6\ mm^3$ were cut from the as-cast alloys and the steady-state zone of the directionally solidified samples by EDM, respectively. All surfaces were mechanically ground with 2000 # abrasive paper prior to compression test to avoid the effect of surface marks. Compression test with the compression axis parallel to the growth direction were conducted in an HT2402 universal test machine at a strain rate of $2 \times 10^{-3}\ s^{-1}$. In this work, four specimens were tested and the average value was employted for each specimen condition. The microstructures were observed by scanning electron microscopy (SEM) using the backscattered electron imaging mode. and optical microscope (OM), the constituent phases were identified by X-ray diffractometer (XRD) and energy dispersive spectroscopy (EDS). The fracture surface morphologies were observed by SEM using the secondary electron imaging mode.

## 3. Results and discussion

### 3.1. As-cast microstructures

The optical micrographs of microstructures of the as-cast NiAl-32Cr-6Mo-xNb($x = 0$, 1, 3 and 5 at%) hypereutectic alloys are shown in Fig. 1. Fig. 1(b), (d), (f) and (h) are the high-magnification optical micrographs of microstructures. The alloy composition of NiAl-32Cr-6Mo largely deviates from the eutectic point, which is generally thought to be NiAl-(34-x)Cr-xMo($0 \leq x \leq 6$, at%) [4,10,11], the liquidus is always higher than the eutectic temperature. Thus, the primary phase has larger undercooling than eutectic [20]. The as-cast microstructure was macroscopically constructed by primary dendrites and eutectic. EDS results indicated the primary dendrite was Cr(Mo) phase (Ni: 6.86%, Al: 8.24, Cr: 66.53% and Mo: 18.37%, at%), while the eutectic consisted of Cr(Mo) and NiAl plates. Some black NiAl particles were precipitated in the Cr(Mo) phase (Fig. 1(a) and (b)). When Nb was added into the NiAl-32Cr-6Mo alloy, the microstructure was strongly affected. The primary Cr(Mo) phase did not show obvious dendritic morphology, and its size sharply decreased. With the increasing content of Nb, the alloy composition deviated from the eutectic point greatly. So the number of the primary Cr(Mo) dendrites gradually increased. Furthermore, due to the increasing undercooling caused by the Nb addition, the size of the eutectic cells decreased.

From Fig. 1(b), it is obvious that the Cr(Mo) dendrites did not show any evidence of faceted growth. Around them, haloes of black NiAl phase were observed, which indicated that NiAl phase must be the preferential phase for eutectic nucleation in the NiAl-Cr(Mo) alloy. Due to the rapid cooling rate, the eutectic microstructures displayed as cellular morphology, the NiAl and Cr(Mo) lamellae were arranged in a radial pattern normal to the cell boundary. Obviously, the addition of Nb had a significant effect on the solidification process, primary Cr(Mo) phase did not show distinct preferred growth direction. Nb atoms affect the diffusion of Ni and Al atoms ahead of the Cr(Mo) phase and Cr and Mo atoms ahead of the NiAl phase. Cooperative growth was destroyed. So the formation of eutectic lamellae was disturbed, NiAl and Cr(Mo) lamellae became short and poorly aligned. With the increasing addition of Nb, the concentration of solute at the cell boundary has changed obviously. Therefore, the eutectic cellular microstructure degenerated, and the NiAl and Cr(Mo) phase were sphericized. Additionally, a new refined microstructure was observed at the grain boundary. When the Nb content was 5%, eutectic cell was not apparent and the microstructure became tanglesome. The volume fraction of the refined microstructure was more.

### 3.2. Constituent phases in directionally solidified NiAl-32Cr-6Mo-3Nb hypereutectic alloy

Fig. 2 displays the scanning electron microscope observations of longitudinal microstructures in the directionally solidified NiAl-32Cr-6Mo-3Nb hypereutectic alloy grown at 6 μm/s. Because of the different imaging modes from the optical microscope, it is clearly seen that the microstructure consisted of a dark phase, a gray phase and a white phase actually. From the EDS test result shown in Table 1, the dark phase and gray phase should be NiAl phase and Cr(Mo) phase, respectively. The NiAl phase and Cr(Mo) phase are arranged alternately, while most of the white phase was semicontinuously distributed at the NiAl/Cr(Mo) boundary. Thus, it can be concluded that the addition of Nb did not change the basic phase constituents in the directionally solidified alloy. In addition, Mo and Nb are hardly solubilized in the NiAl phase while Ni and Al could be solubilized in the Cr(Mo) phase. Compared to the as-cast alloy, the solubility of Ni, Al and Mo in the Cr solid solution in directionally solidified alloy was relatively less. The reason should be that the solute atoms were supersaturated due to the rapid solidification rate in the as-cast alloy. Fig. 3 shows the XRD patterns of the as-cast NiAl-32Cr-6Mo alloy and the directionally solidified NiAl-32Cr-6Mo-3Nb alloy. Both alloys consisted of NiAl and Cr (Mo) phases, but the peak of Laves phase appeared in the directionally solidified NiAl-32Cr-6Mo-3Nb alloy, which indicated the Nb addition results in the formation of $Cr_2Nb$ phase.

For the white phase in Fig. 2, it could be approximatively described as $Nb(Cr_{1-x-y}Ni_xAl_y)_2$, which had the C14 structure in the Cr-Nb binary system by the results of XRD and EDS. The distinction was some substitutions of Ni and Al atoms for Cr atom. The similar result was also found by K.W. Huai et al. in as-cast Ni-33Al-28Cr-5Mo-1Nb alloy [18]. So, the refined microstructure observed at the grain boundary in Fig. 1 should be NiAl + Cr(Mo) eutectic and the Laves phase. From Fig. 2(b), the $Nb(Cr_{1-x-y}Ni_xAl_y)_2$ phase was mainly surrounded by the Cr(Mo) phase, which indicated Laves phase may nucleate and grow from the Cr (Mo) phase interface. At the phase interface, the Nb content was relatively more. When it exceeded the solid solubility, Laves phase would precipite. In addition, some Laves phase directly nucleate and grow from the liquid phase (seen in Fig. 2(c)). With the increasing addition of