Effect of Hf on Microstructure and High-Temperature Strength of a Cast NiAl/Cr(Mo) Alloy

Chuanyong Cui, Jianting Guo, Yihui Qi and Hengqiang Ye

Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110016, P.R. China

A NiAl/Cr(Mo) alloy modified with Hf was fabricated by a vacuum induction melted and drop cast. The alloy was mainly composed of NiAl matrix, Cr(Mo) and Hf-rich phase distributed between NiAl and Cr(Mo) phase boundary and phase transition was also studied. Then it was hot isostatically pressed (HIPed) at 1523 K, 200 MPa for 4.5h. Its high temperature compressive behavior was studied and the deformation features of the alloy could be adequately described by standard power law which is usually used to characterize creep behavior for various metallic material. The stress exponent n as well as the activation energy Q was calculated by fitting the experimental data to the power-law and temperature-compensated power law equation. The possible strengthening mechanism was discussed.

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Keywords: phase transition; deformation; hot isostatic pressing; NiAl–28Cr–5.8Mo–0.2Hf

1. Introduction

In polycrystalline NiAl form, conventional NiAl alloys do not possess adequate strength to be useful at the elevated temperatures needed to compete with nickel-based superalloys and there is little interest today in continuous fiber reinforced NiAl-based composites due to a number of presently irresolvable technical barriers. However, there is NiAl-based eutectic alloy system that have been actively investigated for potential utilization in niche high temperature application. One promising NiAl-eutectic alloy is NiAl/Cr(Mo) system. Directionally solidified NiAl/Cr(Mo) eutectic has been studied for many years because of its higher fracture toughness compared to many Ni-based alloy.

Small addition of refractory metal from Group IVB, in particular Hf, was found to be very effective in improving the high temperature creep strength of NiAl single crystal. Extensive studies on mechanical properties of the single phase (Heusler) and the NiAl-Ni$_2$AlHf two phase alloy have been reported and the two-phase alloys were found to have excellent creep resistance, comparable to conventional nickel-based superalloys.

Directional solidification has been used to produce NiAl single crystal for use in aero-turbine engines. However, the higher melting point of NiAl, close to 1912 K, which was about 300 K higher than the temperature used to process superalloys, pushes the stability of ceramic mold (Al$_2$O$_3$–SiO$_2$) to their limit when in contact with molten NiAl. Therefore the mold-metal reactions are serious issue because of Si contaminant. This uncontrolled addition of Si makes it difficult to understand the microstructure and strengthening mechanism of the proposed alloys. It is necessary to examine the microstructure and strength without Si contaminant.

Based on the above reason, the cast Ni–33Al–28Cr–5.8Mo–0.2Hf (Unless otherwise stated, all compositions are in atomic percent) alloy was selected for research. The microstructure, interface and mechanical properties of cast NiAl–28Cr–5.8Mo–0.2Hf alloy in the HIPed condition were reported.

2. Experimental Procedure

The alloy used for this investigation was Ni–33Al–28Cr–5.8Mo–0.2Hf in nominal. It was melted in a vacuum induction furnace and subsequently cast into ingots with 26 mm in diameter by 200 mm in length. The phase stability was performed on the as-cast state and the mechanical properties were conducted on the HIPed (1523 K, 200 MPa, 4.5 h) condition. Compression tests with a specimen size of 4 x 4 x 6 mm$^3$ were conducted in air at 1273 K and 1373 K and strain rate from 2 x 10$^{-3}$ s$^{-1}$ to 2 x 10$^{-5}$ s$^{-1}$, using a Gleeble 1500 test machine.

The samples for transmission electron microscopy (TEM) observations were prepared for the HIPed materials. After being cut into 3 mm discs with a thickness of 0.5 mm by electro-discharge machine (EDM), they were then thinned by mechanical polishing and dimple grinding to approximately 35 μm. The TEM observation was carried out on a PHILLIPS EM200 transmission electron microscope equipped with X-ray energy dispersive spectrometer (EDXS). High resolution electron microscopy (HREM) observations were performed with a JEM2010 high resolution electron microscopy.

3. Results and Discussion

A typical microstructure of the cast NiAl–28Cr–5.8Mo–0.2Hf alloy is shown in Fig. 1(a). The alloy is composed of three phases, which are Cr(Mo), NiAl matrix and white phase distributed at the NiAl/Cr(Mo) phase boundary. The EDXS result is as follows: Al 2.91, Cr 26.23, Ni 8.84, Hf 62.02, which indicates that the white phase is the Hf-rich phase with a high level of Cr. In order to study the phase stability of Hf-rich phase, the heat treatment is performed on the as-cast state and the EDXS results are shown in Table 1. From Table 1, it can be found that the formation of Heusler phase is dependent on the temperature and cooling rate, i.e. Heusler phase can be formed at the b, d, f, g, h, j condition, while the Hf-rich phases keep their original formation above 1273 K. It should be noted that the Cr content existing in Heusler phase is lower
can diffuse into the Heusler lattice (Cr: 6–11 at%), which lead to the formation of Hf-rich phase at high temperature. While at low temperature, little amount of Cr can exist in the Heusler phase lattice and they don’t influence the stability of Heusler phase, therefore Heusler phase is a stable phase.

According to NiAl-Cr(Mo) phase diagram\(^{19}\) and NiAl-Ni\(_2\)AlHf pseudobinary phase diagram,\(^{18}\) the maximum solubility of Hf in NiAl is less than 5% at the eutectic (NiAl–Ni\(_2\)AlHf) temperature of approximately 1623 K. Hf can be fully dissolved in NiAl phase at the NiAl and Cr(Mo) eutectic temperature, the solidified process of NiAl-28Cr–5.8Mo–0.2Hf alloy could be deduced as follows: the NiAl and Cr(Mo) eutectic reaction occurs at about 1718 K firstly,

\[
L \rightarrow \text{NiAl} + \text{Cr(Mo)}
\]  

(1)

The NiAl phase becomes enriched in Hf, where Hf-rich phase precipitates with decreasing temperature from the NiAl phase.

After the HIPed treatment, there is little change in the morphology of NiAl and Cr(Mo) (Fig. 1(b)). The EDXS result of the white phase is as follows: Ni 6.08, Cr 3.28, Hf 90.64, which indicates the white phase is also Hf-rich phase, whereas the Heusler phase precipitates are found rather than Hf-rich phase in the DS NiAl/Cr(Mo, Hf) composite,\(^{15}\) which may be attributed to Si contaminant and aged treatment of the DS NiAl/Cr(Mo, Hf) composite. A large number of precipitate phase are observed in Cr(Mo) grain, which is identified as NiAl precipitate. Because of the addition of Hf element, Heusler phase precipitates are found in the matrix in the HIPed alloy, as shown in Fig. 1(c), Heusler phase precipitates are entangled with dislocation. TEM results also confirm the Heusler phase, as determined in Fig. 1(d) from the selected area diffraction patterns. Fig. 1(e) is a HREM image viewed along [111] common direction of NiAl and fine Cr(Mo) precipitates. The fine Cr(Mo) precipitates, which are spherical in shape, are coherent with NiAl matrix. The modulation wave observed in NiAl matrix is due to the B\(_2\)–L\(_{10}\) martensitic phase transformation of NiAl.\(^{20,21}\)

Figure 2 is a HREM image viewed along [110] common direction of NiAl and Cr(Mo) after the HIPed treatment. The image shows an abrupt transition from NiAl to Cr(Mo) lattice with no transition layer. The misfit dislocation is clearly visible. Since the point-to-point resolution of JEM-2100 high resolution electron microscope is 0.19 nm, it is unable to resolve (200) spacing of NiAl and Cr(Mo). It can also be seen from Fig. 2 that the interfaces between NiAl and Cr(Mo) are not smooth and straight. The NiAl-TiB\(_2\) interface\(^{22}\) was atomically flat and sharp. In some cases, thin amorphous layers existed at NiAl and TiB\(_2\) interface, which is different from

![Image](Fig. 1 The typical microstructure of the cast NiAl–28Cr–5.8Mo–0.2Hf alloy (a) the as-grown state (b) the HIPed state (c) TEM micrographs of Heusler phase in the NiAl matrix (d) Corresponding electron diffraction pattern taken from NiAl and Ni\(_2\)AlHf phase (e) HREM image viewed along [111] common direction of NiAl and Cr(Mo).]

Table 1 The EDXS results of Hf-rich phase after different heat treatment.

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<thead>
<tr>
<th></th>
<th>a</th>
<th>b(H)</th>
<th>c</th>
<th>d(H)</th>
<th>e</th>
<th>f(H)</th>
<th>g(H)</th>
<th>h(H)</th>
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<td>6.68</td>
<td>3.42</td>
<td>6.03</td>
<td>5.98</td>
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<tr>
<td>Cr</td>
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<tr>
<td>Hf</td>
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<td>3.25</td>
<td>3.69</td>
<td>3.25</td>
<td>50.16</td>
<td>3.25</td>
<td>50.51</td>
<td>3.25</td>
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A, b, c, d, e, f, g, h, j denote different heat treatment, i.e. 1613 K/1 h, air cooled (AC(a)); 1613 K/1 h, furnace cooled (FC(b)); 1473 K/4 h, AC(c); 1473 K/4 h, FC(d); 1273 K/4 h, AC(e); 1273 K/4h, FC(f); 1173 K/2 h, AC(g); 1073 K/2 h, AC(h); 973 K/2 h, AC(j). H denotes Heusler phase.
the present results. Due to the very small lattice mismatch between these two phases, a semi-coherent interface between NiAl and Cr(Mo) is observed.

The region in which misfit dislocations located protrudes into NiAl side of the interface indicating a high growth rate of these cusps during the solidification process of the alloy. Since the segregating of Cr and Mo atoms on misfit dislocation line can result in a reduction in the system’s energy. The curved interface implies the following: (i) The interface was not in its equilibrium state; (ii) there should be a long-range stress field at the interface; (iii) Stress concentration was generated in the vicinity of the misfit dislocation. All of which would enhance segregating of impurities to the interface and drive crack tip through the interface.

The true stress-strain curves transformed from the load-time chart for the alloy are presented in Fig. 3. From this figure, it can be seen that the strength basically decreases with decreasing strain rate at all test temperature. The deformation behavior at slower strain rate of $2 \times 10^{-5} \text{s}^{-1}$ is clearly different from that at higher strain rates $2 \times 10^{-4} \text{s}^{-1}$ and $2 \times 10^{-3} \text{s}^{-1}$. That is to say, after reaching the highest yielding point, the alloy deformed at a slower strain rate displays fast strain softening and then followed by continued deformation at constant stress. On the other hand, those compressed at higher strain rates usually display gradual softening after the highest yield point. This result is very similar to NiAl-eutectic with reactive element system. In most materials, the strain softening during high temperature deformation process generally corresponds to the occurrence of dynamic recovery and re-crystallization, it appears that the high temperature deformation process is associated with those process in the NiAl matrix.

True compressive flow stress-strain rate behavior of the alloy is presented in Fig. 4, where the flow stresses were taken at 3% strain from the true stress-strain diagrams. These data were fitted by linear regression techniques to the power-law equation and temperature-compensated power-law equation, respectively,

$$\dot{\varepsilon} = A\sigma^n$$
$$\dot{\varepsilon} = B\sigma^n\exp\left(-\frac{Q}{RT}\right)$$

Fig. 2 HREM image viewed along $\overline{[1\overline{1}0]}$ common direction of NiAl and Cr(Mo) for the HIPed state.

Fig. 3 True compressive stress-strain diagrams for NiAl–28Cr–5.8Mo–0.2Hf tested at (a) 1273 K (b) 1373 K.
change the activation energy value, however the stress exponent decreases with increasing the Cr(Mo), which shows that the addition of Cr(Mo) can reduce the stress exponent of NiAl. From Table 3, it was found that the stress exponent of cast + HIP processed NiAl/Cr(Mo)-Hf is relatively less than that of DS NiAl–28Cr–6Mo, which may be induced by different fabricated processing. The creep behavior of NiAl-(Ta, Nb) alloy with Laves phase investigated by Zueherer showed that the stress exponent of the alloy fabricated by powder technique is smaller than that of casting. Such difference can be attributed to their different microstructure. Whittenberger, studied extruded and directionally solidified two phase Ni–45Al–10.5Nb with partially aligned single crystalline structure and fine grain size polycrystalline band structure respectively. They found similar behavior. It was stated that a grain boundary sliding mechanism could contribute to plastic flow process in the fine grain structure and hence lower the observed stress exponent, while boundary dependent processes would not be possible in directionally solidified NiAl/NiAlNb composite. Such mechanism may be applicable to the NiAl/Cr(Mo)-Hf system. Additionally, the introduction of the element Hf may also exert influence on the compressive flow behavior. The activation energy for the present eutectic alloy is almost the same as those measured from other Heusler strengthened nickel aluminides and directionally solidified NiAl-based alloys. For example, NiAl–Ni$_2$AlHf alloy possesses activation energy of 435 kJ/mol, while DS NiAl–28Cr–6Mo alloy has an activation energy of 456.6 kJ/mol, which showed that small addition of Hf has little effect on the activity energy of NiAl/Cr(Mo) eutectic system.

In order to compare, the true stress-strain rate behavior of the directionally solidified NiAl–28Cr–6Mo$^{30}$ and HPES NiAl/Cr(Mo),$^{23}$ as well as NiAl–0.7Zr$^{27}$ produced

<table>
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<th>$n$</th>
<th>$R^2$</th>
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<tr>
<td>NiAl/Cr(Mo, Hf), HIP</td>
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<td>8.7</td>
<td>0.98</td>
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<tr>
<td>NiAl/Cr(Mo)</td>
<td>8.11 x 10^{-16}</td>
<td>5.32</td>
<td>0.993</td>
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<tr>
<td>NiAl/Cr(Mo)</td>
<td>3.89 x 10^{-11}</td>
<td>3.31</td>
<td>0.993</td>
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<tr>
<th>Alloy</th>
<th>$A$</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
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<tbody>
<tr>
<td>NiAl/Cr(Mo, Hf), HIP</td>
<td>1.46 x 10^{-14}</td>
<td>4.77</td>
<td>0.993</td>
</tr>
<tr>
<td>NiAl/Cr(Mo)</td>
<td>1.92 x 10^{-11}</td>
<td>3.73</td>
<td>0.996</td>
</tr>
<tr>
<td>NiAl/Cr(Mo)</td>
<td>1.49 x 10^{-8}</td>
<td>2.46</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table 2 Power-law fits of the compressive flow stress-strain rate data for the HIPed NiAl–28Cr–5.8Mo–0.2Hf alloy.
from preallloyed powder, were also included according to quantitative power-law equations. As clearly indicated in Fig. 4, NiAl–28Cr–5.8Mo–0.2Hf is stronger than HPES NiAl/Cr(Mo) and preallloyed powder NiAl–0.7Zr, but still weaker than DS NiAl–28Cr–6Mo. This structure produced by directional solidification may result in better strengthening effect than the disorder structure where NiAl and Cr(Mo) phase are randomly dispersed.

Although the present alloy can’t compete with DS NiAl–28Cr–6Mo alloy, they do show evidently higher strengths than binary NiAl. The addition of Hf, Cr and (Mo) is good strengthening agents with respect to NiAl. At elevated temperature, the facts that dislocation were mainly generated in the NiAl instead of Cr(Mo) grain indicate that the Cr(Mo) constituent has higher yielding than the NiAl constituent. The NiAl precipitate may also contribute to the higher strength of Cr(Mo). The Cr(Mo) precipitates and Heusler phase precipitates in the matrix contribute to inhibit the movement of dislocation and hence increase the strength of the composite through dispersion strengthening.

The stress exponent $n$ is believed to provide an insight into the creep mechanism. The values of 1, 3, 5 are considered to represent the diffusion creep (Coble Creep), viscous glide of mobile dislocation, high temperature climb controlled creep due to lattice self-diffusion, respectively. Raj et al. divided the creep behavior of polycrystalline NiAl into three regions. Region 1, which occurs at low stress, is characterized by $n = 2$ and Region 2 at intermediate stress with $n = 6.5$, while Region 3 occurs at high stress where $n$ is stress dependent. The value of $n$ obtained in the present work, $n = 5.46$, seems to be consistent with their value in Region 2 and high temperature climb controlled creep due to lattice self-diffusion.

4. Conclusion

(1) The cast NiAl–28Cr–5.8Mo–0.2Hf alloy was composed of NiAl matrix, Cr(Mo) and Hf-rich phase. Hf-rich phase can be transformed into Heusler phase at the temperature lower than 1273 K.

(2) After the HIPed treatment, there is little change in the morphology of NiAl and Cr(Mo). Fine Heusler precipitates were found in the NiAl matrix.

(3) The high temperature compressive behavior of the present alloy was studied. The strengthening of the alloy can be attributed to the precipitation strengthening by Ni$_2$AlHf and solid solution strengthening by Cr, Mo, Hf element. Additionally, the strengths of the present alloy did not exceed those of DS NiAl–28Cr–6Mo composite.

Acknowledgements

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