

Mechanical behaviors of NiAl–Cr(Mo)-based near eutectic alloy with Ti, Hf, Nb and W additions

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Abstract: Effects of Ti, Hf, Nb and W alloying elements addition on the microstructure and the mechanical behaviors of NiAl–Cr(Mo) intermetallic alloy were investigated by means of XRD, SEM, EDX and compression tests. The results show that Ni–31Al–30Cr–4Mo–2(Ti, Hf, Nb, W) alloy consists of four phases: NiAl, α -Cr solid solution, Cr_2Nb and $\text{Ni}_2\text{Al}(\text{Ti, Hf})$. The mechanical properties are improved significantly compared with the base alloy. The compression yield strength at 1 373 K is 467 MPa and the room temperature compression ductility is 17.87% under the strain rate of $5.56 \times 10^{-3} \text{ s}^{-1}$, due to the existence of Cr_2Nb and $\text{Ni}_2\text{Al}(\text{Ti, Hf})$ phases for strengthening and Ti solid solution in NiAl matrix and coarse Cr(Mo, W) solid solution phase at cellular boundaries for ductility. The elevated temperature compression deformation behavior of the alloy can be properly described by power-law equation: $\dot{\epsilon} = 0.898 \sigma^{8.47} \exp[-615/(RT)]$.

Key words: NiAl–Cr(Mo)-based alloy; Heusler phase; Cr(Mo,W) solid solution; mechanical properties

1 Introduction

NiAl is a potential high-temperature structure material due to its high melting point, low density, high elastic modulus and excellent oxidation resistance. But, its low room-temperature ductility, poor fracture toughness and inadequate high-temperature strength limit its practical use[1–2]. Fortunately, in recent years, in-situ eutectic NiAl–Cr(Mo) alloy prepared by directional solidification provided room-temperature fracture toughness of $24 \text{ MPa}\cdot\text{m}^{1/2}$ over that of polycrystalline NiAl ($6 \text{ MPa}\cdot\text{m}^{1/2}$)[3]. However, the high temperature strength still needed to be enhanced, compared with the strength of the applied Ni-based superalloys.

GUO et al had added Hf alloying element to NiAl–Cr(Mo) alloy and developed a high-temperature strength alloy of NiAl–28Cr–5.5Mo–0.5Hf[4–6]. However, Hf addition induced Heusler phase, Ni_2AlHf , existing at the NiAl/Cr(Mo) interface, which decreased the bonding of NiAl and Cr(Mo) phase, leading to the decrease of ambient temperature ductility evidently[7]. Ti and Hf were situated at the same column in the element periodic table and both of them could form Heusler phases such as Ni_2AlTi and Ni_2AlHf . Recently,

Ti and Hf co-addition to NiAl–Cr(Mo) alloy was reported to form Heusler phase $\text{Ni}_2\text{Al}(\text{Ti, Hf})$ and $\beta\text{-Ti}(\text{M, M=Hf, Cr, Ni})$ solid solution phase, which improved the strength and ductility at ambient temperature[8].

In recent work, Nb addition to NiAl–Cr(Mo) formed dispersion strengthening Cr_2Nb phase at cellular boundary, which contributed to high temperature strength [9–10]. However, effect of Ti, Nb and Hf co-addition to NiAl–Cr(Mo) alloy has less been reported. Furthermore, It is considerable that misaligned grain boundary is the origination of voids[3]. W, Mo and Cr located at the same column in the element periodic table and W may solve in the Cr(Mo) phase, changing the morphology of Cr(Mo) phase at cellular boundary, which may benefit to ductility. Hence, in consideration of controlling content of Heusler and Laves phases and inducing solid solution phases, 1% Ti, 0.2% Hf, 0.5% Nb and 0.3% W (molar fraction) are added to Ni–33Al–30Cr–4Mo to substitute Al, and the effects of Ti, Hf, Nb and W addition on the microstructure and mechanical properties are investigated.

2 Experimental

The alloy used for this investigation has nominal

compositions of Ni-31Al-30Cr-4Mo-(1Ti, 0.2Hf, 0.5Nb, 0.3W) (molar fraction, %). The material used was arc-melted under an argon atmosphere protection from starting materials of 99.98% Ni, 99.9%Al, 99.98%Cr, 99.9%Mo, 99.76%Ti, 99.7%Hf, 99.7%Nb and 99.95%W (mass fraction) using a non-consumable tungsten electrode. Each alloy button was turned over and remelted four times to get a homogeneous specimen. The alloy buttons were homogeneously treated at 1 523 K for 24 h in air and cooled to room temperature with furnace. The specimens for compression testing were cut from the homogenized buttons with the size of $d4\text{ mm}\times 6\text{ mm}$ column by electro-discharge machining, and all major surfaces were mechanically ground with 800-grit SiC abrasive before compression test. Microstructure of the samples was observed by scanning electron microscope(SEM), primarily using back-scattered electron(BSE) imaging. The compositions were detected by energy dispersive X-ray analysis (EDX) attached to the SEM. X-ray diffraction analysis was used to identify the structure of the phases on a Rigaku D/MAX2200PC using Cu K_{α} radiation. The compression test was conducted in air with a MTS880 machine from room temperature(RT) to 1 373 K and the recorded stress—strain curves were converted to the true stress—true strain curves via the assumption of the constant volume.

3 Results and discussion

3.1 As-cast microstructure

Fig.1 shows the SEM micrographs of Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W). The alloys are composed of four phases: NiAl (dark phase), α -Cr solid solution (gray plate phase and coarse phase), Cr_2Nb (white phase) (Fig.1(b)) and $\text{Ni}_2\text{Al}(\text{Ti}, \text{Hf})$ phase (white phase), identified by XRD pattern (Fig.2).

NiAl and Cr(Mo) plate exhibit a radiate emanating pattern from the cell interior to its boundary and the size of eutectic cell is smaller than that of NiAl-Cr(Mo). Heusler phase $\text{Ni}_2\text{Al}(\text{Ti}, \text{Hf})$ together with Laves phase Cr_2Nb distributes at cellular boundary. Coarse α -Cr solid solution phase with size of about $30\text{ }\mu\text{m}$ exists at the junction of the grains with different orientations.

The chemical compositions of each constituent phase analyzed by EDX are listed in Table 1, indicating that W mainly enriches in coarse α -Cr solid solution (denoted as Cr(Mo, W)) and content of Mo in coarse Cr(Mo, W) phase is larger than that in Cr(Mo) plate. The refractory W element may change the solidification path and the solidification can be described as follows: $L \rightarrow L1 + \text{Cr}(\text{Mo}, \text{W})_{\text{ss}} \rightarrow L2 + \text{Cr}(\text{Mo}, \text{W})_{\text{ss}} + \text{Cr}_2\text{Nb} \rightarrow \text{Cr}(\text{Mo}, \text{W})_{\text{ss}} + \text{Cr}_2\text{Nb} + [\text{NiAl}(\text{Ti}, \text{Hf}) + \text{Cr}(\text{Mo})]$ eutectic $\rightarrow \text{Cr}(\text{Mo}, \text{W})_{\text{ss}} + \text{Cr}_2\text{Nb} + [\text{NiAl}(\text{Ti}) + \text{Cr}(\text{Mo})]$ eutectic + $\text{Ni}_2\text{Al}(\text{Ti}, \text{Hf})$.

It is needed to be mentioned that (Ti, Hf)_{ss} is not

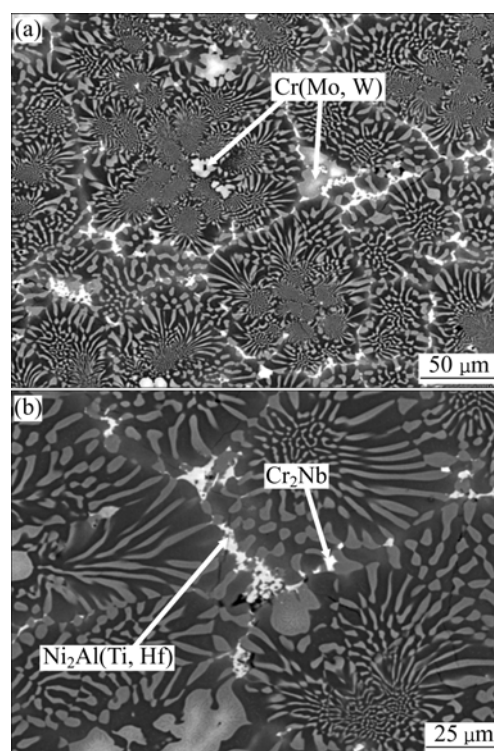


Fig.1 SEM micrographs of as-cast microstructures of Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W) alloy showing different phases: (a) Cr(Mo, W); (b) Cr_2Nb and $\text{Ni}_2\text{Al}(\text{Ti}, \text{Hf})$

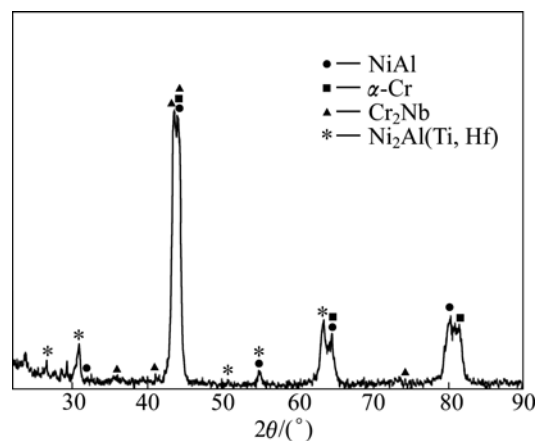


Fig.2 XRD pattern of as-cast Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W) alloy

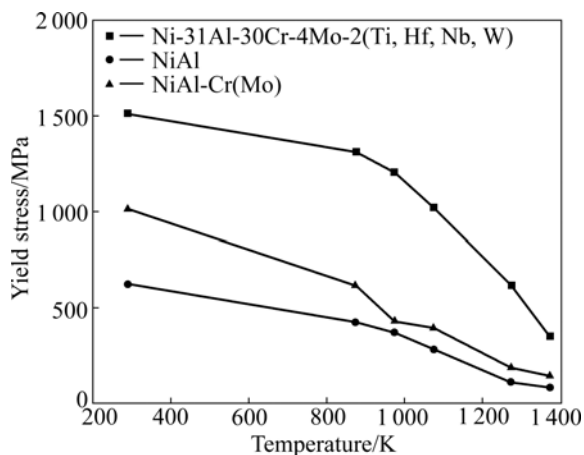
observed in the alloy which precipitates in NiAl-Cr(Mo)-(Ti, Hf) alloy[8]. This may be the effect of refractory W in this alloy.

3.2 Mechanical properties

As shown in Fig.3, the 0.2% offset yield strength decreases with the increase of temperature. However, Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W) shows higher yield strength than NiAl or NiAl-Cr(Mo). For instance, at 1 373 K, the yield strength of Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W) is 467 MPa, about two times higher than

Table 1 Chemical composition of constituent phases in Ni-31Al-30Cr-4Mo-2(Ti,Hf,Nb,W) alloy

Phase	Chemical composition (molar fraction)/%							
	Ni	Al	Cr	Mo	Ti	Hf	Nb	W
NiAl	47.69	46.39	4.57	—	1.35	—	—	—
α -Cr solid solution (Cr(Mo) plate)	7.98	8.36	74.31	8.82	—	—	—	0.53
α -Cr solid solution (Cr(Mo, W))	11.03	8.73	65.10	12.82	—	—	—	2.32
Cr ₂ Nb	13.06	10.00	46.12	4.35	—	—	23.56	—
Ni ₂ Al(Ti, Hf)	46.31	23.18	8.26	—	6.85	15.4	—	—

**Fig.3** 0.2% yield strength as function of temperature under strain rate of $5.56 \times 10^{-3} \text{ s}^{-1}$

that of NiAl-Cr(Mo) (about 140 MPa)[11]. The enhancement of the yield strength attributes to the dispersion strengthening of Ni₂Al(Ti, Hf), Cr₂Nb phases and Ti and W solid solution. The room-temperature yield strength and compressive strength are 1 511 MPa and 2 028 MPa, respectively, which are much higher than those of NiAl and NiAl-Cr(Mo), as listed in Table 2. It is ascribed to Ti solid solution strengthening in NiAl matrix as reported[8,12–13] and W solid solution strengthening in α -Cr, which are confirmed by Vickers hardness in Table 3. The hardnesses of NiAl matrix and Cr(Mo, W) solid solution phase increase distinctly.

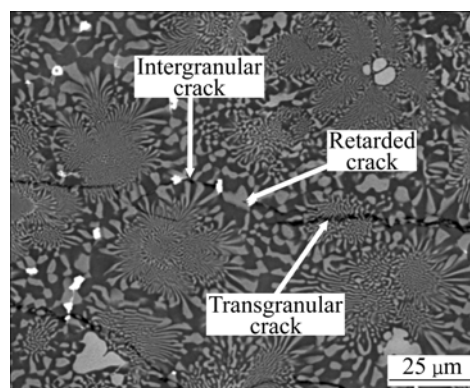
The ambient compression ductility of Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W) alloy calculated from compressive curve is about 17.87%, as listed in Table 2. The crack propagation during compressive deformation is displayed in Fig.4. Generally, the grain boundary is the location of fracture, especially in the brittle Heusler or Laves phases-containing NiAl-Cr(Mo), which trends to exhibit intergranular fracture under load. On the other hand, coarse α -Cr(Mo, W) phase is observed at the grain boundaries to retard the crack propagation, resulting in the fracture characteristic transforming from intergranular model to the mixture of intergranular and transgranular type. Based on the comparison of fracture behaviors, it can be concluded that larger amount of W and Mo solid solution in coarse α -Cr(Mo, W) phase at

Table 2 Results of room-temperature compression test under strain rate of $5.56 \times 10^{-3} \text{ s}^{-1}$

Alloy	Yield strength/MPa	Compressive strength/MPa	Compressive ductility/%
Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W)	1 511	2 028	17.87
NiAl-Cr(Mo)[11]	1 081	1 598	14.20
NiAl[14]	340	—	3.00

Table 3 Room-temperature Vickers hardnesses of NiAl-Cr(Mo)-0.5Hf [15] and Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W) alloy

Alloy	Phase	Vickers hardness
Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W)	Primary NiAl	569
	Eutectic cell	515
	Coarse Cr(Mo, W)	633
NiAl-Cr(Mo)-0.5Hf	Primary NiAl	433
	Eutectic cell	454

**Fig.4** Crack propagation path in compressive deformation of Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W) alloy

the cellular boundary increases the bonding strength of grain boundary to adjust the deformation of grains with different orientations.

The true compressive stress—true strain curves at 1 273–1 373 K with different strain rates are shown in Fig.5. The flow stresses decrease and the samples are softened after peak stress with strain rate changing from 5.56×10^{-3} to $5.56 \times 10^{-5} \text{ s}^{-1}$. At 1 373 K, the sample at strain rate of $5.56 \times 10^{-5} \text{ s}^{-1}$ displays a fast softening after

reaching the peak stress.

Figs.5(c) and (d) show the dependence of the true compressive flow stress on strain rate and these data are fitted to a temperature-compensated power law relationship defined by[15]

$$\dot{\epsilon} = A\sigma^n \exp\left(\frac{-Q}{RT}\right) \quad (1)$$

where A is a constant; n is the stress exponent; Q is the activation energy for deformation; and R is the universal gas constant. The values of A , n , Q and the correlation coefficient (R_d^2) for each fit are given in Table 4. The stress exponent $n=8.47$ higher than that of pure metals ($n=3-5$) reveals that high temperature compressive deformation is conducted by dislocation mechanism [16–18]. The activation energy of the alloy is much

higher than that of NiAl-Cr(Mo) and NiAl, which indicates that the movement of dislocation can be inhibited by precipitation of $\text{Ni}_2\text{Al}(\text{Ti, Hf})$ and Cr_2Nb phases and Ti and W solid solution. The correlation coefficient shows that high temperature deformation can be suitably described by the power law relationship.

4 Conclusions

1) NiAl, α -Cr, Cr_2Nb and $\text{Ni}_2\text{Al}(\text{Ti, Hf})$ phases are observed in Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W) alloy after the addition of W, Ti, Hf and Nb. $\text{Ni}_2\text{Al}(\text{Ti, Hf})$ and Cr_2Nb phases benefit to high-temperature strength. Ti solid solution in NiAl matrix and coarse α -Cr(Mo, W) phase are advantageous to ambient strength and ductility.

2) The additions of W, Ti, Hf and Nb to NiAl-30Cr-

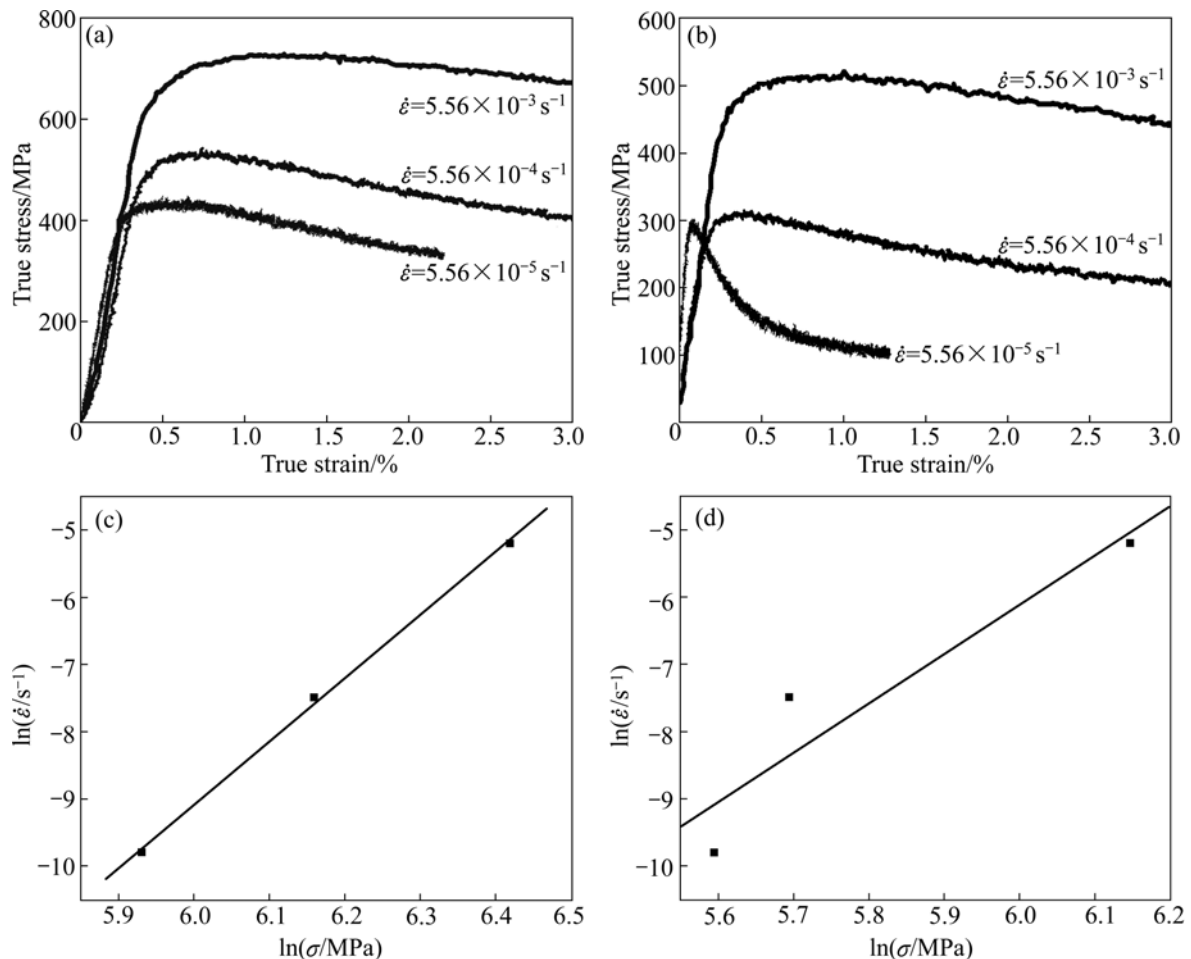


Fig.5 True compressive stress—true strain curves at 1 273 K (a) and 1 373 K (b) and true compressive strain as function of stress at 1 273 K (c) and 1 373 K (d)

Table 4 Temperature-compensated power-law fit of true flow stress and strain rate data

Material	Temperature/K	$Q/(\text{kJ}\cdot\text{mol}^{-1})$	n	A/s^{-1}	R_d^2
Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W)	1 273–1 373	615	8.47	0.898 0	0.956
NiAl-Cr(Mo)[3]	1 273–1 373	456	6.38	0.019 9	—
NiAl[19]	1 100–1 400	314	5.75	0.160 0	0.990

4Mo significantly improve its high-temperature yield strength, room temperature yield strength and ductility.

3) From 1 273 to 1 373 K, the flow stress of Ni-31Al-30Cr-4Mo-2(Ti, Hf, Nb, W) follows power law

relationship: $\dot{\varepsilon} = 0.898\sigma^{8.47} \exp(\frac{-615}{RT})$.

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