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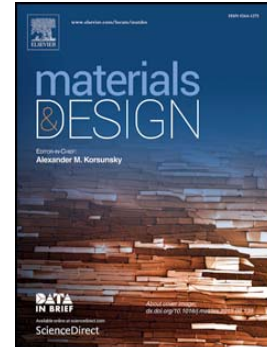
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New phase and deformation behavior in directional solidified NiTiAl based

intermetallic alloy upon cyclic tensile loading-unloading

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Abstract: In the present paper, to understand the nature of newly designed Ni43Ti4Al2Nb2Hf alloys in the case of avoiding shape memory, TEM and HREM were used to reveal the precipitation type, phase composition and its relationship with the hardness. Cyclic tensile loading-unloading test is also carried out to study the deformation behavior. It is observed that a new phase with the approximate composition of $Ti_{36\pm2}$-$Ni_{34\pm2}$-$Nb_{20\pm2}$-$Al_{8\pm1}$-$Hf_{2\pm0.5}$ precipitates in the directional solidified Ni43Ti4Al2Nb2Hf alloy, which is identified to be the base-centered monoclinic lattice with lattice parameters a = 0.987 nm, b = 0.504 nm, c = 1.172 nm, $\alpha = \gamma = 90^{\circ}$, $\beta = 130.18^{\circ}$, and space group C2/c. The hardness of the Ni36Ti20Nb8Al2Hf alloy with same composition to the new phase is more than 810 HV, nearly twice of that of the Ni43Ti4Al2Nb2Hf alloy, which confirms the strengthening effect of the new phase. In addition, the cyclic loading results indicate that the linear recoverable strain is more than 3%, which exhibits the significantly enhanced load capability of this alloy.

Key words: NiTiAl based alloy; Intermetallics; Hardness; Base-centered monoclinic lattice; Cyclic strain-stress response behavior

1. Introduction

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Over the last decade, intermetallics such as nickel aluminides and titanium aluminides have been considered as potential candidates for high temperature applications [1-2]. However, the combination of good strength and good ductility has generally been a dilemma in these intermetallics. Unlike other B2 intermetallics such as NiAl or FeAl, Stoichiometric NiTi has relatively high room-temperature ductility [3]. Meantime, NiTi alloys have also intrinsically good aqueous corrosion resistance [4]. Therefore, it is thought that an intermetallic alloy based on this phase will have sufficient ductility to be used as structural materials in the case of avoiding shape memory [5-6]. For example, it has been developed as a credible candidate material for spacecraft bearing applications [7].

The addition of 8.43 at% Al into B2 NiTi matrix can enhance the compression strength as high as 2300 MPa at room temperature (RT), which is attributed to fine precipitation of coherent L21 (heusler)-Ni_2TiAl compound phases in a NiTiAl matrix [8]. Hence, the Ni_2TiAl (β') and B2-NiTi (β) phase might be expected to form a precipitation hardening system with both good mechanical strength and some ductility, which is similar to the conventional γ/γ' structure of Ni-base superalloys [9-10]. However, the misfit between the NiTi matrix and Ni_2TiAl (β') precipitates in the Ni-Al-Ti system amounts to about 1.5%, considerably larger than the misfit of a few tenths of percent in γ/γ' alloys, that is believed to have a detrimental effect on the creep properties at high temperatures [11-13]. Also, ductility of NiTiAl alloys is gradually reduced as the Al content is increased, as Heusler phase forms primary dendrites, embrittling the material when Al content is above 10.95 at.% [8]. Thus, the compositional control of Al is essential to guarantee the ductility in NiTiAl alloys. In addition, high melting point elements, such as Nb, Hf, Mo and etc, also exhibit the potential in enhancing the integrative mechanical properties at

elevated temperature of NiTiAl alloys. As potential high-temperature structural materials, addition of Nb contributes to the dramatic improvement of oxidation resistance at 1073K in NiTiAlNb alloy [14-15]. Moreover, it is reported that the addition of larger-sized Hf or Mo into the NiTiAl alloy can take effect of solution strengthening and dramatically reinforce the alloy [16-17]. In our previous work, the RT tensile strength of the Nb and Hf modified NiTiAl alloy can be achieved as high as more than 1900 MPa, nearly reaching the level of ultra-high strength steel, and no Heusler phase formation in the alloy [18]. In particular, a new phase has been found in this B2-typed multi-element NiTiAlNbHf alloy, but little is known about the formation, characteristics, role and relationship of this new phase with mechanical property. It is well known that many investigations about NiTi shape memory alloy (SMA) have been focusing on superelasticity or pseudoelasticity behavior and specific properties (transformation temperature, microhardness, indentation modulus) using cyclic loading technology [19-21]. The SMA NiTi with near-equiatomic composition may deform by a reversible, thermoelastic transformation between a high-temperature, cubic (B2) parent austenitic phase and a low-temperature, monoclinic (B19′) martensitic phase [22-24]. However, to the best of our knowledge, no study exists on the mechanical behavior of NiTiAlNbHf alloy where an austenitic matrix deforms without the presence of martensite phase. Without such information, it is not possible to systemically optimize the B2 NiTiAl based alloy for future structural material applications. In the present paper, to understand the nature of NiTiAlNbHf series alloys, TEM and HREM were used to reveal the microstructure in details, especially the new phase, and cyclic tensile loading test is also carried out to study its relationship with the mechanical property.

2. Experimental procedure

2.1. Processing

The nominal composition of the alloy used in the present study is Ni43Ti4Al2Nb2Hf (at%). Master ingots were made from pure elements (99.76 wt% Ti, 99.98 wt% Ni, 99.99 wt% Al, 99.98 wt% Nb and 99.9 wt% Hf) in a water-cooled copper crucible arc-melting furnace under argon atmosphere. To ensure composition homogeneity, the ingots were melted four times. Before the DS experiment, the bar stock for DS was cut by wire-electrode cutting to 14 mm in diameter and 220 mm in total length from the master alloy ingots. After grinding, cleaning and drying, the bars were enclosed in a home-made Y_2O_3/Al_2O_3 double layer ceramic tube, which was 240 mm in length, 20 mm in outer diameter and 14.5 mm in inner diameter [25]. The DS experiments were carried out in a vertical Bridgman furnace with W-cylinder heating and liquid metal cooling. Before the DS experiments, the chamber of the furnace was evacuated at a 10^{-3} Pa level and backfilled with high purity argon to a pressure of 0.05 MPa. Then, the furnace was heated to 1550 ℃ to melt the alloy. After reaching the holding time of 20 min, the ceramic tube and the melt inside were drawn into the Ga-In-Sn cooling liquid.

2.2. Microstructural studies

The microstructural samples were sampled from the centers of the DS bar stock, which are the steady-state growth regions. The samples were cut in transverse section and then ground and polished. The microstructure and phase compositions were examined using a JXA8100 electro-probe microanalyzer (EPMA), which was equipped with energy dispersive X-ray spectroscopy (EDS). The phase types were analyzed with a D/MAX-2500 X-type X-ray diffractometer (XRD) with Cu K α radiation (voltage: 40 kV; current: 200 mA; scanning speed

of 6°/min; scanning range of 10–90°). Thin foils for transmission electron microscopy (TEM) observation were prepared using the argon ion thinning technique. The TEM imaging and selected area diffraction pattern (SADP) were performed on a JEOL-2100F electron microscope. EDS was also performed on the JEOL 2100F TEM operating at 200 kV and equipped with a Schottky field-emission gun (FEG) and an Oxford ultrathin-window EDS detector.

2.3. Hardness and Cyclic loading test

Vickers hardness measurements were carried out on polished sample surface. 980 mN load was applied for 15 s using a diamond Vickers indenter (FM800, Japan). More than five indents were performed on each sample, and average hardness values were achieved among these five indents. The tensile loading specimens were in the gauge size of 18mm×3mm×2mm. The tensile direction is parallel to the directional solidification growth direction. The tensile loading tests were carried out using an SANS-CMT5504 test machine. Axial strain was measured using an YYJ-2/10 type extensometer. The cyclic tensile loading is at a speed of 0.05mm/min.

3. Results and discussion

3.1. The precipitates in the DS Ni43Ti4Al2Nb2Hf based alloy

Fig. 1(a) show the typical microstructure of directional solidified Ni43Ti4Al2Nb2Hf (at%) alloys, the phases details in the interdendritic area is magnified in Fig. 1(b). It can be indicated that the microstructure consisted of grey matrix, dark second phase, white second phase, light grey phase which is adjacent to the dark and white phases. These phase morphologies are the same as the results investigated by Pan LW et al [16]. But, in order to quite appropriate to study the composition of each phase, here, accurate TEM-EDS spectra collected from each contrast have

been carried out and corresponding datum are shown in Fig.1c-f.

Quantitative TEM-EDS data indicates that the composition of matrix with grey contrast is the near equi-atomic NiTi matrix phase, in which small amounts of Al, Hf and Nb are dissolved. In addition, the black one represents the Ti_2Ni phase, while the white region distributes β-Nb phase with Nb content as high as up to 76.74 at%. The SAED patterns of Ti_2Ni and β-Nb phases are shown in Fig.2. As reported by Meng et al. [15], the Ti_2Ni phase can strengthen the NiTi matrix phase at room temperature. Zhang et al. [26] thought that the β-Nb phase is a plasticity phase, whereas the Ti_2Ni phase is a brittleness phase at room temperature. As for the composition of light grey region, which has been once thought to be the same as the white β-Nb phase but more Al, Ti, Hf and Ni atoms dissolved, equivalently β-Nb (Ti, Ni, Al, Hf) phase [27-28]. In the present work, more detailed and accurate observation about this phase has been done. First, it is determined with a relatively stable composition of 36 ± 2 at% Ti, 34 ± 2 at% Ni, 20 ± 2 at% Nb, 8 ± 1 at% Al and 2 ± 0.5 at% Hf, which is namely X phase for simple. In order to observe each element's distribution intuitively, the EDS element maps are performed, as seen in Fig.3. Distinct phase boundaries can be observed between X phase and dark Ti_2Ni or white β-Nb phases. In Comparison with Ti_2Ni and β-Nb phases, an obvious difference is that more Al dissolved in X phase, in addition to this, much less Nb content compared with the β-Nb phases. Actually, viewed X phase at a higher magnification by TEM, it is also found that X phase has totally different lattice structure from Ti_2Ni and β-Nb, or any other existing phase in the Ni-Ti-Al-Nb-Hf series alloy. Based on the above observation, it has been possible to deduce that X phase is previously unreported in the NiTi based alloy. Thus, it is necessary to make clear of the details of X phase.

3.2. The structure of the X phase

Because X phase is large enough to make a SAED study from a single precipitate, hence, Fig. 4 (a-f) shows a set of diffraction tilt series in six different zone axis orientations acquired from X phase (as shown in Fig. 4(g)). Due to the foil sample from the coarse column grain formed by of directional solidification, it is hard to get a set of SAED patterns (EDPs) covering the whole orientation triangle from 0º to 90º. In the sequence of Fig. 4(a) → (b) → (c), the diffraction spots pair marked by the red arrows and A was kept visible when rotating the sample. Similarly, in the sequences of Fig.4 (a) → (d) → (f), the diffraction spots pair marked by the yellow arrows and B was kept visible during rotating, while in the sequences of Fig. 4(a) → (e), the diffraction spots pair marked by green arrows and C was kept visible during rotating. These EDPs can be indexed a base-centred monoclinic lattice with a = 0.9872nm, b = 0.5042nm, c = 1.172nm, α=γ=90º and β=130.18º. The obtained lattice parameters were then used to calculate the angles between the zone axes shown in Fig. 4. All the experimental and calculated tilting angles (ϕ_{exp} and ϕ_{cal}) between neighboring EDPs are indicated in Table 1. As can be seen from Table 1, the experimental angles between two zone axes $[U_1V_1W_1]$ and $[U_2V_2W_2]$ are also in a good agreement with the calculated ones, therefore the crystal structure of X phase was confirmed to be a base-centred monoclinic.

In order to determine the unit cell geometry of X phase, a series of Convergent Beam Electron Diffraction (CBED) and SAED patterns of different orientations was recorded. The first Zone Axis Pattern (ZAP) was indexed as [$\bar{1}$02] and the corresponding CBED pattern which has a (2mm) symmetry (Fig. 5(a) and (b)). It can be seen from Table 2 that the (2mm) symmetry of projection Whole Pattern(WP) CBED gives the $2mm1_R$ projection diffraction group, which relates to four diffraction groups, namely: $2m_Rm_R$、 2mm, $2mm1_R$ (three diffraction group not allowed for

monoclinic lattice) and $2_R mm_R$ (corresponding to 2/m point group). The second ZAP was indexed

as [1$\bar{1}$2] (Fig. 5(c)), projection WP CBED taken along [1$\bar{1}$2] show a symmetry of (2) (see Fig.

5(d)), thus it corresponds to the 21_R diffraction groups (see Table 2), which relates to the three

diffraction groups of 2_R, 21_R (both diffraction groups correspond to 2/m point group) and 2

(corresponding to 2 point group). Since a (2mm) plus a (2) 'net' symmetries are typical of a

monoclinic crystal system [29]. It further confirms that the crystal system of X phase is a

base-centred monoclinic lattice.

The summary of the point group deduction is presented in Table 3. According to Table 3,

three types of zones axis patterns are required to identify the point group for monoclinic. Due to

the TEM foil with preferred orientation of [001] resulted from directional solidification, it is hard

to acquire the [010] ZAP. Taking into account the symmetries of [$\bar{1}$02] and [1$\bar{1}$2] projections, the

point group of the structure of the X phase can be established as 2/m. Based on the

abovementioned the base-centred monoclinic of X phase, 2/m point group corresponds C2/m or

C2/c space group. In addition, some diffraction discs in the [1$\bar{1}$2] CBED pattern (Fig. 4d) are

marked by yellow circles, which exhibit a dark line, which corresponds to a Gjonnes-Moodie (GM)

line. Due to the absence of screw axes in a base-centred monoclinic, it is induced the presence of c

glide planes in the X phase. Thus, the correct space group describing the symmetry of the X phase

is C2/c.

HREM observation along the main zone axes of the X phase has revealed some structural

details of the precipitate. Figure 6 show the HREM image and the corresponding EDPs. In Fig.

6(a), the (200), (110) and ($\bar{1}$10) lattice planes are marked which correspond to spots (200), (110)

and ($\bar{1}$10) respectively in the EDP along [001] direction (as shown in the inset of Fig. 6(a)).

Similarly, the other HREM images and the corresponding EDPs along [1$\bar{1}$2], [011] and [012]

directions are seen in Fig. 6(b), (c) and (d) and the right top corners figures. The different planes

spacing are measured from HREM results, and all the lattice planes from HREM results are found

to be coincident with the crystal lattice of X phase, which further confirm the base-centred

monoclinic of this phase.

3.3. Role of X phase on the hardness

According to Pan et al, the ultra-high RT tensile strength can been achieved, even more than

1900 MPa in this alloy, owing to the presences of the Ti_2Ni and β-Nb phases [15-16,18]. But it is

not yet clear about the role of X phase on the mechanical behavior in this alloy. So, in order to

evaluate the hardness of the new phase, we specially design and fabricate a new alloy with the X

phase composition, using arc-melting furnace with the same processing parameters to the present

master alloy. The nominal composition of this new alloy is Ni36Ti20Nb8Al2Hf (at%), for simple,

which is namely 20Nb alloy. Fig. 7(a) shows the microstructure of the arc-casting 20Nb alloy and

the corresponding XRD results is shown in Fig. 7(b). It is seen from Fig. 7(a) that the

microstructure of the 20Nb alloy comprised of most grey phase, accompanied by dark grey

B2-NiTi, white β-Nb and a few dark Ti_2Ni particles (as shown in the inset of Fig. 7(a)). The

TEM-SAED pattern shown in Fig. 7(c-d) confirms that the grey phase is just the above-mentioned

X phase. In addition, due to remarkable increase in the volume fraction of light grey X phase, the

B2-NiTi phase is not distributed continuously any more, and the X phase changes to be the matrix

phase. Although the phase morphology of 20Nb alloy is apparently different from that of

Ni43Ti4Al2Nb2Hf alloy, each phase composition is exactly the same as that of Ni43Ti4Al2Nb2Hf

alloy, as can be seen from the EDS results (Table. 4). According to the XRD results (Fig. 7(b)),

there are four phases distributed in the Nb20 alloy, which is consistent with the observation by

SEM. For comparison, Fig. 8 gives the Vickers hardness of two alloys. The hardness of the

arc-melted Ni43Ti4Al2Nb2Hf alloy is about 400 HV, after directional solidification, the hardness

improves to about 450 HV. By contrast, it is worth noticing that the hardness of 20Nb alloy is

about 810 HV, nearly twice of that of the former. It is convincing that the increasing of X phase

can prominently enhance the NiTiAl based alloy. More detailed investigation on the 20Nb alloy is

being carried out.

3.4. Cyclic strain-stress response behavior

Extensively studies on the cyclic deformation behavior of NiTi SMA have indicated that NiTi

possesses the excellent superelasticity or pseudoelasticity, as much as 8% strain, based on the

phase transformation between the cubic B2-phase (austenite) and the monoclinic B19' phase

(martensite) [30]. However, so far, very few investigations have been performed on the

NiTiAlNbHf alloy (B2 austenite structure). And, to the best of our knowledge, no martensitic

phase or intermediate R phase occur in the present alloy. Thus, to have a better understanding the

phase stability and deformation behavior of this alloy, cyclic tensile loading and unloading test

(controlling by strain) has been performed. The uniaxial loading direction is taken along with the

growing direction of DS Ni43Ti4Al2Nb2Hf alloy.

Fig. 9(a) shows the strain-stress curves of 25 cycles at a constant maximum strain of 2%, it

can be seen that the strain-stress curve keeps unchangeable linear relationship. Further increase in

the maximum strain of 3% and continuing 10 cycles, it is still remained the linear recoverable

strain (superelastic strain) behavior, as shown in Fig. 9(b). Generally, a maximum of overall

deformation strain is less than 1% for traditional structural materials like steel and some intermetallic alloys, such as NiAl, TiAl and etc. However, as evidenced by cyclic tensile tests, the linear recoverable strain is more than 3% in this DS Ni43Ti4Al2Nb2Hf alloy, which exhibits the significantly enhanced load capability. Therefore, it is indicated that the present alloy possess the superior performance in combination of high hardness and high levels of superelastic behavior, which can withstand extreme loading conditions without incurring permanent surface damage. In addition, our previous work found that the linear elastic strain can be achieved as high as 4.27%, coupled with the tensile strength of 1972MPa [27]. Though much more research will be required to understand the NiTiAlNbHf material, the results obtained thus far point to a very bright future for many applications where extreme loading is unavoidable.

4. Conclusions

The NiTiAl-based intermetallic alloy with B2 structure was fabricated by directional solidification as a potential candidate for high temperature structural material applications. The detailed microstructure, Vickers hardness and superelasticity deformation behavior of the alloy were studied. The main results can be summarized as follows:

1. In the DS Ni43Ti4Al2Nb2Hf alloy, a new phase (named X phase) appears in the interdendritic area, with the composition of about $Ti36\pm2-Ni34\pm2-Nb20\pm2-Al8\pm1-Hf2\pm0.5$ (at%) determined by TEM-EDS technology.

2. The lattice structure of the X phase is identified to be base-centered monoclinic lattice with lattice parameters, a = 0.987 nm, b = 0.504 nm, c = 1.172 nm, $\alpha = \gamma = 90º$, $\beta = 130.18º$. The space group of the X structure was determined to be C2/c on the basis of and CBED

observations.

3. The increasing of X phase can prominently enhance the NiTiAl-based alloy. The Vickers hardness of the DS Ni43Ti4Al2Nb2Hf alloy is about 450 HV. For comparing the influence of X phase, the hardness of 20Nb alloy with the X phase composition is measured to be more than 810 HV, nearly twice of that of the former.

4. The remarkably recoverable, superelastic strain (above 3%) deformation behavior is exhibited in DS Ni43Ti4Al2Nb2Hf alloy with B2 austenite structure, which indicates that the alloy possesses the significantly enhanced load capability.

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Captions of Tables:

Table. 1 Experimental and calculated angles Φ_{exp} and Φ_{cal} between zone axes $[U_1V_1W_1]$ and

$[U_2V_2W_2]$.

Table. 2 Projection WP CBED symmetries of diffraction groups.

Table. 3 Relation between the relevant diffraction groups and monoclinic crystal point groups.

Table. 4 TEM-EDS results of each phase in 20Nb alloy.

Captions of Figures:

Fig.1. Typical cross-section microstructure of DS Ni43Ti4Al2Nb2Hf alloy (a) and enlarged

interdendritic area (b), EDS spectra of NiTi (c), β-Nb phase (d), Ti_2Ni phase (e) and new phase (f).

Fig. 2 SAED patterns of β-Nb phase (a,b,c) and Ti_2Ni phase (d,e,f) in DS Ni43Ti4Al2Nb2Hf

alloy.

Fig. 3 Morphologies of the interdendritic phases (a) and EDS element map for Ti (b), Nb (c), Ni

(d), Al (e) and Hf (f) from the same area.

Fig. 4 Series of SAED patterns at different zone axes. In the sequence of (a) → (b) → (c), the

diffraction spots pair (marked by the red arrows and A) was kept visible when rotating the sample.

Similarly, in the sequences of (a) → (d) → (f) and (a) → (e), the diffraction spots pair (marked by

the yellow arrows and B, green arrows and C) were kept visible during rotating, respectively.

Fig. 5 First incidence ZA [$\bar{1}$02] SAED patterns (a) and CBED (b), second incidence ZA [1$\bar{1}$2]

SAED patterns (c), and CBED (d).

Fig. 6 HREM image of DS Ni43Ti4Al2Nb2Hf alloy and the corresponding SAED patterns along

[001] (a), [1$\bar{1}$2] (b), [011] (d) and [012] (d).

Fig. 7 Microstructure (a) and XRD pattern (b) of 20Nb alloy, and SAED pattern corresponding to

the X phase in 20Nb alloy along [001](c) and [011](d).

Fig. 8 Average microhardness of the present Ni43Ti4Al2Nb2Hf alloy by arc-melting and directional solidification, compared with Nb20 alloy by arc-melting process.

Fig. 9 Evolution of stress–stain curves of DS Ni43Ti4Al2Nb2Hf alloy during loading–unloading cycling: (a) maximum strain of 2% and 3% (b).

Table.1

$U_1V_1W_1$	$U_2V_2W_2$	Φ_{exp} (°)	Φ_{cal} (°)
001	$\bar{1}04$	8.06	7.82
001	$\bar{1}02$	14.2	14.2
001	$0\bar{1}2$	12.14	12.86
001	$0\bar{1}1$	23.28	24.84
001	$\bar{3}34$	22.41	23.96
001	$\bar{1}33$	22.14	24.34

Table. 2

Projection diffraction groups	Corresponding diffraction groups	Projection WP CBED symmetry
1_R	$1,1_R$	1
21_R	$2,2_R,21_R$	2
$m1_R$	$m_R,m,m1_R$	m
$2mm1_R$	$2m_Rm_R,2mm,2_Rmm_R,2mm1_R$	2mm
41_R	$4,4_R,41_R$	4
$4mm1_R$	$4m_Rm_R,4mm,4_Rmm_R,4mm1_R$	4mm
31_R	$3,31_R$	3
$3m1_R$	$3m_R,3m,3m1_R$	3m
61_R	$6,6_R,61_R$	6
$6mm1_R$	$6m_Rm_R,6mm,6_Rmm_R,6mm1_R$	6mm

Table. 3

Point group	[010]	[U0W]	[UVW]
2/m	21_R	$2_R mm_R$	2_R
m	1_R	m	1
2	2	m_R	1

Pratial table taken from [29]

Table. 4

Phase	Composition(at%)				
	Al	Ti	Ni	Nb	Hf
NiTi phase	1.73	42.15	52.51	2.14	1.47
X phase	8.99	35.95	34.19	19.31	1.56
β-Nb phase	2.96	23.51	2.30	71.23	0
Ti$_2$Ni phase	3.09	56.49	34.94	5.15	0.33

Fig. 1

Fig. 1
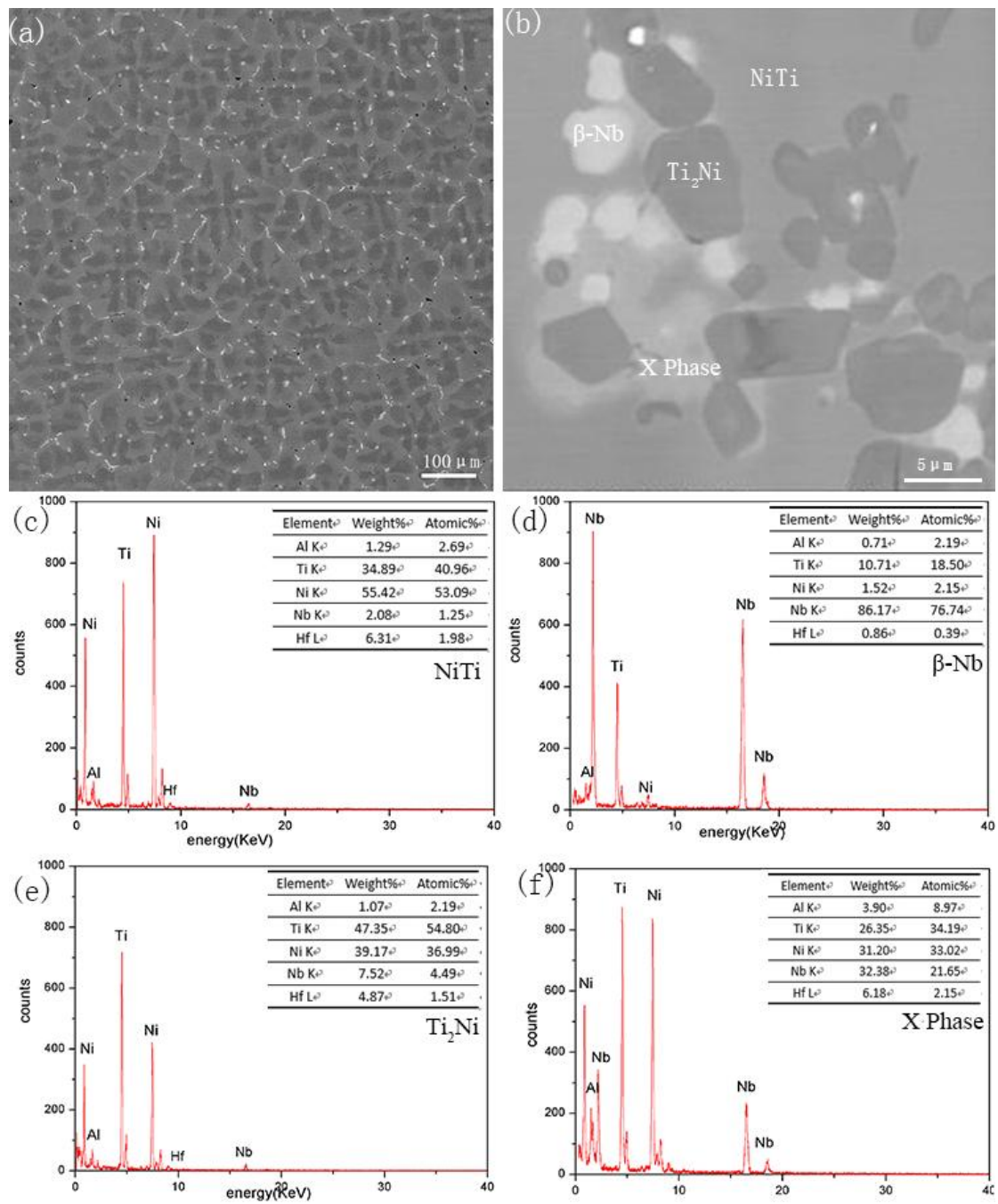
Fig. 2
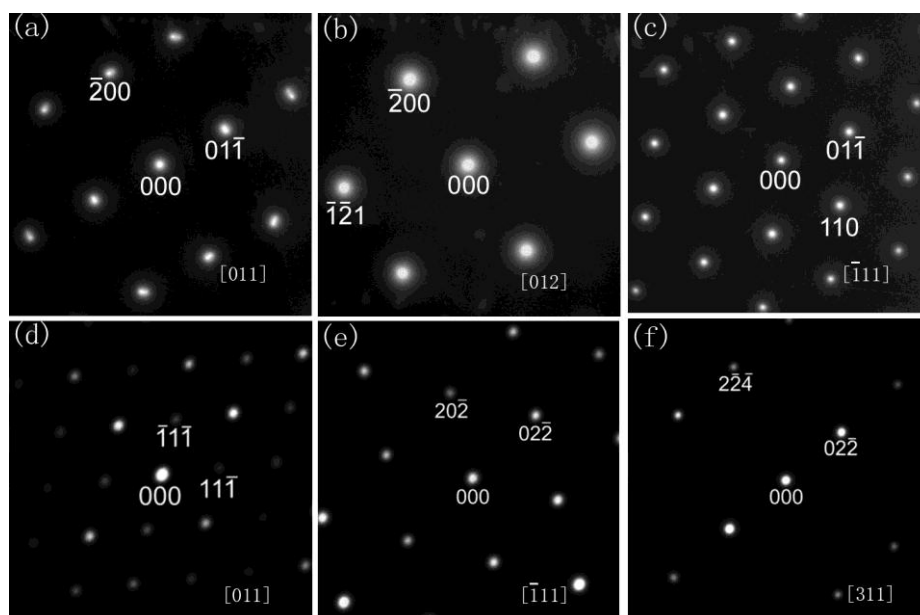
Fig. 3
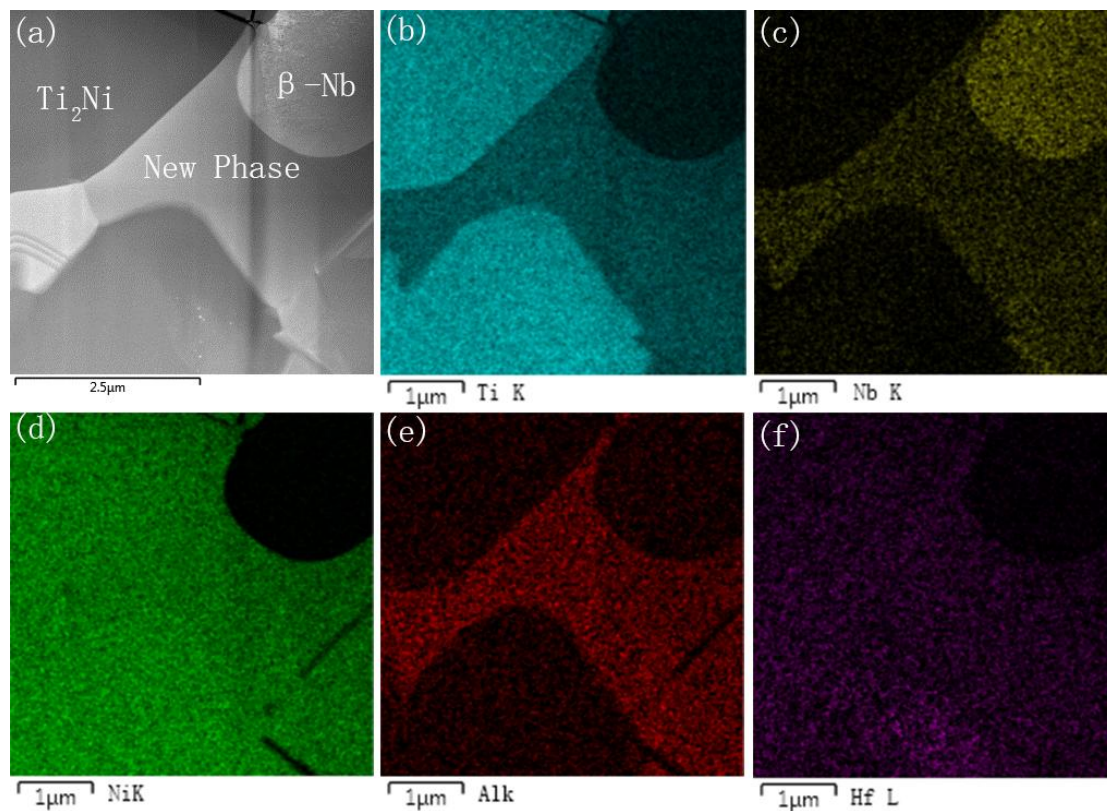
Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Microstructure of the directional solidified Ni43Ti4Al2Nb2Hf alloy

EDS element map of the interdendritic phases

Series of SAED patterns of the X phase at different zone axes

Microstructure and XRD pattern of the 20Nb alloy

SAED pattern corresponding to the X phase in 20Nb alloy

Vickers hardness

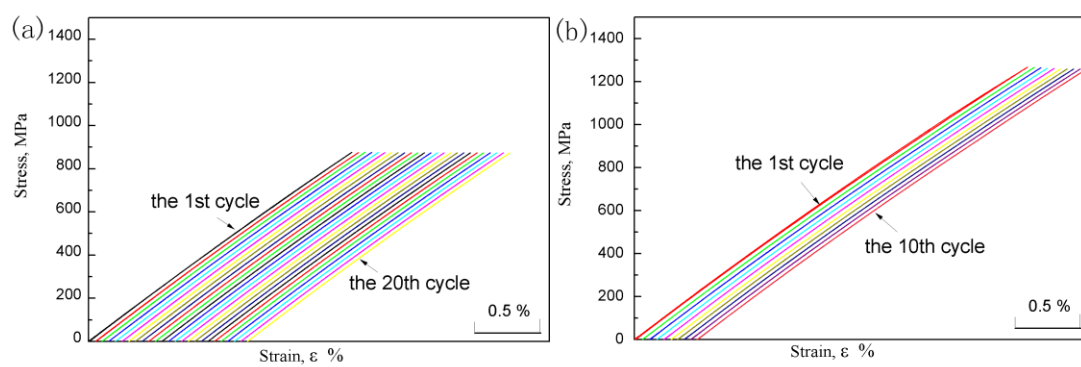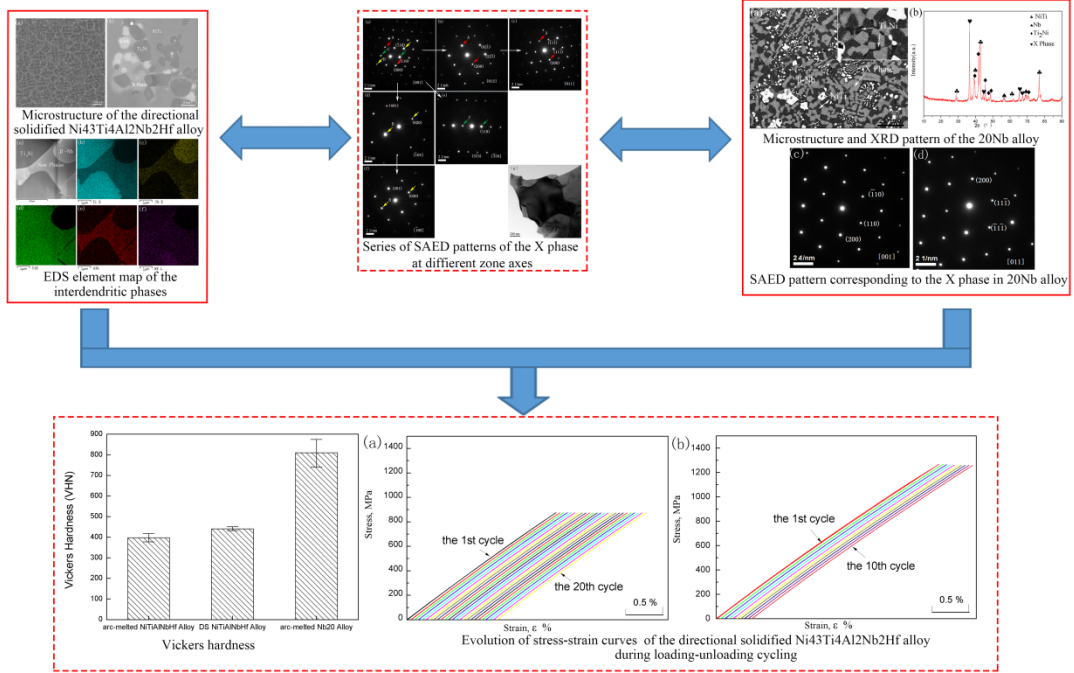Evolution of stress-strain curves of the directional solidified Ni43Ti4Al2Nb2Hf alloy during loading-unloading cycling

Graphical abstract

Highlights

➢ The microstructure of directional solidified Ni43Ti4Al2Nb2Hf(at%) alloy is comprised of B2-NiTi matrix, Ti_2Ni phase, β-Nb phase and a new phase with the composition of Ti36±2-Ni34±2-Nb20±2-Al8±1-Hf2±0.5 (at%).

➢ The new phase is identified to be base-centered monoclinic lattice with lattice parameters, a = 0.987 nm, b = 0.504 nm, c = 1.172 nm, $\alpha = \gamma = 90°$, $\beta = 130.18°$.

➢ The new phase dramatically increases the strength of the directional solidified NiTiAl-based alloy.

➢ The directional solidified Ni43Ti4Al2Nb2Hf alloy exhibits remarkably recoverable, superelastic strain (above 3%) deformation behavior.