Metallophysics and Advanced Technologies
Металофіз. новітні технол.
Metallofiz. Noveishie Tekhnol.
2020, vol. 42, No. 5, pp. 603–610
https://doi.org/10.15407/mfint.42.05.0603
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PHASE TRANSFORMATIONS

PACS numbers: 61.66.Dk, 62.20.fg, 64.70.kd, 81.30.kf, 81.40.Ef, 81.65.Kn

Martensitic Transformation in Quenched Hf–Nb Alloys

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Martensitic transformation and shape memory effect are investigated in Hf–Nb alloys. Niobium content varies in a range of 15 at.% to 50 at.%. Prior to investigation samples are quenched in water. Phase composition, microstructure and functional properties are investigated. For the first time the presence of a martensitic-type phase transition, accompanied by the shape memory effect, is observed in the quenched $Hf_{75}Nb_{25}$ alloy. While for alloys with a higher concentration of hafnium, the quenching temperature will be obviously higher than 1500°C.

Key words: Hf–Nb alloys, martensitic transformation, shape memory.

Проведено дослідження загартованих стопів системи Hf–Nb з концентрацією Ніобію від 15 ат.% до 50 ат.% на предмет протікання мартенситного перетворення та наявності ефекту пам'яті форми. Вивчено мікроструктуру стопів, їх кристалічну будову, методом триточкового вигину досліджені функціональні властивості. Вперше в загартованому стопі $Hf_{75}Nb_{25}$ виявлено наявність фазового переходу мартенситного типу, супроводжуваного ефектом пам'яті форми. Для стопів з більш високою концентрацією Гафнію температури гартування 1500°C явно недостатньо.

Ключові слова: стопи Hf–Nb, мартенситне перетворення, ефект пам'яті форми.

Проведены исследования закалённых сплавов системы Hf–Nb с концентрацией ниобия от 15 ат.% до 50 ат.% на предмет протекания мартенситного превращения и наличия эффекта памяти формы. Изучены микро-

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Citation: S. Kedrovskyi, Yu. Koval, V. Slepchenko, and O. Bezsmertna, Martensitic Transformation in Quenched Hf–Nb Alloys, *Metallofiz. Noveishie Tekhnol.*, **42**, No. 5: 603–611 (2020), DOI: 10.15407/mfint.42.05.0603.

структура сплавов, их кристаллическое строение, методом трёхточечного изгиба исследованы функциональные свойства. Впервые в закаленном сплаве $Hf_{75}Nb_{25}$ обнаружено наличие фазового перехода мартенситного типа, сопровождаемого эффектом памяти формы. Для сплавов с более высокой концентрацией гафния температуры закалки 1500°C явно недостаточно.

Ключевые слова: сплавы Hf–Nb, мартенситное превращение, эффект памяти формы.

(Received November 26, 2019)

1. INTRODUCTION

Alloys based on transition metals of IV and V groups of the periodic table found wide application in field of functional materials [1–3]: firstly, due to possible martensitic transformation (MT) and shape memory effect (SME); secondary, due to their good anticorrosion and biomedical properties [4–7]. Titanium, zirconium and hafnium are the most common base for that type of alloys. These metals have close physical and chemical properties, as well as equal number of valence electrons. Another common thing for all of listed above metals is that they exist in two crystal modifications—low-temperature α (h.c.p.) and high-temperature β (b.c.c.). It should be noted that the temperature of allotropic transformation ($\alpha \to \beta$) of titanium and zirconium has relatively close values of 883 and 863°C, respectively, while hafnium transformation occurs at almost two times higher temperature—1743°C [1, 8]. Addition of niobium into the alloy is a practical way to stabilize the β-phase and reduces the temperature of $\alpha \to \beta$ transformation [1, 2]. Furthermore, niobium forms solid solutions with titanium, zirconium and hafnium [1, 8].

According to [1, 9], the formation of hexagonal α' and orthorhombic α'' martensitic phases occurs in quenched Ti–Nb alloys. It should be noted that critical concentration of niobium for stabilizing of the β-phase must in the range of 28–36 at.% [2, 10, 11]. Meanwhile investigation of quenched alloys in Zr–Nb system confirmed shape memory effect in alloys with niobium concentration between 7 at.% and 14 at.% [12, 13], while concentration of niobium necessary for stabilization of the β-phase found to be close to 20 at.% [1].

Hafnium possesses a similar to titanium and zirconium physical and chemical properties. Moreover, Hf–Nb and Ti–Nb systems have similar view of the phase diagrams. Unlike titanium and zirconium, hafnium has an electronic *f*-shell, which leads to higher temperatures of allotropic transformation. Therefore, depending on the chemical composition, the quenching temperatures will be in a range of 1300–1700°C. In turn, this leads to the complexity of experimental investigation.

It can be assumed that in Hf–Nb system similar martensitic phase transformation occurs. Another assumption can be made regarding Hf–Nb alloys functional properties, such as superelasticity and shape memory effect. If it is so, the Hf–Nb alloys may be a new step towards development of functional alloys with a high-temperature shape memory effect and high degree of biocompatibility.

2. EXPERIMENT

Preparation of samples was done by vacuum arc re-melting in an argon atmosphere (residual pressure $P = 0.05$ MPa). For samples of $Hf_{100-x}Nb_x$ alloys ($x = 15$, 20, 25, 50) were smelted from pure charge components (hafnium 99.99% and niobium 99.99%). Mass of each ingot was 30 g. Deviation of the chemical composition did not exceed 0.01 at.%. After melting test samples in the form of plates measuring 0.3×3×30 mm and samples ∅10×5 mm were cut from the central part of the ingots. Quenching was done from $T = 1500$°C into water at room temperature. While holding time was 1 min. Oxidized layer was mechanically removed. Microstructure of samples was investigated by using of an integrated optical microscope for operation in reflected light—AXIOVERT 40 MAT. Prior to that chemical etching at room temperature were done. Following etchant was used HNO_3 (45%) + HF (5%) + H_2O (50%). The determination of the MT parameters and the presence of the SME were carried out using the three-point bending method [14].

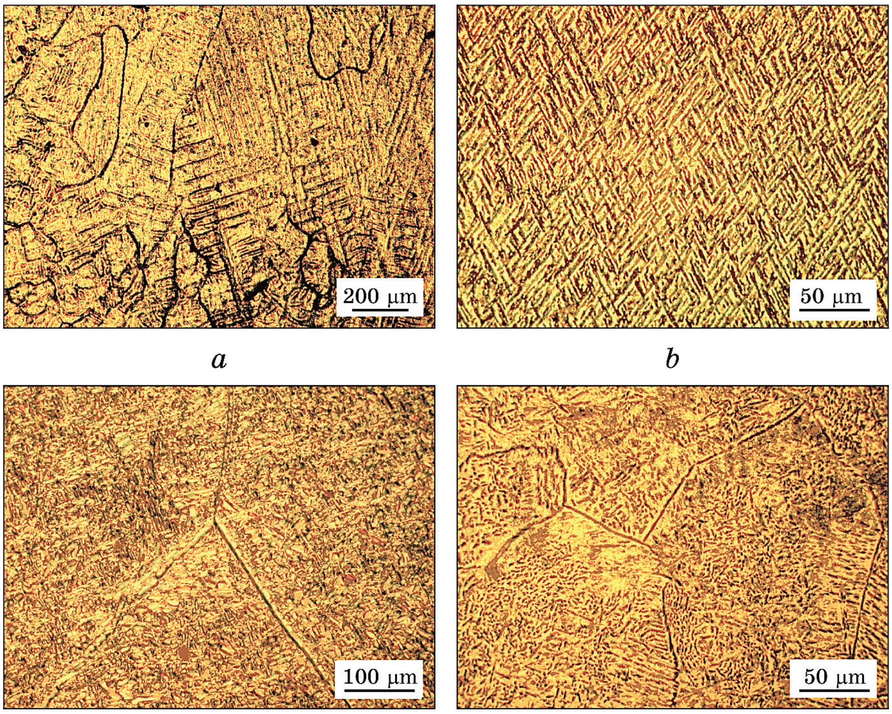
For X-ray phase analysis, a diffractometer STOE STADI MP was used. The shooting was carried out at room temperature in a discrete mode with a step of 0.04° according to the Bragg–Brentano method in CuK_α monochromatic radiation with a wavelength of 0.154 nm.

3. RESULTS AND DISCUSSION

Based on analysis of Ti–Nb and Zr–Nb phase diagrams and temperature ranges of the MT in these alloys, it can be assumed that in the Hf–Nb system the martensitic-type phase transformation exists at niobium concentrations up to 30 at.%. Therefore, following alloy was investigated $Hf_{100-x}Nb_x$ (where $x = 15$, 20, 25, 50 at.%). According to [1] MT in alloys based on transition metals of group IV usually occurs after quenching from temperatures above the polymorphic transformation line.

Microstructure analysis of the quenched $Hf_{50}Nb_{50}$ alloy revealed a structure similar to the nonequilibrium β-phase (b.c.c.) structure typical for Ti–Nb and Zr–Nb alloys [1, 6, 9, 15, 16,]. This fact allows us to assume that if MT occurs in this alloy, then its characteristic temperatures must be below room temperature. With a decrease in the concentration of niobium to 25 at.%, the formation of a distinct acicular structure typical for martensitic phase occurs (Fig. 1, *b*). The microstructure patterns of quenched from a temperature of 1500°C $Hf_{80}Nb_{20}$ and $Hf_{85}Nb_{15}$ alloys do not exhibit a characteristic martensitic structure (Fig. 1, *c*, *d*). The microstructure of these samples looks like as the incompletely recrystallized structure. This may indicate that the quenching point of these alloys should be at a higher temperature. Increased oxidation of hafnium during quenching from temperatures >1500°C can lead to a significant oxidation of the samples, what makes the further investigation process difficult.

The phase composition of the studied samples in the state after quenching was determined by X-ray diffraction. It was found that in the $Hf_{85}Nb_{15}$, $Hf_{80}Nb_{20}$ and $Hf_{50}Nb_{50}$ alloys (Fig. 2, *a*, *c* and *d*) there are bcc reflections of the β-phase of the niobium solid solution in hafnium. Also in inclusions of h.c.p. α-phase of hafnium were found in investigated samples. The presence of b.c.c. β-phase reflexes pointed out that in the alloys the start point of direct MT can be below room tempera-



a *b* *c* *d*

Fig. 1. Microstructure of quenched from 1500°C alloys: $Hf_{50}Nb_{50}$ (*a*), $Hf_{75}Nb_{25}$ (*b*), $Hf_{80}Nb_{20}$ (*c*), $Hf_{85}Nb_{15}$ (*d*).

ture.

Meanwhile, the phase composition of the $Hf_{75}Nb_{25}$ alloy has certain differences, since in addition to the β phase, the presence of an unidentified phase was revealed. The general form of the X-ray diffraction pattern is typical for structures with syngonies of the middle and lower categories (Fig. 2, *b*). Therefore, it can be assumed that this phase represents the martensitic type of the structure. According to [17, 18] $Hf_{50}Nb_{50}$ alloy has a b.c.c. lattice at room temperature.

In order to detect the shape memory effect in quenched samples of Hf–Nb alloys, thermomechanical tests were carried out according to the three-point bending scheme with continuous heating and cooling. Martensitic transformation and incomplete shape recovery, which was ~95%, were found only in the $Hf_{75}Nb_{25}$ alloy (Fig. 3). The characteristic temperatures of martensitic transformations correspond to the fol-

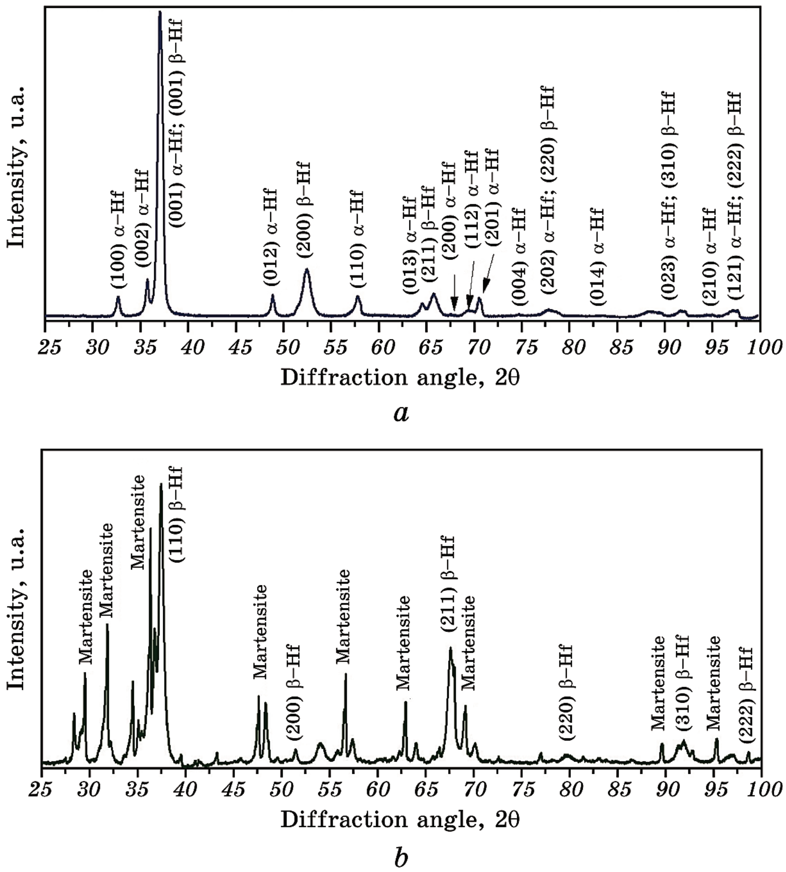
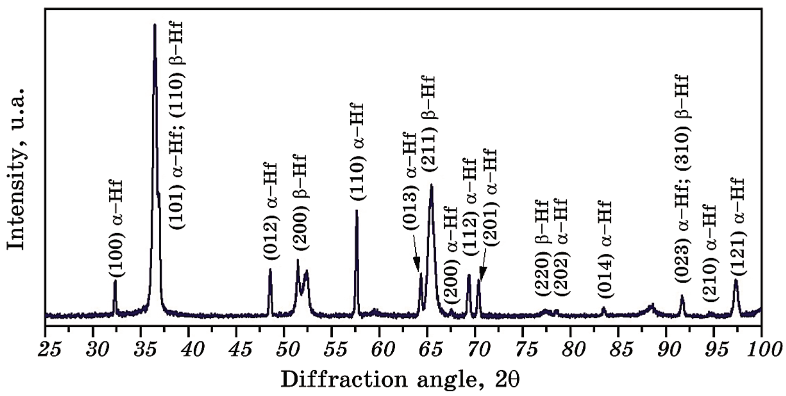
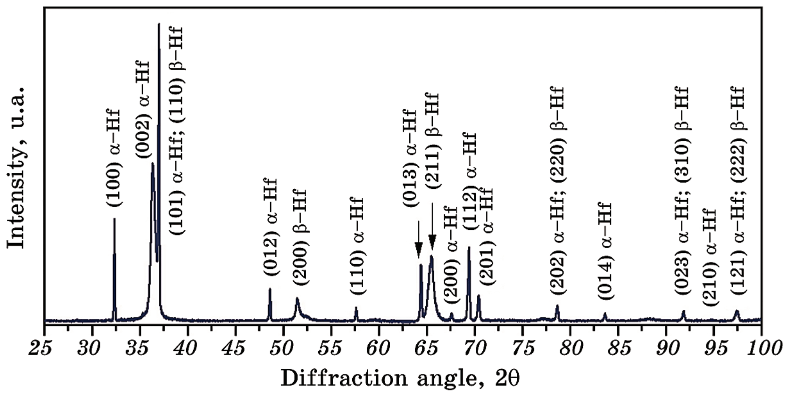


Fig. 2. X-ray diffraction patterns of alloys $Hf_{50}Nb_{50}$ (*a*), $Hf_{75}Nb_{25}$ (*b*), $Hf_{80}Nb_{20}$ (*c*), $Hf_{85}Nb_{15}$ (*d*) (quenching: $T = 1500$°C; $\tau = 1$ min).



c



d

Continuation of Fig. 2.

lowing values: direct M_S = 220°C, M_F = 70°C, and reverse A_S = 140°C, A_F = 280°C.

The fact of detection of MT in one of Hf–Nb alloys and genetically associated with it the shape memory effect, taking into account the MT in previously studied Ti–Nb and Zr–Nb systems [10] and [12], may indicate the presence of a consistent pattern of the effect between the allotropism of IV group metal elements (Ti, Zr, Hf) to the martensitic transition in alloys with an element of V group (Nb).

4. CONCLUSION

Presence of a martensitic-type phase transition is observed, for the first time, in the quenched $Hf_{75}Nb_{25}$ alloy. It was found that MT accompanied by the shape memory effect. Selected concentration range of studied alloys of Hf–Nb system gave general understanding of pro-

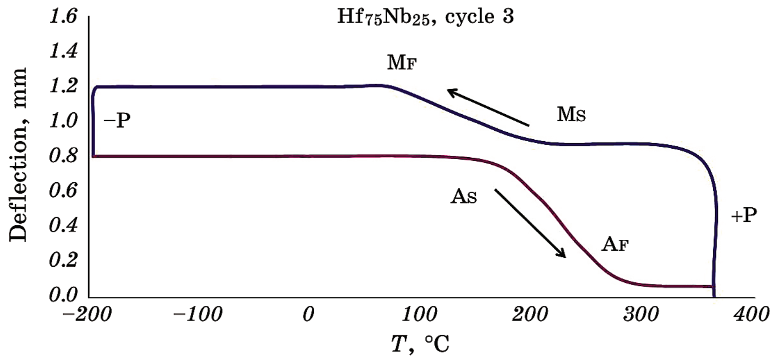


Fig. 3. Temperature dependence of the deformation accumulation and recovery for the $Hf_{75}Nb_{25}$ alloy, cycle 3.

cesses and behaviour of this promising system. That is why further research with reducing the range of the Nb content has scientific potential. In addition, in order to obtain a functional alloy with a high-temperature shape memory effect based on this system, it is necessary to continue the search for alloying components that could increase the MT temperatures.

REFERENCES

1. S. Banerjee and P. Mukhopadhyay, *Pergamon Materials Series*, **12**: 840 (2007).
2. A. V. Dobromyslov and V. A. Elkin, *Scr. Mater.*, **44**: 905 (2001).
3. H. Y. Kim , T. Sasaki, K. Okutsu, J. I. Kim, T. Inamura , H. Hosoda, and S. Miyazaki, *Acta Mater.*, **54**: 423 (2006).
4. Q. Guo, Yo. Zhan, H. Mo, and G. Zhang, *Materials and Design*, **31**: 4842 (2010).
5. V. Brailovski, S. Prokoshkin, M. Gauthier, K. Inaekyan, S. Dubinskiy, M. Petrzhik, and M. Filonov, *Mater. Sci. Eng. C*, **31**: 643 (2011).
6. T. Ahmed and H. J. Rack, *J. Mater. Sci.*, **31**: 4267 (1996).
7. J. A. Davidson, K. P. Daigle, and P. Kovacs, *Artificial Organs*, **20(6)**: 513 (1996).
8. H. Okamoto, *J. Phase Equilibria*, **12**, Iss. 2: 211 (1991).
9. S. Banumathy, R. K. Mandal, and A. K. Singh, *J. Appl. Phys.*, **106**: 093518 (2009).
10. Yu. M. Koval’, S. S. Kovbosha, V. V. Odnosum, V. M. Slipchenko, and G. S. Firstov, *Metallofiz. Noveishie Tekhnol.*, **32**, No. 12: 1681 (2010) (in Russian).
11. T. Inamura, Y. Fukui, H. Hosoda, K. Wakashima, and S. Miyazaki, *Mater. Sci. Eng.*, **25**: 426 (2005).
12. S. N. Kedrovsky, Yu. N. Koval’, and V. N. Slepchenko, *Metallofiz. Noveishie Tekhnol.*, **36**, No. 12: 1651 (2014) (in Russian).
13. F. Okabe, H. Y. Kima, and S. Miyazaki, *Scr. Mater.*, **162**: 412 (2019).
14. V. V. Martinov and L. G. Handros, *FMM*, **39**, No. 5: 1037(1975) (in Russian).
15. N. I. Taluc, *Zakonomernosti Strukturnykh i Fazovykh Prevrashcheniy v*

Tsirkonii i Ego Splavakh s Perekhodnymi Metallami IV–VIII Grupp Periodicheskoy Sistemy Elementov (Thesis of Disser. for Dr. Phys.-Math. Sci.) (Yekaterinburg: 2006) (in Russian).
16. R. Kondo, N. Nomura, Suyalatu, Y. Tsutsumi, H. Doi, and T. Hanawa, *Acta Biomater.*, **12**: 4278 (2011).
17. W. A. Jackson, A. J. Perkins, and R. F. Hehemann, *Metallurgical Transactions*, **1**: 2014 (1970).
18. Wendell B. Jones, R. Taggart, and D. H. Polonis, *Metallurgical Transactions A*, **9**: 723 (1978).