

Available online at www.sciencedirect.com

Chinese Journal of Aeronautics 22(2009) 658-662

**Chinese
Journal of
Aeronautics**
www.elsevier.com/locate/cja

Effects of Nb Content on Yield Strength of NiTiNb Alloys in Martensite State

Xiao Fu, Ma Guojun, Zhao Xinqing*, Xu Huibin

School of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100191, China

Received 26 April 2009; accepted 16 November 2009

Abstract

Two near single-phase NiTiNb alloys— $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ and $\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$ —are prepared and studied by means of scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), differential scanning calorimetry (DSC) and tensile tests in order to unearth the effects of Nb-atom solid solution in NiTi phase on the yield strength induced by self-accommodation of martensite variants. The results show that the yield strength of near single-phase NiTiNb alloys varies inversely with the amount of Nb-atoms solid-dissolved in NiTi phase. From the results out of the prior and current studies, it can be surmised that the effects of Nb content on the yield strength of NiTiNb alloys in martensite state depend on the coaction. Nb solid solution weakening mechanism and β -Nb phase composite strengthening mechanism. This inference might be a satisfactory explanation to the fact that the yield strength of $(\text{NiTi})_{50-0.5x}\text{Nb}_x$ alloys in martensite state begins with decline and then rises when the Nb content increases.

Keywords: NiTiNb alloy; martensite; yield strength; Nb content

1. Introduction

NiTi-based shape memory alloys (SMA) with excellent shape memory effect (SME) and superelasticity (SE) have applications in various fields, such as aeronautics and astronautics, mechanical electronics, medical implanting technology and automatic control systems^[1]. Furthermore, NiTi shape memory alloys are also one of the most important damping materials applied in lots of devices to reduce and absorb vibration and noise^[1-7]. The high damping mechanism of NiTi shape memory alloys is associated with the detwinning process of martensite variations or martensite transformation. Accordingly, shape memory alloys used as a sort of high damping materials in engineering applications must be in the martensite state.

However, NiTi shape memory alloys in martensite state possess very low yield strength due to the reorientation of martensite variants or occurrence of detwinning in the deformation process^[1]. This would limit

the application of NiTi alloys as a high strength damping material in engineering practices^[2-3,7]. Therefore, it becomes an urgent task to develop a new material which has both high yield strength and high damping capacity appropriate for working under room or higher temperature conditions. In this respect, many researchers have viewed tailoring alloy's composition as a potential effective approach to associate these two contradictory properties^[8].

NiTiNb alloys have drawn attention thanks to their microstructurally characteristic in-situ composite structure. For instance, $\text{Ni}_{47}\text{Ti}_{44}\text{Nb}_9$ has the primary NiTi phases in matrix with the eutectic of β -Nb phase and NiTi phase embedded inside^[6,9-12]. In the earlier researches, a series of NiTiNb alloys with this structure were prepared and investigated^[6,11-12]. The as-rolled alloy samples possessive of a lot of β -Nb phase exhibited much higher yield strength in tensile tests than the as-rolled $\text{Ni}_{50}\text{Ti}_{50}$ ones^[13]. This proved the β -Nb phase composite mechanism which is in position to strengthen NiTiNb alloys. However, it was found to be quite strange that, in $(\text{NiTi})_{50-0.5x}\text{Nb}_x$ alloys, as Nb content increases from 0% to 20%, its yield strength firstly declined and then soared substantially. This caused researchers to suppose not only one mechanism which would play role in affecting the alloys' properties when Nb content increases. If true, then it is necessary to find out what the other mechanism is and

*Corresponding author. Tel.: +86-10-82338559.

E-mail address: xinqing@buaa.edu.cn

Foundation items: National Natural Science Foundation of China (50971009); Science Fund for Creative Research Groups (50921003); Aviation Science Foundation of China (2009ZF51059)

how it behaves in the alloys. Only if this problem is settled, the correct approach can be figured out to prepare high damping NiTiNb alloys with high yield strength.

This article prepares as-rolled $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ and $\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$ alloy samples and determines their microstructures, transformation behavior and mechanical properties, and compares them with those of as-rolled $\text{Ni}_{50}\text{Ti}_{50}$ alloy samples.

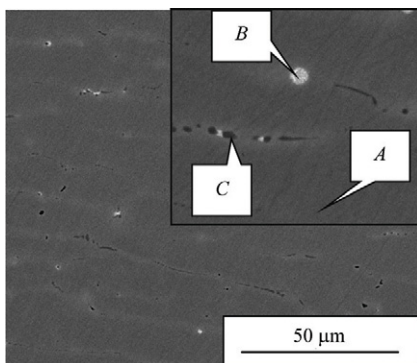
2. Experimental

$\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ and $\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$ alloy samples were prepared by arc melting Ti (99.8 wt%), Ni (99.96 wt%) and Nb (99.9 wt%) in a water-cooled copper hearth. The ingots weighing about 100 g were repeatedly melted four times for alloying homogenization. The ingots thus obtained were then hot rolled at 850 °C into plates 1.2 mm thick. The specimens for differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and tensile tests cut from the plates were annealed at 850 °C for 40 min and quenched in water. The $\text{Ni}_{50}\text{Ti}_{50}$ alloy for comparison is prepared in the same way. The transformation behavior of specimens was measured by DSC using a Netzsch 204 F1 analyzer at the rate of 5 °C/min. An MTS-880 mechanical tester was used to determine the stress-strain curves. An observation of microstructure and quantitative analysis of composition were performed on a FEI Quanta600 SEM equipped with an energy dispersive X-ray analyzer of IE-350 type made by Oxford Instruments.

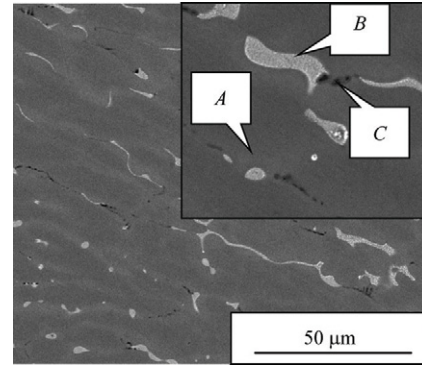
3. Results and Discussion

3.1. Microstructure of near single-phase NiTiNb alloys

Fig.1 shows the SEM images of as-cast $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ and $\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$ alloy samples. The analysis by energy dispersive spectroscopy (EDS) indicates that the dark region (A) represents the NiTi phase and the black region (C) the $(\text{Ti, Nb})_4\text{Ni}_2\text{O}$ phase, which is brittle to the detriment of ductility. The bright region (B) is the eutectic of TiNi phase and β -Nb phase with the composition over the whole area listed in Table 1.



(a) $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$



(b) $\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$

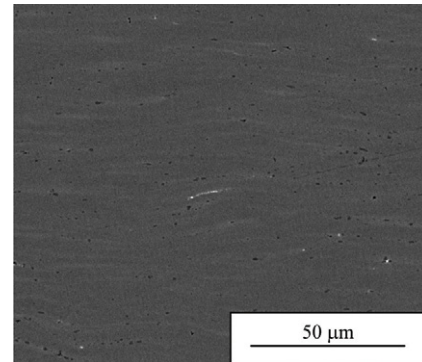
Fig.1 SEM images of as-cast NiTiNb alloy samples.

Table 1 EDS compositions of $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ and $\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$ alloys

		at%		
Area		Ni	Ti	Nb
As-cast sample	$\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$	48.48	49.41	2.11
	$\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$	48.03	47.61	4.36
Matrix of as-cast sample	$\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$	48.89	49.38	1.73
	$\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$	49.25	47.65	3.10
As-rolled sample	$\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$	48.31	49.55	2.14
	$\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$	47.82	47.83	4.36
Matrix of as-rolled sample	$\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$	48.66	49.55	1.79
	$\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$	48.53	47.77	3.70

Fig.2 shows the SEM images of as-rolled $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ and $\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$ alloy samples. It seems that the eutectics have been crashed and dispersed in NiTi phase to form some Nb-rich phases, which are hardly brought out in as-rolled $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$ alloy samples, but zoned just like slim silk in as-rolled $\text{Ni}_{49.5}\text{Ti}_{46.5}\text{Nb}_4$ alloy samples.

According to composition analysis by EDS (see Table 1), it is indicated that most Nb-atoms of the alloy have dissolved in NiTi phase and the amount of solid-dissolved Nb-atoms in the NiTi phase of both as-rolled alloy samples stands at 1.79% and 3.70% respectively. Moreover, the as-rolled samples show higher Nb solid solution in NiTi phase than the as-cast samples.



(a) $\text{Ni}_{50}\text{Ti}_{48}\text{Nb}_2$

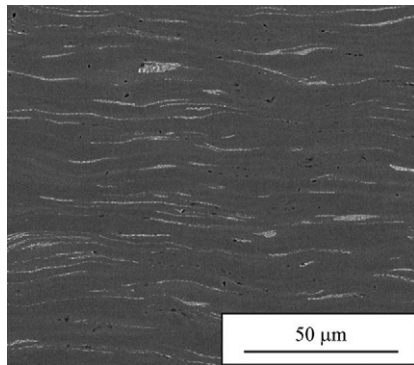
(b) Ni_{49.5}Ti_{46.5}Nb₄

Fig.2 SEM images of as-rolled NiTiNb alloy samples.

Fig.3 shows the transformation behavior of as-rolled Ni₅₀Ti₄₈Nb₂ and Ni_{49.5}Ti_{46.5}Nb₄ alloy samples. The DSC results display that the martensite transformation in Ni₅₀Ti₄₈Nb₂ alloy starts at 8 °C while Ni_{49.5}Ti_{46.5}Nb₄ alloy at -9 °C. Their exothermic and endothermic peaks are shorter and wider than those of Ni₅₀Ti₅₀ alloy. In Fig.3, M_s is the martensitic transformation start temperatures, A_s the austenitic transformation start temperatures. As shown in Table 1, it is clear that the more the Nb-atoms have dissolved in NiTi phase, the shorter and wider the peaks become by DSC analysis. This implies that Nb-atoms that have dissolved in NiTi phase might not disperse homogeneously. According to

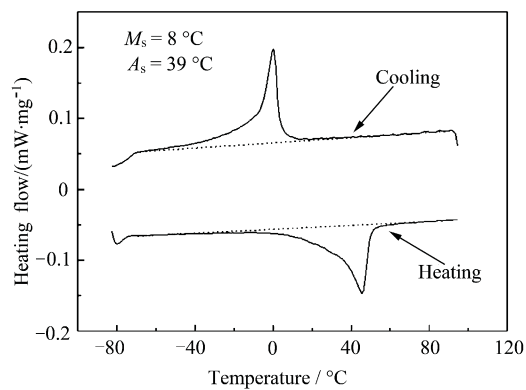
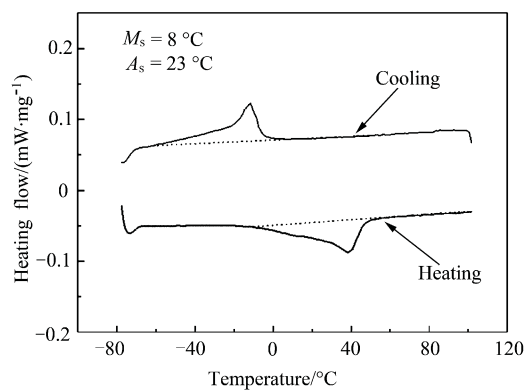
(a) Ni₅₀Ti₄₈Nb₂(b) Ni_{49.5}Ti_{46.5}Nb₄

Fig.3 DSC curves of as-rolled NiTiNb alloy samples.

authors' previous experimental investigation, martensite transformation temperature of NiTiNb alloys can be controlled by adding Nb. Because Nb-atoms tend to replace Ni-atoms^[11], the higher the Nb content and the Ni/Ti ratio are, the lower the martensite transformation temperature results are^[6,11]. Thus the transformation temperature of micro-areas in NiTi phase varies as the amount of solid-dissolved Nb-atoms changes.

3.2. Mechanical property of TiNiNb alloys

Since it was documented that the lowest yield strength can be obtained at the temperatures near M_s point^[14], all tensile tests were carried out at $M_s - 15$ °C to ensure the samples staying in martensite state. Before the test was undertaken, the specimen was first heated to 100 °C, preserved for 1 min and then cooled to the prefixed test temperature, i.e. $M_s - 15$ °C. Fig.4 illustrates the stress-strain curves of as-rolled Ni₅₀Ti₄₈Nb₂ and Ni_{49.5}Ti_{46.5}Nb₄ alloys. For the purpose of comparison, Fig.4 also indicates the stress-strain curve of as-rolled Ni₅₀Ti₅₀ alloy at $M_s - 15$ °C.

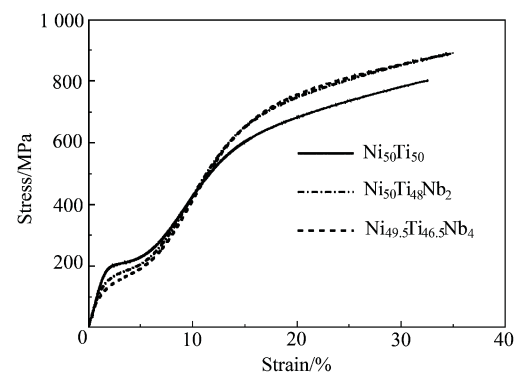


Fig.4 Stress-strain curves of as-rolled samples in tensile tests.

From Fig.4, it can be observed that the yield strength of as-rolled Ni₅₀Ti₄₈Nb₂ and Ni_{49.5}Ti_{46.5}Nb₄ alloys at $M_s - 15$ °C is under 160 MPa, much lower than that of as-rolled Ni₅₀Ti₅₀ alloy, 196 MPa. Fig.5 illustrates the detailed relationship between the yield

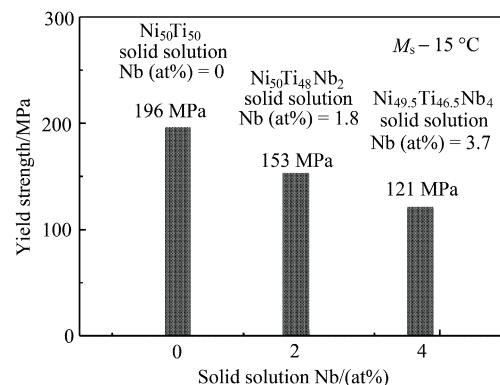


Fig.5 Influences of Nb-atoms in solid solution on yield strength of as-rolled near single-phase NiTiNb alloy.

strength at $M_s - 15^\circ\text{C}$ and the amount of Nb-atoms in solid solution.

From Fig.5, it is quite easy to discover that the yield strength of near single-phase NiTiNb alloys declines as the amount of Nb-atoms in solid solution increases in an approximately linear manner. This bears a relation to authors' prior work on $(\text{NiTi})_{50-0.5x}\text{Nb}_x$ ($x = 0, 5, 10, 15, 20$) alloys, which evidenced the effects the Nb content can exert on the microstructure, yield strength and damping capacity of $(\text{NiTi})_{50-0.5x}\text{Nb}_x$ alloys^[13]. Fig.6 quotes the relationship between yield strength and Nb content in $(\text{NiTi})_{50-0.5x}\text{Nb}_x$ alloys.

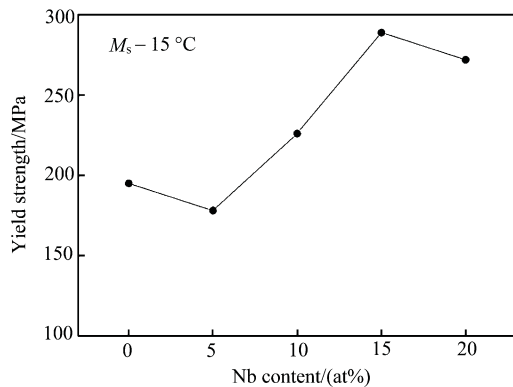


Fig.6 Influences of Nb content on yield strength of as-rolled $(\text{NiTi})_{50-0.5x}\text{Nb}_x$ ($x = 0, 5, 10, 15, 20$) alloys^[13].

According to the results from the previous and on-going studies, it stands to reason that it is the coaction of two mechanisms, Nb solid solution mechanism and β -Nb phase composite mechanism, that decides the effects of Nb content on yield strength of NiTiNb alloys. By Nb solid solution mechanism is meant that dissolution of Nb-atoms in NiTi phase leads to decreasing the yield strength of single NiTi phase as evidenced by this study. By β -Nb phase composite mechanism is meant that a great number of free Nb-atoms form a lot of β -Nb fiber-shaped phases, which act as strengtheners to enhance the yield strength^[13]. Fig.7 schematizes the aforementioned co-active phenomena.

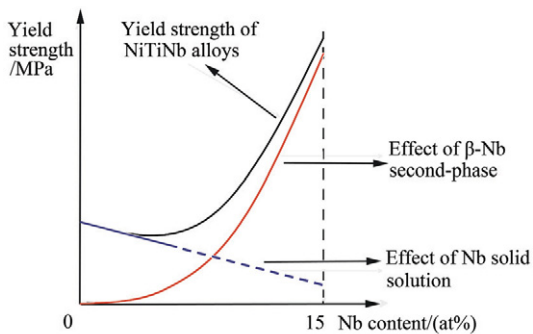


Fig.7 Schematic representation of Nb solid solution mechanism and β -Nb phase composite mechanism.

When Nb content is relatively low, for example below 5%, a majority of Nb-atoms dissolve in NiTi phase of the NiTiNb alloys, in which the Ni content is approximately equal to Ti content. In this case, the Nb solid solution mechanism plays a primary role in affecting the yield strength making it decline as Nb content increases.

The amount of Nb-atoms solid-dissolved in NiTi phase can allegedly hardly exceed 6 at%^[13]. This is the reason why a larger section of the declined line in Fig.7 indicating the effects of Nb solid solution mechanism appears as a dash line. The more the Nb content is, the more the β -Nb phase emerges. When Nb content exceeds 10 at%, major portion of Nb content would exist as β -Nb phase, which puts the β -Nb phase composite mechanism into action in the case of high Nb content. The yield strength rises with β -Nb phase increasing.

This inference could satisfactorily explain why the yield strength of $(\text{NiTi})_{50-0.5x}\text{Nb}_x$ alloys follows first decline with a subsequent considerable rise with the Nb content increasing from 0 at% to 15 at%. However, it is still unclear why the yield strength again turns down once Nb content exceeds 15 at%. Maybe, this is because almost all the Nb content (about 20 at%) would form eutectics so as to make it difficult to retain some big fiber-shaped β -Nb phases, which are more likely to strengthen the alloy than the smaller ones.

4. Conclusions

This article has made it clear that the yield strength of near single-phase NiTiNb alloys declines in an approximate linear manner with Nb solid solution increasing in NiTi phase.

It is surmized that effects of Nb content on yield strength of NiTiNb alloys depend upon the coaction of two mechanisms, i.e., Nb solid solution mechanism and β -Nb phase composite mechanism. When the alloy contains lower Nb, the former mechanism plays a primary role. When it contains higher Nb, the former mechanism gives way to the latter one.

References

- [1] Otsuka K, Ren X. Physical metallurgy of Ti-Ni-based shape memory alloys. *Progress in Materials Science* 2005; 50(5): 511-678.
- [2] van Humbeeck J. Damping capacity of thermoelastic martensite in shape memory alloys. *Journal of Alloys Compounds* 2003; 355(1-2): 58-64.
- [3] Cai W, Lu X L, Zhao L C. Damping behavior of TiNi-based shape memory alloys. *Materials Science and Engineering: A* 2005; 394(1-2): 78-82.
- [4] Wu S K, Lin H C. Damping characteristics of TiNi binary and ternary shape memory alloys. *Journal of Alloys Compounds* 2003; 355(1-2): 72-78.
- [5] Cai W, Meng X L, Zhao L C. Recent development of TiNi-based shape memory alloys. *Current Opinion in Solid State & Materials Science* 2005; 9(6): 296-302.

- [6] Xiao F, Ma G J, Zhao X Q, et al. A novel TiNiNb shape memory alloy with high yield strength and high damping capacity. Proceedings of the SPIE, the International Society for Optical Engineering. 2007; 6423: 64232L.
- [7] Rajagopalan S, Little A L, Bourke M A M, et al. Elastic modulus of shape-memory NiTi from in situ neutron diffraction during macroscopic loading, instrumented indentation, and extensometry. Applied Physics Letters 2005; 86(8): 081901.
- [8] Schaller R. Metal matrix composites, a smart choice for high damping materials. Journal of Alloys Compounds 2003; 355(1-2): 131-135.
- [9] Piao M, Miyazaki S, Otsuka K, et al. Effects of Nb addition on the microstructure of Ti-Ni alloys. Materials Transactions JIM 1992; 33(4): 337-345.
- [10] Piao M, Miyazaki S, Otsuka K. Characteristics of deformation and transformation in $\text{Ni}_{44}\text{Ti}_{47}\text{Nb}_9$ shape memory alloy. Materials Transactions JIM 1992; 33(4): 346-353.
- [11] Zhao X Q, Yan X M, Yang Y Z, et al. Wide hysteresis NiTi(Nb) shape memory alloys with low Nb content (4.5 at.%). Materials Science and Engineering: A 2006; 438: 575-578.
- [12] He X M, Rong L J, Yan D S, et al. TiNiNb wide hysteresis shape memory alloy with low niobium content. Materials Science and Engineering: A 2004; 371(1-2): 193-197.
- [13] Xiao F, Zhao X Q, Xu H B, et al. Damping capacity and mechanical property of NiTiNb shape memory alloys. Acta Metallurgica Sinica 2009; 45(1): 626-632. [in Chinese]
- [14] Melton K N, Mercier O. The mechanical properties of NiTi-based shape memory alloys. Acta Materialia 1981; 29(2): 393-398.

Biography:

Xiao Fu Born in 1981, he received B.S. degree from Beijing University of Aeronautics and Astronautics in 2003 and then became a Ph.D. candidate there. His main research interest lies in smart materials.
E-mail: xf@mse.buaa.edu.cn