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## Relationship between phase composition and corrosion resistance of Ni-Ti-Nb based shape memory alloys<sup>①</sup>

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**[Abstract]** The stability and microstructure of Ni-Ti-Nb based shape memory alloys were investigated after alloyed with elements Zr, Cr and V. In artificial seawater (3.5% NaCl) and physiological solution (5% NaCl+ 0.1% H<sub>2</sub>O<sub>2</sub>), the results show that the alloying elements influence the corrosion behavior of Ni-Ti-Nb alloys. Generally, Zr improves the corrosion resistance of Ni-Ti-Nb alloy, Cr reduces its corrosion resistance and V does not change the property. In order to investigate the reason of the difference, the relation of the phase components and corrosion resistance of Ni-Ti-Nb based shape memory alloys were studied by element analysis and SEM.

**[Key words]** Ni-Ti-Nb; corrosion resistance; phase components; shape memory alloy

**[CLC number]** TG 139.6

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### 1 INTRODUCTION

Ni-Ti-Nb alloys, on account of their shape memory and phase transformation hysteresis, have been paid attention by researchers for many years and proposed for various applications<sup>[1-5]</sup>. The results show that the phase transformation hysteresis due to  $\beta$ -Nb particles in Ni-Ti matrix can be obtained by part losing of shape memory effect. Concerning above, quaternary Ni-Ti-Nb based shape memory alloys have been studied in the research to enhance the rate of shape memory effect, to adjust phase transformation temperatures and to decrease the alloy price by adding elements Zr, Cr and V. In this paper, the corrosion behavior of Ni-Ti-Nb based alloys has been studied. At the meaning time, in order to improve knowledge on corrosion behavior of Ni-Ti-Nb based alloys, the relationship between the phase components and their corrosion behavior was investigated.

### 2 MATERIAL PREPARATION

Ni-Ti-Nb based shape memory alloys were prepared in a cold crucible by magnetic suspension furnace under a controlled protective argon followed by quenching into an iron mould. On the basis of Ni-44Ti-9Nb, the compositions of the three quaternary alloys were designed as follows (mole fraction, %): Ni-44Ti-8Nb-V; Ni-44Ti-8Nb-Cr; Ni-44Ti-8Nb-Zr.

The ingots were hot forged and rolled at 750~900 °C, then cold rolled to a thickness of 3 mm. All specimens (10 mm × 10 mm) were cut from the plates and annealed at 850 °C for 30 min in evacuated quartz.

Each of specimens was connected to a wire by means of point welding. Then the exposed surface of the specimens was limited in cylinder by cold mounting using a thermosetting resin, which acted as an insulator for the other sides in the test system. Specimens used in polarization test were polished by 1000# silicon carbide paper, and then put in air for 24 h. The corrosive agent of microstructure is 8% HF + 15% HNO<sub>3</sub>+ 77% distilled H<sub>2</sub>O.

### 3 TEST TECHNIQUE

Anodic polarization is used to study the corrosion behavior of metals showing passivity behavior in these tests. Potentiodynamic cyclic corrosion tests were carried out at 30 °C in artificial seawater (3.5%) and artificial physiological solution (5% NaCl + 0.1% H<sub>2</sub>O<sub>2</sub>), in which oxygen was not driven out. Assistant electrode is Pt plate and saturated calomel electrode was used as comparing electrode in tests. Experiment parameters, the controlling of polarized course and the data collection were conducted in computer program by Monte Carlo method. The step of voltage was 0.2 mV/min. The microstructures of Ni-Ti-Nb based alloys were observed under Hitachi X650 SEM.

### 4 RESULTS AND DISCUSSION

A passive oxide surface film is the basis of the corrosion resistance of Ni-Ti-Nb alloy. The corrosion damage of Ni-Ti-Nb alloys was caused mainly by pitting in corrosive solutions in former study<sup>[6]</sup>.

Generally, NiTiNb shape memory alloy is of excellent corrosion resistance. Above a certain voltage, the current remains low over a reasonably wide range of potential. But above a critical potential known as the pitting potential, the passive film break up, pitting occurs and the current increases rapidly<sup>[7]</sup>. The polarization curves were shown in Fig. 1. Their break potentials ( $E_b$ ) are: in artificial sea water, Ni44Ti9Nb,  $E_b = 440$  mV; Ni44Ti8NbCr,  $E_b = 380$  mV; Ni44Ti8NbZr,  $E_b = 1430$  mV; Ni44Ti8NbV,  $E_b = 452$  mV; in artificial physiological solution Ni44Ti9Nb,  $E_b = 714$  mV; Ni44Ti8NbCr,  $E_b = 624$  mV; Ni44Ti8NbZr,  $E_b = 1510$  mV; Ni44Ti8NbV,  $E_b = 720$  mV.

Comparing the data, we conclude that adding Cr, Zr and V to NiTiNb alloy changes its behavior of corrosion resistance. In the two environments, element Zr enhances the corrosion resistance obviously, while element Cr reduces the ability of corrosion resistance of NiTiNb alloy. The cases were caused mainly by the distribution of alloying elements in their microstructure, which influences their polarized potential. The components of phases in NiTiNb based alloys are listed in Table 1.

The microstructures of NiTiNb based alloys are shown in Fig. 2.

The microstructure form and phase composition in NiTiNb based alloys were different in some way. Comparing the microstructure, the  $\beta$ -Nb particles in NiTiNbZr alloy is partly separated with each other and does not form a net entirely, which is different from the others where  $\beta$ -Nb phases are almost cor-

**Table 1** Results of EPMA analysis for each phase in present alloys (mole fraction, %)

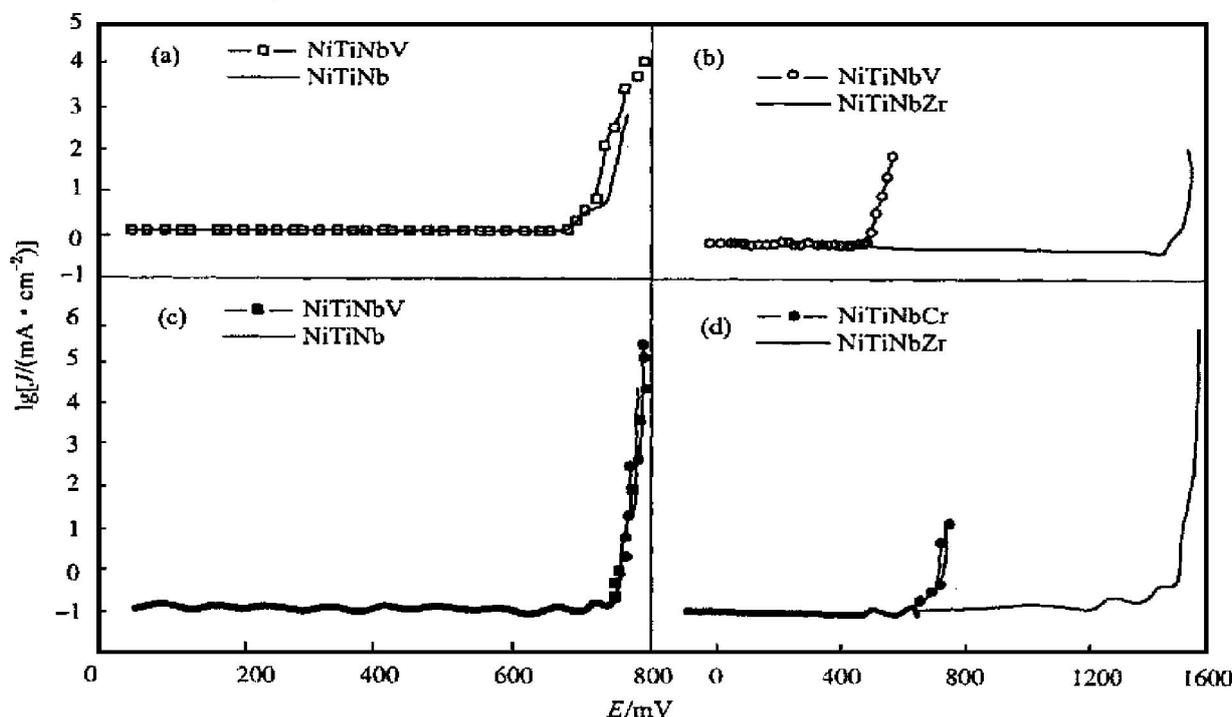
Alloy	Phase	Ni	Ti	Nb	V, Cr, Zr
NiTiNb	NiTi matrix	48.52	46.64	4.84	-
	$\beta$ -Nb phase	9.37	12.51	78.12	-
	(Ti, Nb) <sub>2</sub> Ni	33.66	60.27	6.07	-
NiTiNbV	NiTi matrix	46.67	47.28	4.24	0.81
	$\beta$ -Nb phase	9.82	10.89	75.21	4.09
NiTiNbCr	NiTi matrix	47.4	47.05	4.85	0.70
	$\beta$ -Nb phase	9.05	11.26	77.13	2.56
NiTiNbZr	NiTi matrix	48.07	47.54	4.39	0
	$\beta$ -Nb phase	9.32	10.82	78.33	1.53

nected together. Except for  $\beta$ -Nb particles are indifferent states in the NiTi matrix phase, alloying elements existed in different distributions. Analyses of energy spectrum have shown that element V not only existed in NiTi matrix, but also in  $\beta$ -Nb particle, and partly segregated in crystal interfaces, while element Zr distributed into the  $\beta$ -Nb particle and scarcely in NiTi matrix. Element Cr mainly existed in NiTi matrix and  $\beta$ -Nb particles. It is the different distribution of elements and microstructures that affects their corrosion resistance.

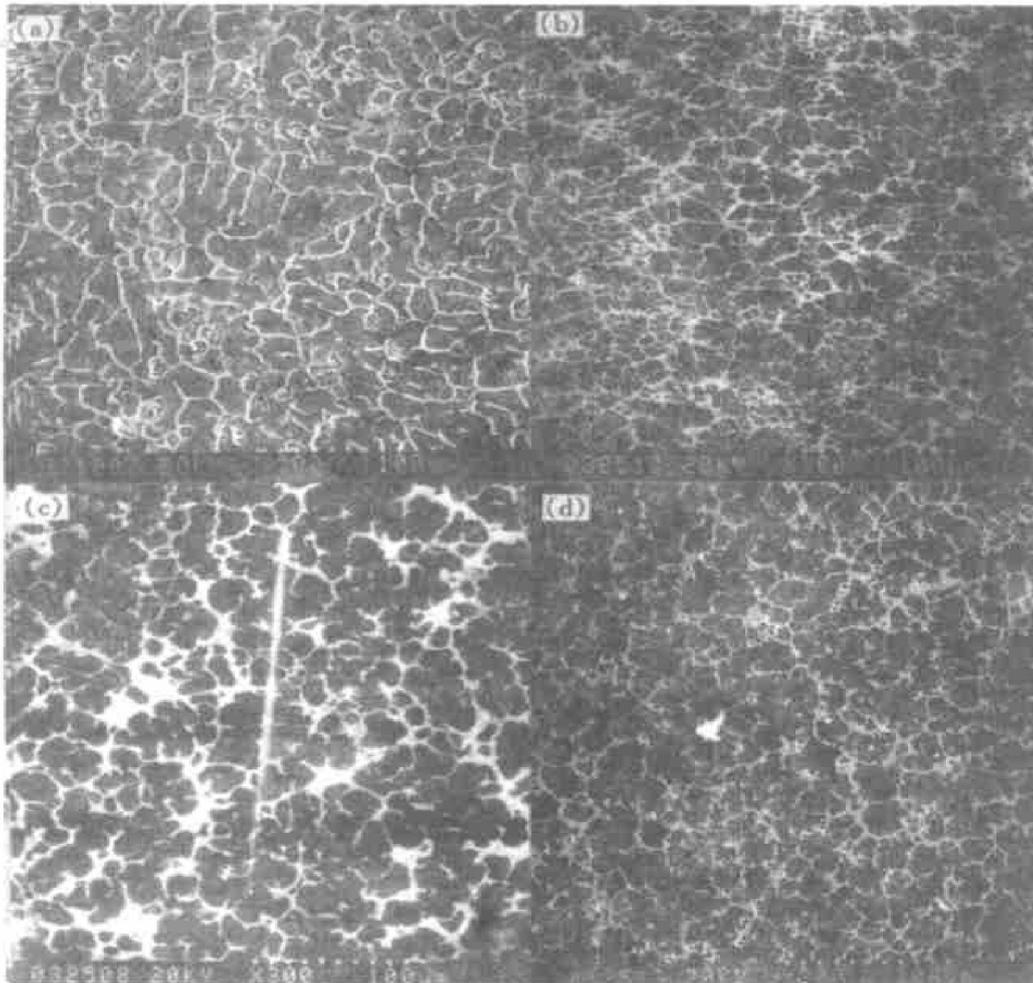
## 5 CONCLUSIONS

1) Potentiodynamic tests point out a satisfactory behavior of NiTiNb shape memory alloys in artificial seawater and physiological solution environment.

2) The corrosion resistance difference of the NiTiNb based alloys mainly correlates with their mi-



**Fig. 1** Polarization curves of TiNiNb based alloys  
(a) —In artificial seawater; (b) —In physiological solution



**Fig. 2** SEM images of NiTiNb based alloys  
(a) NiTiNb alloy; (b) NiTiV alloy; (c) NiTiNbZr alloy; (d) NiTiNbCr alloy

microstructure and their phase composition. Alloying element Zr considerably enhances the corrosion resistance of NiTiNb shape memory alloy, element Cr reduces its corrosion behavior and element V does not change this property obviously.

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