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# Martensitic transformation behavior in Ti–Ni–X (Ag, In, Sn, Sb, Te, Tl, Pb, Bi) ternary alloys

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#### A B S T R A C T

The microstructures and transformation behaviors of Ti–Ni–X (Ag, In, Sn, Sb, Te, Tl, Pb, Bi) ternary alloys were investigated using electron probe micro-analysis (EPMA), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and Micro Vickers hardness tests. All specimens consisted of Ti–Ni matrices and second phase particles. Ag, In and Sn were soluble in Ti–Ni matrices with a limited solubility  $(\leq$ 1.0 at%), while Sb, Te, Tl, Pb and Bi were not soluble. Two-stage B2-R-B19' transformation occurred in Ti-48.8Ni-1.2Ag, Ti-49.0Ni-1.0In and Ti-49.0Ni-1.0Sn alloys, while one-stage B2-B19' transformation occurred in Ti–49.0Ni–1.0Ag, Ti–49.0Ni–1.0Sb, Ti–49.0Ni–1.0Te, Ti–49.0Ni–1.0Pb and Ti–49.0Ni–1.0Bi alloys. Micro Vickers hardness of the alloys displaying the B2-R-B19' transformation (Hv 250–368) was much larger than that  $(<$ Hv 200) of the alloys displaying the B2-B19' transformation. Solid solution hardening was an important factor for inducing the B2-R transformation in Ti–Ni–X (X = non-transition elements) alloys.

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# 1. Introduction

The B2-R transformation is very attractive for many actuator applications because of low transformation hysteresis and high fatigue life. Several methods for inducing the B2-R transformation in Ti–Ni alloys, such as thermo-mechanical treatment [\[1,2\],](#page--1-0) aging of Ni-rich alloys [\[3,4\],](#page--1-0) addition of a third element to an equiatomic Ti–Ni alloy  $[5-8]$ , rapid solidification  $[9,10]$  and grain refinement [\[11\]](#page--1-0) have been developed. Unlike thermo-mechanical treatment, aging and rapid solidification, the third element addition method does not require additional heat treatment such as annealing or aging or a complicated process such as melt spinning or melt overflow. Iron, molybdenum, chromium and cobalt have been known to induce the B2-R transformation in Ti–Ni alloys [\[5–8\].](#page--1-0) Iron, chromium and cobalt are 3d transition elements and molybdenum is a 4d transition element. Therefore, the addition of 3d or 4d elements to an equiatomic TiNi alloy seems to be necessary for inducing the B2-R transformation.

There have been few studies carried out on the effects of nontransition elements on martensitic transformation of Ti–Ni alloys [\[12–15\].](#page--1-0) The addition of aluminum, which has the electronic configuration [Ne] $3s<sup>2</sup>3p$ , to an equiatomic TiNi alloy has been

reported to induce the B2-R transformation [\[12\].](#page--1-0) The addition of tin ([Kr] $4d^{10}5s^25p^2$ ) to an equiatomic TiNi alloy displayed the B2-R transformation [\[13\]](#page--1-0). However, there is a discrepancy in the effect of Sn on the martensitic transformation behavior of Ti–Ni alloys. In the 47.5Ti–47.5Ni–5Sn and 45Ti–45Ni–10Sn alloys, the B2-R phase transformation is not observed [\[14\]](#page--1-0). Moreover, the B2-R transformation is not observed in Ti–Ni–Ag alloys with an Ag content of 0.1205–0.2633 wt% [\[15\].](#page--1-0) This suggests that effects of nontransition elements on martensitic transformation of Ti–Ni alloys are still controversial.

In this study, Ag, In, Sn, Sb, Te, Tl, Pb and Bi, which are not 3d or 4d transition elements, are added to an equiatomic TiNi alloy in order to investigate the effect of non-transition elements on the martensitic transformation of Ti–Ni alloys. The microstructures and phase transformation behavior of the ternary alloys were investigated and then the empirical criterion of alloy composition for inducing the B2-R transformation was deduced.

## 2. Experimental procedure

Ti–49.0Ni–1.0Ag, Ti–484.8Ni–1.2Ag, Ti–49.0Ni–1.0In, Ti– 49.0Ni–1.0Sn, Ti–49.0Ni–1.0Sb, Ti–49.0Ni–1.0Te, Ti–49.0Ni– 1.0Tl, Ti–49.0Ni–1.0Pb and Ti–49.0Ni–1.0Bi (at%) alloys were prepared from sponge Ti (99.95%), pure Ni (99.99%), Ag (99.9%), In (99.999%), Sn (99.99%), Sb (99.99%), Te (99.9999%), Tl (99.9%), Pb (99.9%) and Bi (99.99%) by vacuum arc melting under an

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atmosphere of high purity argon. The ingots were turned over and remelted six times to ensure homogeneity. The ingots obtained were homogenized at 1273 K for 86.4 ks under high purity argon atmosphere. Specimens for electron probe micro-analysis (EPMA), differential scanning calorimetry (DSC), X-ray diffraction (XRD) and the hardness test were cut from the homogenized ingots. They were annealed at 1123 K for 3.6 ks in a vacuum followed by iced water quenching. All specimens were electropolished after heat treatment with an electrolyte consisting of 95% CH<sub>3</sub>COOH and 5%  $HClO<sub>4</sub>$  by volume.

The microstructural features of the alloys and compositions of various phases were evaluated by EPMA (JXA-8100, JEOL). In order to study the martensitic transformation behaviors of the alloys, DSC measurements were taken at a heating and cooling rate of 0.17 K/s using TA Instrument DSC-2010. The crystal structures of the alloys were investigated by XRD using  $CuK<sub>α</sub>$  radiation by successively changing the experimental temperatures with a scanning rate of  $2^{\circ}/$ min. Micro Vickers hardness tests were performed at room temperature with 500 g load. For each specimen, the average hardness value was taken from 12 test readings.

### 3. Results and discussion

Fig. 1(a)–(i) shows back-scattered electron images of Ti–49.0Ni– 1.0Ag, Ti–484.8Ni–1.2Ag, Ti–49.0Ni–1.0In, Ti–49.0Ni–1.0Sn, Ti– 49.0Ni–1.0Sb, Ti–49.0Ni–1.0Te, Ti–49.0Ni–1.0Tl, Ti–49.0Ni–1.0Pb and Ti–49.0Ni–1.0Bi (at%) alloys, respectively. Most of the samples are found to consist of a gray-colored matrix, black-colored particles and white-colored particles, except a Ti–49.0Ni–1.0In alloy, where white-colored particles are not observed. The chemical compositions of the matrices and particles in Fig. 1 were investigated using electron probe micro-analysis (EPMA) and the results obtained are shown in [Table](#page--1-0) 1. It is found that small amounts of Ag, In and Sn are soluble in the matrices with a limited solubility (  $\leq$  1.0 at%), while Sb, Te, Tl, Pb and Bi are not soluble in the matrices. The ratio of Tito Ni in black-colored particles designated by A1–I1 in Fig. 1 is close to 2:1; thus the particles are thought to be  $Ti<sub>2</sub>Ni$ . A small amounts of Ag is soluble in Ti<sub>2</sub>Ni, while In, Sn, Sb, Te, Tl, Pb, Bi are not soluble. Whitecolored particles designated by A2–I2 contain a high concentration of ternary elements, suggesting that the majority of ternary elements exist in white-colored particles. A2 and B2 are known to be TiAg as will be mentioned later. From a previous study [\[13,17\],](#page--1-0)  $Ti<sub>3</sub>Sn$  is formed in Ti–Ni–Sn alloys when the Sn content is greater than 1.5 at%. However, the chemical composition of the D2 particle is found to be largely deviated from  $Ti<sub>3</sub>Sn$ . Details of the D2 phase are not yet known.

[Fig.](#page--1-0) 2(a)–(i) shows the DSC curves of Ti–49.0Ni–1.0Ag, Ti– 484.8Ni–1.2Ag, Ti–49.0Ni–1.0In, Ti–49.0Ni–1.0Sn, Ti–49.0Ni– 1.0Sb, Ti–49.0Ni–1.0Te, Ti–49.0Ni–1.0Tl, Ti–49.0Ni–1.0Pb and Ti–49.0Ni–1.0Bi (at%) alloys, respectively. The shape of the DSC curves is largely dependent on the alloy composition. The alloys containing In, Sn Te, Pb and Bi display two DSC peaks on each



Fig. 1. Back-scattered electron images of Ti-Ni-X alloys. Details on the chemical composition of the particles designated by arrows as well as the matrices are shown in [Table](#page--1-0) 1.

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