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Effect of alloy composition on the B2–R transformation in rapidly solidified Ti–Ni alloys

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ABSTRACT

Microstructures and martensitic transformation behavior of 52.7Ti–Ni, 52.0Ti–Ni, 51.1Ti–Ni and 49.7Ti–Ni (at%) alloy ribbons were investigated by means of optical microscopy, transmission electron microscopy, differential scanning calorimetry, X-ray diffraction and thermal cycling tests under constant load. Very fine Ti_2Ni particles less than 20 nm which induced the B2-R transformation by suppressing the B2–B19′ transformation were observed in the ribbons. A temperature difference (ΔT) between T_R* and M_s* almost kept constant with increasing Ti content from 49.7 at% to 52.0 at% (∼8 K), above which it increases largely (∼17 K), which was ascribed to the fact that volume fraction of Ti_2Ni particles almost kept constant with increasing Ti content from 49.7 at% to 52.0 at% (∼8%), above which it increases largely (∼18%).

1. Introduction

The B2 (cubic)–R (trigonal) transformation is known to be suitable for highly sensitive actuator applications because of small transformation hysteresis [1,2]. Several methods for inducing the B2–R transformation in Ti–Ni binary alloy system such as thermo-mechanical treatment [3,4], aging [5–7], rapid solidification [8–11] have been developed. Among them, rapid solidification is particular of interest because it does not need additional processes such as annealing and aging for inducing the B2–R transformation and enable us obtain thin ribbons directly from melt.

Rapidly solidified Ti–Ni alloys are known to show characteristic microstructures much different from slowly solidified Ti–Ni alloys. Very fine Ti_2Ni particles (less than 20 nm) embedded in Ti–Ni matrix are observed in rapidly solidified near equiatomic Ti–Ni alloys which do not include the particles in equilibrium state [9–12]. This is ascribed to the fact that rapid solidification enhances formation of Ti_2Ni particles by suppressing the TiNi phase nucleation [13]. Metastable Ti_2Ni particles affect martensitic transformation and mechanical properties such as shape memory effect and superelasticity of Ti–Ni based shape memory alloys. Ti_2Ni particles coherent with Ti–Ni matrix suppress the formation of the B19′ (monoclinic) martensite and thus the B2–R transformation occurs before the B2–B19′ transformation starts to occur [9–11]. Also they increase the critical stress for slip and thus enhance the superelasticity comparing with slowly solidified alloys [14].

Microstructural features of rapidly solidified Ti–Ni alloys are expected to depend on alloy compositions since amount of metastable Ti_2Ni particles would be dependent on alloy compositions. Microstructural change with alloy compositions is considered to affect transformation behavior and mechanical properties of rapidly solidified Ti–Ni alloys. To the best of our knowledge, however, the relationship between alloy compositions and microstructures is not studied well in rapidly solidified Ti–Ni alloys. In this study, therefore, Ti–Ni alloy ribbons with various Ti-content were prepared by melt spinning and then their microstructures and martensitic transformation behavior were investigated. Also a relationship between microstructure and martensitic transformation behavior was discussed.

2. Experimental procedure

52.7Ti–Ni, 52.0Ti–Ni, 51.1Ti–Ni and 49.7Ti–Ni (at%) pre-alloys were prepared by arc melting. Billet charges of about 15 g cut from the pre-alloys were placed into quartz crucibles and the chamber of the melt spinning system had been pumped down to less than 1×10^{-3} Pa before re-melting. After re-melting, it was ejected through the nozzle on the outer surface of the rotating quenching wheel made of copper. Melt spinning temperature and the linear velocity were 1703 K and 31 m/s, respectively. Samples for differential scanning calorimetry (DSC), X-ray diffraction (XRD), optical microscopy (OM), transmission electron microscopy (TEM) and thermal cycling tests under constant load were cut from the ribbons and then electropolished with an electrolyte of 95% CH_3COOH and 5% $HClO_4$ in volume.

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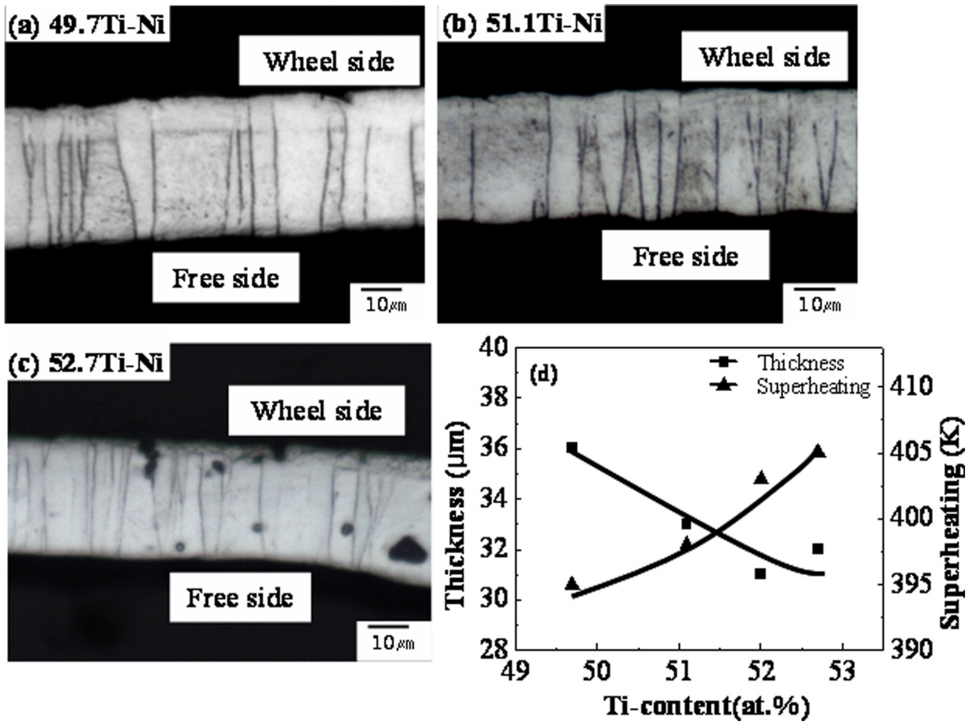

Fig. 1. (a)–(c) Optical micrographs of cross-sections of 49.7Ti–Ni, 51.1Ti–Ni and 52.7Ti–Ni (at%) alloy ribbons, respectively and (d) relationship between Ti-content and average thickness of ribbons.

Transformation behavior and temperatures were investigated by means of DSC and XRD. DSC measurements were made using TA-DSC with a cooling and heating rate of 0.17 K/s. XRD experiments were made using CuKα with successively changing experimental temperature. TEM observations were made using JEOL-2010 at an accelerating voltage of 200 kV. Samples for TEM observation were prepared by twin-jet method using an electrolyte of 97% CH_3COOH and 3% $HClO_4$ in volume. OM observations were made after etching the ribbons in a solution of H_2O:HCl:H_2O_2 (3:2:1). Thermal cycling tests under the various applied stress with a cooling and heating rate of 0.017 K/s were made for investigating the shape memory effect. Samples for thermal cycling tests under constant load were prepared by removing wheel side of as-spun ribbons. Average sample size was 3.0 mm (width) × 19.5 μm (thickness) × 50.0 mm (length) and gauge length was 30.0 mm.

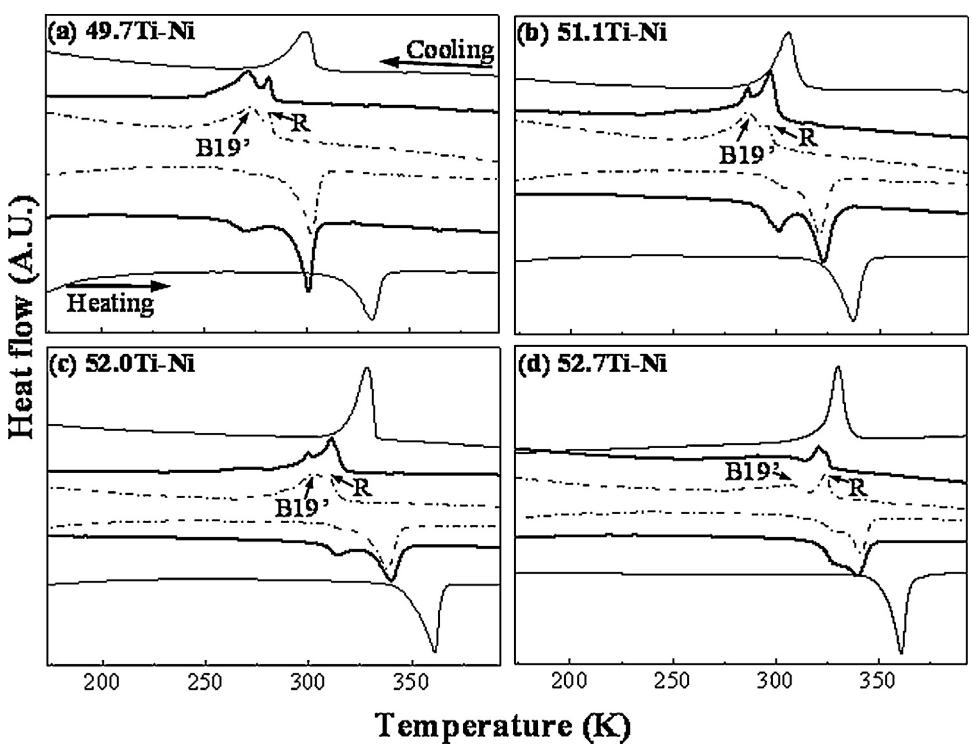

Fig. 2. DSC curves of Ti–Ni alloys ingots (thin solid line), ribbons (thick solid line) and ribbons after removing wheel side (dotted lines).