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Transformation behavior and shape memory characteristics of thermo-mechanically treated Ti–(45−x)Ni–5Cu–xV (at%) alloys

Jae-young Jang [a], Su-jin Chun [a], Eunsoo Choi [b], Yinong Liu [c], Hong Yang [c], Tae-hyun Nam [a,*]

[a] Division of Materials Scince and Engineering and ERI, Gyeongsang National University, 501 Jinjudaero, Jinju, Gyeongnam 660-701, Republic of Korea
[b] Department of Civil Engineering, Hongik University, Seoul, Republic of Korea
[c] School of Mechanical Engineering, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

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ABSTRACT

Transformation behavior, shape memory characteristics and superelasticity of thermo-mechanically treated Ti–(45−*x*)Ni–5Cu–*x*V (at%) ($x = 0.5–2.0$) alloys were investigated by means of differential scanning calorimetry, transmission electron microscopy, X-ray diffractions, thermal cycling tests under constant load and tensile tests. The B2–B19′ transformation occurred when V content was 0.5 at%, above which the B2–B19–B19′ transformation occurred. The B2–B19 transformation was not separated clearly from the B19–B19′ transformation. Thermo-mechanically treated Ti–(45−*x*)Ni–5Cu–*x*V alloys showed perfect shape memory effect and transformation hysteresis(ΔT) of Ti–43.5Ni–5.0Cu–1.5V and Ti–43.0Ni–5.0Cu–2.0V alloys was about 9 K which was much smaller than that of a Ti–44.5Ni–5.0Cu–0.5V alloy(23.3 K). More than 90% of superelastic recovery ratio was observed in all specimens and transformation hysteresis ($\Delta\sigma$) of a Ti–44.5Ni–5.0Cu–0.5V alloy was about 70 MPa, which was much larger than that of a Ti–43.0Ni–5.0Cu–2.0V alloy (35 MPa).

1. Introduction

The B2(cubic)–B19(orthorhombic) martensitic transformation is very promising for many applications because of large transformation elongation and moderate transformation hysteresis. The B2–B19 martensitic transformation has been observed in Ti–Ni–Cu alloys with Cu content more than 10 at% [1,2].

Unfortunately Ti–Ni–Cu alloys with Cu content more than 10 at% are so brittle that cold working is not possible. Therefore, from a practical point of view, it is desirable to develop new alloys showing the B2–B19 transformation with good workability. Since Ti–Ni–Cu alloys with Cu content less than 10at% shows good workability comparable with near equiatomic Ti–Ni alloys, it is desirable to induce the B2–B19 transformation in Ti–Ni–Cu alloys with low Cu-content.

Ternary Ti–Ni–X alloys made by substitution of Fe, Al, Co, Cr, Mo for Ti in near equiatomic Ti–Ni alloys induce the B2–R transformation, and thus transformation occurs in two-stage, B2–R–B19′ [6–10]. Those elements are believed to induce the B2–R transformation by suppressing the B2–B19′ transformation. Since Cu is effective to induce the B2–B19 transformation, substitution of Fe, Al, Co, Cr, Mo for Ti in Ti–Ni–Cu with low Cu content may induce the B2–B19 transformation by suppressing the B2–B19′ transformation. In fact, substitution of Fe and Mo for Ti induced the B19 martensite in a Ti–45Ni–5Cu alloy [3,5].

For inducing the B2–B19 transformation in Ti–Ni based alloys, substitution of elements which can decrease the density of state at the Fermi energy level is recommended [11]. In fact, substitution of V for Ni in a Ti–45Ni–5Cu alloy induced the B2–B19 transformation because the number of the valence electron of V is smaller than that of Ni and therefore, the density of state at the Fermi energy level decreased [4]. Since the previous study was made on solution treated alloys, the shape memory characteristics and superelasticity were not good enough [4]. For improving the shape memory characteristics and superelasticity, thermo-mechanical treatment was made on Ti–Ni–Cu–V alloys. The purpose of the present study is to investigate of transformation behavior, shape memory characteristics and superelasticity of thermo-mechanically treated Ti–(45−*x*)Ni–5Cu–*x*V (at%) ($x = 0.5–2.0$) alloys.

2. Experimental procedure

Ti–(45−*x*)Ni–5Cu–*x*V (at%) ($x = 0.5$, 1.0, 1.5, 2.0) alloys were prepared by vacuum induction melting in a graphite crucible. The alloy ingots were hot rolled at 1123 K into a sheet with a thickness of 1.2 mm. The hot rolled sheet was cold rolled by 30%. Specimens for differential scanning calorimetry (DSC), X-ray diffraction(XRD), thermal cycling tests under constant load, tensile tests and transmission electron microscope (TEM) observation were cut from the cold rolled sheet. All specimens were heat treated at

* Corresponding author.
E-mail address: tahynam@gnu.ac.kr (T.-h. Nam).

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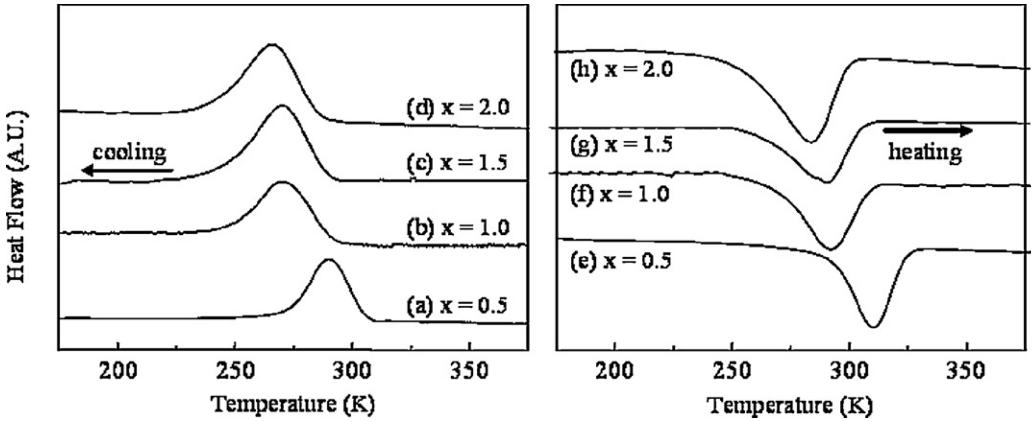

Fig. 1. DSC curves of thermo-mechanically treated Ti–(45.0−*x*)Ni–5.0Cu–*x*V alloys.

673 K for 3.6 ks followed by iced water quenching. After heat treatments, specimens were electropolished using an electrolyte which consists of 95%CH_3COOH and 5%$HClO_4$ in volume. Specimens for TEM observation were prepared by twin-jet method with an electrolyte which consists of 97%CH_3COOH and 3%$HClO_4$ in volume.

Transformation behavior was investigated by means of DSC, XRD and TEM. Heating and cooling rate for DSC was 0.17 K/s. XRD experiments were made at room temperature using Cu Kα with a scanning rate of 2°/min. TEM observations were made using JEOL 2010 operated at an accelerating voltage of 200 kV. In order to investigate the shape memory characteristics, thermal cycling tests were carried out by heating and cooling the specimen under various applied stresses. Elongation on cooling and its recovery on heating were measured by linear variable differential transformer. The superelasticity was examined by tensile test at various temperatures with a strain rate of 10^{-4}/s.

3. Results and discussion

3.1. Transformation behavior

Fig. 1 shows DSC curves of thermo-mechanically treated Ti–(45−*x*)Ni–5Cu–*x*V alloys. Clear DSC peaks are observed on each cooling and heating curve in all specimens, which move toward lower temperature with increasing V content. In order to explain the DSC curves, XRD experiments were made at 223 K and then XRD patterns obtained are shown in Fig. 2. In the patterns of a Ti–44.5Ni–5.0Cu–0.5V and Ti–44.0Ni–5.0Cu–1.0V alloys, diffraction peaks corresponding to the B19′ martensite are observed. In the patterns of Ti–43.5Ni–5.0Cu–1.5V and Ti–43.0Ni–5.0Cu–2.0V alloys, diffraction peaks corresponding to the B19 martensite and the B19′ martensite are observed simultaneously.

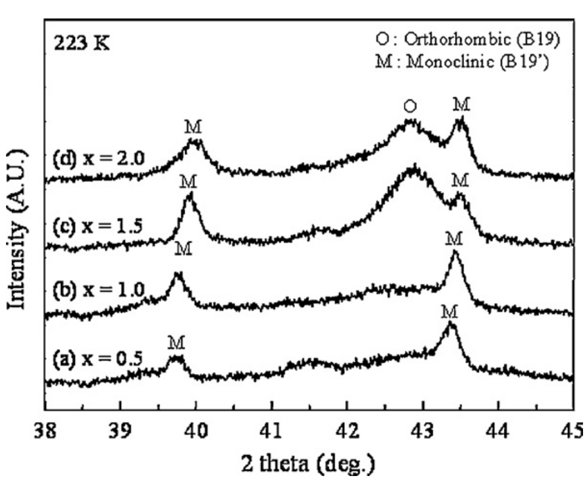

Fig. 2. XRD patterns of thermo-mechanically treated Ti–(45.0−*x*)Ni–5.0Cu–*x*V alloys.

TEM observation was made on Ti–44.0Ni–5.0Cu–1.0V and Ti–43.0Ni–5.0Cu–2.0V alloys, then results obtained are shown in Fig. 3. From the electron diffraction pattern of Fig. 3(b), it is found that the B2 parent phase and B19 martensite coexist in Fig. 3(a).

The B19 martensite was not observed in the XRD pattern of Fig. 2(b). This is ascribed to the fact that X-ray diffraction was made at 223 K, which is enough low for finishing the B19–B19′ transformation. Fig. 3(c) and (d) are a bright field image of a Ti–43.0Ni–5.0Cu–2.0V alloy and the corresponding diffraction pattern, respectively. The B2 parent phase with high density of dislocations is observed.

From Figs. 1–3, it is known that transformation behavior of thermo-mechanically treated Ti–(45−*x*)Ni–5Cu–*x*V alloys depends largely on V content. The B2–B19′ transformation occurs when V content is 0.5 at%, above which the B2–B19–B19′ transformation occurs. This means that substitution of V for Ni in a Ti–45Ni–5Cu alloy induces the B2–B19 transformation. However, the B2–B19 transformation is not separated clearly from the B19–B19′ transformation, although it was separated clearly in solution treated Ti–(45−*x*)Ni–5Cu–*x*V alloys [4].

Dislocations introduced by thermo-mechanical treatment are believed to make the B2–B19 overlapped with the B19–B19′. Similar result was observed in a thermo-mechanically treated Ti–40Ni–10Cu(at%) alloy [12].

3.2. Shape memory characteristics and super-elasticity

Elongation vs. temperature curves of thermo-mechanically treated Ti–(45−*x*)Ni–5Cu–*x*V alloys are shown in Fig. 4. All curves in the figure were obtained under the applied stress of 120 MPa. Since the one-stage B2–B19′ transformation occurs in a Ti–44.5Ni–5.0Cu–0.5V, the elongation developed on cooling in Fig. 4(a) is ascribed to the B2–B19′ transformation. Since the two-stage B2–B19–B19′ transformation occurs in Ti–44.0Ni–5.0Cu–1.0V, Ti–43.5Ni–5.0Cu–1.5V and Ti–43.0Ni–5.0Cu–2.0V alloys, the elongation developed on cooling in Fig. 4(b)–(d) is attributed to the B2–B19–B19′ transformation. However, the elongation associated with the B2–B19 is not separated from that associated with the B19–B19′ transformation. Elongation occurred on cooling is recovered completely on heating in all samples.

Transformation hysteresis (ΔT) of Ti–44.5Ni–5.0Cu–0.5V and Ti–44.0Ni–5.0Cu–1.0V alloys is measured to be 23.3 K and 17.6 K, respectively. On the other hand ΔT of Ti–43.5Ni–5.0Cu–1.5V and Ti–43.0Ni–5.0Cu–2.0V alloys is measured to be 9.2 K and 9.7 K,