Determination of Heat of Transformation in a Cold-Rolled Martensitic TiNi Alloy

H.C. LIN and S.K. WU

We studied the heat of transformation, $\Delta H$, in martensitic transformations in a cold-rolled equiatomic TiNi alloy with differential scanning calorimetry (DSC), X-ray diffraction (XRD), and microhardness measurements. Results of our experiment indicate that the martensite stabilization and stress-induced parent (SIP) B2 phase are introduced when the TiNi martensite is cold rolled at room temperature. The SIP formation seems to be related to the lattice softening phenomenon occurring in the martensite, while the $\Delta H$ value of the first reverse martensitic transformation decreases enormously for the cold-rolled equiatomic TiNi alloy. We are proposing possible explanations for these results: (1) the occurrence of SIP, which reduces the transformable martensite volume; (2) the release of accumulated elastic energy induced by the cold rolling; and (3) the recovery of defects induced by cold rolling and release of the heat of recovery. We also found that the retained dislocations can depress the martensitic transformation temperatures and induce the R-phase transformation after the occurrence of the first reverse martensitic transformation.

I. INTRODUCTION

Among many shape memory alloys, TiNi alloys are the most popular because they can be deformed in a ductile manner to more than 50 pct strain prior to fracture and show the shape memory effect or pseudoelasticity (PE) over a wide range of strain up to 8 pct.\textsuperscript{[1]} The transformation behavior and mechanical properties in TiNi binary alloys\textsuperscript{[2-6]} and TiNiX ternary alloys\textsuperscript{[7-10]} have been studied extensively. These studies have confirmed that transformation behaviors and mechanical properties can be affected by internal stresses induced by many thermal-mechanical treatments, including thermal cycling,\textsuperscript{[11,12]} aging treatment in Ni-rich alloys,\textsuperscript{[13-16]} and annealing immediately following cold working.\textsuperscript{[17,18]}

Many recent articles have reported deformation behavior and stress effects in TiNi alloys\textsuperscript{[17,18,20,21]} and stated that the stress in these alloys significantly affects the start and finish transformation temperatures and induces the R-phase transformation and that the microstructure with dislocations or precipitates impedes the movement of martensite interfaces and depresses the $M_s$ point. All of these reported studies, however, were conducted on TiNi specimens which had been deformed with subsequent annealing. TiNi specimens that have been deformed but not annealed are seldom studied, although some results have been implied in the reports.\textsuperscript{[22,23,24]} In our previous article,\textsuperscript{[19]} we discussed the effects of cold rolling on the martensitic transformation of equiatomic TiNi alloy primarily through transmission electron microscope (TEM) observation and internal friction measurement. We observed the phenomenon of martensite stabilization in the cold-rolled Ti$_{50}$Ni$_{50}$ alloy at room temperature. We expected the deformed structures, such as distorted martensite and dislocations/vacancies, to impede the reverse martensitic transformation by imposing a frictional stress on the martensite/martensite and martensite/parent interfaces. This would cause the reverse martensitic transformation temperatures to shift to higher values, since the transformation would require additional driving force to overcome the frictional stress. In this study, we plastic-deformed the equiatomic TiNi alloy by cold rolling at room temperature and then conducted differential scanning calorimetry (DSC), X-ray diffraction (XRD), and microhardness measurements. In the following sections, we systematically describe the transformation heat exhibited in this deformed TiNi alloy and its relation to the degree of cold rolling.

II. EXPERIMENTAL PROCEDURE

We used the conventional tungsten arc melting technique to prepare the equiatomic TiNi alloy. Titanium (purity, 99.7 pct) and nickel (purity, 99.9 pct), totalling about 60 g, were melted and remelted at least six times in an argon atmosphere. Pure titanium buttons were also melted and used as a getter. The mass loss during melting was negligible. The as-melted button was homogenized at 1050 °C for 72 hours and quenched in water, then hot-rolled to a plate of 3-mm thickness. Specimens for cold rolling were carefully cut from the plate with a low-speed diamond saw. These specimens were then annealed at 800 °C for 2 hours and cooled in a vacuum furnace. After annealing, some specimens were cold-rolled at room temperature to a 5, 10, 20, and 40 pct reduction in thickness and then subjected to the DSC, XRD, and microhardness measurements. The temperature increase in the specimens during the cold-rolling process was very slight, even in the 40 pct thickness-reduced specimen.

A Du Pont 9990 thermal analyzer equipped with a quantitative scanning system 910 DSC cell was used to run controlled heating and cooling on samples encapsulated in an aluminum pan. Temperatures ranged from $-60$ °C to $+300$ °C with a heating/cooling rate of 10 °C/min. The heat of transformation, $\Delta H$, was automatically calculated from the area under the DSC peak.
with the equipment software packages. The XRD analysis was carried out at room temperature with the PHILIPS* PW1710 X-ray diffractometer under the conditions of CuKα radiation, 30 kV tube voltage, and 20 mA current. The specimen size for XRD was 20 by 20 mm. Specimens for the hardness testing were mechanically polished and then measured in the Vickers microhardness tester with a 1000-g load at room temperature. For each specimen, the hardness value, Hv, was averaged from at least five test readings.

III. EXPERIMENTAL RESULTS

A. DSC Measurement on the Cold-Rolled Specimens

Figure 1 shows the DSC curves for the 5 pct cold-rolled Ti₆₀Ni₅₀ specimen in the first heating cycle and subsequent cooling and heating cycles. Compared with the experimental results of the internal friction testing[19] and electrical resistance measurements,[20] the DSC peaks shown in Figure 1 are associated with the martensitic transformation of B₂ ↔ B₁₉' (B₂: parent phase, CsCl-type structure; B₁₉': martensite, monoclinic distortion of the B₁₉ structure). The first heating curve shows an endothermic reaction, with \( \Delta H = 16.55 \, \text{J/g} \) and the peak temperature \( A₁^* \) near 101.9 °C. The cooling curve, however, shows an exothermic reaction, with \( \Delta H \) being 24.16 J/g and the peak temperature \( M₁^* \) near 37.9 °C. In the second heating curve, \( A₁^* \) appears at 75.7 °C, with \( \Delta H = 24.57 \, \text{J/g} \).

Figures 2(a) and (b) show the DSC curves of the first heating cycle and subsequent cooling and heating cycles, respectively, for the 20 pct cold-rolled specimen. In Figure 2(a), peak \( A₁^* \) appears at 135.4 °C. In Figure 2(b), there are two separate peaks on the cooling run, \( M₁^* = 8.0 \, \text{°C} \), \( R₂^* = 52.1 \, \text{°C} \). On the heating run, there is a duplex peak contributed by both the martensitic and R-phase transformations. When the measurement on the cooling run is stopped at 37 °C (between \( M₁^* \) and \( R₂^* \) temperatures) and again resumed, the peak \( R₂^* \) appears after the peak \( A₁^* \) at about 63.3 °C (shown as the dashed line in Figure 2(b)). This means that \( B₁₉' \rightarrow R \) transformation occurs before \( R \rightarrow B₂ \) transformation. The DSC curves for both the as-annealed and 10 pct cold-rolled specimens are similar to those shown in Figure 1, except for the difference of peak temperatures and \( \Delta H \) values, and, hence, are omitted here. All experimental results, including peak temperatures and \( \Delta H \) values, are summarized in Table I. The data in Table I are also plotted in Figures 4 and 5 for \( A₁^* \) and \( R₂^* \) phase, rhombohedral structure). However, on the following heating run, only an endothermic peak \( A₂^* \) appears at 67.3 °C. If cooling is stopped at 37 °C (between \( M₂^* \) and \( R₂^* \) temperatures) and then resumed, another peak \( R₂^* \) appears before the \( A₂^* \) peak at about 57.4 °C (shown as the dashed line in Figure 2(b)). This implies that the martensite phase is more stable than the R phase before transforming to \( B₂ \) phase during the heating cycle. Figure 2(b) indicates that the transformation sequence of the 20 pct cold-rolled specimen is \( B₂ \rightarrow R \rightarrow B₁₉' \) on cooling and \( B₁₉' \rightarrow B₂ \) on heating.

Figures 3(a) and (b) show the same curves as Figures 2(a) and (b), this time for the 40 pct cold-rolled specimen. In Figure 3(b), there are also two separate peaks on the cooling run, \( M₂^* = 8.0 \, \text{°C} \), \( R₂^* = 52.1 \, \text{°C} \). On the heating run, there is a duplex peak contributed by both the martensitic and R-phase transformations. When the measurement on the cooling run is stopped at 37 °C (between \( M₂^* \) and \( R₂^* \)) and again resumed, the peak \( R₂^* \) appears after the peak \( A₂^* \) at about 63.3 °C (shown as the dashed line in Figure 3(b)). This means that \( B₁₉' \rightarrow R \) transformation occurs before \( R \rightarrow B₂ \) transformation. The DSC curves for both the as-annealed and 10 pct cold-rolled specimens are similar to those shown in Figure 1, except for the difference of peak temperatures and \( \Delta H \) values, and, hence, are omitted here. All experimental results, including peak temperatures and \( \Delta H \) values, are summarized in Table I. The data in Table I are also plotted in Figures 4 and 5 for \( A₁^* \) and \( R₂^* \)