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Shape memory and superelasticity of nanograined Ti-51.2 at.% Ni alloy processed by severe plastic deformation via high-ratio differential speed rolling

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ABSTRACT

A novel method of producing nanograined Ni-rich superelastic NiTi alloys in sheet form was proposed using a combination of severe plastic deformation via high-ratio differential speed rolling (HRDSR) and post-deformation annealing. The HRDSR-processed microstructure was composed of heavily deformed austenite and martensite grains, and amorphous phases. After annealing at 673 K, the severely deformed microstructure with no functional properties evolved to the nanograined structure (20–70 nm) composed of austenite and martensite nanograins and sub-nanograins through static recovery or continuous static recrystallization process. The nanograined microstructure had a high resistance to martensitic transformation upon cooling and slip deformation during straining. As a result, the HRDSR-processed alloy annealed at 673K exhibited superior superelasticity compared to the alloys with coarse grains. At the higher annealing temperature of 873 K, the micron-sized recrystallized grains with low dislocations developed through discontinuous static recrystallization process. In this case, deformation during straining was governed by the detwinning of twinned martensite, and as a result, shape memory effect was more significantly pronounced than superelasticity.

1. Introduction

Equiatomic and near equiatomic NiTi shape memory alloys (SMAs) with the shape memory effect (SME) and superelasticity (SE) have been widely used in various medical devices such as medical implants, guide wires for catheters, stents and orthodontic arch wires [1,2]. The occurrence of plastic deformation in the NiTi alloys during prestraining or cyclic deformation, however, can cause degradation of the SE and SME. To suppress plastic deformation, improving the strength of NiTi SMAs is important, especially in the trend of miniaturization of medical devices [3].

Precipitation and grain refinement have been proposed as methods of increasing the critical stress for dislocation slip in NiTi alloys. For precipitation hardening, it has been reported that fine (< 15 nm) and densely dispersed Ni_4Ti_3 precipitates that form during aging at temperatures between 473 and 873 K in Ni-rich NiTi alloys [4–6] effectively resist the motion of dislocations. For grain refinement, severe plastic deformation (SPD) has been demonstrated to quite effective. For example, equal channel angular pressing (ECAP), which was conducted on a Ti-50.9 at.% Ni alloy at 723 K for 8 passes, refined the grain size from 60 to 80 μm to 300–400 nm [7]. Several authors showed that SPD based on cold working led to partial amorphization of NiTi alloys, resulting in the formation of microstructures composed of a mixture of nanocrystalline and amorphous phases [8–12]. Nakayama et al. [8] showed that after 50% cold rolling, a Ti-50.2 at.% Ni sample became nanocrystalline with some amorphous region. Tsuchiya et al. [9] showed that thin wires of Ti–50.9 at.% Ni alloy processed by cold drawing of 50–70% area reduction had an amorphous phase coexisting with the nanocrystalline B2 austenite phase. Waitz et al. [10] showed that after high pressure torsion (HPT) deformation, almost complete amorphization was obtained in Ti-49.7 at.% Ni alloy containing B19′ martensite phase. Subsequent isothermal annealing led to the formation of nanocrystalline structures with grain sizes in the range of 5–350 nm. Jiang et al. [11] applied local canning compression as an SPD method to Ti-50.9 at.% Ni alloy and observed nanocrystallization and amorphization after compressive deformation. Sergueeva et al. [12] showed the presence of an amorphous phase and nanocrystalline B2 phases in Ti-50.6 at.% Ni alloy after HPT and the formation of a homogeneous

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nanocrystalline structure after heat treatments at 673–773 K. Some researchers reported that nanocrystallization of the amorphous phase by appropriate heat treatment could improve the mechanical properties and the functional properties of NiTi SMAs. Tsuchiya et al. [9] showed that amorphous/nanocrystalline Ti–50.9 at.% Ni wires after annealing at 573 K exhibited a large superelastic strain (~5%). Delville et al. [13] applied the short-time heat treatment via pulsed electric current to as-drawn Ti-50.9 at.% Ni alloy wires and showed that partially re-crystallized microstructure with nanograins exhibited a high degree of SE (~6%).

In obtaining the amorphous/nanocrystalline phase for NiTi alloys in plate or sheet form, the HPT method has a limitation in terms of the size and dimension of the materials and cold rolling may be not a practical method because it requires many rolling passes and cracking is prone to occur during rolling due to severe work hardening. A high-ratio differential speed rolling (HRDSR) process was proposed by Kim et al. [14,15] for production of ultrafine-grained metals in sheet form. As HRDSR requires a much lower roll force and induces a much larger amount of shear strain compared to conventional rolling, SPD can be applied in HRDSR through fewer rolling passes at lower temperatures. Recently, Kim and his colleagues [16] showed that HRDSR could be used in producing the ultrafine grained Fe-based shape memory alloys with enhanced recovery stress.

In the present study, HRDSR was applied to a Ni-rich Ti-51.1 at.% Ni alloy to obtain the nanograined microstructure. The microstructural evolution during HRDSR was observed, and the annealing effect on the rolled microstructures was examined. Finally, the SE and SME of the as-HRDSRed and annealed alloys were evaluated, and their correlation with the microstructures was investigated and discussed.

2. Experimental Procedures

The 2.4-mm thickness NiTi alloy plates with a nominal composition of Ti-51.1 at.% Ni was purchased from SMA Co., Ltd. (Kyonggi do, Korea). The amounts of Ni and Ti elements in the alloy were analyzed using inductively coupled plasma optical emission spectrophotometers (ICP-OES, PerkinElmer Optima 8300): 51.14 at.% Ni-48.68 at.% Ti. According to the statement of manufacturer, the plates were prepared through hot rolling. The as-received samples were annealed at 1123 K for 120 min and then cooled by water quenching. The material obtained after cooling is hereafter referred to as the solution annealed (SA) sample. The SA sample was subjected to HRDSR without the sample preheating. The speed ratio between the upper and lower rolls was set to 2. The surface temperatures of the rolls were maintained at 423 K during rolling. HRDSR was conducted to a final thickness of 1.2 mm (50% reduction in total) using a single pass. Post-HRDSR annealing was conducted at two temperatures (673 and 873 K) for annealing times up to 2 h. Strip-shaped tensile samples (with a thickness of 1.2 mm, a width of 2 mm and a gauge length of 15 mm) were prepared with the gauge length parallel to the rolling direction. The SA, as-HRDSRed and annealed HRDSR samples were cooled in liquid nitrogen before microstructural observation and mechanical tests.

The microstructures of the as-HRDSRed, and HRDSRed samples annealed at 673 K for 30 min were observed using a field emission transmission electron microscope (JEM 2001 F, 200 keV) equipped for energy dispersive X-ray spectroscopy (EDS). The samples were jet-polished with a solution composed of 60% methyl alcohol (CH_3OH), 30% glycerin ($C_3H_8O_3$) and 10% nitric acid (HNO_3), and then ion milled.

The recovery stress of the SA, as-HRDSRed, and HRDSRed samples was measured after loading to 8% strain at an initial strain rate of $5 \times 10^{-4}\,s^{-1}$ followed by unloading and heating the sample under a displacement constraint condition to 473 K at a rate of 1 K/s with a heating gun. Then, the sample was cooled at a rate of 1 K/s to room temperature (293 K).

The recovery strains of the SA, as-HRDSRed, and HRDSRed samples were measured after tensile loading to pre-strains of 8% followed by unloading and heating up to 473 K at a rate of 1 K/s using a heating gun. During heating, the crosshead of the tensile testing machine was programmed to move automatically to remove the stress generated in the sample (above 4 MPa) due to a reverse martensitic transformation during the heating process. This permitted the measurement of the recovery strain in a nearly stress-free state.

A differential scanning calorimeter (DSC, Perkin-Elmer DSC7) was used to determine the transformation temperatures of the SA, as-HRDSRed and annealed HRDSR samples by scanning in the temperature range from 175 to 425 K at heating and cooling rates of 10 K/min.

X-ray diffraction (XRD) was carried out on the samples using a Philips X'Pert Pro diffractometer with CuKa radiation (λ = 1.5418 Å) at ambient temperature.

Electron back-scattering diffraction (EBSD) analysis with scanning step sizes of 0.1–2.5 μm was used to characterize the microstructures of the SA, as-HRDSRed, and HRDSRed samples. To prepare the sample for EBSD analysis, the surface of the samples was sectioned parallel to the longitudinal axis of the rolled samples, mechanically ground using SiC paper and then ion milled. The EBSD data were processed using TSL-OIM analysis software, and the data points with a confidence index below 0.1 were removed from the EBSD data.

3. Results and Discussion

3.1. Microstructures and Phase Transformations

Fig. 1(a) shows the inverse pole figure (IPF) map of the SA sample. The microstructure is composed of recrystallized grains with the average size of 35.6 μm. Fig. 1(b) shows the DSC curve of the SA sample, where the peaks corresponding to the B2-B19′ on cooling and the reverse B19′-B2 transformations on heating are observed. The transformation temperatures of the martensite and austenite start (M_s and A_s), peak (M_p and A_p) and finish temperatures (M_f and A_f) determined from the DSC curve are summarized in Table 1. Fig. 1(c) shows the XRD pattern of the SA sample, indicating that B2 austenite is the parent phase. A peak for B19′ martensite is also observed, suggesting a coexistence of B19′ martensite in the B2 matrix at room temperature.

Fig. 2(a)–(d) and Fig. 3(a)–(d) show the DSC curves of the as-HRDSRed sample and the HRDSRed samples annealed at 673 and 873 K for different annealing times. The transformation temperatures measured from the DSC curves are listed in Table 1. After HRDSR, the peak intensities and the amounts of heat associated with the martensitic and austenitic transformation considerably decreased (Fig. 2(a)). This result indicates that defects such as dislocations and vacancies produced during severe plastic deformation by HRDSR suppressed the martensitic transformation during cooling. After annealing of the as-HRDSRed sample at 673 K for 5, 30 and 60 min (Fig. 2(b)–(d)), the following changes were observed. First, for all the cases, the amounts of heat associated with the martensitic and austenitic phase transformations considerably increased compared to that for the as-HRDSRed sample, implying that post-SPD annealing reduced the density of defects, which inhibit the movement of the austenite–martensite transformation interfaces [17]. Second, for all the cases, during the heating stage, multiple-step phase transformation (R-B19′ and B19′-B2) appeared. During cooling, multiple-step phase transformation (B2-R and R-B19′) also occurred, although the second peak was not so obvious as the first one. Appearance of R peak in the sample heavily deformed by HRDSR agrees with the reports by other investigators [17,18] that the defects induced during cold working have the effect of promoting the R-phase transformation in NiTi SMAs. The high internal stresses induced by dislocations has been suggested to be responsible for the R-phase transformation [18]. Third, for all the cases, a mixture of R, B19′ and B2 is expected to exist at room temperature.

The HRDSRed samples annealed at 873 K for different times (Fig. 3(a)–(d)) show different DSC characteristics compared to those of