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# Superelastic properties of nanocrystalline NiTi shape memory alloy produced by thermomechanical processing

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**Abstract:** Effects of thermomechanical treatment of cold rolling followed by annealing on microstructure and superelastic behavior of the $Ni_{50}Ti_{50}$ shape memory alloy were studied. Several specimens were produced by copper boat vacuum induction melting. The homogenized specimens were hot rolled and annealed at 900 °C. Thereafter, annealed specimens were subjected to cold rolling with different thickness reductions up to 70%. Transmission electron microscopy revealed that the severe cold rolling led to the formation of a mixed microstructure consisting of nanocrystalline and amorphous phases in $Ni_{50}Ti_{50}$ alloy. After annealing at 400 °C for 1 h, the amorphous phase formed in the cold-rolled specimens was crystallized and a nanocrystalline structure formed. Results showed that with increasing thickness reduction during cold rolling, the recoverable strain of $Ni_{50}Ti_{50}$ alloy was increased during superelastic experiments such that the 70% cold rolled−annealed specimen exhibited about 12% of recoverable strain. Moreover, with increasing thickness reduction, the critical stress for stress-induced martensitic transformation was increased. It is noteworthy that in the 70% cold rolled−annealed specimen, the damping capacity was measured to be 28 J/cm$^3$ that is significantly higher than that of commercial NiTi alloys.

**Key words:** nanocrystalline material; shape memory alloy; superelasticity; thermomechanical processing

## 1 Introduction

NiTi shape memory alloy (SMA) is one of the most important engineering materials which possesses two unique properties named superelasticity and shape memory effect [1,2]. Shape memory effect of NiTi SMA refers to its ability to recover original shape when it is heated to the temperature above the austenite finish temperature ($A_f$) after experiencing a certain deformation in the martensitic phase. Superelasticity of NiTi SMA refers to its nonlinear recoverable deformation behavior at the temperature above $A_f$, which is attributed to the stress-induced martensite transformation under loading and the spontaneous reversion of the transformation under unloading [3,4]. In addition to mentioned characteristics, NiTi SMA has high corrosion resistance, favorable biocompatibility and high damping capacity. Therefore, it has been employed in many applications including biomedical, aerospace, oil–gas, automotive, robotics and telecommunication industries [5]. The functional properties of SMA such as the recovery strain, shape recovery rate, recovery stress, temperature range of shape recovery and transformation yield stress, are structure-sensitive ones. Therefore, various thermomechanical treatments like cold rolling and subsequent annealing causing a well-developed dislocation substructure or nanocrystalline structure are effectively used for improving the superelastic properties of SMAs [6−8]. Cold rolling improves the superelastic behavior with increasing the critical stress for dislocations slip relative to critical stress for twinning mechanism [1]. Besides, NiTi shape memory alloys are prone to be amorphous by cold rolling. Post deformation annealing will result in the formation of a nanocrystalline structure if the optimum thermomechanical course is selected [6−8]. Nanocrystalline shape memory alloys have superior properties over their coarse grained counterparts. PROKOFIEV et al [9] reported that the formation of nanocrystalline structure in NiTi led to a higher strength of the alloy, with the effect on superelasticity, narrow hysteresis and low residual strain. RYKLINA et al [10] have shown that the nanostructures in NiTi alloy led to increasing the recovery strain as

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compared to the coarse-grained counterparts. MEI et al [11] demonstrated that the elastic modulus of nanostructured NiTi increases dramatically. TSUCHIYA et al [12] produced nanocrystalline NiTi wire with high tensile strength and high elastic modulus. DELVILLE et al [13] and MALARD et al [14] prepared nanostructured NiTi wire by means of cold drawing and heat treatments. They found that the NiTi wire with nanocrystalline structure possesses perfect superelasticity with a recoverable strain of 8%.

The tensile properties and transformation behavior of the nanostructured $Ti_{50}Ni_{50}$ shape memory alloy prepared by copper boat induction melting followed by thermomechanical treatment were discussed in previous works [15,16]. In the current research, the effect of thermomechanical processing comprised cold rolling followed by annealing on the superelastic properties of an equiatomic NiTi shape memory alloy is investigated.

## 2 Experimental

$Ni_{50}Ti_{50}$ (mole fraction, %) cast ingots were prepared by a home-made copper-boat vacuum induction melting system. The as-cast cylindrical ingots were homogenized at 900 °C for 4 h in a vacuum furnace followed by cold water quenching. After homogenization, the ingots were hot rolled at 900 °C into a sheet of 2.5 mm in thickness and then annealed at 900 °C for 1 h followed by water quenching. The annealed specimens were cold rolled with 20%−70% thickness reduction at room temperature. Based on the crystallization temperatures determined from calorimetric measurements, post deformation annealing was conducted at 400 °C for 1 h in vacuum.

Transformation behavior and microstructure evolution of the $Ni_{50}Ti_{50}$ alloy were investigated by means of differential scanning calorimetry (DSC NETZSCH 200F3), X-ray diffraction (XRD Philips X'Pert with Cu $K_\alpha$ radiation) and field emission transmission electron microscopy (TEM JEOL−2100F) techniques. DSC measurements were made with a cooling and heating rate of 10 °C/min. The crystallite size, residual microstrain and dislocation density of all samples which were subjected to various cold reductions are determined by analyzing the XRD patterns via the Rietveld software, Materials analysis using diffraction (MAUD) [17]. Details of method of analysis have been reported elsewhere [17−20]. After fitting the theoretical curve on the XRD pattern of samples, related values of microstructural parameters (such as crystallite size and microstrain) for each XRD peak were provided by software. The value of the dislocation density ($\rho$) was calculated [21] from the average values of the crystallite size ($D$) and microstrain $(\varepsilon^2)^{0.5}$ (output data of MAUD software) by the following equation:

$$\rho=\frac{3\sqrt{2\pi}(\varepsilon^2)^{0.5}}{Db} \tag{1}$$

where $b$ is the absolute value of Burgers vector.

Samples for TEM were prepared by polishing with a twin-jet electro-polisher (Struers, Tenupol-5) in a solution of 90% acetic acid glacial and 10% perchloric acid at 15 °C under 35 V. TEM observations were made at the operating voltage of 200 kV. Tensile test was carried out according to ASTM-F2516 (standard test method for tension testing of nickel−titanium superelastic materials) with a strain rate of $1\times10^{-3}$ $s^{-1}$ at room temperature. All tensile test specimens were cut along the rolling direction.

## 3 Results and discussion

The as-homogenized microstructure was composed of coarse grains with an average size of 50 μm. The XRD results show that the homogenized NiTi specimen consists of $B2$ austenite and $B19'$ martensite phases. DSC curves of the homogenized specimen are shown in Fig. 1. In this figure, DSC peaks corresponding to the $B2$−$B19'$ on cooling and the reverse $B19'$−$B2$ transformation on heating are clearly seen ($M_s$=54 °C, $M_f$=26 °C, $A_s$=61 °C, $A_f$=93 °C). It should be noted that the two-phase microstructure of the homogenized sample, as characterized by XRD at room temperature, is not consistent with the transformation temperatures, determined by DSC. The reason is believed to be due to the higher cooling rate (about 10000 °C/min) during quenching from the homogenization temperature compared with the one used in the DSC test (e.g. 10 °C/min) [15,16]. As already reported by CHANG et al [22], the $M_f$ is significantly reduced by increasing the cooling rate. As a consequence, a complete $B2$ to $B19'$ transformation may not take place during the quenching stage leading to the two phase microstructure.

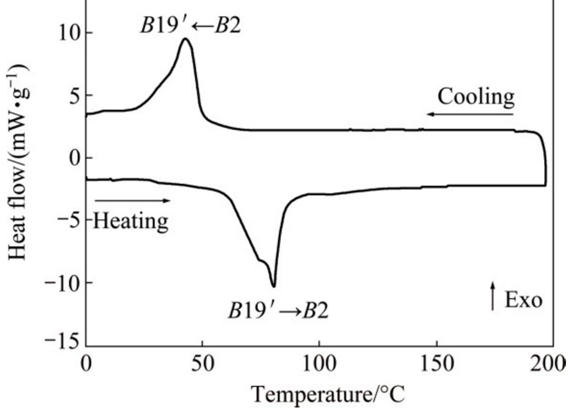


**Fig. 1** DSC curves of homogenized $Ni_{50}Ti_{50}$ specimen