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Structure refinement of shape memory alloys under severe electroplastic rolling

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ABSTRACT

It is shown that the deformability of $Ti_{49.2}Ni_{50.8}$ and $Ti_{50.0}Ni_{50.0}$ alloys rolled with electric current is considerably greater than that obtained by cold rolling. The influence of deformation with an electric current on features of the microstructure was investigated. It was demonstrated that strong grain refinement to size of 60-120 nm accompanies the electroplastic rolling process. At the same annealing temperature, the alloy with the initial martensitic structure has a larger grain size. These differences can probably be explained by the different recrystallization temperatures of deformed martensite and austenite. The intensity of strain hardening was compared for both alloys after electroplastic rolling (EPR). The reasons for the different behaviour in the EPR process are discussed.

Keywords: *Nanostructure, Shape Memory Alloys, Electroplastic Rolling, Deformability.*

1. Introduction

At present production, research and application of shape memory TiNi-based alloys for medicine and structure elements is a promising area of materials science. The functional and mechanical properties of TiNi alloys can be enhanced considerably by ultrafine-grained or nanograined structure formation during severe plastic deformation (SPD) [1, 2]. However, it is difficult to solve this problem by traditional metal working methods, because it is not possible to introduce large strain by cold deformation without breakage [3] or by hot deformation without strength decreases [4]. Hot rolling helps to achieve high strain values of the TiNi alloy, but high temperatures lead to significant reductions in hardness and strength [4]. Long enough, it has been shown that the elongation to failure of metallic materials can be enhanced by use of the electroplastic effect (EPE) at tension [5]. This is why successful attempts were later made to apply current for cold rolling $Ti_{49.3}Ni_{50.7}$ alloy in course-grained (CG) and ultrafine-grained (UFG) states [6], and then thoroughly research EPE at tension $Ti_{49.3}Ni_{50.7}$ alloy. The availability of using EPE was confirmed for strength and deformability enhancement [7, 8]. It was found that electroplastic rolling (EPR) in combination with post-deformation annealing leads to the formation of a nanostructure in the $Ti_{49.3}Ni_{50.7}$ alloy. It is shown that EPR increases the deformability of $Ti_{49.3}Ni_{50.7}$ by 1.5–2 times in comparison with cold deformation without current. Post-deformation annealing in the temperature range of 400–500 °C leads to the formation of a nanocrystalline structure and to the achievement of high strength and functional properties of the $Ti_{49.3}Ni_{50.7}$ [8]. In addition, it turned out that cold rolling with current can significantly reduce the elastic modulus of shape memory alloys, which is important for the use of bone implants [9].

At once the TiNi-based shape memory alloys have various compositions, and their influence on the EPR processing is unknown. Difference in alloy chemical composition leads to different phase compositions: B2 austenite or B19' martensite at room temperature, and, apparently, to differences in the structural formation during deformation. Therefore, it is important to understand whether and what is the difference in the structure, properties and deformation ability of these alloys processed by the electroplastic rolling.

The aim of this paper is to study the deformability, microstructure, and microhardness of $Ti_{50.0}Ni_{50.0}$ and $Ti_{49.2}Ni_{50.8}$ alloys processed by EPR.

2. Experimental details

The investigation has been performed on hot-rolled bars of $Ti_{49.2}Ni_{50.8}$ and $Ti_{50.0}Ni_{50.0}$ alloys with dimensions of Æ 6.1 × 135 mm. The bars were heated at 750 °C for 1 hour and quenched in water to homogenize the alloy before the experiments. At room temperature, the alloys had the B2 austenite and B19' martensite structures, respectively, after quenching. The martensitic temperatures of the alloys at cooling and heating at the speed of 20 °/min were measured by differential scanning calorimetry (DSC) method and are shown for the initial state in Table 1.

Samples were subjected to EPR until the appearance of visible cracks or destruction of the sample to compare their deformability ($e = \ln S_0/S_f$, where e is the true strain and S_0 and S_f are the initial and final cross-sectional areas before and after deformation, respectively). EPR was conducted on a rolling mill with calibrated rollers. The size of calibers was varied from 1 to 7 mm. The rolling mill was equipped with a pulse current generator. Current was provided to the deformation zone using a sliding contact (negative pole) of the specimen and one of the rolls (positive pole), respectively. The following current mode and current regimes were selected based on the previously found values of the critical current density j_{cr} and the condition of the minimum thermal effect. Failure to comply with these requirements can lead to a lack of EPE or strong heating, which prevents the structure refinement. EPR was carried out step by step on the bar under a pulse unipolar current with current density j = 100 A/mm^2 and 140 A/mm^2, a pulse duration of 120 × 10^{-6} s, frequency of 1000 Hz, speed of 5 cm/min, and single reduction per pass of 50 μm. The last parameter determines the intensity of plastic deformation over the section and crack resistance of the material. After each step, samples were cooled in water to avoid heating. The bar was turned 90° along the longitudinal axis and the rolling direction was changed to the opposite one before each subsequent pass.

Samples for further research were selected with true strain (diameter) e = 0.8 (Ø 4 mm), 1.2 (Ø 3.4 mm), 1.4 (Ø 3 mm), and 3.6 (Ø 1 mm). The microhardness of the cross-section of the rolled sample was measured on a PMT-3 under 100 g load for 20 s.

The microstructure was studied by transmission electron microscopy (TEM) using a Tesla BS-540 microscope. Foils for TEM were obtained by cutting, mechanical thinning, and electrolytic polishing of the samples. The selected area of electron diffraction patterns (SAEDP) was about 1 μm^2.

3. Results and discussion

The deformability of $Ti_{50.0}Ni_{50.0}$ and $Ti_{49.2}Ni_{50.8}$ alloys rolled with and without a current is shown in Table 2. The values of true strain correspond to the appearance of visible cracks in the EPR or destruction.

The table 2 shows that rolling with a current increases the deformability by a factor of 6–10 for

Table 1- The martensitic temperatures of the alloys in the initial state

Chemical composition	Treatment	Martensitic temperatures (°C)				Phase state at room temperature
		Ms	Mf	As	Af	
$Ti_{49.2}Ni_{50.8}$	Quenching (750 °C/water)	–5	–37	-5	17	B2 austenite
$Ti_{50.0}Ni_{50.0}$		45	25	58	77	B19' martensite

Table 2- Deformability of alloys rolled with current (j = 100 A/mm²) and without current

Alloy	Phase composition	True strain without current, $e_{j=0}$	True strain with current, e_j
$Ti_{49.2}Ni_{50.8}$	Austenite	0.1	1.2
$Ti_{50.0}Ni_{50.0}$	Martensite	0.6	3.6*

* The size of calibres was 1 mm

both alloys compared to rolling without a current. The table also shows that the deformability of the $Ti_{50.0}Ni_{50.0}$ alloy is higher than that of the $Ti_{49.2}Ni_{50.8}$ alloy with and without current. The use of a pulse current provides deformation of the $Ti_{50.0}Ni_{50.0}$ alloy without breakage up to a strain of e = 3.6 or more. The true strain corresponding to fracture was not defined in this experiment because of the limitation of the small calibre.

Comparison of the microhardness evolution during the EPR process allows the intensity of strain hardening to be estimated (Fig. 1). The microhardness of the $Ti_{49.2}Ni_{50.8}$ alloy is higher in comparison with $Ti_{50.0}Ni_{50.0}$ alloy before and after deformation. Microhardness measurements showed an increase in comparison with the initial undeformed state for both alloys during EPR processing. However, the degree of strain hardening (slope of curves) differs between alloys. The curves show that $Ti_{49.2}Ni_{50.8}$ alloy is hardened more intensively.

The structure of alloys processed by any plastic deformation including EPR is heterogeneous, which is why post-deformation annealing is commonly used. The investigated alloys were annealed at 500 °C for 1 hour to obtain the grain structure and to optimize the mechanical properties. The microhardness of both alloys decreased as a result of annealing. After annealing, the difference in microhardness of the deformed alloys is much lower than in the deformed state before annealing (Fig. 1, points 3 and 4).

Current density has a great influence on the intensity of strain hardening. Thus, the degree of strain hardening in $Ti_{49.2}Ni_{50.8}$ alloy decreases more than twofold when the current density increases from 100 to 140 A/mm^2 (Fig. 2). The degree of hardening is lower in alloy processed by EPR with higher current density. In addition the current density of 140 A/mm^2 improves the deformability by a factor of three.

Figure 3 shows the microstructures of both alloys after annealing at 450 and 500 °C for 1 hour. In the alloy with initial austenitic structure after EPR (e = 1.2) and subsequent annealing at 500 °C a nanostructure with an average grain size of 90 nm was obtained (Fig. 3a). Annealing at 500 °C in the alloy with initial martensitic structure leads to grain structure formation with a rather larger grain size of 120 nm (Fig. 3b). Nevertheless a grain nanostructure with a size of 60 nm is formed after annealing at 450 °C (Fig. 3c). Analysis of diffraction patterns suggests that $Ti_{49.2}Ni_{50.8}$ alloy has a mainly austenitic structure after EPR and annealing at 500 °C, but in $Ti_{50.0}Ni_{50.0}$ alloy a mixed austenitic–martensitic structure is formed.

The present study showed that rolling with a current greatly improves the deformability of each of the alloys in comparison with rolling without a current (Table 1). This is explained by the electroplastic effect, which has a great influence on the unblocking of dislocations ("electronic wind") [5].

$Ti_{50.0}Ni_{50.0}$ alloy with an initial martensite structure has a much larger deformability in comparison with $Ti_{49.2}Ni_{50.8}$ alloy with an initial B2 austenite structure after EPR at room temperature (Fig. 1). Apparently mechanical twinning of B19' phase and twinning of B2 phases (from return martensitic transformation) can develop together in the alloy with initial martensitic structure. This effect can increase the deformability of the alloy. At the same time, $Ti_{49.2}Ni_{50.8}$ alloy has a much higher deformability which becomes comparable

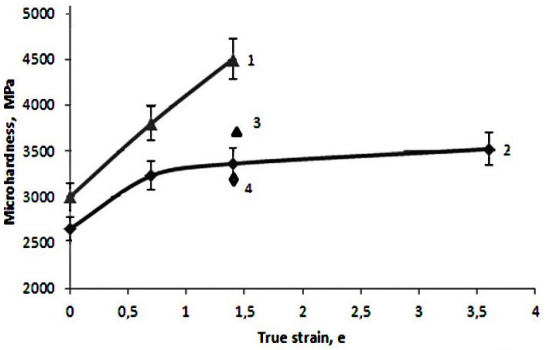

Fig. 1- Microhardness dependence on true strain with EPR (j = 100 A/mm^2): (1) $Ti_{49.2}Ni_{50.8}$, (2) $Ti_{50.0}Ni_{50.0}$, (3) $Ti_{49.2}Ni_{50.8}$ + annealing at 500 °C, (4) $Ti_{50.0}Ni_{50.0}$ + annealing at 500 °C.

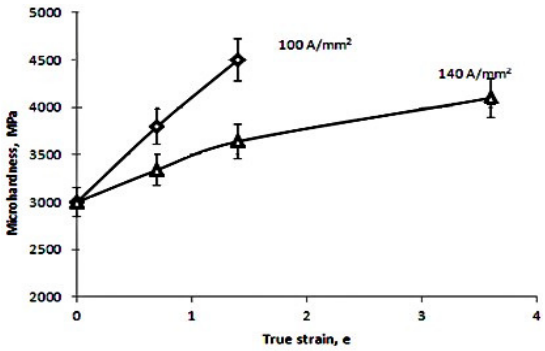

Fig. 2- Influence of current density on strain hardening in $Ti_{49.2}Ni_{50.8}$ alloy.

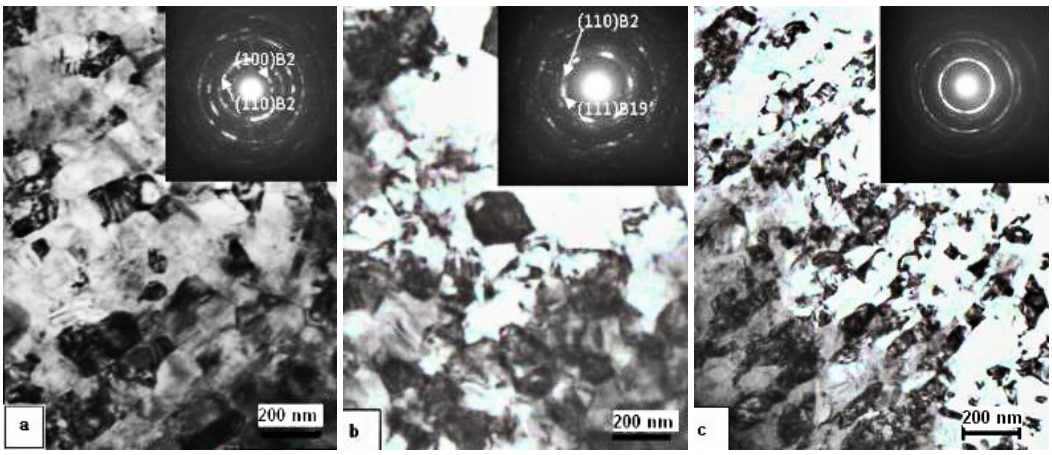

Fig. 3- Microstructures and SAEDP of alloys after EPR and annealing: (a) $Ti_{49.2}Ni_{50.8}$, e = 1.2 + annealing at 500 °C for 1 hour; (b) $Ti_{50.0}Ni_{50.0}$, e = 1.4 + annealing at 500 °C for 1 hour; (c) $Ti_{50.0}Ni_{50.0}$, e = 1.4 + annealing at 450 °C for 1 hour.

Table 3- The martensitic temperatures of the alloys after EPR

Chemical composition	Treatment	The martensitic temperatures, °C				Phase state at room temperature
		Ms	Mf	As	Af	
$Ti_{49.2}Ni_{50.8}$	e=1.2 + annealing (500 °C)	20	-34	19	31	B2 austenite
$Ti_{50.0}Ni_{50.0}$	e=1.4 + annealing (500 °C)	37	13	51	70	mixed austenitic–martensitic structure
	e=1.4 + annealing (450 °C)	41	-1	45	59	

with that of $Ti_{50.0}Ni_{50.0}$ alloy if the current density increases from 100 to 140 A/mm^2 (Fig. 2). The level of microhardness decreases, but it is 1.5 times higher than that of $Ti_{50.0}Ni_{50.0}$ alloy after EPR with less current density.

$Ti_{49.2}Ni_{50.8}$ alloy is more intensively strengthened and has a higher level of microhardness with increasing EPR strain. This can probably be explained by an excess of Ni atoms in the initial BCC lattice of $Ti_{49.2}Ni_{50.8}$ alloy. The main reason for the distinction in hardening intensity is the different deformation mechanisms of B2 phase in $Ti_{49.2}Ni_{50.8}$ alloy and B19' phase in $Ti_{50.0}Ni_{50.0}$ alloy. Also, the elastic modulus makes a significant contribution to the intensity of hardening, as it is proportional to the stresses occurring in the material. As the elastic modulus E of austenitic phase is almost two times greater than the elastic modulus E of martensitic phase [10], it makes an essential contribution to the level of hardening of $Ti_{49.2}Ni_{50.8}$ alloy, which is higher than that of $Ti_{50.0}Ni_{50.0}$ alloy at the same true strain. Finally, more intensive hardening of $Ti_{49.2}Ni_{50.8}$ alloy during the EPR process can be explained by strengthening of Ti_3Ni_4 particles in over-stoichiometric alloy. These particles can appear because of local heating upon current transmission.

The structures of $Ti_{49.2}Ni_{50.8}$ and $Ti_{50.0}Ni_{50.0}$ alloys after post-deformation annealing also have differences (Fig. 3a, b). At the same annealing temperature, the alloy with the initial martensitic structure has a larger grain size. These differences can probably be explained by the different recrystallization temperatures of deformed martensite and austenite. Microstructural studies have also shown differences in the phase composition after the EPR and after annealing. $Ti_{49.2}Ni_{50.8}$ alloy after EPR and annealing at 500 °C has mainly austenitic structure, whereas mixed austenitic–martensitic structure is formed in $Ti_{50.0}Ni_{50.0}$ alloy. This is related to the influence of deformation on the temperature range of martensitic transformation [2]. The mixed austenitic–martensitic structure in $Ti_{50.0}Ni_{50.0}$ alloy was also confirmed by DSC (Table 3).

4. Conclusions

1. EPR increases the deformability of $Ti_{49.2}Ni_{50.8}$ and $Ti_{50.0}Ni_{50.0}$ alloys in comparison with rolling without a current. The deformability enhancement is stronger when the current density is higher. Deformability after EPR of $Ti_{50,0}Ni_{50,0}$ alloy is several times higher than the deformability of $Ti_{49,2}Ni_{50,8}$ alloy.

2. Microhardness and strain hardening during EPR processing in $Ti_{49,2}Ni_{50,8}$ alloy are higher than in $Ti_{50,0}Ni_{50,0}$ alloy.

3. Post deformation annealing of $Ti_{49,2}Ni_{50,8}$ and $Ti_{50,0}Ni_{50,0}$ alloys at 450–500 °C leads to nanostructure formation with a grain size of 60–120 nm.

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