The Influence of the Surface Layer on the Combination of Properties of Thin TiNi Alloy Wires

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Abstract—We have studied the influence of the surface layer on the parameters of the multiply repeated shape memory effect, developing stresses, characteristic temperatures, and intervals of martensitic transformations in thin (1 mm diameter) wires made of TiNi-based alloys. Examination of the surface layer structure showed that, in 1-mm-diameter TN-1V grade alloy wire, the oxide layer is about 15 μm thick and consists mostly of titanium, nickel, oxygen, and carbon. Removal of this surface layer leads to an increase in the maximum accumulated deformation, shift of the temperature interval of formation toward higher temperatures, and increase in the strength and plasticity characteristics.

Thin wires made of biocompatible TiNi-based alloys of various grades (TN-10, TN-20, TN-KhE, and TN-1V) are widely used in medicine for manufacturing mesh implants, which is possible due to the unique properties of superplasticity and shape memory inherent in these alloys [1]. The compositions of these alloys have been selected so as to ensure the process of shape recovery proceeding in a convenient temperature interval. During the process of wire formation, initial ingots are subjected to various thermomechanical treatments, which lead to the formation of a modified surface layer of significant thickness. Indeed, the surface layer on TiNi wires with diameters below 90 μm has a volume comparable to that of the remaining matrix part and, hence, significantly influences the mechanical properties of the whole wire [2]. A number of works have been devoted to studying the character and sequence of martensitic transformations (MTs) in wires of binary TiNi alloys with diameters of 3.5, 3, and 2 mm [3–5]. However, data on the influence of a modified surface layer on parameters of the multiple shape memory (MSM) effect, developing stresses, and MTs in TiNi wires for medicinal applications with the most frequently used diameter of 1 mm are, to the best of our knowledge, absent in the available literature, which makes studying these effects topical.

The present work was aimed at analysis of the dependence of the shape-forming parameters of TiNi alloys under MSM effect conditions, developing stresses, and accumulated deformation for TN-1V grade wire 1 mm in diameter with and without z modified surface layer. As is known, a nickel titanium alloy wire represents a composite material comprising a matrix (inner volume of TiNi alloy) and a shell (oxidized surface layer) with substantially different properties [6].

We have studied 50-mm-long wires of a TiNi alloy of TN-1V grade with 1-mm diameter obtained by multiple drawing via spinnerets with intermediate annealing at 800°C. To obtain a wire with minimum thickness of the oxidized surface layer, some samples were etched in a mixture of hydrofluoric and nitric acids ($H_2O : HNO_3 : HF = 2 : 2 : 1$). The alloy composition was determined by energy-dispersive X-ray (EDX) analysis in a JEOL JSM 6500F scanning electron microscope (SEM). The MSM effect parameters were studied under condition of tensile testing at a constant load of 2 kgf. The temperature dependence of electric resistivity $\rho(T)$ was studied by potentiometric techniques. The developing stresses and mechanical properties were determined by conventional methods on an Instron testing machine.

Examination of the surface layer of samples in the SEM with an EDX attachment showed that the thickness of a modified surface layer on a 1-mm-diameter TN-1V wire amounts to an average of 15 μm. The EDX analysis of this layer showed the presence of titanium, nickel, oxygen, and carbon (Figs. 1a, 1b). Analysis of the distribution profiles of elements revealed significant segregation of oxygen in the near-surface layer (Fig. 1c), which was indicative of the formation of an oxidized layer. In addition to oxides, this layer contained carbides. The oxidized layer on TiNi alloy surface was reported [7, 8] to consist of a combination of oxides (TiO_2, Ti_2O_5, etc.) with inclusions of
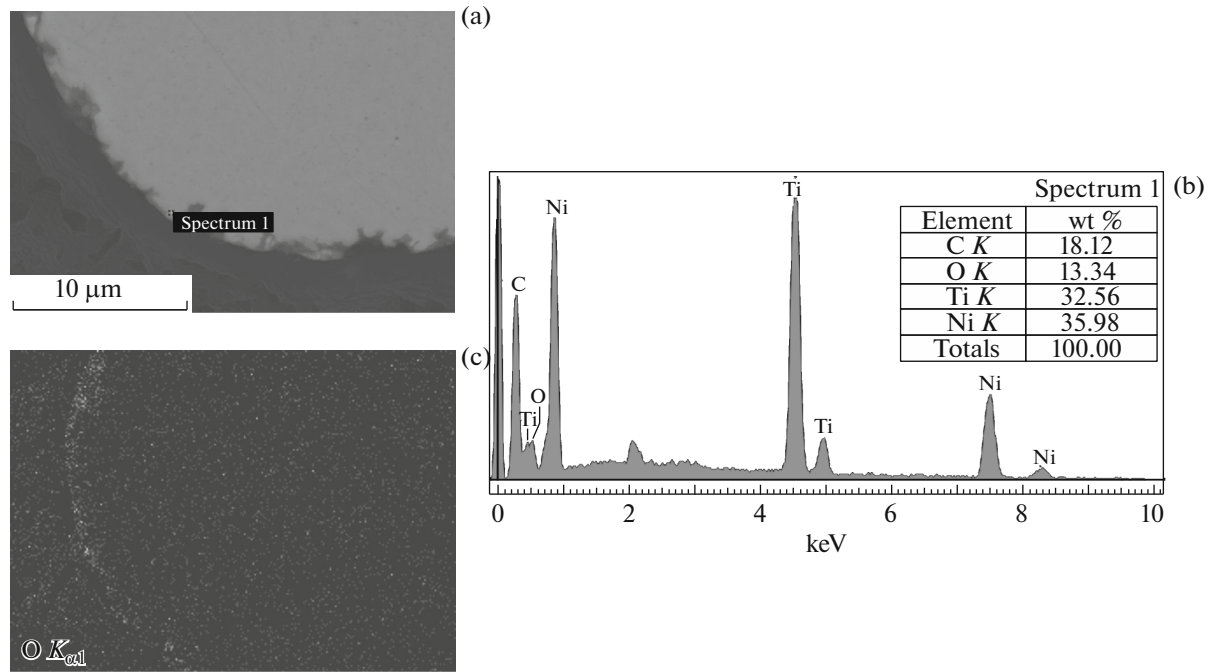
Fig. 1. Surface structure and composition of TiNi wire: (a) SEM image, (b) EDX spectrum measured at the site indicated in image (a), and (c) map of oxygen distribution on the wire surface.
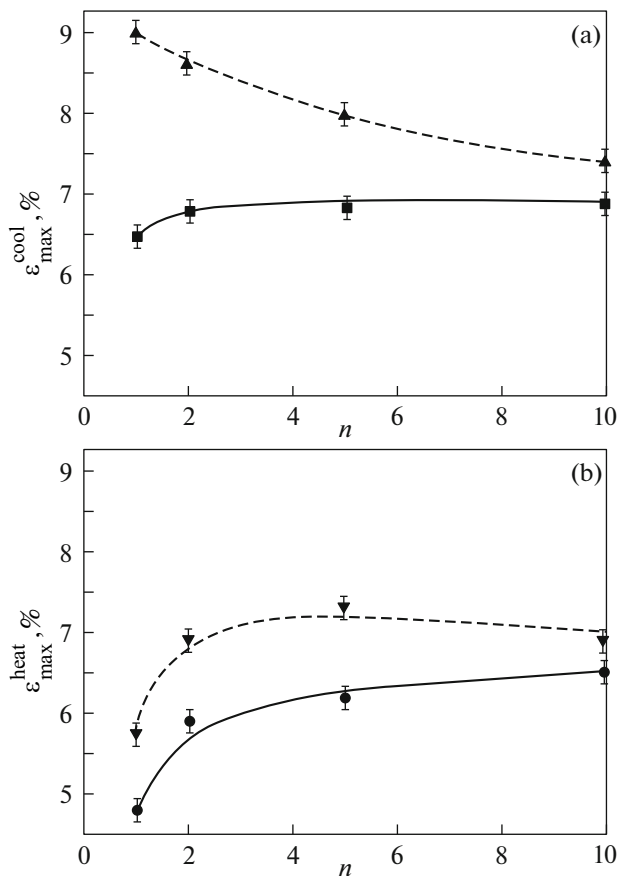

Fig. 2. Plots of the maximum deformation accumulated on (a) cooling and (b) heating vs. number of thermal (cooling–heating) cycles for 1-mm-diameter TN-1V wires with (solid curve) and without (dashed line) a modified surface layer.

Ti_4Ni_2O and Ti_4Ni_2C phases formed due to the penetration of oxygen and carbon into Ti_2Ni intermetallide (a technological impurity that is always present in TiNi alloys). The matrix mostly consists of titanium and nickel with rather insignificant amount of oxygen ($O < 2$ at %). The concentration of nickel in the matrix phase exceeds that of titanium, a large amount of which is spent on the formation of Ti_4Ni_2O and Ti_4Ni_2C phases.

Since the SM effect is only characteristic of the inner matrix of TiNi wire, the modified surface layer of considerable thickness will not contribute to the total accumulation of deformation. This is confirmed by the experimental temperature dependences of accumulated deformation $\varepsilon(T)$ presented in Fig. 2. Indeed, in the samples with a retained surface layer, the SMS effect is characterized by not very large deformation accumulated on cooling (ε_{max}^{cool}) and heating (ε_{max}^{heat}), in contrast to the samples from which this layer was removed by etching. After removal of the modified surface layer, the maximum accumulated deformation on cooling increased from 6.5 to 9% and that on heating increased from 4.7 to 5.7%. Thermal cycling leads to total growth in the accumulated maximum deformation.

The residual deformation per one heating cycle decreases in the course of repeated thermal cycling. The value of total residual deformation accumulated as a result of thermal cycling should be distinguished from the residual deformation upon every cycle, which is the difference of maximum deformation upon cool-

Table 1. Mechanical properties and parameters of martensitic transformations in TiNi-based alloy (TN-1V grade) wires with and without a modified surface layer

Characteristic	Notation	Wire with surface layer	Wire without surface layer
Ultimate stress at break	σ_b, MPa	940	1065
Total accumulated deformation	ε_b, %	40.5	50.8
Elastic deformation	ε_{elast}, %	0.1	0.1
Martensite deformation	ε_{marten}, %	6.4	6.9
Plastic deformation	ε_{plast}, %	34	43.8
Minimum MT stress	σ_{min}^{Ms}, MPa	170	138
Maximum MT stress	σ_{max}^{Md}, MPa	318	290
MT start temperature on cooling	M_s, °C	25	30
MT finish temperature	M_f, °C	10	12
Reverse MT start temperature	A_s, °C	Determination hindered	
Reverse MT finish temperature	A_f, °C	50	60
MT temperature interval	$(A_f - M_f)$, °C	60	70

ing and reversible deformation upon heating. The total residual deformation grows in the course of thermal cycling, since the microstresses accumulated in a sample during straining in the martensite or two-phase state exhibit relaxation due to plastic shear. The residual deformation in every cycle for the samples without surface layer (3.3%) is higher than that for the samples with this layer (1.7%). Thus, the surface layer plays the role of a limiting factor for MT in the course of thermal cycling. For this reason, the samples with retained surface layer exhibit worse shape memory but possess higher strength characteristics (Table 1).

Removal of the surface layer leads to increase in characteristic temperatures of the forward MT (M_s, M_f) and reverse MT (A_f), since the elimination of this factor hindering the motion of the interface allows the MT to start and finish earlier (Table 1).

We have also determined the temperature dependence of developing stresses in TN-1V samples under conditions of tensile straining during recovery of the initial shape caused by heating above the MT temperature. Removal of the surface layer leads to decrease in the minimum and maximum MT stress (Table 1). Measurements of the strength characteristics showed that the samples without modified surface layers possessed an ultimate strength that was 120 MPa greater and 10% higher plasticity as compared to the initial wire. These samples can withstand greater straining due to, predominantly, growing plasticity contribution to the total accumulated deformation and insignificantly increased martensitic component of deformation. Removal of the surface layer prevents the appearance of microcracks at the surface layer/inner volume interface, which lead to the premature fracture of wire samples under tensile testing conditions.

Thus, an about 15 μm-thick surface layer in 1-mm-diameter TN-1V wires represents an oxidized layer consisting predominantly of titanium, nickel, oxygen, and carbon. This modified surface layer significantly influences the whole combination of properties of TiNi alloys. Removal of this layer leads to about 30% increase in the maximum accumulated deformation and shifts the temperature interval of forming by more than 50°C toward higher temperatures. In addition, the minimum and maximum stresses of MT exhibit shift upon removal of the surface layer, being the additional factor of stiffness of the material tested. The etched samples exhibited 120 MPa greater ultimate strength and 10% higher plasticity as compared to the initial wire.

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