Surface microstructure and B2 phase structural state induced in NiTi alloy by a high-current pulsed electron beam

L.L. Meisner [a,b], M.G. Ostapenko [a,c,*], A.I. Lotkov [a], A.A. Neiman [a]

[a] Institute of Strength Physics and Materials Science SB RAS, 2/4 Akademichesky Ave., Tomsk 634021, Russia
[b] National Research Tomsk State University, 36 Lenin Ave., Tomsk 634036, Russia
[c] National Research Tomsk Polytechnic University, 30 Lenin Ave., Tomsk 634036, Russia

ABSTRACT

In the work, we studied structural phase states in surface layers of electron beam-irradiated nickel-titanium (NiTi) alloy depending on beam energy density. The surface of NiTi specimens was exposed to pulsed irradiation (pulse duration $\tau = 150\,\mu s$, number of pulses $N = 5$) by a low-energy high-current ($I = 70\,A$) electron beam with surface melting at electron beam energy densities $E_1 = 15\,J/cm^2$, $E_2 = 20\,J/cm^2$, and $E_3 = 30\,J/cm^2$. The surface layer structure was examined by X-ray diffraction analysis and transmission electron microscopy. It is found that in the NiTi specimens irradiated at $E \leq 20\,J/cm^2$, the layer that contains a martensite phase resides not on the surface but at some depth from it. In the NiTi specimens irradiated at $E_3 = 30\,J/cm^2$, the entire modified surface zone is characterized by a two-phase state in which the B19′ phase dominates over the B2 phase. It is supposed that a barrier to B2 → B19′ martensite transformation in the melted NiTi layer irradiated at $E \leq 20\,J/cm^2$ is high inhomogeneous residual stresses varying with depth from the irradiated surface.

© 2014 Elsevier B.V. All rights reserved.

Now, stable interest is being shown in ion, electron, and plasma flows as a means for precision modification of structural phase states and surface properties of metal materials [1–3]. Experiments demonstrate that these methods of surface modification of NiTi-based alloys increase their corrosion resistance and fatigue strength and provide their surface hardening [4–6]. Among the methods of surface modification of metals and alloys, pulsed electron beam treatment is gaining wide acceptance. The main distinguishing feature of pulsed electron beam treatment is high electron beam energy density per unit treated surface area (10^9–$10^{12}\,J/cm^2$). A short electron beam of high energy density produces dynamically varying temperature fields in surface layers thus providing their superfast heating with the result that the layers are melted and then rapidly quenched ($\sim 10^9\,K/s$) [5]. Besides, the dynamic elastic stress fields formed in the melted layer can induce large strains in the subsurface layer beneath it [7,8]. So, nonequilibrium structural phase states may arise not only in the melted layer but also in the intermediate and core layers. It is these structural phase states that

are considered responsible for changes in physicochemical and mechanical surface properties of materials and for their improvement which is unattainable by conventional surface treatment methods [3,4,6,8–12].

Apparently, the surface properties of NiTi alloy after electron beam treatment are defined by the structural phase state in its modified surface zone. At the same time, as shown previously [12], the final surface microstructure and properties of electron beam-treated materials depend directly on the treatment parameters: on the electron beam energy density, pulse duration, and number of pulses. Therefore, attaining the best surface properties of NiTi alloy requires studies to provide an optimum choice of these parameters. Analysis of the available data suggests that the evolution of structural states formed in the modified NiTi surface zone and their changes depending on the parameters of pulsed electron beam treatment are poorly studied and are thus not quite clear. The lack of experimental data gives no way to exactly determine what modes and parameters of electron beam treatment are most appropriate to NiTi-based alloys to preserve their shape memory property or superelasticity.

The objective of the work was to study the mechanisms of structural phase state formation in NiTi surface layers under low-energy pulsed electron beam irradiation depending on the electron beam energy density.

* Corresponding author at: Institute of Strength Physics and Materials Science SB RAS, 2/4 Akademichesky Ave., Tomsk, 634021, Russia.
E-mail address: artifakt@ispms.tsc.ru (M.G. Ostapenko).

1. Material and research techniques

The alloy under study was melted from iodide titanium and NO-grade nickel in an electric arc furnace (with six-fold remelting of the ingot). The ingot was homogenized at $T = 1273$ K for 6 h and then cooled in the furnace. The test specimens of dimensions of 15 mm × 15 mm × 1 mm prepared from the ingot were subjected to chemical surface cleaning in acid solution ($HNO_3/HF = 3/1$), annealing at $T = 1073$ K for 1 h with subsequent cooling in the furnace, and then to electrolytic polishing in acid solution ($CH_3COOH/HClO_4 = 3/1$) cooled to $T = 273$ K. As a result, the initial NiTi specimens at room temperature were in the two-phase state: a B2 phase (∼95 vol.%) and a Ti_2Ni phase (∼5 vol.%). The lattice parameter of the B2 phase (bcc structure, CsCl ordering) was $a_{B2}^0 = 3.0132 \pm 0.0005$ Å . The start temperature of direct B2 → B19′ martensite transformation for the alloy was $M_S = 290$ K. This temperature was defined as the temperature at which first peaks of the B19′ martensite phase appeared in X-ray diffraction of the alloy on cooling and was measured with a TTK-450 X-ray camera and XRD-6000 diffractometer (Shimadzu, Japan). The equipment used in the study and mentioned hereinafter was provided by Tomsk Materials Science Center for Collective Use of Tomsk State University and Shared Use Center "Nanotekh" of ISPMS SB RAS (Tomsk, Russia).

The chemical composition of the B2 phase was measured with a Wave 500 wavelength dispersive spectrometer (Oxford Instruments) and an EVO 50 scanning electron microscope (Zeiss, Germany). According to the obtained data, the Ti–Ni ratio in the B2 phase corresponded to $Ti_{49.5}Ni_{50.5}$.

The NiTi specimens were subjected to pulsed (pulse duration $\tau = 150$ μs, number of pulses $N = 5$) surface irradiation by a low-energy high-current ($I = 70$ A) electron beam with surface melting under the conditions of high vacuum (∼10^{-6} Pa) with oil-less pumping. The beam energy density was constant ($E = $ const) and was either $E_1 = 15$ J/cm^2, or $E_2 = 20$ J/cm^2, or $E_3 = 30$ J/cm^2. Thus, there were three groups of specimens the treatment for which differed only in electron beam energy density.

X-ray diffraction (XRD) analysis before and after electron beam treatment was performed at room temperature on a DRON-7 diffractometer (Burevestnik, Russia) in Co-K$_\alpha$ radiation with a Fe-filter for cutoff of β-radiation and on a Shimadzu XRD-6000 diffractometer (Shimadzu, Japan) in Cu-K$_\alpha$ radiation with a monochromator for cutoff of β-radiation. The phase composition and the structure of surface and deeper layers were analyzed using X-ray diffraction in symmetric (Bragg–Brentano) and asymmetric geometries. The imaging conditions and the choice of X-ray wavelengths, β-filters, and glancing incidence angles α for NiTi specimens were described in detail in our previous papers [13,14].

In the XRD study, we took into account the following: (1) the structural parameters obtained from X-ray data are integral structural characteristics of the material volume penetrated by an X-ray beam; (2) the material volume penetrated by an X-ray beam depends on the Bragg angle 2θ: the higher the angle 2θ, the larger this volume and hence the larger the X-ray penetration depth into the material; (3) the representative material volume in X-ray diffractometry in Bragg–Brentano (symmetric) geometry is maximal. Thus, it was considered that the X-ray data on structural parameters of the B2 phase in symmetric geometry characterized mainly deep layers in which the initial state of this phase was preserved after electron beam treatment. The X-ray data on structural parameters of the B2 and B19′ phases in asymmetric geometry characterized structural phase states in surface layers of thickness corresponding to a chosen glancing incidence angle α (α is the angle between the specimen surface plane and the direction of a primary incident X-ray beam). X-ray diffraction patterns were taken at glancing incidence angles $\alpha = 3°–12°$. The analyzed layer thickness h was estimated by the formula [15]:

$$h = -\ln(1 - R)/\mu k, \qquad (1)$$

where R is the radiation absorbed by a layer of thickness h (taken to be $R = 0.99$); μ is the linear absorption coefficient of NiTi; $k = (1/\sin\alpha + 1/\sin\delta)$ is the coefficient that takes into account diffraction geometry; $\delta = (2\theta - \alpha)$ is the angle between the X-ray beam reflected from the plane ($h\,k\,l$) and the specimen plane; θ is the Bragg angle of a family of lattice planes ($h\,k\,l$).

The microstructure of NiTi surface layers before and after electron beam treatment was examined on a JEM 2100 transmission electron microscope (JEOL, Japan) at an accelerating voltage of 200 kV. Foils of lateral specimen sections for transmission electron microscopy were prepared by a special procedure which allowed one to preserve the irradiated surface and to examine the structure at a specified depth from the surface.

The lattice parameter a_{B2} of the B2 phase was determined by a precision method with construction of extrapolation dependences of a_{B2}^{hkl} on the function $1/2(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$ [16]. The measurement accuracy for the lattice parameter was $\triangle a = \pm 0.0005$ Å.

2. Results and discussion

2.1. Phase composition in the modified NiTi surface zone

For XRD analysis, as noted in the previous section, we used two different X-ray diffraction geometries. As estimated by formula (1), the layer thicknesses for which the integral structural parameters of the phases were determined varied in the following ranges: for symmetric geometry, from ∼12 to ∼30 μm (depending on the diffraction angle θ); for asymmetric geometry, from ∼0.3 to ∼2.8 μm at $\alpha = 3°$, from ∼0.5 to ∼5.2 μm at $\alpha = 6°$, and from ∼0.9 to ∼20 μm at $\alpha = 12°$. This means that the examined region in symmetric geometry included not only the layer modified by electron beam treatment (the thickness of this layer, according to the previous data [13], is no greater than ∼10 μm) but also its adjacent deeper layer which did not experience direct electron beam action. In asymmetric geometry, the contribution of these core layers to X-ray diffraction patterns decreased with decreasing the glancing incidence angle α.

Fig. 1 shows X-ray diffraction patterns in symmetric geometry for NiTi before (a) and after electron beam treatment (b–d). It is seen that the X-ray pattern of the initial NiTi specimen contains peaks of only two phases: B2 (NiTi) and Ti_2Ni. The B2 phase is textured such that the X-ray pattern lacks the main (200)$_{B2}$ peak (in the range of angles $2\theta \sim 71°–72°$). After electron beam treatment of the NiTi specimens at different energy densities $E_1 = 15$ J/cm^2 (b), $E_2 = 20$ J/cm^2 (c), and $E_3 = 30$ J/cm^2 (d), a series of common effects is observed on all X-ray patterns: (1) the presence of new peaks the most intense of which are found in the vicinity of the (1 1 0)$_{B2}$ peak; (2) the absence of peaks of the Ti_2Ni phase; and (3) the appearance of the (2 0 0)$_{B2}$ peak on the X-ray pattern (b) suggesting that the B2 phase texture in the NiTi specimens is changed after electron beam treatment at $E_1 = 15$ J/cm^2. Interpretation of the X-ray patterns shows that the new peaks correspond to the B19′ martensite phase with monoclinic structure (space group P2$_1$/m). Comparison of the X-ray patterns reveals that increasing the electron beam energy density increases the intensity of B19′ peaks. Estimation of the relative volume content of the B2 and B19′ phases from the total intensity of their peaks shows that the percentage of the martensite phase increases from ∼5 vol. % in the NiTi specimen irradiated at $E_1 = 15$ J/cm^2 to ∼80 vol. % in the NiTi specimen irradiated at $E_3 = 30$ J/cm^2.