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The gradient structure of the NiTi surface layers subjected to tantalum ion beam alloying

S L Girsova¹, T M Poletika¹, L L Meisner¹² and E Yu Schmidt²

¹Institute of Strength Physics and Material Science SB RAS, 2/4 Akademichesky ave., Tomsk, 634055, Russia
²National Research Tomsk State University, 36 Lenin ave., Tomsk, 634050, Russia
poletm@ispms.tsc.ru

Abstract. The NiTi shape memory alloy has been modified by ion implantation with Ta to improve the surface and biological properties. The elemental and phase composition and structure of the surface and near-surface layers of NiTi specimens after the Ta ion implantation with the fluency \( D = 3 \times 10^{17} \text{ cm}^{-2} \) and \( D = 6 \times 10^{17} \text{ cm}^{-2} \) are examined. The methods of Auger electron spectroscopy (AES), transmission electron microscopy (TEM), and electron dispersion analysis (EDS) are used. It is found that a nonuniform distribution of elements along the depth of the surface layer after the ion implantation of NiTi specimens, regardless of the regime, is accompanied by the formation of a number of sublayer structures.

1. Introduction
Shape memory alloys are known to enjoy wide applications, e.g. NiTi alloy is employed in biomedical industry for the manufacture of implants. To overcome the problem of Ni release and to improve the biological, chemical, and mechanical properties, many surface treatment techniques are used [1]. Thus, the ion beam implantation gained recognition as an effective method for the deposition of thin protective layers on the surface of NiTi alloys [2]. A complex gradient structure would form in surface layers of as-treated NiTi alloys; a significant change would also occur in their phase composition. The mechanisms involved are still unclear. This might be due to the lack of reliable experimental evidence for structural changes occurring in the surface and near-surface layers of treated materials. The aim of the given study is to investigate the surface layer structure of as-treated material at the nanoscale levels. The study is carried out for test specimens made of NiTi alloy, which were modified by the Ta-ion beam implantation; the surface layer of as-treated alloy is found to possess an enhanced biocompatibility and satisfactory X-ray contrast range [3, 4]. The ion beam implantation would cause oxide layers, TiO₂ included, to form on the surface of Ti and Ti-based alloys, which is liable to enhance the biocompatibility, chemical stability, non-toxicity, and absorptive capacity of as-treated material [2, 4].

2. Experimental
The study was carried out on test specimens of NiTi alloy (the alloy composition is Ni₅₀.₅Ti₄₉.₅; the alloy structure is B2). The specimen surface was polished before the treatment. The Ta-ion beam modification was performed with a DIANA-3 ion implanter unit using pulsed Ta-ion beams; the fluency \( D = 3 \times 10^{17} \text{ cm}^{-2} \) and \( D = 6 \times 10^{17} \text{ cm}^{-2} \); the average accelerating voltage was 80 kV and the pulse repetition frequency was 50 Hz. By ion implantation, the specimens were heated to the
temperature ≤473 K. Using the method of Auger electron spectroscopy (AES), the layer-by-layer analysis was made for the element composition of the modified specimen surface using a SHUNA-2 (NR TPU, Russia). The defect structure studies were carried out with the aid of transmission electron microscopy (TEM) on JEM 2100 (JEOL) at the accelerating voltage of 200 kV. The cross-section specimens were prepared by the ion thinning method on EM 09100IS (JEOL). The equipment used in the study and mentioned hereinafter was provided by the Shared Use Center of the ISPMS SB RAS (Tomsk, Russia).

3. Element concentration profiles (AES)

Figure 1 illustrates profiles obtained for near-surface layers of as-treated specimens by AES. Irrespective of the dose, oxide layers enriched with Ti and O atoms form on the specimen surface. O and C atoms are adsorbed from the residual atmosphere of the vacuum chamber of the ion implanter. The oxide layer thickness is 10 nm and 30 nm for the fluency \( D = 3 \times 10^{17} \text{ cm}^{-2} \) and \( D = 6 \times 10^{17} \text{ cm}^{-2} \), respectively. Oxide layers were found to contain such concentrations of O and Ti that are sufficient for the formation of stoichiometric dioxide \( \text{TiO}_2 \).

The important parameter characterizing the state of NiTi surface layers is the content of Ni atoms. The Ni concentration profiles obtained for oxide sublayers are displaced with depth. The above results indicate that the as-treated specimen surface is depleted of Ni. The AES data presented in Figure 1 suggests that the latter effect might be due to Ni-O bonds, being more readily reduced relative to Ti-O bonds [5]; besides, the preferential sputtering of Ni atoms, which is four times higher than that of Ti, might be responsible for the same effect [6]. Due to surface layers being depleted of titanium, Ti atoms are accumulated in areas with a low content of oxygen and titanium. Hence, in the concentration profiles obtained for the ion-modified layer the maxima of Ti and Ni are shifted relative to one another. The Ta concentration profile obtained for oxide layers is also displaced with depth (Figure 1). The maximum Ta content is found to occur at the depth 20÷30 and 50 ÷ 60 nm in going down to the lower boundary of oxides, respectively, for the regimes \( D = 3 \times 10^{17} \text{ cm}^{-2} \) and \( D = 6 \times 10^{17} \text{ cm}^{-2} \). The ion-modified surface layer for both as-treated specimens has the thickness 80 nm and 100 nm.

![Figure 1](image1.png)

**Figure 1.** Element concentration profiles within surface layers of NiTi specimens with implanted Ta: fluency \( D = 3 \times 10^{17} \text{ cm}^{-2} \) (a) and fluency \( D = 6 \times 10^{17} \text{ cm}^{-2} \) (b).

4. Surface layers structure (TEM)

Using the TEM technique, the surface layer structure is examined. It is found that a nonuniform distribution of elements along the depth of surface layers after the Ta ion implantation, regardless of the regime, is accompanied by the formation of a number of different sublayers. Thus, two main layers are found, i.e. the upper oxide layer and the lower-lying layer of the material in the amorphous state.
The surface layer structure of NiTi specimens subjected to the Ta-ion implantation is illustrated in Figure 2. The upper oxide sublayers are 20÷30 nm thick. The diffraction analysis data suggests that oxide layers preferably include TiO$_2$ modifications, i.e. brookite and rutile. For specimens with a higher irradiation dose $D = 6 \times 10^{17}$ cm$^{-2}$, the oxide layer structure is more complex (Figure 2). It is seen that there are two layers: the light outer layer and the dark one adjacent to the lower boundary of the oxide. The observed contrast suggests that the dark crystalline underlayer contains atoms of heavier element tantalum. We can assume that this is due to the linear dependence of both the depth and the width of the Ta concentration profile of the ion treatment regime. Thus, with increasing irradiation dose, the maximum implantable element expands with overlapping O and Ta distribution profiles, which implies the existence of nanoparticles of Ta oxides. Indeed, an increase in the dose of irradiation is accompanied by a rise of temperature and the number of radiation-induced defects, thus increasing the diffusion mobility of heavier atoms. However, there is no reliable experimental TEM data confirming the presence of tantalum oxide in implanted layers of NiTi.

![Figure 2](image)

**Figure 2.** TEM images of surface layers of NiTi subjected to the Ta-ion implantation with the fluency $D = 3 \times 10^{17}$ cm$^{-2}$: (a) a bright-field image of surface layers and a nanodiffraction (NBD) pattern of the amorphous ion-modified layer (the probe on the specimen size 30 nm); 1) the oxide layer (nanocomposite ceramics); 2) the amorphous layer; 3) the near-surface crystalline layer; (b) NBD pattern of the near-surface oxide layer, zone axis [-345] of TiO$_2$ brookite (indicated by the arrow); (c) EDS data obtained for the surface layer, which reveals a layer containing localized Ta atoms.

The amorphous layer has a thickness of 80 nm and 100 nm for the regimes $D = 3 \times 10^{17}$ cm$^{-2}$ and $D = 6 \times 10^{17}$ cm$^{-2}$, respectively (Figure 2a). The NBD pattern obtained for the latter near-surface amorphous layers of both implanted NiTi specimens has a characteristic broad diffuse halo corresponding to reflection {110} B2, which exhibits a short-range order (Figure 2a). It is believed that distortion-type amorphization takes place, thus causing distortion of the original NiTi crystal at the scale level of a unit cell [7]. It should be noted that, regardless of the dose, the variation in the TEM image contrast suggests that the amorphous material layer has a darker zone 30÷40 nm thick and a lower-lying lighter zone (Figure 2a). According to the sorption $Z$-contrast (here $Z$ is the atomic number of elements, $Z_{Ta} = 73$), the element tantalum is localized in the former zone. In support of this view, the energy dispersion analysis is made for the amorphous layer, which suggests that a Ta-enriched layer really exists (Figure 2c). It was found that the thickness of this layer is independent of the ion treatment regime.

A thin defect sublayer is found to occur between the modified amorphous layer and the substrate for both ion-treated specimens; it is characterized by an inhomogeneous TEM contrast (Figures 2 and 3). Generally, such an intermediate layer has a high internal stress level and contains all kinds of
defects, e.g. point defects, dislocation loops, etc., as well as nanophases on the base of alloy components [8]. Due to the formation of an ion-modified (amorphous) surface layer, the material volume would change significantly. This would cause significant dilatation and an increase in the compressive stress level in the near-surface layer, thereby initiating plastic yielding of the material [2]. The effect of dilation is observed for the near-surface layer of NiTi alloy subjected to the ion implantation treatment to the depth \( \geq 10 \text{ \mu m} \) [9]. It should be noted that this effect becomes stronger with increasing irradiation dose. The effect is manifested in the formation of dislocations, dislocation loops, and network substructures (Figure 2e). Modified near-surface layers have low dislocation density, which is largely due to recovery processes initiated by high temperature. The overall picture is diverse and inhomogeneous; in particular, the deformation structure varies significantly. Thus, traces of the martensitic R-phase are observed in the form of individual lamellae or groups of lamellae. The formation of the R-phase should be due to the shifting temperature interval of martensitic transformations as well as the suppression of the B19' phase formation in thin near-surface layers by the implantation treatment [2].

![Figure 3](image-url)  
**Figure 3.** TEM images of surface layers of NiTi alloy subjected to the Ta-ion implantation with \( D = 6 \times 10^{17} \text{ cm}^{-2} \): (a) a bright-field image; the oxide layer enriched with Ta is indicated by the arrow; (b) a bright-field image of the amorphous layer; an NBD pattern of the amorphous layer (the probe on the specimen size 25 nm); 1 — the oxide layer (nanocomposite ceramics); 2 — the amorphous layer; 3 — the near-surface crystalline layer.

4. **Conclusion**

It is found that a nonuniform distribution of elements along the depth of the surface layer of NiTi after ion implantation, regardless of the regime, is accompanied by the formation of a number of different nanolayer structures. Thus, two main layers are found: the oxide layer and the ion-modified amorphous layer. The oxide layer contains preferably titanium oxide TiO\(_2\). With increasing irradiation dose, we observe an increase in the thickness of the oxide layer and changes in its structure, resulting in the formation of two-layer nanocomposite ceramics. Ta atoms are localized in the lower-lying amorphous layer \( \leq 100 \text{ nm} \) thick. With increasing irradiation dose, the maximum implant element is not only shifted into the specimen, but also expands with overlapping O and Ta distribution profiles. This is due to the linear dependence of both the depth and the width of the concentration profile of Ta in the ion treatment regime. The AES and EDS data show a significant loss in the Ni oxide layer, which is an important factor when using NiTi in medicine as implants. The effect of dilation was manifested in the formation of dislocations and dislocation loops and network substructures.
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