

# Peculiarities of structure and hardening of Ni-Ti alloy surface layers formed by $^{84}\text{Kr}^{15+}$ ions irradiation at 147 MeV energy at high temperatures

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**Abstract.** The consistent patterns of changes in nanostructure and nanohardness of Ni-Ti alloy after irradiation with  $^{84}\text{Kr}^{15+}$  ions with 147 MeV energy to the fluence of  $1 \cdot 10^{19} \text{ m}^{-2}$  at 250 and 300°C temperatures depending on phase composition have been experimentally studied. It was shown that significant (44 – 94%) softening of surface layers for the single-phase and two-phase Ni-Ti alloys is connected with the formation of bubble nanostructured defects and complete sputtering of the process layers. The role of nanostructure in roughness of the irradiated Ni-Ti alloy surface of various phase composition has been established.

## 1. Introduction

During modification of NiTi alloys for medical application the great attention should be paid to the surface [1]. The papers [2-4] showed that as a result of irradiation with inert gases heavy ions of MeV-energy the structure and properties of the modified surface layers of Ni-Ti alloy vary considerably depending on exposure parameters and phase composition. So, the nanostructured defects in the form of bubbles ( $^{40}\text{Ar}^{8+}$ ) or tracks ( $^{84}\text{Kr}^{15+}$ ,  $^{132}\text{Xe}^{22+}$ ) were revealed on the surface of Ni-Ti alloy of various phase composition after irradiation under comparable parameters of  $A/Z$ ,  $E_{\text{nucl}}$ ,  $Ft$ ,  $J_{\text{beam}}$  and  $T_{\text{irrad}}$  [3, 4]. Transformation of the track structure into the granular structure occurs during irradiation with  $^{84}\text{Kr}^{15+}$  ions to the fluences of  $\leq 5 \times 10^{19} \text{ ion/m}^2$  [5]. In this case radiation hardening is observed near the Ni-Ti single-phase alloy surface layer modified with krypton ions, but in the case of argon ions irradiation it is observed at the depth of  $\geq 100 \text{ nm}$  only [2]. This is associated with the running processes of ion polishing and sputtering typical for krypton ions and lighter argon ions, respectively [2, 3]. The main reason for surface layers softening of Ni-Ti two-phase alloy is the radiation-induced phase transformation  $B19 \rightarrow B2$  [3, 5].

The represented results are obtained for Ni-Ti alloy of various phase composition, irradiated with heavy ions of MeV energy at the temperature of  $\leq 100^\circ\text{C}$ . The exposure at high temperatures, as shown in [6, 7], contributes to stabilization or improving certain properties of the nickel-titanium based alloys retaining the shape memory effect.

The aim of this work is to study the effect of high temperature MeV-energy krypton ions exposure on the change in nanostructure and nanohardness of the surface layers of Ni-Ti alloy of various phase composition.



## 2. Experimental methods and material

The Ni-Ti alloy was studied in two structural-phase states: two-phase and single-phase. The experimental two-phase Ni-Ti alloy of the following composition: 53.46 wt.% Ni - 46.54 wt.% Ti, consisting primarily of NiTi with the B2 structure (austenite), NiTi with B19' structure (martensite), a small content of Ti, excessive Ni as a solid solution, and technological particles close in their composition to  $Ti_2Ni(C)$  [2, 3]. The experimental samples of two-phase alloy Ni-Ti were cut from a massive forget plate across the rolling direction using spark cutting. The sample surfaces were mechanically ground and then polishing on a woolen cloth using GOI polishing paste. The surface quality was estimated by optical metallographic analysis. The samples size was  $15 \times 3.9 \times 0.35 \text{ mm}^3$ . The experimental samples of single-phase Ni-Ti alloy with the B2 structure (austenite) were prepared by annealing the two-phase samples in the vacuum ( $\sim 10^{-4} \text{ Pa}$ ) furnace chamber for 1 hour at  $230 \pm 30 \text{ }^\circ\text{C}$  [2].

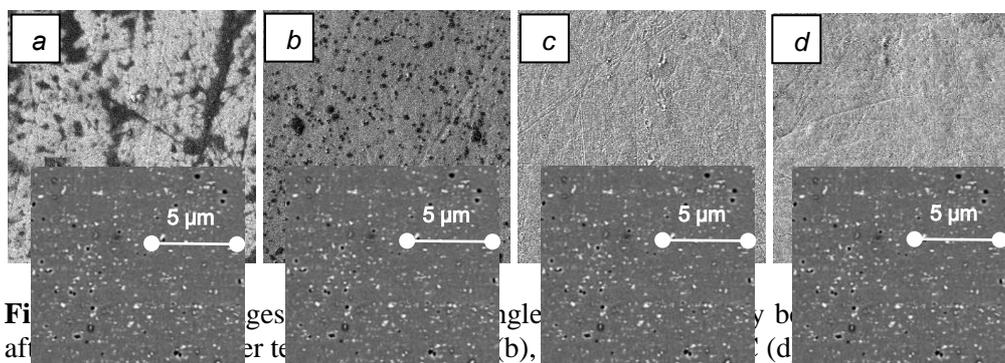
Irradiation of  $^{84}\text{Kr}^{15+}$  ions at 147 MeV (1.75 MeV/nucl.) energy up to the fluence  $1 \times 10^{19} \text{ ion/m}^2$  was performed with DC-60 accelerator (Astana, Kazakhstan) at 250 and  $300^\circ\text{C}$  temperatures. Accuracy of irradiation temperature maintenance was  $\pm 5^0$ . The radiation treatment area was  $\sim 1 \times 10^{-4} \text{ m}^2$ .

The study of surface layers microstructure and elemental analysis was performed by scanning electron microscopy (SEM) using the microscope JSM-7500F (JEOL, Japan). The analyzed depth was about  $1 \mu\text{m}$ . The degree of surface layers hardening was evaluated according to the results of nanohardness measurements by sclerometry [2] using the nanohardness gage "NanoScan-Compact" (Russia) at the applied load of  $1 \pm 200 \text{ mN}$ . The accuracy was 1% for nanohardness measurement. The surface roughness was evaluated according to the scanned images.

## 3. Experimental results and discussion

SEM-images at low magnifications of surface layers structure of the single-phase Ni-Ti alloy after irradiation with  $^{84}\text{Kr}^{15+}$  ions at 250 and  $300^\circ\text{C}$  temperatures are shown in figure 1c,d. For comparison purpose also shows the microstructure of the single-phase Ni-Ti alloy before (figure 1a) and after irradiation with  $^{84}\text{Kr}^{15+}$  ions at  $T_{\text{irrad}} \leq 100^\circ\text{C}$  (figure 1b). Analysis of the obtained experimental data showed that interaction of  $^{84}\text{Kr}^{15+}$  ions with the surface of the single-phase Ni-Ti alloy at high temperatures results in the sputtering processes of friable film consisting of  $Ni_4Ti_3$  compound and ion surface polishing, according to X-ray diffraction studies.

It was found that the sputtering processes of the strain-hardened  $Ni_3Ti_3O$  [3] layer and the ion surface polishing also occur for the two-phase Ni-Ti alloy, however at all selected irradiation temperatures. Regardless of the structural-phase state the microstructure of Ni-Ti alloy surface is characterized by high quality after high temperatures exposure as the result of the  $^{84}\text{Kr}^{15+}$  ions polishing process (figure 1c,d).

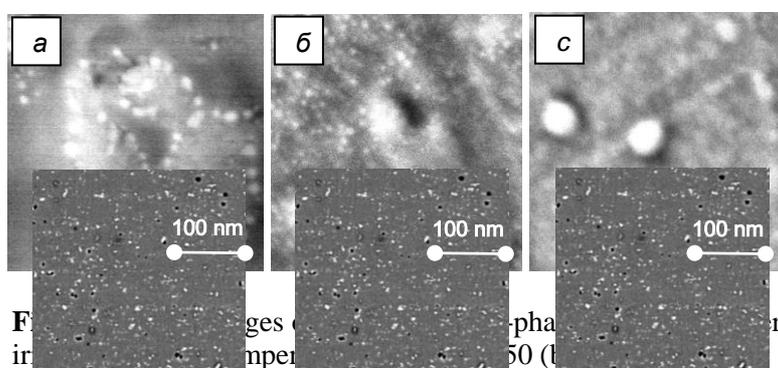


SEM-images at high magnifications of surface layers structure of the two-phase Ni-Ti alloy after irradiation with  $^{84}\text{Kr}^{15+}$  ions at  $T_{\text{irrad}} \leq 100^\circ\text{C}$  [3,4], 250 and  $300^\circ\text{C}$  are shown in figure 2. We can see that as  $T_{\text{irrad}}$  increases to  $250^\circ\text{C}$  formation of rare light bubbles up to 80 nm on the background of small bubbles (about 10 nm) occurs instead of tracks formation (figure 2b). At further increase of  $T_{\text{irrad}}$  to  $300^\circ\text{C}$

the size of large bubbles is reduced to 50-60 nm, while the size of small bubbles grows to 25-30 and 15-20 nm (figure 2c). The number of larger bubbles decreases almost twice and the number of smaller bubbles remains small.

Similar patterns of exposure temperature effect on the surface layers structure were also revealed for the single-phase Ni-Ti alloy. However, compared to the two-phase Ni-Ti alloy, the size of large bubbles after irradiation at  $T_{\text{irrad}} = 250^{\circ}\text{C}$  is less (to 70 nm), and the number of small bubbles (about 10 nm) grows. And on the contrary, the size of large bubbles grows to 100 nm, and the size of small bubbles grows to 50 and 20-30 nm during irradiation at  $T_{\text{irrad}} = 300^{\circ}\text{C}$ .

We shall note that the characteristic heterogeneity of elemental composition of the non-irradiated Ni-Ti alloy of various structural-phase states improves after irradiation with  $^{84}\text{Kr}^{15+}$  ions at high temperatures. However, the almost uniform elemental composition was found only for the single-phase Ni-Ti alloy after irradiation at  $T_{\text{irrad}} = 300^{\circ}\text{C}$ .



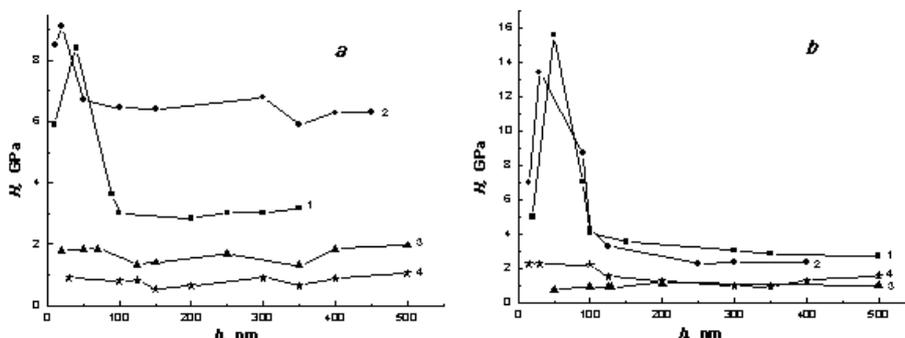
The results of nanohardness measurements depending on surface layer thickness are shown in figure 3. According to these data, firstly, the sharp softening of Ni-Ti alloy occurs during exposure at high temperatures regardless of its structure-phase state. Near the surface the single-phase Ni-Ti alloy softens at 44 and 74% at 250 and  $300^{\circ}\text{C}$  temperatures, respectively (figure 3a, curves 3 and 4) compared with non-irradiated alloy (figure 3a, curve 1). The degree of softening for the two-phase Ni-Ti alloy is much higher: 94 and 85% respectively after irradiation at 250 and  $300^{\circ}\text{C}$  temperatures (figure 3b, curve 3 and 4). The hardening effect of the single-phase Ni-Ti alloy after irradiation at  $T_{\text{irrad}} \leq 100^{\circ}\text{C}$  (figure 3a, curve 2) is noted in [2].

Secondly, the character of H (h) – curves modified at high temperatures of Ni-Ti alloys differs from similar curves for non-irradiated Ni-Ti alloys and after irradiation at  $T \leq 100^{\circ}\text{C}$  by the following: there is no maximum near the surface (figure 3a,b). It points to complete sputtering during exposure process at high temperatures of the surface technological layers:  $\text{Ni}_4\text{Ti}_3$  film and deformation-hardened layer of  $\text{Ni}_3\text{Ti}_3\text{O}$  40 and 50 nm thick, respectively. Maxima shift on H (h) – curves to the modified surface is 20 and 30 nm, respectively, for the two-phase (figure 3a, curve 2) and the single-phase Ni-Ti alloy (figure 3b, curve 2) during irradiation at  $T_{\text{irrad}} \leq 100^{\circ}\text{C}$ , which indicates their partial sputtering

Thirdly, the nanohardness value near (up  $\geq 130$  nm) Ni-Ti alloy surface is practically independent from its structural-phase state after exposure at high temperatures (figure 3ab, curves 3 and 4). This fact is consistent with the formation of bubbles nanostructured defects at high temperatures, similar in size and concentration (figure 2), and sputtering of technological layers. It can be concluded that the surface layers of single-phase and two-phase Ni-Ti alloys, modified at high temperatures, are characterized by austenitic structure-phase state.

Let us consider the dependence of surface layers nanohardness value from the quality of exposed surface, i.e. its roughness. The results of the arithmetic mean values of roughness height  $R_a$  obtained by measuring of the roughness curves for the studied Ni-Ti alloys are shown in table 1. We shall mainly note a significant decrease in roughness for Ni-Ti alloys after irradiation at  $T_{\text{irrad}} \leq 100^{\circ}\text{C}$  compared with the non-irradiated state, when the track nanostructured defects (figure 2 a) are observed on the surface [3, 4].

The roughness value for the single-phase Ni-Ti alloy is slightly lower than for the two-phase alloy, which is mainly due to the large size of track nanostructured defects at almost the same amount of them [4].



**Figure 3.** Dependence of nanohardness single-phase (a) and two-phase Ni-Ti alloy (b) before (curve 1) and after irradiation under temperature  $\leq 100$  (curve 2), 250 (curve 3) and 300 $^{\circ}$ C (curve 4) on thickness of surface layer.

For irradiation at high temperatures the roughness value, on the contrary, increases compared to non-irradiated Ni-Ti alloys, except for single-phase alloy irradiated at  $T_{\text{irrad}} = 300^{\circ}\text{C}$  (table 1). The main reason of roughness increase for the modified surface of both alloys is the formation of nanostructured bubble defects (figure 2b) with the size 1.6 - 2 times lower than for track nanostructured defects (figure 2a). According to analysis of the above-mentioned SEM - data, the roughness reduction is caused by contribution of small bubbles ( $T_{\text{irrad}} = 250^{\circ}\text{C}$ ) or its increasing by reducing the number of large and small bubbles ( $T_{\text{irrad}} = 300^{\circ}\text{C}$ ).

Thus, it was found that the roughness value of Ni-Ti alloy surface irradiated at various temperatures depends on the type of nanostructured defects, their size and number. The larger nanostructured defects, the lower the surface roughness. Decrease of nanostructured defects number leads to its increase.

**Table 1.** Roughness of Ni-Ti alloy surface, irradiated at various temperatures

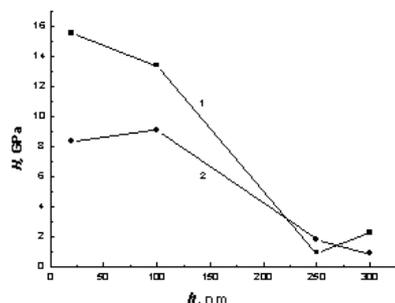
Ni-Ti alloy	Roughness (nm)			
	Non-irradiated	$\leq 100^{\circ}\text{C}$	250 $^{\circ}\text{C}$	300 $^{\circ}\text{C}$
Single-phase	9.04	3.48	13.34	7.19
Two-phase	13.85	3.89	15.03	17.91

Changes of maximum nanohardness value for two-phase (curve 1) and single-phase (curve 2) Ni-Ti alloys, depending on the temperature of  ${}_{84}\text{Kr}^{15+}$  ions irradiation, are presented in figure 4. Firstly we shall note that the magnitude of the surface layer nanohardness for the non-irradiated two-phase Ni-Ti alloy is determined by hardness of  $\text{Ni}_3\text{Ti}_3\text{O}$  compound, NiTi martensitic phase with the B19 structure and NiTi austenitic phase with the B2 structure, while the contribution in the non-irradiated single-phase Ni-Ti alloy nanohardness is stipulated by hardness of  $\text{Ni}_4\text{Ti}_3$  compound and NiTi with the B2 structure.

As a result of irradiation at  $T_{\text{irrad}} \leq 100^{\circ}\text{C}$  the value of surface layer nanohardness for the two-phase Ni-Ti alloy is reduced due to competition of the contributions from the processes of track nanostructured defects accumulation (figure 2b), partial sputtering of the process layer (figure 3b), complete transfer of martensite to austenite  $\text{B19}' \rightarrow \text{B2}$  [3, 5] and contribution of NiTi with the B2 structure [3]. The predominance of the contribution from the process of track nanostructured defects accumulation [4] over the contribution from the partially sputtering of the process layer (figure 2a) is the cause of hardening of the single-phase Ni-Ti alloy surface layer after irradiation at  $T_{\text{irrad}} \leq 100^{\circ}\text{C}$ .

A significant (44 - 94%) softening of the surface layers of single-phase and two-phase Ni-Ti alloys after irradiation at high temperatures, as found in this study, is connected to the complete sputtering of

the process layers and formation of bubble-type nanostructured defects, size and number of which is significantly less than for the track nanostructured defects.



**Figure 4.** Dependence of  $H_{\max}$  two-phase (curve 1) and single-phase Ni-Ti alloy (curve 2) on  $T_{\text{irrd}}$ .

#### 4. Conclusion

Thus, as a result of the study it is shown that a significant (44 - 94%) softening near the surface of two-phase and single-phase Ni-Ti alloys after irradiation with  $^{84}\text{Kr}^{15+}$  ions at 250 and 300°C to a fluence of  $1 \cdot 10^{19} \text{ m}^{-2}$  is associated with a full sputtering of the technological layers and formation of nanostructured bubble defects. It is found that the value of roughness for the Ni-Ti alloy surface exposed at 100-300°C temperatures depends on the type of nanostructured defects, their size and number. Thus, the larger nanostructured defects, the lower the surface roughness. Reduction of nanostructured defects number leads to roughness increase.

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