Structure and Mechanical Properties of Multi-Functional Layer Deposited on Surface of Ni–Ti Shape Memory Alloy

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A thin layer, about 25 nm thick, was produced in glow discharge deposition process on the surface of the NiTi shape memory alloy. Structural and chemical studies revealed that the layer consisted of two sublayers. About 7 nm thick one, adhering closely to the NiTi substrate and formed from the nanocrystalline titanium nitride was followed by 17 nm of the amorphous titanium oxide layer. The technological parameters of the glow discharge process caused that the presence of the R-phase in the matrix was identified.

Keywords: NiTi, shape memory alloy, glow discharge deposition, titanium nitride, titanium oxide, multi-layer cover

1. Introduction

NiTi alloys are known from the occurrence of shape memory phenomena.1) Hence, they have found wide applications as materials for implants and medical tools.2–5) In order to improve their functional properties, their surface is covered by various layers that simultaneously fulfill several functions. One of the materials used to modify the NiTi surface are titanium oxide and/or titanium nitride.4,5) Depending on the technological parameters—including temperature—a layer with various types of structures (from crystalline to nanocrystalline and amorphous) can be obtained. However, the temperature of the processes strongly affects the NiTi substrate. Also, it often leads to the degradation of the parent phase into equilibrium phases, which do not exhibit shape memory properties. In the present work, a two-step low-temperature glow discharge treatment was used, which allowed for the formation of an amorphous-nanocrystalline layer simultaneously with maintaining the presence of phases undergoing the martensitic transformation.

2. Experimental Procedure

A commercial NiTi alloy with chemical composition of 50.6 at% nickel and 49.6 at% titanium was used as a substrate for layer deposition. Rectangular samples were cut and subjected to quenching from 1173 K. This treatment ensures that the alloy reveals presence of the B2 parent phase at the room temperature. Next, the surface was cleaned, ground and polished in SiO2 suspensions with the final gradation of 0.1 μm. A glow discharge technique was used for layer deposition. Process was carried out at 573 K in two steps with total time of 1500 s. For the first 900 s, the surface was nitrided and then oxidized. It was expected, that a nitride layer would form on the alloy surface followed by an oxide one.

The structure of the deposited layer and the alloy was examined by X-ray diffraction using the technique of constant incidence angle of the primary beam (GIXD) and microscopic observations. X-ray examinations were carried out on a X’Pert PRO diffractometer equipped with an Euler cradle and an X-ray tube with a copper anode. The X-ray diffraction patterns were measured at the room temperature. For phase identification, reference standards from the International Center for Diffraction Data (ICDD) PDF-4 database were used.

Microscopic observations were done in the transmission electron microscope (TEM): JEOL JEM 3010 (accelerating voltage of 300 kV) and Tecnai G2 FEG super TWIN (accelerating voltage of 200 kV). The samples were prepared from: covered surface and cross-section of the layer. From the covered surface, sample was cut in-plane and thinned from the substrate side. The coated side of the sample remained unchanged. Thin foils were prepared using electrochemical method, at room temperature, in a solution of sulfuric acid in methanol in 1:5 ratio.

The cross-section of the layer was observed in a sample cut perpendicular to the covered surface. The sample was prepared using the focused ion beam technique (FIB) using QUANTA 200 3D Dual Beam equipped with Omniprobe in situ micromanipulator. For protective purposes, the sample surface was covered with a thin layer of platinum.

Mechanical properties of the deposited layer were studied using Triboindenter Ti 950 (Hysitron) equipped with Berkovitch pyramid. On the deposited surface, 10 various and random places were selected. Around each of them 25 (5 × 5 points grid) indentations were made with the maximum force rising from 0.1 mN to 4 mN.

3. Results and Discussions

Impact of the applied glow discharge process on the surface of the NiTi alloy was studied using GIXD technique. X-ray diffraction patterns were measured at incidence angle
of 0.2; 0.3; 0.5 and 1 degree. It has been known, that lowering of the incidence angle causes decrease of a penetration depth. As a result of that, X-ray diffraction pattern contains information from the area close to the surface. Hence, it was expected, that the diffraction pattern measured at the incidence angle of 0.2° of primary beam.

**Table 1 Structural parameters calculated from Rietveld refinement compared to ICDD data for identified phases.**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Calculation</th>
<th>ICDD 04-015-2441</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Titanium nitride</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>Fm 3m</td>
<td></td>
</tr>
<tr>
<td>Lattice parameter</td>
<td>a₀/Å</td>
<td>a₀/Å</td>
</tr>
<tr>
<td>111</td>
<td>0.2413</td>
<td>0.2434</td>
</tr>
<tr>
<td>200</td>
<td>0.2089</td>
<td>0.2108</td>
</tr>
<tr>
<td>220</td>
<td>0.1478</td>
<td>0.1491</td>
</tr>
<tr>
<td>311</td>
<td>0.1260</td>
<td>0.1271</td>
</tr>
<tr>
<td>222</td>
<td>0.1207</td>
<td>0.1217</td>
</tr>
<tr>
<td>400</td>
<td>0.1045</td>
<td>0.1054</td>
</tr>
<tr>
<td><strong>NiTi matrix: R-phase</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>P3</td>
<td></td>
</tr>
<tr>
<td>Lattice parameter</td>
<td>a₀/Å</td>
<td>c₀/Å</td>
</tr>
<tr>
<td>0.7358</td>
<td>0.5284</td>
<td>0.7354</td>
</tr>
</tbody>
</table>

Due to the fact that titanium, in comparison to nickel, posses greater affinity to form compounds with nitrogen or oxygen. In the presence of a nitrogen atmosphere, used at a first in glow discharge, titanium from NiTi matrix migrated to the surface and formed titanium nitride. This was confirmed by the presence of the TiN phase. The calculation showed that lattice parameter of titanium nitride is about 0.0036 nm lower than the one in the standard (Table 1). The ICDD data (about 50 files in the database) show, that the lattice parameters may vary from 0.4295 nm (card no 04-017-6803) to 0.4216 nm (card no 04-015-2441) dependently on the stoichiometry of the compound and the content of the impurities resulting from technological processes. Decrease of the lattice parameter indicates that the chemical composition of the titanium nitride, formed on the surface, is slightly deviated from the stoichiometric one. This fact may have its source in the next step of the glow discharge process—the introduction of oxygen atmosphere. However, X-ray examinations did not show the presence of a crystalline oxide phase on the surface of the alloy. However, in the angular 2θ range between 22° and 30°, broad maximum can be distinguishable. The analysis showed that its 2θ position was 26.6° and half width of 6°. These data indicate that it was diffusion effect and the maximum was characteristic for presence of an amorphous phase.

More detailed information on the structure of the created layer was brought by the results of the microscopic examinations. Figure 2(a) shows a TEM image of the cross-section of the layer. Along the line marked as a STEM-line, the chemical composition was measured at distance of 400 nm. The distribution of elements is shown in Fig. 2(b). In order to keep the transparency of the figure, only the distance between 100 nm and 350 nm (marked with bold line) was shown. Based on the analysis of the chemical composition, it was found that the layer contained titanium, oxygen and nitrogen. The nickel content in the layer area decreased practically to zero. Introduction of the oxygen in the second part of the glow discharge process caused a further migration of titanium towards the surface of the layer; hence its presence along the whole thickness of the layer was identified. It is noteworthy, that such application of the deposition conditions led to formation of about 25 nm thick layer free of nickel. The consequence of titanium diffusion to the surface was an increase in the nickel content in the matrix, at a depth of about 60 nm below the layer. Consequently, the amount of titanium in the alloy matrix decreased. The measured chemical composition in this area showed the presence of: 37.9 at% of titanium and 62.1 at% of nickel.

Structure of the layer and its sublayers is shown in Fig. 3(a). The diffraction pattern recorded from the area marked with the circle “Z” showed the presence of nanocrystalline material. First of all, diffraction rings, originating from the protective platinum cover, were visible. In addition, several diffraction spots were distributed on a described in the literature. Presence of the R-phase indicates that the surface modification does not affect the structure of the NiTi matrix. However, as it will be shown later from the microscopy observations, the surface area of the matrix reveals the structural changes resulting from the layer deposition process.

Fig. 1 X-ray diffraction pattern measured at 0.2° of incidence angle of primary beam.
ring with a radius corresponding to the interplanar distance of 0.1449 nm, characteristic for family of crystallographic plane \{220\} of titanium nitride. Dark field image (Fig. 3(b)) made in one of 220 spots, shows that the bright area forms the strip adhering to the NiTi substrate side. Taking into account the results from the chemical composition analysis and the identification of diffraction images, it can be concluded that this sublayer is composed of titanium nitride nanocrystalline grains, with a characteristic columnar structure. Moreover, additional ring located between the primary beam and 111 platinum ring was observed. This may indicate that the remaining sublayer area (between titanium nitride and platinum) is amorphous. As shown from the analysis of the chemical composition, this region contains oxygen and titanium—in 2:1 ratio. This fact suggests that the sublayer is composed of amorphous titanium oxide and will be described later using results obtained for an in-plane cut sample. It can be found from the high resolution image (Fig. 3) that the thickness of the TiN sublayer is about 7 nm, while the thickness of the titanium oxide sublayer is about 17 nm. Received results are consistent with the linear distribution of the elements presented in Fig. 2(b).

As mentioned earlier, the substrate area located directly under the layer shows increased nickel content in relation to titanium, which has relocated to the layer. The electron diffraction pattern recorded from the area marked as “A” (Fig. 4(a)), indicates the presence of two diffuse diffraction rings, characteristic for nanocrystalline material and/or strongly stressed one. The determined interplanar distances were characteristic for the \{110\} and \{211\} crystallographic planes of the B2 parent phase (ICDD card no 01-076-3614). However, its chemical composition, with the predominance
of a higher content of nickel, was strongly deviated from the stoichiometric one. Below this area, the NiTi matrix is composed of the R-phase. Its presence was confirmed by the phase identification of the electron diffraction pattern obtained from area marked as “B” (Fig. 4(a)) and the results received from X-ray examinations.

In order to confirm the structure/amorphousness of the sublayers creating the deposit, microscopic observations were carried out on an in-plain cut-out sample and polished with a classical electrochemical method (Fig. 4(b)). Identification of the electron diffraction pattern, recorded from the area characteristic for the largest thickness (denoted as “C”), confirmed the occurrence of R-phase in the NiTi substrate. In diffraction pattern, obtained from the area characterized by lower contrast (characteristic for a smaller thickness), the characteristic ring of diffraction from crystallographic planes {002} of titanium nitride was visible. Its character confirms nanocrystalline structure of TiN. In addition, a diffuse ring (near the trace of the primary beam) characteristic for the scattering of electrons on the amorphous material was also clearly distinguished. The presence of amorphous phase was definitely confirmed by the diffraction obtained from the smallest thickness area—marked as “E”. This is the area, in which the additional analysis of the chemical composition indicated the presence of 66 at% and 34 at% for oxygen and titanium, respectively. This fact confirms the amorphousness of titanium oxide sublayer located in the upper area of the cover.

The presence of the coating as well as its structure and sequence of the sublayers affected the mechanical properties of the NiTi alloy with modified surface. The hardness and reduced Young’s modulus determined versus the penetration depth of the indenter showed significant differences (Fig. 5). Both, hardness and Young’s modulus revealed elevated

![Fig. 4 TEM image of the cross-section specimen with SAD patterns measured at regions A and B (a), in-plain sample (prepared by electrochemical etching) with SAD patterns measured at regions C, D and E (b).](image)

![Fig. 5 Hardness (a) and reduced Young’s modulus (b) versus penetration depth.](image)
values in the subsurface areas in relation to the depth at which only the R-phase was identified.

At the depth, which corresponds to the thickness of the oxide/nitride layer, the hardness decreases from about 14 to about 5 GPa. In the subsurface area of the NiTi matrix, it takes values from about 5 to about 4 GPa and at depth from 75 nm to 250 nm it lowers down to about 3 GPa. The obtained results remain in good agreement with the data presented in literature. The literature data revealed that the hardness of crystalline or nanocrystalline titanium oxide, which depends on the chemical composition, crystallite size, state of internal stresses, defect structure, crystallographic orientation of grains, layer thickness and substrate type, may range from 2 to 8 GPa.9) However, there is no literature report regarding hardness of the amorphous form of titanium oxide. In contrast to the titanium oxide, the hardness of the nitride oxide, also conditioned by the structural state, can take value from 3 up to 30 GPa.10) For a NiTi alloy, depending on the phase state, these values differ slightly and may range from about 3 GPa (for the parent phase) to about 5 GPa for martensite.14) A similar course, depending on the thickness changes and structural state, showed the value of the reduced Young’s modulus. In the layer area, it ranged from 55 to about 95 GPa. They are characteristic for titanium nitride and oxide.9,11) In the near-surface area of the NiTi matrix, where the parent phase has been identified, the Young’s modulus value varied from about 30 GPa to about 50 GPa. These values are about 2 times higher than measured for the area containing the R-phase. The literature data show that the Young’s modulus for the B2 parent phase range from about 60 GPa up to 180 GPa, depending on ratio of nanoindentation.14) Also, these values vary depending on the phase composition. In general, Young’s modulus is two times higher for the B2 parent phase (41–75 GPa) than the B19’ martensite (28–41 GPa). The R-phase shows the similarity of the module’s value to martensite.14) In the present work, it was shown that in the subsurface area, the Young’s modulus values range from 30 to 50 GPa. This fact confirms the results of structural studies indicating the formation of the B2 phase structure in the matrix, just below the layer. In the R-phase area, the module is close to the martensite and range from 20 to 30 GPa.

4. Conclusions

The glow discharge conditions allow for the formation of a protective layer on the surface of the NiTi alloy consisting of an amorphous titanium oxide and a nanocrystalline titanium nitride sublayer. The layer, approximately 25 nm thick, does not contain nickel and adheres closely to the substrate. The mechanical properties (hardness and reduced Young’s modulus) of the layers are several times higher than those of the NiTi substrate.

REFERENCES