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Experimental and numerical analysis of tensile properties of Ti-13Nb-13Zr alloy and determination of influence of anodization process

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Abstract

Due to their excellent mechanical properties and corrosion resistance, titanium-based materials are widely represented in aeronautics, chemical industry and medicine, where they are considered the best replacement for damaged hard tissues. In order to obtain optimal properties for medical applications, commercially pure titanium (cpTi) is often alloyed. The β-type titanium alloys containing Nb, Zr, Ta, Mo, Sn have attracted considerable attention, due to their unique combinations of high strength, low modulus of elasticity, superior corrosion resistance and biocompatibility. Also, titanium-based materials can be processed by surface modifications, including the anodization, which belongs to the group of chemical nanostructured surface modifications. Analysis of microstructure of two-phase Ti-13Nb-13Zr (TNZ) alloy was done by Scanning Electron Microscopy (SEM). Characterisation of surface, obtained by anodization in the H_3PO_4 + NaF solution, during 90 minutes process, was performed by SEM. Micro Tensile Specimens (MTS) were cut from TNZ and anodized TNZ disks and were subjected to the tensile test using servo-hydraulic testing machine *Instron 1255*. Stereometric measurement of strain at the surface of the MTS during tension was done using the *Aramis system*. Results showed that anodization process led to a creation of heterogeneous layer of nanotubes. Anodized TNZ alloy had lower elastic modulus and tensile strength comparing to the initial alloy. In order to better understand tensile behaviour, numerical analysis of non-anodized alloy was done. The 3D numerical model of MTS, which simulated the tensile test, was made in *Abaqus* software package. Good correlation between experimental and numerical results was obtained.

Keywords: Electrochemical anodization; Finite element method; Tensile properties; Ti-13Nb-13Zr alloy

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1. Introduction

Due to their excellent mechanical properties and corrosion resistance, titanium-based materials are widely represented in aeronautics, chemical industry and medicine, where they are considered the best replacement for damaged hard tissues. One of the most important features that leads to serious limitations in the usage of titanium based materials in medicine is their higher modulus of elasticity when compared with the bones [1]. Lower modulus of elasticity, closer to the value of the bone, reduces the risk of structural damage and loosening of surrounding bone tissue, as well as rejection of the implant by human body. In order to obtain optimal properties for medical applications, commercially pure titanium (cpTi) is often alloyed. Today, scientific works are focused on the development of alloys whose elements are less toxic for human organism then Al and V. The β-type titanium alloys containing Nb, Zr, Ta, Mo, Sn have attracted considerable attention, due to their unique combinations of high strength and ductility, lower modulus of elasticity, superior corrosion resistance and biocompatibility. Also, it was found that β phase, which contains β-stabilizer such as Nb, Zr, Ta, Mo, Sn, has the lowest modulus of elasticity, namely around 35 GPa, compared to the other phases that could be formed in titanium alloys [1]. In addition to optimizing the chemical composition of the alloys, the porosity of the titanium based material allows reduction of the modulus of elasticity. At a porosity of about 30%, the value of the modulus of elasticity is almost equal to that of the surrounding bone tissue [2].

Nanostructured surface modifications of the titanium alloys create a surface morphology of few nanometres in size, increasing the roughness, changing the topography from micro to the level of nano size. These methods can be classified into four categories: Mechanical, Physical, Biochemical and Chemical [3]. The chemical methods for surface modification of titanium alloys are used to improve biocompatibility, corrosion resistance, wear, eliminate contamination of the surface, decrease of modulus of elasticity [4, 5]. Some of the most commonly used chemical methods are chemical treatments, electrochemical treatments, namely electrochemical anodization (anodic oxidation), sol-gel process and chemical vapor deposition. The electrochemical anodization process results in formation of nanostructured oxide layer composed of TiO_2-based nanotubes, with thickness in the range from 10 nm to 40 μm [6]. The most significant advantage of anodization is possibility to control the shape of the nanotubular oxide layer and its dimensions by electrochemical anodization parameters (solution, current, anodizing time and potential).

The aim of this study is to show how electrochemical anodization process influences the physical (modulus of elasticity) and mechanical (tensile strength and yield strength) properties of the two-phase Ti-13Nb-13NZ alloy and show correlation between experimental and numerical results for non-anodized alloy.

2. Materials and Methods

The conventional Ti-13Nb-13Zr alloy (TNZ) was produced by rolling as two-phase α+β alloy. The chemical composition of the TNZ alloy was obtained using X-ray fluorescence analysis and it was: 71.38% of titanium, 14.56% of niobium, 13.44% of zirconium and 0.34% of mercury. One group of the TNZ alloy samples were subjected to electrochemical anodization process in order to obtain nanostructured modified surfaces. For electrochemical anodization, disk-shaped sample with the radius of 28 mm and thickness of 2.28 mm was cut, polished and then cleaned in alcohol, acetone and distilled water. The process was carried out at room temperature, in H_3PO_4 + NaF solution, at a potential of 25 V and during 90 minutes. In order to analyze characteristics of the microstructure and nanostructured modified surfaces of TNZ alloy, scanning electron microscope (SEM) MIRA3 TESCAN was used, while chemical composition of nanostructured modified surface was determined using energy dispersive spectrometer (EDS).

In order to determine the tensile characteristics, Micro Tensile Specimens (MTS) with rectangular cross-section were cut from non-anodized and anodized TNZ disk and were subjected to the tensile test using servo-hydraulic testing machine *Instron 1255*. The stereometric measurement of strain at the surface of the MTS during tension was done using the *Aramis system*. The MTS had gage section of 0.86 mm×2 mm×8.8 mm. The MTS and its dimension are presented in Fig. 1a. More details about the tensile testing and the Aramis system can be seen in [7]. Numerical model of non-anodized MTS, which simulated the tensile test, was formed in the software package Abaqus. In 3D model of MTS, a quarter-geometry representation was sufficient, as shown in Fig. 1b.

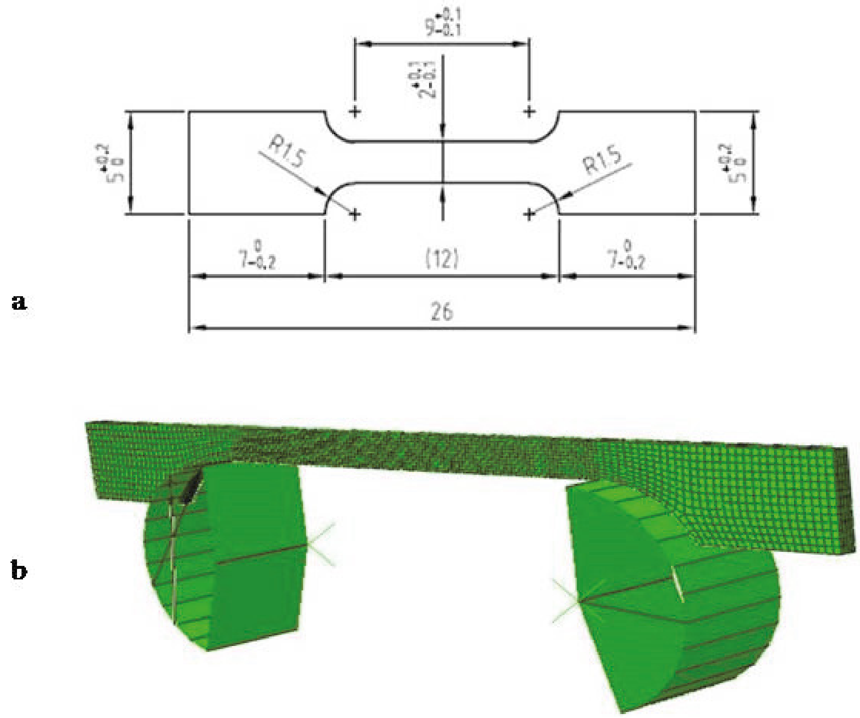

Fig. 1. (a) Micro tensile specimen and its dimensions; (b) 3D model of the micro tensile specimen and finite element mesh.

The Finite Element Method (FEM) calculations were made in Abaqus software package, by using the quadratic interpolation with reduced integration, FE type C3D20R. The behaviour of the material was elasto-plastic, defined by the curve true stress - true strain. This curve is formed based on the part of the nominal stress - nominal strain experimental curve up to the ultimate tensile strength: $\varepsilon_{true} = \ln(\varepsilon_{nom} + 1)$, $\sigma_{true} = \sigma_{nom}(1 + \varepsilon_{nom})$, with added point of the final fracture: $\sigma_f = E_f/A_f$, $\varepsilon_{f=} \ln\left(A_0/A_f + 1\right)$. For the considered specimen geometry, it turned out that it is very important to apply the Bridgeman correction, i.e. that the stress triaxiality has an important role after the neck has been formed. The equation for cylindrical specimen is applied; according to [8], it is applicable to the specimen with rectangular cross-section.

3. Results and Discussion

3.1. Characterization of materials

Fig. 2 (a) shows typical microstructure of two-phase Ti-13Nb-13Zr alloy [8]. As can be seen from the SEM images the alloy consists of of two phases - α' acicular martensitic phase and β phase, which were shown using the X-ray diffraction (XRD) in [7]. After electrochemical anodization process nanostructured modified surface which consists of the nanotubes is obtained, Fig 2 (b). The nanostructured surface formed after electrochemical anodization consists of nanotubes and has inhomogeneous morphology. As can be seen, morphology has longer nanotubes with smaller radius and shorter nanotubes with bigger radius. The differences in the values of the radii are large, ranging approximately from 46 nm to 85 nm. This large difference properly indicates the inhomogeneity of nanostructured modified surface. The chemical analysis of the nanostructured modified surface shows presence of O, Ti, Zr and Nb with values of 42.1%, 39.0%, 11.6%, 7.2%, respectively. These results are in accordance with many papers [9, 10] which deal with nanostructured surface modification of the Ti-13Nb-13Zr alloy. Also, previous work has shown that increase of anodizing time leads to reduction of the inhomogeneity of morphology [11].

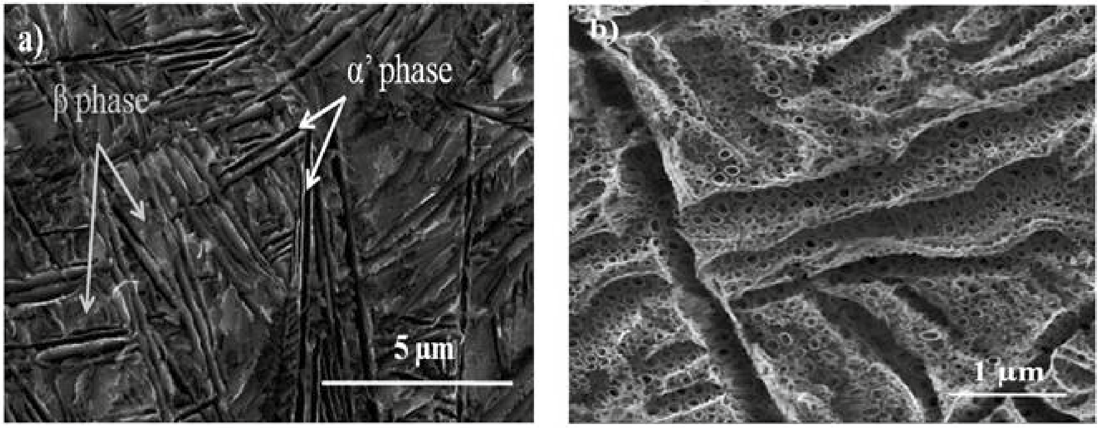

Fig. 2. (a) Microstructure of the Ti-13Nb-13Zr alloy [8]; (b) nanostructured modified surface after electrochemical anodization process.

3.2. Measurement of physical and mechanical properties

The values of physical (modulus of elasticity E) and mechanical properties (tensile strength R_m and yield strength $R_{p0.2}$) of the Ti-13Nb-13Zr alloy before and after electrochemical anodization are presented in Table 1. The curves nominal stress - nominal strain of the Ti-13Nb-13Zr alloy before and after electrochemical anodization, obtained after tensile testing, are presented in Fig. 3 [7].

Table 1. Physical and mechanical properties of the Ti-13Nb-13Zr alloy before and after electrochemical anodization. modif. from [7]

Physical and mechanical properties	E / GPa	$R_{p0.2}$ / MPa	R_m/ MPa
CG TNZ	79.11	618.77	757.97
Anodized CG TNZ	63.21	499.63	611.77

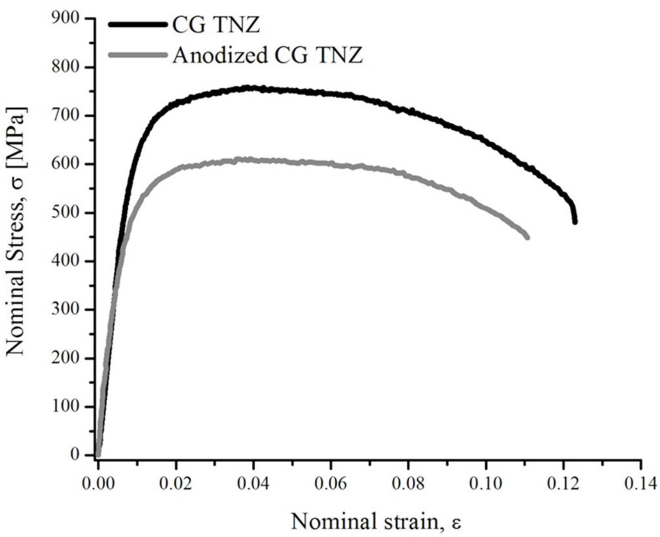

Fig. 3. Nominal stress - nominal strain curves of Ti-13Nb-13Zr alloy before and after electrochemical process. [7]

As can be seen in Fig. 3. and Table 1. the electrochemical anodization process conducts notable reduction of the values of R_m, $R_{p0.2}$. The value of R_m of anodized Ti-13Nb-13Zr alloy is reduced from 757.97 MPa to 611.77 MPa, while the value of $R_{p0.2}$ is reduced from 618.77 to 499.63 MPa. Also, the electrochemical anodization process leads to reduction in the value of E. Namely, the value of E of anodized Ti-13Nb-13Zr alloy is reduced from 79.11 GPa to 63.21 GPa. The decrease in the value of the modulus of elasticity is particularly significant because the approximate values of the bone allow for better mechanical biocompatibility of the implants. The effect of nanostructured surface modification on physical and mechanical properties has not been sufficiently studied, but there are a number of papers indicating that the values of these biomaterial properties can be reduced after electrochemical oxidation due to the formation of a porous structure on the surface [12, 13]. As stated in the section 3.1., the nanostructured surface formed after electrochemical anodization during 90 minutes at 25 V consists of nanotubes which have inhomogeneous morphology, between which furrows are formed. The formed furrows can effect as cracks, and have a high influence on the values of the physical and mechanical properties [7]. Further, the nanotubes and the thin oxide layer on which they are formed are rather brittle, unlike the base material (alloy) which exhibits ductile behaviour. The stereometric method is applied in the tensile testing. Fig. 4 presents behaviour of the MTS during the tensile testing which was showed using Aramis system (the MTS of non-anodized TNZ alloy is presented). Fig.4a shows strain at the force of 1.211 kN, while *dl* is 0.716 mm, the creation of neck, which indicates the existence of a ductile fracture, occurs at 0.825 kN when *dl* is 1.08 mm, Fig.4 b.

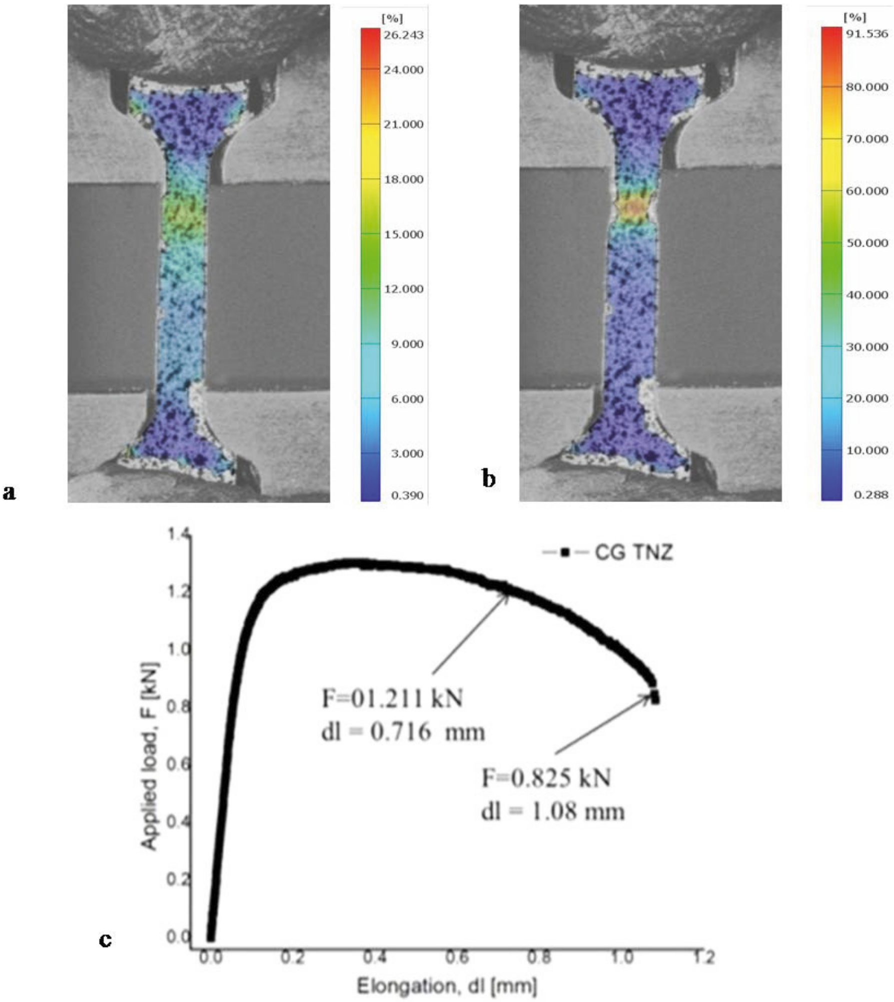

Fig. 4. The view of specimen during tensile testing by stereometric method at different loading levels.

3.3. Numerical examination of the Ti-13Nb-13Zr tensile behaviour

Fig. 5 presents plastic strain obtained on the MTS, instant before the failure when elongation is 1.08 mm; obviously, high plastic strain values are concentrated in the necking region.

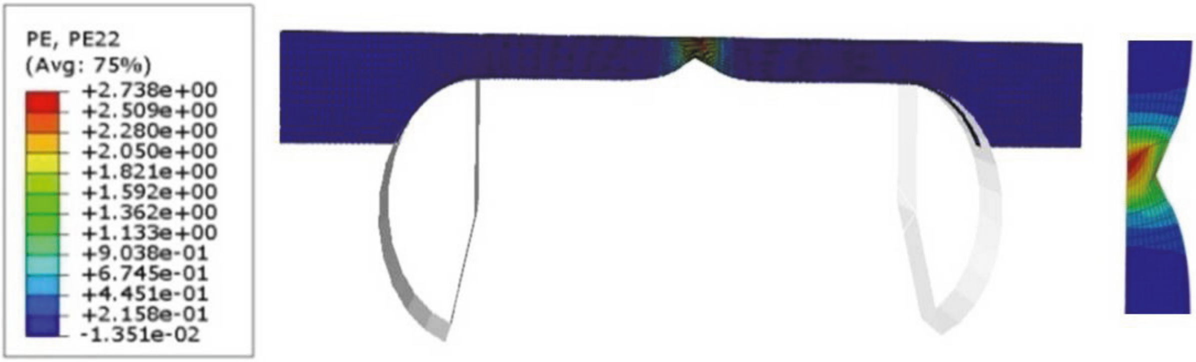

Fig. 5. The field of plastic strain of the MTS of TNZ alloy, instant before fracture.

The curve nominal stress - nominal strain of the Ti-13Nb-13Zr alloys obtained using FEM is shown in Fig. 6, along with the experimental curve. As mentioned previously, Bridgeman correction has a significant effect for this geometry, and higher forces/stresses are predicted (in the part of the curve between the maximum loading and final failure) if this correction is not taken into account.-Fig. 6. shows that the elastic part of the curve obtained using FEM is the same as for the curves obtained by experimental procedure. Also, can be concluded that the highest nominal stress is the same for the both curves, while nominal strain is the higher for the curve obtained using FEM. The tensile strength obtained by experimental procedure and using FEM is the same, around 757.97 MPa. The nominal strain for the curve obtained using FEM is 0.14 (elongation of 14 %) while the nominal strain obtained by experimental procedure is 0.12 (elongation of 12%). At high strain values, damage development is significant, which is not taken into account in the model.

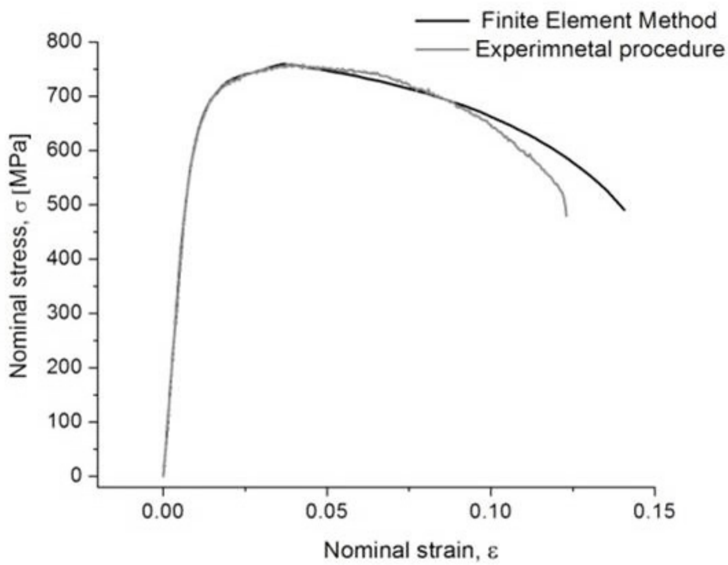

Fig. 6. Comparison of the nominal stress- nominal strain curves obtained by the experimental procedure and using FEM

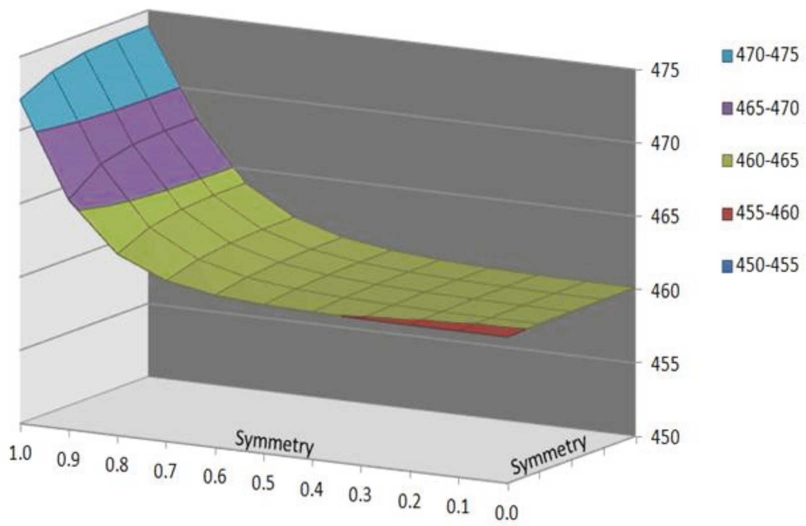

Fig. 7. Distribution of longitudinal stress S_{22} along the cross-section of MTS.

In the numerical model, the distribution of the longitudinal stress S_{22} along the cross-section before reaching the yield stress is also considered, Fig. 7; since the cross-section represents one quarter of the specimen, the symmetry planes are marked. It can be concluded that the difference is less than 3.5 %. These differences become even smaller at the maximum loading. Such distributions are similar to the ones for round tensile specimen (RT), so it can be concluded that the MTS specimen cross-section shape (rectangular) does not influence the obtained material properties significantly. The finite element analysis presented in this section is performed on the material in the original state, i.e. without anodization. However, a rather large difference between the anodized and non-anodized alloy is obtained experimentally (Fig. 3), much higher than typically reported in the literature. In our initial numerical analyses, addition of the nanotubular structure geometry on the surface resulted in a negligible decrease in predicted yield and tensile strength. Therefore, further examination will have to include the analysis of local damage initiation at the bases of the nanotubes (on nano and micro level), as well as its development through the material. It could be assumed that the micro-cracks initiate in the thin brittle oxide layer between the nanotubes and the base material at relatively low loading levels, and then continue to grow through the ductile base material. This mechanism leads to decrease of the load carrying capacity, but does not change the trend of the stress-strain curve (Fig. 3), i.e. the specimen fails by ductile fracture, because the brittle oxide layer on the surface is thin in comparison with the specimen dimensions. This is an interesting topic for further examination, having in mind that surface treatment by annodization (which causes changes only in the very thin surface layer) caused a significant decrease of the load carrying capacity of the tensile specimen.

4. Conclusions

The obtained results showed that electrochemical anodization process led to creation of an inhomogeneous nanotubular oxide layer consisting of nanotubes with different dimensions (diameter, wall thickness and length) on the surface. As one of the consequences, the tensile testing on micro tensile specimens (MTS) revealed that anodized TNZ alloy has lower physical and mechanical properties. These differences are larger than those reported in the literature; very few studies which deal with tensile properties of the materials with surface nanotubular layers could be found. The finite element method (FEM) calculations for simulation of the tensile test of the TNZ alloy not subjected to annodization were conducted in *Abaqus* software package. Based on the experimental tensile testing, true stress - true strain curve is formed. A reasonably good agreement between the experimental and numerical results was obtained when this curve is applied in numerical analysis of the tensile test. Variation of the axial stress along the specimen cross section is examined, in order to assess the influence of the specimen shape on the stress distribution.

Acknowledgment

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