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## Original Research Article

# Elastic modulus of nanocrystalline titanium evaluated by cyclic tensile method

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## ABSTRACT

The present study is devoted to examinations of the elastic modulus with the use of the uniaxial tensile test. The commercial purity titanium Grade 2 in the two states i.e. microcrystalline (mc-Ti) and nanocrystalline (nc-Ti) were examined. Bulk nc-Ti was fabricated by hydrostatic extrusion (HE) which is one of the severe plastic deformation methods (SPD). The elastic modulus of mc-Ti and nc-Ti were compared with the aim to analyze the influence of the nanostructure of titanium on its elastic modulus. The mc-Ti and nc-Ti samples were subjected to uniaxial tensile tests at various strain rates and various values of stress.

Generally, higher elastic modulus values were obtained in microcrystalline titanium. The elastic modulus of mc-Ti was evaluated at 107 GPa on average, whereas the elastic modulus of nc-Ti was 94 GPa on average. The nanocrystalline titanium had a lower elastic modulus than its microcrystalline counterpart by 13% on average, which can be attributed to the presence of significant volume of amorphous regions in the structure. Moreover, in this case a lower standard deviation of all the results was obtained. In most cases, with higher applied stress (load) the value of the modulus was lower, whereas at higher strain rates its value was higher.

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## 1. Introduction

In the last years nanomaterials have been the subject of many investigations and publications [1]. One of the features of these materials, which is best examined and described, is their mechanical behavior [2]. It is commonly known that compared with their microcrystalline counterparts, nanomaterials are characterized by higher values of the yield stress, tensile strength, and hardness, whereas their plasticity and fracture toughness are lower [3]. Another basic parameter which

describes the mechanical behavior of materials is their modulus of elasticity –  $E$ . In the case of nanomaterials there are however some problems with determining the elastic modulus. The possible relation between the value of this modulus and the structure of nanomaterials is difficult to describe. This is so since these materials are fabricated by various methods, various types of samples are prepared for their examinations, and various methods are employed for measuring their properties. That the results obtained thus far are not unequivocal can result from the fact that there are a variety of factors which affect the value of the elastic modulus in a given nanomaterial.

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In general, the value of the elastic modulus is defined by the three basic parameters: (1) forces of interactions between the atoms, which are associated with their equilibrium positions i.e. the equilibrium between the attractive and repulsing forces, (2) the bonding forces between the atoms, and (3) lattice constant of the elementary cell. Hence, in practice, the elastic modulus depends on the following factors:

- (a) Chemical composition of the material, i.e. the purity and alloying elements. It has been found that, in titanium, the presence of oxygen, nitrogen, carbon, and aluminum results in an increase of the elastic modulus  $E$ , whereas vanadium and molybdenum decrease its value. It has been demonstrated that an increase of the Sn content in the Ti8VSn alloy results in a decrease of the elastic modulus, which is attributed to the lattice expansion of the material. [4]. Moreover, the elastic modulus appeared to depend on the kind, volume fraction, distribution, and morphology of the individual constituent phases [5], just as in the case of developed new type alloys intended for medical applications [6].
- (b) Crystallographic orientation of a single grain, and, in anisotropic materials, the direction of action of the loading force. This is the case of pure titanium because of the difference in the constant of elementary cells of the lattice.
- (c) Structural defects present in the material, such as the share of the grain boundaries in the material volume related to the grain size [7], the porosity, micro-cracks [8] and dislocation density. For example, Fougere et al. [9] suggested that the effect of porosity in decreasing the Young's modulus is the dominant structural feature. There are also studies which propose reduction of the Young's modulus by introducing pores [10]. The effects associated with structural defects are especially important in nanomaterials which contain great numbers of defects of various types. It should be noted that the occurrence and number of defects and, thus, the value of the elastic modulus, depend very often on the method employed for producing a given nanomaterial.
- (d) Temperature of the material (i.e. the elastic modulus decreases with increasing temperature). The decrease of the elastic modulus during heating is due to an increase of the equilibrium interatomic distance. This is an effect of thermal expansion of material and weakening of the forces of interatomic bonds.

A method commonly known and long used for measuring the Young's modulus is the uniaxial tensile of the sample. The advantage of this method lies in that the tension is uniformly applied (along the measurement length) to the entire volume of the sample within its elasticity range. This method gives a macroscopic view on the properties of a relatively large volume of the material. In the present study, the volume of nanocrystalline titanium produced by hydrostatic extrusion was relatively large (i.e. bulk). The uniaxial tensile method, described above, permitted the present authors to determine the elastic modulus in the macroscopic scale, and at the same time to examine a relatively large volume of the nc-Ti.

The recent literature reports indicate that, at the present, the method most often used for measuring the Young's

modulus is nanoindentation [6,7,11–13] whose main feature is that it examines samples with a relatively small volume. The nanoindentation method is also often used in surface engineering. As an example it can be mentioned the examinations of the Young's modulus of pure titanium after a modification of its surface described in ref. [11]. Huang et al. [12] used this method for measuring the Young's modulus of the nanostructured surface layers produced by the surface mechanical attrition treatment (SMAT). The nanoindentation method has however a drawback in that the results can be false because of a possible adverse influence of the substrate on which the nanostructured layer is deposited, the anisotropy of the material, or local defects. Moreover, the result obtained by this method can also depend on the surface preparation procedure employed such as e.g. the mechanical treatment which generates stress and, in consequence, the strengthening of near-surface zone.

Other methods employed for measuring the elastic modulus include e.g. the free resonance vibration method [4], ultrasonic techniques [6], or electromagnetic acoustic resonance method, the latter being used for e.g. examining porous pure Ti and the Ti6Al4V alloy [10]. Cao et al. [14] determined the Young's modulus of nanocrystalline titanium produced by powder milling and consolidation by measuring the velocity of ultrasonic wave propagation.

It seems that the use of the uniaxial tensile method for measuring the elastic modulus of bulk nanocrystalline titanium has never been described in the literature. Therefore, the results obtained in the present study and their analysis will provide an innovatory contribution to the knowledge about nanometals.

Summing up there is the need to determine the Young's modulus of nanometals including the nanocrystalline titanium and the uniaxial method is proposed. The aim of this study was to examine the elastic properties of mc-Ti and nc-Ti and to determine the possible influence of the structure on the Young's modulus. The next goal was to explain what phenomenon causes possible differences. The study was also concerned with the effect of the strain rate and values of stress (i.e. load) applied during the tensile tests on the value of elastic modulus.

## 2. Materials and processing

The material investigated was commercial pure titanium Grade 2 (Table 1) in the two states: (1) as a microcrystalline titanium (mc-Ti), and (2) as a nanocrystalline titanium (nc-Ti). The nc-Ti was produced by plastic forming (i.e. hydrostatic extrusion – HE) of the mc-Ti (i.e. initial state). The mc-Ti material was delivered in the form of a rod with  $\varnothing 33$  mm. To produce nc-Ti, the mc-Ti rod was subjected to multi-pass HE process. The cold extrusion process was conducted at room temperature. The fabrication of nc-Ti was realized in 12 passes of extrusion during which the rod diameter was gradually reduced (i.e.  $\varnothing 33$  mm  $\rightarrow$   $\varnothing 25$  mm  $\rightarrow$   $\varnothing 20$  mm  $\rightarrow$   $\varnothing 16$  mm  $\rightarrow$   $\varnothing 14$  mm  $\rightarrow$   $\varnothing 12$  mm  $\rightarrow$   $\varnothing 10$  mm  $\rightarrow$   $\varnothing 9$  mm  $\rightarrow$   $\varnothing 8$  mm  $\rightarrow$   $\varnothing 7$  mm  $\rightarrow$   $\varnothing 6$  mm  $\rightarrow$   $\varnothing 5.5$  mm  $\rightarrow$   $\varnothing 5$  mm). In effect, nc-Ti was in the form of a rod with the  $\varnothing 5$  mm diameter (Fig. 1).

During each pass plastic deformation is induced in the material. The sum of deformation induced by all the extrusion

**Table 1 – Chemical composition of mc-Ti and nc-Ti examined in the present study.**

| Element            | N    | C    | H     | Fe   | O    | Other max | Ti      |
|--------------------|------|------|-------|------|------|-----------|---------|
| Amount of mass [%] | 0.02 | 0.01 | 0.004 | 0.05 | 0.22 | 0.3       | ≥99.396 |

passes is defined as the accumulated strain which is described by the formula:  $\epsilon = 2 \ln(D_s/D_f)$  (1) (where:  $D_s$  – starting diameter,  $D_f$  – final diameter after extrusion). The total accumulated strain induced in nc-Ti was 3.8. Another parameter is the reduction of the cross-section area defined as:  $R = P_s/P_f$  (2) (where:  $P_s$  is the surface area of the rod cross-section before extrusion, and  $P_f$  is the surface area of cross-section after the extrusion). The total reduction achieved in nc-Ti by the HE was 43.5.

The hydrostatic extrusion, which is classified within the severe plastic deformation (SPD) methods, was realized at the Institute of High Pressure Physics, Polish Academy of Sciences, within the framework of a project coordinated by the Faculty of Materials Science and Engineering, Warsaw University of Technology. The principle of HE method was described in detail in Ref. [15,16]. The properties of these two materials and hydrostatic extrusion process were described in more detail in our earlier publication [16,17].

Prior to the extrusion, the average equivalent diameter of the grains in microcrystalline titanium, measured on a transverse cross-section, was 20  $\mu\text{m}$  (Fig. 2a). On a longitudinal



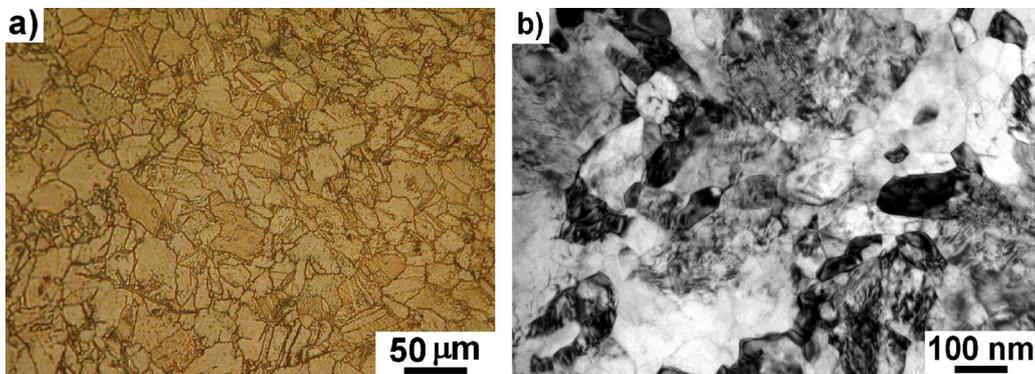
**Fig. 1 – View of bulk nc-Ti in the form of rods with a diameter of  $\varnothing 5$  mm.**

cross-section the grains were slightly elongated in the direction of the axis of the rod. The hydrostatic extrusion was realized in 12 stages after which the microstructure was refined to the nanometric scale. On the transverse cross-section, the average equivalent diameter of the nano-grains was  $E(\text{deg}) = 55 \text{ nm}$  (Fig. 2b). On the longitudinal cross-section, the grains were elongated in the direction of extrusion, i.e. in parallel to the axis of the rod. The basic properties of these two states are given in Table 2. The yield stress and ultimate tensile strength of the nc-Ti material were excellent and its strength was more than twice as high as that of the mc-Ti.

### 3. Examination procedure and test parameters

The investigated materials were subjected to uniaxial tensile tests at various strain rates and various stresses. The aim of this work was to analyze the potential influence of the grain size and tensile tests parameters on the value of elastic modulus. All the tests were conducted at room temperature. The examination procedure and the tests parameters are given in Table 3.

An example of the sample intended for the tensile test is shown in Fig. 3. The mc-Ti samples (prepared from the rod in the as-delivered state) and the nc-Ti samples (cut out from the nc-rod obtained after the hydrostatic extrusion) were of the standard type (with the length-to-diameter ratio equal to 5) and had the same dimensions. Their transverse cross-sections were circular, the axes were parallel to the axis of the initial



**Fig. 2 – Structure, observed on a transverse cross-section, of: (a) mc-Ti; (b) nc-Ti.**

**Table 2 – Basic properties of the mc-Ti and nc-Ti materials examined in the present study.**

| Properties state      | Average grain size – transverse section | Yield stress [MPa] | Ultimate tensile strength [MPa] | Elongation A [%] |
|-----------------------|---|--------------------|---------------------------------|------------------|
| mc-Ti (initial state) | 20 $\mu\text{m}$                        | 357                | 482                             | 21.1             |
| nc-Ti (after HE)      | 55 nm                                   | 1040               | 1141                            | 5.6              |

**Table 3 – Procedure and the parameters of the uniaxial tensile tests.**

| Strain rate<br>$\dot{\epsilon}$ [1/s] | Range of applied stress i.e. minimum–maximum [MPa] |        | Number of cycles |
|---------------------------------------|--|--------|------------------|
|                                       | mc-Ti  | nc-Ti  |                  |
| $3.3 \times 10^{-4}$ (slower strain)  | 10–150   | 10–500 | 5                |
|                                       | 10–250   | 10–800 | 5                |
| $3.3 \times 10^{-3}$ (faster strain)  | 10–150   | 10–500 | 5                |
|                                       | 10–250   | 10–800 | 5                |

**Fig. 3 – View of a sample prepared for the uniaxial tensile test and its basic dimensions.**

mc-Ti and nc-Ti rod, respectively (the axis of the nc-Ti rod coincided with the extrusion direction).

The uniaxial tensile tests were conducted at two constant strain rates which differed from one another by a factor of 10. One strain rate was  $\dot{\epsilon} = 3.3 \times 10^{-4}$  [1/s] (slower straining) which corresponded to the slower movement of the traverse ( $V = 0.005$  mm/s). The other strain rate was  $\dot{\epsilon} = 3.3 \times 10^{-3}$  [1/s] (faster straining), which corresponded to the faster movement of the machine traverse ( $V = 0.05$  mm/s).

The ranges of the stress applied to the samples during the tensile tests were selected individually for each material examined, in dependence on its yield stress and so as not to exceed its elasticity range. For each state, the aim was that the stress ranges should differ significantly from one another and both were lower than the yield stress in order that the effect of the micro-plasticity was as low as possible. The applied stress ranges have been taken at about 40% and 70% of the yield stress. Each sample was subjected to a loading cycle during which the stress increased from its minimum to maximum

**Table 4 – Data analysis performed in this work.**

| Comparison of the results   | Possible factors affecting modulus $E$      |
|---|---|
| mc-Ti versus nc-Ti  | Effect of the nanostructure i.e. grain size |
| Strain rate: $3.3 \times 10^{-4}$ [1/s] versus $3.3 \times 10^{-3}$ [1/s] | Influence of the strain rate                |
| Stress e.g.: 10–500 [MPa] versus 10–800 [MPa]                             | Influence of the stress range               |

value and than in the reverse direction from the maximum to minimum value. This sequence meant one loading cycle. During each test conducted at given parameters this cycle was repeated 5 times. In the calculations, only data recorded when the stress was increasing were utilized.

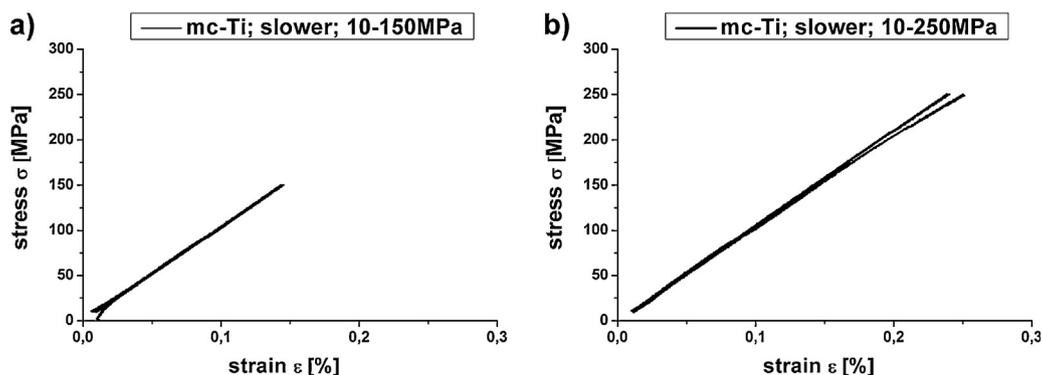
The tensile tests were carried out according to Norm PN-91 H-04310 in a vertical MTS 858 universal hydraulic testing machine equipped with an electromechanical extensometer. The loading force was measured using a digital converter. During the test, the loading force and displacements were recorded. The results were utilized for plotting the strain–stress curve and calculating the arithmetic mean of the elastic modulus for each case examined.

#### 4. Results and discussion

The results obtained during the realization of the present research project deliver data which enable a thorough analysis of the effect of several factors on the elastic modulus of nanomaterials (see Table 4).

Figs. 4 and 5 show some exemplary strain–stress curves recorded during 5 loading–unloading cycles of the uniaxial tensile tests. Only the curves conducted at the slower strain rate  $\dot{\epsilon} = 3.3 \times 10^{-4}$  [1/s] has been presented.

Fig. 4a is the strain–stress curve obtained for mc-Ti during the 5 loading–unloading cycles within the range of lower stress i.e. from 10 to 150 MPa. It can be seen that all the plots are identical, all are rectilinear and parallel to one another (Fig. 4a). Hence the value of the elastic modulus  $E$  is almost the same and the standard deviation SD is very small (Table 5). In the test conducted at the same slow strain but with more severe load (10–250 MPa), Fig. 4b, the strain–stress plots are also identical except that obtained during the first

**Fig. 4 – mc-Ti samples tested at slower strain rate within the stress range: (a) 10–150 MPa; (b) 10–250 MPa.**

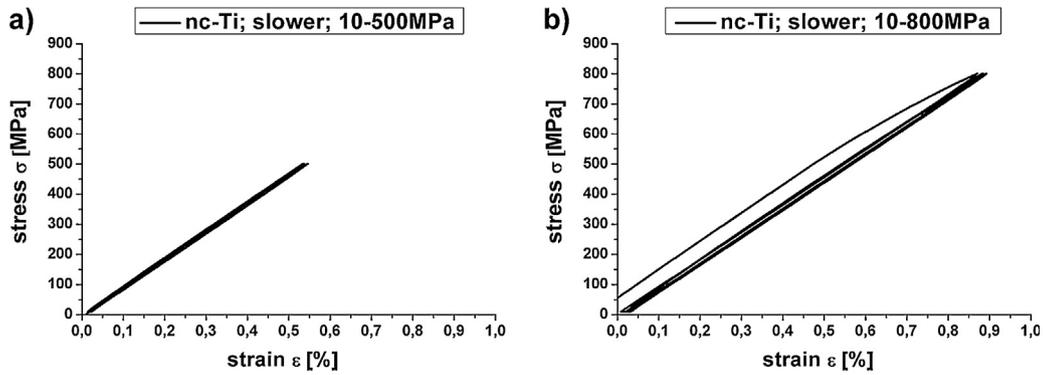


Fig. 5 – nc-Ti samples tested at slower strain rate within the stress range: (a) 10–500 MPa; (b) 10–800 MPa.

loading-unloading cycle which is slightly different (and thus the result is lower by 3 GPa) because of the setting of the sample to the holder. In the curves obtained during 2–5 cycles the standard deviation SD was very small (Table 5).

In the test conducted for mc-Ti with the higher strain rate and the stress range 10–150 MPa the strain–stress curves were similar, and thus the calculated value of the Young’s modulus was almost the same. However here too, the exception was the curve obtained during the first cycle when the sample set to the holder, its slope slightly differed from that of the other curves and, in consequence, the result differed from those obtained in cycles 2–5 where the results are identical (Table 5). The analogous effect has been observed for stress range 10–250 MPa.

Fig. 5a shows the strain–stress curves obtained for nc-Ti in the test conducted with the lower strain rate under stress ranging from 10 to 500 MPa. The curves obtained in the individual cycles are identical and all are rectilinear and parallel to one another (Fig. 5a). Hence the calculated values of the elastic modulus are identical and the standard deviation value is exceptionally small (SD = 0.31; Table 6). At the same slow strain rate but under heavier stress (10–800 MPa range) the results obtained in the cycles 2 to 5 are identical and the

coefficient SD is very small. The only exception is the curve obtained in the first cycle which slightly differs from the others (Fig. 5b) as a result of the setting of the sample to the holder. Hence the value of the elastic modulus calculated based on this curve is lower by about 3 GPa than those obtained from the other curves (Table 6).

The strain–stress curves obtained for nc-Ti at the higher strain rate and subjected to lower stress (10–500 MPa) were identical (parallel and with the same slope) in cycles 2 to 5 and slightly different in cycle 1. Under heavier stress (10–800 MPa) the slight difference in the slope of the curves appeared in cycles 1 and 5 and, hence the calculated value of the elastic modulus of this cycles was here minimally lower. In spite of this, the values of the modulus calculated from the cycles 2–4 were similar.

All the results, including the calculated values of the elastic modulus  $E$ , obtained for the mc-Ti and nc-Ti samples are given in Tables 5 and 6.

Based on these results it can be concluded that: (1) irrespective of the test parameters, in all the variants of the test the nanocrystalline titanium had lower elastic modulus than its microcrystalline counterpart by, on average, about 13%; (2) in all the cases, at the higher strain rate (i.e. faster

Table 5 – Results obtained for mc-Ti samples in the uniaxial tensile tests;  $E$  – elastic modulus [GPa],  $\sigma$  – stress [MPa],  $\epsilon$  – strain, SD – standard deviation, CV – coefficient of variation.

| Strain rate $\dot{\epsilon}$ [1/s] | Cycle No. | Results: mc-Ti sample     |      |      |                           |      |      |
|------------------------------------|-----------|---------------------------|------|------|---------------------------|------|------|
|                                    |           | Stress range 10–150 [MPa] |      |      | Stress range 10–250 [MPa] |      |      |
|                                    |           | $E = \sigma/\epsilon$     | SD   | CV   | $E = \sigma/\epsilon$     | SD   | CV   |
| $3.3 \times 10^{-4}$ (slower)      | 1         | 104.65                    | 2.56 | 0.02 | 101.96                    | 2.57 | 0.03 |
|                                    | 2         | 103.37                    | 2.32 | 0.02 | 105.01                    | 1.60 | 0.02 |
|                                    | 3         | 103.79                    | 1.59 | 0.02 | 105.08                    | 1.64 | 0.02 |
|                                    | 4         | 104.28                    | 1.19 | 0.10 | 105.15                    | 1.90 | 0.02 |
|                                    | 5         | 104.14                    | 1.97 | 0.02 | 105.12                    | 2.17 | 0.02 |
|                                    | Average   | 104.05                    | 1.93 | 0.04 | 104.46                    | 1.98 | 0.02 |
| $3.3 \times 10^{-3}$ (faster)      | 1         | 124.12                    | 6.23 | 0.05 | 103.83                    | 3.42 | 0.03 |
|                                    | 2         | 112.18                    | 1.73 | 0.02 | 108.94                    | 0.97 | 0.01 |
|                                    | 3         | 111.79                    | 2.07 | 0.02 | 109.35                    | 1.28 | 0.01 |
|                                    | 4         | 110.56                    | 2.70 | 0.02 | 109.24                    | 1.32 | 0.01 |
|                                    | 5         | 110.85                    | 3.48 | 0.03 | 109.09                    | 1.69 | 0.02 |
|                                    | Average   | 113.90                    | 3.24 | 0.03 | 108.09                    | 1.74 | 0.02 |

**Table 6 – Results obtained for nc-Ti samples in the uniaxial tensile tests; E – elastic modulus [GPa],  $\sigma$  – stress [MPa],  $\varepsilon$  – strain, SD – standard deviation, CV – coefficient of variation.**

| Strain rate $\dot{\varepsilon}$ [1/s] | Cycle No. | Results: nc-Ti sample     |      |       |                           |      |      |
|---------------------------------------|-----------|---------------------------|------|-------|---------------------------|------|------|
|                                       |           | Stress range 10–500 [MPa] |      |       | Stress range 10–800 [MPa] |      |      |
|                                       |           | $E = \sigma/\varepsilon$  | SD   | CV    | $E = \sigma/\varepsilon$  | SD   | CV   |
| $3.3 \times 10^{-4}$ (slower)         | 1         | 93.21                     | 0.29 | <0.01 | 88.83                     | 1.99 | 0.02 |
|                                       | 2         | 93.99                     | 0.33 | <0.01 | 91.48                     | 0.70 | 0.01 |
|                                       | 3         | 94.15                     | 0.32 | <0.01 | 91.79                     | 0.62 | 0.01 |
|                                       | 4         | 94.25                     | 0.31 | <0.01 | 91.94                     | 0.57 | 0.01 |
|                                       | 5         | 94.26                     | 0.29 | <0.01 | 91.92                     | 0.57 | 0.01 |
|                                       | Average   | 93.97                     | 0.31 | <0.01 | 91.19                     | 0.89 | 0.01 |
| $3.3 \times 10^{-3}$ (faster)         | 1         | 94.74                     | 1.28 | 0.01  | 92.70                     | 2.29 | 0.02 |
|                                       | 2         | 97.61                     | 0.27 | <0.01 | 95.22                     | 1.20 | 0.01 |
|                                       | 3         | 98.10                     | 0.29 | <0.01 | 95.55                     | 1.13 | 0.01 |
|                                       | 4         | 98.35                     | 0.36 | <0.01 | 95.68                     | 1.12 | 0.01 |
|                                       | 5         | 98.43                     | 0.38 | <0.01 | 85.39                     | 5.67 | 0.07 |
|                                       | Average   | 97.45                     | 0.52 | <0.01 | 92.91                     | 2.28 | 0.02 |

straining), the elastic modulus was higher; (3) the effect of loading on the value of the elastic modulus was not significant and could not be estimated unequivocally. In most cases the elastic modulus decreased under heavier load. It should be noted that the conclusions, formulated above, are not invalidated when omitting the results obtained in the extreme cycles disturbed by the setting of the sample to the holder.

The analysis of the calculated values of the elastic modulus should take into account the effect of micro-cracks [8] and pores [10]. However in the present experiments this effect can be excluded. If microcracks and pores are significantly numerous in the nc-material, its tensile strength should be reduced, what did not happen. Moreover, their presence had not been confirmed by metallographic examinations. The nc-Ti obtained was a solid polycrystal and its strength was threefold higher than that of the initial mc-Ti. Besides, if the nc-Ti contained numerous microcracks and pores, it had failed during the multiple repetition of the tensile cycles, which obviously did not happen.

Based on the present knowledge about nanometals and the factors on which the value of the Young's modulus depends, it can be supposed that the nanostructure itself may also have an influence on the elastic properties of the material. In fact, compared to their microcrystalline counterparts, the decrease of Young's modulus of nanometals has been already observed but in materials with relatively small grains (5–30 nm) [7]. Knowing that the Young's modulus depends on the interactions between the atoms and on the lattice constants of the elementary cell, this result can be explained by the presence of large regions with disturbed periodicity of the atom positions in which the nano-grains neighbor with one another through highly disordered grain boundaries. In these disordered regions, the average space between the atoms is increased [7,9] and the lattice constants of the elementary cell are changed. It should be realized that in the case of so small nano-grains, amorphous regions (i.e. boundary regions, triple points, and grain boundaries) occupy a significant volume of the material and that such regions are more liable to elastic deformation and hence their Young's modulus is lower. In effect these amorphous regions can have influence on the macroscopic elastic properties of the entire material [7,8]. It

should be noticed that the average grain size decreased from 20  $\mu\text{m}$  (mc-Ti) to 55 nm (nc-Ti). Therefore, the grain refinement was 364. Such a significant reduction of the grain size resulted in an intensive increase of the number of grain boundaries in the material, which have influence on its elastic properties.

All these factors can explain the difference between the elastic modulus of mc-Ti and nc-Ti, observed in the present experiments. An additional explanation may be the fact that in the amorphous regions and regions with disturbed periodicity present in nanometals, the number of interatomic bonds per unit surface area is smaller, which, under load, results in lower stress. During hydroextrusion process the chemical composition of the pure titanium remains unchanged. Thus, the chemical composition of both mc-Ti and nc-Ti is the same. Therefore the metallurgical explanation related to the influence of the other phases, alloying elements, and foreign atoms can be excluded.

It should however be noted that Huang et al. [12] obtained nanocrystalline titanium in which the Young's modulus was higher than that in microcrystalline titanium. They produced a nanostructured layer, about 50  $\mu\text{m}$  thick, on cp-titanium by using the surface mechanical attrition treatment (SMAT). The material had inhomogeneous grains with an average size of 150 nm. The Young's modulus of the initial material, measured by the indentation method, was 116.3 GPa which was typical for the raw microcrystalline titanium, but on the nc-Ti surface it was higher, namely 134 GPa which is difficult to explain. Perhaps this result can be attributed to the inhomogeneity and gradient structure of the material. Other investigators [14] report that they obtained the modulus  $E = 118$  GPa (which is also a high value) in almost fully dense nanocrystalline titanium with an average grain size of 41 nm. The method of this material production was mechanical ball milling and hot powder consolidation. Possible explanation is that treatments of this type induce compressive stresses which may be responsible for this higher value of the elastic modulus when measured by the nanoindentation method.

The differences between the results obtained by different investigators and the lack of any clear theory which explains the effect of nanostructure on the Young's modulus may result from the fact that, in the studies reported, the nanometals

**Table 7 – Exemplary values of the Young's modulus ( $E$ ) of pure titanium (YS – the yield stress, UTS – the ultimate tensile strength).**

| Material      | Alloy    | YS [MPa] | UTS [MPa] | Elongation [%] | Modulus $E$ [GPa] | Ref. |
|---------------|----------|----------|-----------|----------------|-------------------|------|
| 99.8 pure Ti  | $\alpha$ | 140      | 235       | 50             | 100–145           | [4]  |
| cp-Ti Grade 1 | $\alpha$ | 170      | 240       | 24             | 102.7             | [5]  |
| cp-Ti Grade 2 | $\alpha$ | 275      | 345       | 20             | 102.7             | [5]  |
| cp-Ti Grade 3 | $\alpha$ | 380      | 450       | 18             | 103.4             | [5]  |
| cp-Ti Grade 4 | $\alpha$ | 480–655  | >550      | 15             | 100–120           | [4]  |

were produced by different techniques and the modulus was measured by different methods. Moreover the samples examined had differing geometries, volumes, and structure.

The values of the elastic modulus of pure microcrystalline titanium are contained within a wide range from 100 to 150 GPa. The value commonly used in calculations is most often 110–114 GPa. Some available literature data for this material are given in Table 7. There are also reports concerning the Young's modulus of microcrystalline cp-Ti measured by the nanoindentation or ultrasonic method in which the average value of this modulus ranges between 119 and 121 GPa, respectively [6]. Summing up, the values of the Young's modulus obtained in the present study for mc-Ti are in agreement with the literature data concerning pure titanium (Table 7), whereas the results obtained for nc-Ti are lower than those known for microcrystalline titanium.

The increase of the Young's modulus with increasing strain rate observed in the present study can be attributed to the sensitivity of the material to changes of the strain rate. This effect was also observed e.g. in the experiments conducted by Sakai et al. [18] where, the calculated value of the elastic modulus of gold has depended on the strain rate. The effect of the increased strain rate (on the Young's modulus and also on the yield stress) which induces shortening the straining time (i.e. shortens the time of the effect of temperature) is similar to the effect of a decrease of temperature since it is known that, at a decreased temperature, the vibration amplitude of the atoms decreases and the stress necessary for their deformation, both plastic and elastic, increases.

In this work, the Young's modulus was slightly lower when measured in the range of heavier stress. This can be attributed to the fact that, the stress–strain curve was not exactly rectilinear. The recorded stress was not equally proportional to the strain within the entire measurement range. This can be attributed to the micro-plasticity of certain isolated subgrains (reversible when the load is removed) as a result of which the Young's modulus may be decreased. This effect was also observed e.g. in nanocrystalline gold and aluminum [19].

## 5. Summary and conclusions

Titanium in the microcrystalline state (mc-Ti) with an average grain size of 20  $\mu\text{m}$  and the titanium in the nanocrystalline state (nc-Ti) with an average grain size of 55 nm were investigated. The nc-Ti was characterized by enhanced mechanical properties such as microhardness, yield stress and ultimate tensile strength. The aim of this study was to

examine the elastic properties of both these states and to determine the influence of their structure on the Young's modulus. The elastic modulus was determined by the uniaxial tensile tests using standard samples. Based on the results obtained it can be concluded:

1. The values of the elastic modulus obtained for microcrystalline titanium (mc-Ti) are in agreement with the literature data.
2. Irrespective of the test parameters, all the values of the elastic modulus obtained for nc-Ti were slightly lower (by about 13%) than those of its microcrystalline counterpart.
3. The intensive growth of amorphous regions in the structure, such as grain boundaries or dislocations, affects the elastic properties of titanium.
4. Strain rate affects the value of the elastic modulus of titanium Grade 2 evaluated by a tensile tests.
5. Value of the stress insignificantly affects the value of the elastic modulus.

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## REFERENCES

- [1] K.S. Kumar, H. Van Swygenhoven, S. Suresh, *Acta Materialia* 51 (2003) 5743–5774.
- [2] M.A. Meyers, A. Mishra, D.J. Benson, *Progress in Materials Science* 51 (2006) 427–556.
- [3] M. Kulczyk, W. Pachla, A. Mazur, R. Diduszko, H. Garbacz, M. Lewandowska, W. Łojkowski, K.J. Kurzydłowski, *Materials Science Poland* 23 (3) (2005) 839–846.
- [4] H. Matsumoto, S. Watanabe, S. Hanada, *Materials Science and Engineering A* 448 (2007) 39–48.
- [5] M. Niinomi, *Materials Science and Engineering A243* (1998) 231–236.
- [6] P. Majumdar, S.B. Singh, M. Chakraborty, *Materials Science and Engineering A* 489 (2008) 419–425.
- [7] Y. Zhou, U. Erb, K.T. Aust, G. Palumbo, *Scripta Materialia* 48 (2003) 825–830.
- [8] H. Huang, F. Spaepen, *Acta Materialia* 48 (2000) 3261–3269.
- [9] G.E. Fougere, L. Riester, M. Ferber, J.R. Weertman, R.W. Siegel, *Materials Science and Engineering A* 204 (1995) 1–6.
- [10] K. Zhu, C. Li, Z. Zhu, C.S. Liu, *Journal of Materials Science* 42 (2007) 7348–7353.

- [11] G.B. de Souza, C.E. Foerster, S.L.R. da Silva, F.C. Serbena, C.M. Lepienski, C.A. dos Santos, *Surface and Coatings Technology* 191 (2005) 76–82.
- [12] L. Huang, J. Lu, M. Troyon, *Surface and Coatings Technology* 201 (2006) 208–213.
- [13] P. Wieciński, J. Smolik, H. Garbacz, K.J. Kurzydłowski, *Thin Solid Films* 519 (2011) 4069–4073.
- [14] H.S. Cao, J.J. Hunsinger, O. Elkedim, *Scripta Materialia* 46 (2002) 55–60.
- [15] K. Topolski, W. Pachla, H. Garbacz, *Journal of Materials Science* 48 (2013) 4543–4548.
- [16] K. Topolski, H. Garbacz, W. Pachla, K.J. Kurzydłowski, *Solid State Phenomena* 140 (2008) 191–196.
- [17] K. Topolski, H. Garbacz, K.J. Kurzydłowski, *Materials Science Forum* 584–586 (2008) 777–782.
- [18] S. Sakai, H. Tanimoto, H. Mizubayashi, *Acta Materialia* 47 (1999) 211–217.
- [19] J. Rajagopalan, J. Han, M.T. Saif, *Science* 315 (2007) 1831–1834.