The influence of the crystallographic texture and phase composition of Ti-Nb-Zr alloys with shape memory and superelasticity on their functional properties

M M Zaripova, M G Isaenkova, V A Fesenko and A V Osintsev
Institute of Nuclear Physics and Engineering, National Research Nuclear University
MEPhI (Moscow Engineering Physics Institute), Moscow, 115409, Russian Federation

MMZaripova@mephi.ru

Abstract. Currently, Ti-Zr-Nb-based biocompatible alloys are considered as prospective for medical applications. In this work, the mechanisms of the formation of the crystallographic texture of five alloys Ti-(17-19)Zr-(14-16)Nb (at.%) have been compared. The presence of martensitic transformations during the rolling process determines the features of the formed texture. At the initial stage of deformation ($\varepsilon = 50\%$), the texture $\{112\}<011>$ is formed in all five alloys. With an increase of the degree of deformation to 92%, the texture dissipates somewhat, which is due to an increase in the fraction of the martensitic phase in the foils. Recrystallization of rolled foils ($\varepsilon = 92\%$) at 650°C leads to an exacerbation of the texture component close to $\{100\}<011>$, the blurring of which varies in different alloys. Cyclic tensile tests along three directions: the rolling direction (RD), the transverse direction, at an angle of 45° to the RD showed the presence of anisotropy in the samples. It was shown, that the effect of superelasticity is orientation- and structure-dependent, and the anisotropy of mechanical properties.

1. Introduction
At present, Ti-Zr-Nb-based alloys (TNZ), having biomechanical and biochemical compatibility with bone tissue, are considered as prospective for medical purposes. These alloys contain only safe chemical elements permitted for medical application, have high corrosion resistance in environments of the body, characterized by a low modulus of elasticity 40-60 GPa, comparable to that of bone tissue, and the effect of superelasticity guaranteed above 0.5%. The effects of superelasticity in such alloys are realized due to the reversible martensite transformation $\beta$ (body-centered cubic lattice) $\leftrightarrow \alpha''$ (orthorhombic lattice). It becomes relevant to create in a superelastic alloys such a crystallographic texture that would ensure an increase in their functional and operational characteristics.

Hypoallergenic alloys based on Ti-Nb, alloyed with additional elements biocompatible with human organisms [1]: Zr, O, N, Ta, Al, Pt, etc. are promising alloys for biomedical purposes.

It is becoming urgent to create in an alloy with shape memory effect (SME) and superelasticity (SE) such a crystallographic texture that provides an increase in the functional and operational characteristics necessary for them.

The aim of this work is to determine the effect of the crystallographic texture on the properties of shape memory alloys and superelasticity based on Ti-Zr-Nb and the possibility of controlling the
properties by changing it during deformation and subsequent annealing. It is also necessary to choose an alloy with the most stable functional properties.

2. Materials and methods of their research
The work was carried out on foils made of Ti-(17-19)Zr-(14-16)Nb alloys (at.%) (Table 1). The ingots of the indicated alloys were melted in an arc furnace MEPhI-9 in an argon atmosphere, homogenized in a vacuum furnace at a temperature of 1000°C for 2 h, and quenched in water to fix the β structure of the alloy. Then the samples were forged at a temperature (at 900°C, ε ≈ 40%) in order to refine the grain size of the original workpiece. Further, on a laboratory rolling mill, cold rolling of the plates was carried out to degrees of deformation of 92-97%, calculated from the change in the thickness of the plate. Subsequent heat treatment in a temperature range of 650-900°C for 0.5 h in a vacuum oven.

Table 1. Composition of studied alloys, at.%

| №  | Ti   | Zr   | Nb   |
|----|------|------|------|
| 1  | 67.6 | 17.9 | 14.5 |
| 2  | 66.4 | 18.4 | 15.2 |
| 3  | 65.4 | 18.4 | 16.2 |
| 4  | 67.4 | 17.1 | 15.5 |
| 5  | 65.1 | 19.3 | 15.2 |

According to the data of [2, 3], this regime of thermomechanical processing corresponds to the formation in the alloy of a nanosubstructure with a subgrain size of less than 100 nm. Holding at 600°C for half an hour leads to the manifestation of the best functional fatigue life of the alloy.

X-ray analysis of the structural state of foils, including determination of phase composition, an evaluation of the structure perfection by means of the X-ray line profile analysis, and texture estimation, was performed on X-ray diffractometers DRON-3, DRON-3M and D8 Discover with the Cu kα-radiation. The texture was analyzed in terms of the direct pole figures {110}, {100}, {112} and {111} recorded by reflections (110), (200), (112) and (222), respectively, using the standard tilt method [4, 5]. For X-ray studies, samples of 17x17 mm² were cut from rolled and annealed foils, which were etched in a mixture of acids (HNO₃:H₂O:HF = 9: 9: 2) at 30-50 μm to lighten their surface.

Mechanical tests were carried out on the versatile electromechanical machine Instron 5966 (Pₘₐₓ = 10 kN). Tensile tests of the investigated foils were performed at 3 directions: in the rolling direction (RD), transvers direction (TD) and at an angle of 45° to the RD. In addition, cyclic tests (stretching to a few percent deformations followed by complete unloading of the sample) were performed in the same directions.

Uniaxial tension tests were also carried out. Tensile test specimen dimensions: thickness 0.5 ± 0.1 mm, width 1.5 ± 0.5 mm, and working area length 14 mm. To determine Young's modulus from the tensile test results, the digital image correlation technique [6] was used by means of an optical extensometer. The elastic modulus was calculated using the VIC-3D software [7].

3. Results and discussion

3.1 Phase composition
Typical fragments of the diffraction spectra of the foils of the alloy Ti-18Zr-15Nb (at.%) are shown in Figure 1, in which the reflection indices for the β-phase and the additional α″-phase are indicated in different colors. It should be mentioned, that the phase composition for samples of other alloys changes in a similar way.
From the spectra, it can be seen that foils deformed to 92–93% consist mainly of the β-phase and are characterized by broad X-ray reflections, which is due to the presence of a large number of defects in the deformed material. The lines of the additional (martensitic) αʺ-phase are also visible, which indicates the occurrence of martensitic transformations during deformation (rolling).

![Diffraction spectra of Ti-18Zr-15Nb (at.%) alloy samples.](image)

**Figure 1.** Diffraction spectra of Ti-18Zr-15Nb (at.%) alloy samples.

Because of annealing at temperatures of 650 and 900°C in all five alloys, the crystal structure of the annealed foils is improved, as evidenced by the decrease in the half-width (FWHM) of the X-ray lines. In the case of annealing TNZ alloys at a temperature of 650°C with subsequent quenching in water, the foils also remain in the β-phase state, however, reflections of the additional αʺ-phase are also visible, while annealing at 900°C after quenching does not allow the precipitation of αʺ-phase.

### 3.2 Texture analysis

Considering that during rolling of materials with SME and SE, a significant fraction of plastic deformation can occur in the additional phase, which is formed in the alloy due to martensitic transformation, it is necessary to analyze the patterns of texture formation in such alloys.

At the initial stage of deformation (ε = 50%) in all five alloys, the \{112\}<011> texture is formed. As the degree of deformation increases to 92–93%, the texture is somewhat scattered, which is due to an increase in the proportion of the martensitic phase in the deformed foil. Moreover, in two alloys (Ti-18Zr-16Nb and Ti-19Zr-15Nb (at.%)), in comparison with the others, the process of reorientation of grains is inhibited and, as a consequence, the formation of a crystallographic texture due to the high value of the critical shear stresses. However, in the Ti-17Zr-15Nb (at.%) alloy, the texture becomes sharper.

The regularities of changes in the rolling texture as a result of annealing at different temperatures are revealed. The recrystallization of rolled (up to 92–97%) foils at a temperature of 650°C for 0.5 h leads to a sharpening of the texture component close to \{100\}<011>, the blurring of which varies in different alloys. For example, in alloy 18-15, the texture \{100\}<011> is blurred in the \{112\}<110> and \{110\}<100> directions (Figure 2). After annealing at 900°C for 0.5 h, a one-component sharp texture \{100\}<011> is formed in the samples of all five alloys.

### 3.3 Results of tensile tests

Mechanical properties and deformation behaviour are also strongly dependent on the formed crystallographic texture. Cyclic tensile tests showed the presence of anisotropy in the samples of all five alloys (Figure 2). Moreover, the greatest anisotropy is observed at an angle of 45° to the RD due to the formed crystallographic texture.
Figure 2. Results of cyclic tensile tests and texture analysis of foils (ε = 92%) obtained at room temperature: a) Ti-18Zr-15Nb (at.%), annealed at 650°C for 0.5h; b) Ti-18Zr-15Nb (at.%), annealed at 900°C for 0.5h; c) Ti-17Zr-15Nb (at.%), annealed at 650°C for 0.5h; d) Ti-17Zr-15Nb (at.%), annealed at 900°C for 0.5h.

As mentioned above, a sharper texture is formed in samples of alloy 17-15 than in alloy 18-15. For this reason, for these two alloys, which are close in composition, the shape of the stress-strain curves is different (Figure 2a, c). Moreover, specimens cut at an angle of 45° to RD from alloy 18-15 exhibit superelasticity, while specimens from alloy 17-15 exhibit a shape memory effect.

Mechanical tensile also show the presence of anisotropy of mechanical properties in all five alloys, both in the deformed and in the annealed states. After annealing at 900°C, a sharper texture is formed in the samples of all five alloys compared to annealing at 650°C. Therefore, there is a strong dependence of the yield stress and elongation of the sample on the direction in which stretching is performed.

From the diagrams shown in Figure 3, it can be concluded that in the samples annealed at 900°C for 0.5 h we observe a large elongation to break. To reveal the nature of this phenomenon in the materials under study using the digital correlation method, it was revealed that, along with the occurrence of martensitic transformation, the effect of a running (blurred) neck appeared, since it moves along the length of the sample without causing localized compression. With such a quasi-uniform deformation, a large elongation is achieved when the sample is stretched. However, large elongation in the alloys is also supposed to be due to transformation-induced plasticity (TRIP) and twinning-induced plasticity (TWIP) effects [8–10].

More than that, most often, specimens cut at an angle of 45° to the rolling direction are stretched to lower percent of deformation. This is also due to the crystallographic texture formed during the previous thermo-mechanical treatment. Texture {100}<011> is formed (Figure 2,b), where crystals
with different orientations are oriented along different directions (RD || <011>, TD || <011>, at an angle 45° to RD || <100>).

![Stress vs Strain Diagram](image1.png)

**Figure 3.** Tensile test results obtained at room temperature on Ti-18Zr-15Nb (at.%) alloy specimens annealed at 900°C for 0.5 h.

![Young's Modulus Scheme](image2.png)

**Figure 4.** Scheme for measuring Young's modulus using the example of a Ti-18Zr-15Nb (at.%), sample cut along the RD annealed at 650°C, 0.5 h.

During tensile tests, it was found that the stress-strain diagrams of specimens made of alloys with SE and SME for the first and second test cycles differ significantly. In most alloys, in the first cycle, there is no inflection point indicating the occurrence of an martensitic transformations, but already in the second and subsequent cycles, the zone in which the phase transformation occurs is clearly visible. Based on this, it was decided to measure Young's modulus not only at the first deformation cycle, but also at the second, in order to compare the values obtained before and after the phase transformation. The scheme used to measure Young's modulus is shown in Figure 4.

Based on the results obtained, the values of Young's modulus for samples of all five alloys in the unloaded state are 45–93 GPa, which corresponds to the value of Young's modulus for bone tissue. Young's modulus for alloy 18-15 at different directions:

- E₁ = 55 GPa;
- E₂₁ = 45 GPa;
- E₂₂ = 27 GPa.

It was assumed that E₁ and E₂₁ should be equal (since both values are in the elastic region of deformation). Based on the data obtained, for all specimens E₁ > E₂₁, that is, after the first test cycle, the value of the elastic modulus decreases. With each subsequent cycle of "load-unloading", the restoration of the shape more and more approaches the initial value (residual deformation tends to zero, for many samples on the fifth cycle it is completely absent), that is, the material "trains". We consider that such a dislocation substructure is formed in the samples, which allows martensite crystals to be oriented in a certain way, thereby reducing the energy for their formation in subsequent cycles and the stress of activation of this process. The manifestation of plasticity at the first stages of stretching may be due to the reorientation of grains with the {112} orientation, formed during annealing of the foils as a result of recrystallization and were at the beginning of the test in an orientation unstable with respect to the acting load.
4. Conclusions

1. Based on cyclic tests of annealed foils, it was shown that all the investigated Ti-Zr-Nb-based alloys are characterized by either superelasticity or shape memory effect, i.e. able to restore their initial shape.

2. It is shown that a weak (blurred) crystallographic texture is formed in deformed samples, which becomes sharper in subsequent annealing. Moreover, in samples with superelasticity, a similar texture is formed, as well as in samples with shape memory effect.

3. It has been established that alloys with stable functional properties are alloys Ti-18Zr-15Nb, Ti-18Zr-16Nb and Ti-19Zr-15Nb (at.%). To obtain optimal properties, it is necessary to conduct annealing at a temperature of 650°C for 0.5 h.

4. It has been established that alloys with stable functional properties, i.e. with high properties of superelasticity, with a maximum fraction of elastic deformation during cycling, with minimum stresses for activating martensitic transformations, are alloys Ti-18Zr-15Nb, Ti-18Zr-16Nb and Ti-19Zr-15Nb (at.%), for which the content of zirconium ranges from 18.4 to 19.5 at.%, and niobium – from 15.2 to 16.2 at.%. To obtain optimal properties, it is necessary to carry out annealing at a temperature of 650°C for 0.5 h, because annealing at t = 900°C leads to significant grain growth and sharpening of the crystallographic texture, which leads to an increase in the anisotropy of properties and their instability.

5. The Young's modulus of all annealed samples varies from 45 to 93 GPa.

Acknowledgements

This work was supported by Competitiveness Growth Program of the Federal Autonomous Educational Institution of Higher Education National Research Nuclear University MEPhI (Moscow Engineering Physics Institute) (agreement No.02.a03.21.0005).

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