Biomechanical compatibility study of a nickel-free medical TiNbZr shape memory alloy

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Abstract. Biomechanical compatibility of a Ti - (20-30) Nb - 5Zr shape memory alloy was studied. The tensile strength study was carried out. The best properties are observed for the Ti-28Nb-5Zr composition with a wire diameter of 1200 μm, adapted to work in a living organism. The dependence of the change in strength and plasticity on the annealing temperature exhibits minimal extrema. The best characteristics are noted at 800 °C.

1. Introduction
Superelasticity, delayed response to action, low Young's modulus is characteristic of materials biomechanical compatibility and is inherent for shape memory alloys, for example, NiTi [1–2]. Therefore, nitinol is actively used in medicine.

However, the properties of the material highly depend on the surface state, which followed the method of production: different degrees of defectiveness, impurities, an surface Ni content. The marvelous properties of the alloy at the same time accompanied by some difficulties in their traditional methods processing [3-4]. Also the toxic nickel contained in a high concentration and the possibility of the corrosive destruction of the product in the working environment limit its applicability [5-8].

nevertheless, it was shown that shape memory alloys can be obtained from non-toxic metals [9-14]. The shape memory effect was found in titanium alloys with a tantalum, niobium, and molybdenum content of 20-40%. Zirconium also acts as a beta-stabilizer but also prevents the formation of an brittle ω-phase. The smaller size of zirconium compared to other designated metals caused a decrease in the bond strength between its atoms, which is connected with a decrease in elasticity Young's modulus. The superelasticity and shape memory effect were found for alloys with the zirconium content less than 8 at. %.

Thus, these alloys is interesting materials for medical production. This work was aimed at studying the biomechanical compatibility of the Ti-Nb-Zr alloy.
2. Materials and methods
The tensile strength study was carried out on an INSTRON 3382 universal testing machine with a
tensile speed of 1 mm/min. The initial calculated length was measured with an error of ± 0.1 mm. The
initial diameter was measured with an error of ± 0.001 mm. The sample was fixed in the grips of the
testing machine so that the extreme marks limiting the calculated length were spaced from the grips of
the machine at a distance of at least two diameters of the test sample. The grippers ensured that the
sample did not slip during testing. Testing of the wire with the determination of the relative
elongation, yield strength, and ultimate resistance was carried out according to the methods of GOST
1497-84. The processing of test results in determining the characteristics of mechanical properties was
carried out following GOST 1497-84 using the INSTRON Bluehill 2.0 software. 3-7 samples were
tested for one experimental point. The values of the conventional yield stress, tensile strength, relative
elongation, and Young's modulus were determined.

3. Results and discussion
The results of mechanical tests are shown in Table 1. It can be seen that the best properties are
observed for the alloy with 28 at.% Nb when a wire diameter is

\[ \text{1200 \mu m} \]

Indicators of strength and ductility after heat treatment at maximum temperature are comparable to or exceed those for Ti – 6Al – 4V [15], Ti – Nb – Sn [16-17], Ti – 25Ta [ 18], or Ti – Nb [19].

| №  | Composition and diameter (mm) | Processing | Rel. extension (%) ±0.1 | Yield strength (MPa) ±10 | Tensile strength (MPa) ±10 | Young's modulus (GPa) |
|----|-------------------------------|------------|-------------------------|--------------------------|---------------------------|-----------------------|
| 1  | Ti-25Nb-5Zr d=0.4             |            | 1.09                    | 688                      | 812                       | 41.770                |
| 2  |                              |            | 1.47                    | 604                      | 819                       | 42.789                |
| 3  |                              | after drawing | 1.24                    | 658                      | 821                       | 38.637                |
| 4  | Ti-25Nb-5Zr d=0.7             |            | 2.38                    | 531                      | 643                       | 31.636                |
| 5  |                              |            | 1.83                    | 577                      | 666                       | 39.829                |
| 6  |                              |            | 2.12                    | 575                      | 665                       | 46.480                |
| 7  | Ti-28Nb-5Zr d=1.2             |            | 1.62                    | 603                      | 695                       | 37.802                |
| 8  |                              |            | 1.98                    | 595                      | 726                       | 41.447                |
| 9  |                              |            | 2.05                    | 545                      | 694                       | 37.012                |
| 10 | Ti-30Nb-5Zr d=0.55            |            | 0.81                    | 618                      | 648                       | 46.804                |
| 11 |                              |            | 1.10                    | 458                      | 640                       | 41.918                |
| 12 |                              |            | 0.80                    | 639                      | 674                       | 50.496                |
| 13 | Ti-25Nb-5Zr d=0.4 ultrasound + annealing 600°C, 20 min, vacuum | | 0.28 | 601 | 620 | 43.281 |
| 14 |                              |            | 1.71                    | 527                      | 707                       | 42.800                |
| 15 |                              |            | 2.71                    | 591                      | 715                       | 44.092                |
| 16 | Ti-25Nb-5Zr d=0.7             |            | 3.13                    | 572                      | 750                       | 42.079                |
| 17 |                              |            | 1.88                    | 570                      | 738                       | 38.574                |
| 18 |                              |            | 3.76                    | 648                      | 756                       | 24.768                |
| 19 | Ti-28Nb-5Zr d=1.2 ultrasound + annealing 500°C, 1 h, vacuum | | 6.57 | 397 | 596 | 31.071 |
| 20 |                              |            | 6.15                    | 458                      | 601                       | 39.801                |
| 21 |                              |            | 5.57                    | 486                      | 590                       | 33.547                |
| 22 | Ti-30Nb-5Zr d=0.55            |            | 1.15                    | 435                      | 557                       | 39.143                |
Firstly annealing at 500 °C promoted a high increase in plasticity and, on the contrary, a decrease in strength and Young's modulus, which then always decreased with an annealing temperature increase. It is possible that the alloy sample deformed during the drawing process is significantly weakened because the dislocation density is significantly reduced.

Plasticity falls at 600 °C but reached high values at temperatures 700-800 °C. Thus, the deformation is lowest for the samples treated at 600 °C. Perhaps in this moment, the destruction of the metastable β-phase inhomogeneously starts over the grain volume decreasing the plasticity characteristics. Then, the metastable β-phase destroys uniformly becoming a stable beta or mixed $\beta+\alpha$, in connection with which there is an increase in strength and plasticity [20-21].

### 4. Conclusions

Thus, a new functional material for medical purposes was obtained, adapted from the point of view of biomechanical compatibility to work in a living organism. The Ti-28Nb-5Zr alloy has the best characteristics.

| 23 | 5Zr d=0.55 | 1.41 | 444 | 592 | 47.293 |
| 24 | | 1.83 | 332 | 581 | 41.186 |
| 25 | Ti-25Nb-5Zr d=0.7 | 1.76 | 511 | 732 | 30.576 |
| 26 | | 2.03 | 548 | 751 | 38.816 |
| 27 | | 1.85 | 557 | 741 | 37.785 |
| 28 | Ti-28Nb-5Zr d=1.2 | 6.49 | 419 | 614 | 29.725 |
| 29 | annealing 600C, 1 h, vacuum | 3.64 | 492 | 611 | 34.741 |
| 30 | | 4.05 | 573 | 614 | 36.636 |
| 31 | Ti-30Nb-5Zr d=0.55 | 1.42 | 445 | 590 | 41.650 |
| 32 | | 1.74 | 363 | 600 | 38.662 |
| 33 | | 1.07 | 492 | 594 | 41.892 |
| 34 | Ti-25Nb-5Zr d=0.7 | 2.49 | 398 | 788 | 28.419 |
| 35 | | 1.71 | 442 | 774 | 33.011 |
| 36 | | 1.46 | 572 | 791 | 40.879 |
| 37 | Ti-28Nb-5Zr d=1.2 | 5.43 | 511 | 661 | 28.343 |
| 38 | annealing 700C, 1 h, vacuum | 7.87 | 477 | 671 | 28.229 |
| 39 | | 6.62 | 493 | 668 | 30.425 |
| 40 | Ti-30Nb-5Zr d=0.55 | 1.75 | 527 | 710 | 37.917 |
| 41 | | 1.40 | 541 | 711 | 43.462 |
| 42 | | 1.52 | 544 | 727 | 42.576 |
| 43 | Ti-25Nb-5Zr d=0.7 | 0.20 | 378 | 424 | 44.424 |
| 44 | | 0.55 | 640 | 800 | 36.191 |
| 45 | | 1.27 | 625 | 881 | 39.975 |
| 46 | Ti-28Nb-5Zr d=1.2 | 2.39 | 581 | 745 | 19.905 |
| 47 | annealing 800C, 1 h, vacuum | 1.99 | 682 | 955 | 23.794 |
| 48 | | 2.38 | 642 | 820 | 21.942 |
| 49 | Ti-30Nb-5Zr d=0.55 | 1.85 | 623 | 841 | 42.091 |
| 50 | | 2.64 | 529 | 840 | 32.267 |
| 51 | | 2.33 | 631 | 838 | 40.393 |
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