D. ĆUBELA

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# THE RESEARCH OF TECHNOLOGICAL PARAMETERS INFLUENCE ON THE PROCESS OF NITINOL FABRICATION AND PLASTIC DEFORMATION

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*Preliminary Note - Prethodno priopćenje*

Titanium and nickel alloy, with 48 - 55 at. % Ni (rest Ti), named Nitinol has property of thermal and mechanical memory and its properties and application depends strongly on a fabrication processes. Nitinol was produced in semi-industrial conditions. Testing results of the quality of the obtained alloy are related to technological parameters of the production and processing. The aim of this work is to give an answer to the question which technological parameters are most influential and possible for the quality control what kind of corrections regarding literature instructions are needed for successful production of Nitinol for given conditions.

***Key words:*** *Nitinol (titanium and nickel alloy), thermal and mechanical memory, superelasticity, technological parameters*

**Istraživanje utjecaja tehnoloških parametara na proces izrade i plastične deformacije nitinola.** Legura titana i nikla, s 48 - 55 at. % Ni (ostatak Ti), nazvana Nitinol, ima svojstva tenničke i mehaničke memorije i ta svojstva su jako ovisna o procesu izrade legure. Nitinol je proizveden u poluindustrijskim uvjetima. Rezultati ispitivanja kvalitete dobivene legure povezani su s tehnološkim parametrima proizvodnje i prerade. Cilj rada je odrediti koji tehnološki parametri su od najvećeg utjecaja na kvalitet, te je li potrebna kakva korekcija (s obzirom na literaturne navode) za uspješnu proizvodnju Nitinola za dane uvjete.

***Ključne riječi:*** *Nitinol (legura titana i nikla), memorija, superelastičnost, tehnološki parametri*

## INTRODUCTION

The alloy of titanium and nickel in a composition range 48 - 55 at. %Ni (the rest Ti), known by the name Nitinol [1] belongs to the group of alloys called Shape Memory Alloys (SMA) [2]. These alloys have properties of thermal and mechanical memory.

Nitinol is an alloy whose properties and the area of application strongly depends on the process of production and there are still unresolved problems connected with: the precise control of chemical composition, conditions of cold and hot deformation, treatment of superelasticity and shape memory [3, 4].

The aim of research is to produce the equiatomic Nitinol alloy (50 at. % Ti and 50 % at. Ni) in the shape of wire with a diameter of 1 mm and by testing the quality of the acquired Nitinol alloy and connecting the results with technological parameters of the production in the semi industrial condition at the Metallurgical Institute “Kemal Kapetanović” in Zenica give an answer to the question which technological parameters for given condition had decisive impact on the quality and whether and by which corrections it is possible to produce this alloy at the Institute.

## EXPERIMENTAL RESEARCHES

The starting raw materials for this research were Nickel MOND in the shape of balls, purity 99,95 % and Ti 99,68 %. The melting aggregate is a vacuum inductive furnace with the power of 20 KW. $Al_2O_3$, MgO, CaO and graphite pot were used for the lining of the melting pot. The mass of the charge for all cast ingots was 2 kg, 1100 g balls of Ni and 900 g plates of Ti. Charges for ingots A1, M1, M2, G1 and G2 were cleaned only with alcohol and charges for ingots G3 and C1 were cleaned with the water solution of $HNO_3$ and HF acids. Seven ingots were cast from eight charges. The second charge from the pot with the linen of $Al_2O_3$ was not possible to cast because of the high degree of reaction between the linen and the charge. The first charge was partially cast into ingots A1. Two ingots were obtained from the pot with the linen of MgO (M1 and M2), three from the graphite pot (G1, G2, G3) and one from the pot with the linen of CaO (C1).

D. Ćubela, Faculty of Metallurgy and Material Science University of Zenica, Zenica, Bosnia and Herzegovina

Shape of ingot was inverse conical with dimension 45 × 45 mm (mean value) × 110 mm.

The ingots M1, M2, G1 and G2 were not heat-treated after the casting. After the casting, ingot A1 was annealed at 1000 °C/1h/air and G3, C1 at 1000 °C/72h/water.

Before the forging all ingots were heated in a chamber furnace without a protective atmosphere. The forging of all ingots were carried out at an air hammer with force of 20 kN. From seven ingots only G3 were successfully forged into a bar with diameter 26 mm. The hot rolling of the bar Ø 26 mm was carried out in eight passes to diameter 12 mm at the rolling-mill SKET Ø 350 mm. Before the rolling the bar was preheated at 400 °C/1h and heated at 850 °C/15 min. The bar was heated at 850 °C/5 min. after each pass. The rolling to diameter 8 mm was carried out in four passes at a small laboratory rolling-mill Ø 230 mm in the same way.

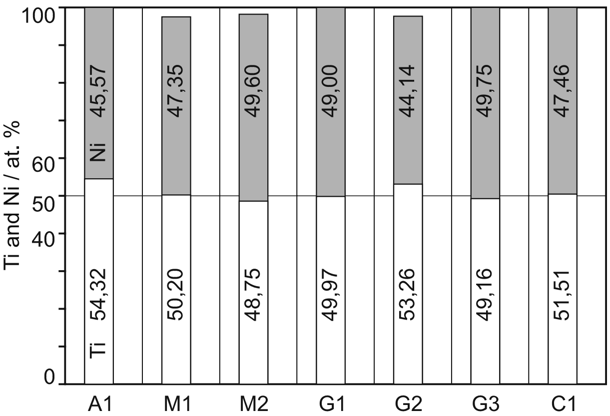



Figure 1. **The content of Ti and Ni into obtained ingots**
Slika 1. **Sadržaj Ti i Ni u izrađenim ingotima**

After rolling, the bar was annealed at 650 °C/1h/water. The cold drawing was first tried at combine drawing machine SCHUMAG. At each attempt the bar cracked brittle. Therefore it was decided that the bar should be returned to hot rolling to diameter 8 mm. Afterwards, the drawing was attempted at the big ARBOGA machine and it was unsuccessful again.

## RESULTS AND DISCUSSION

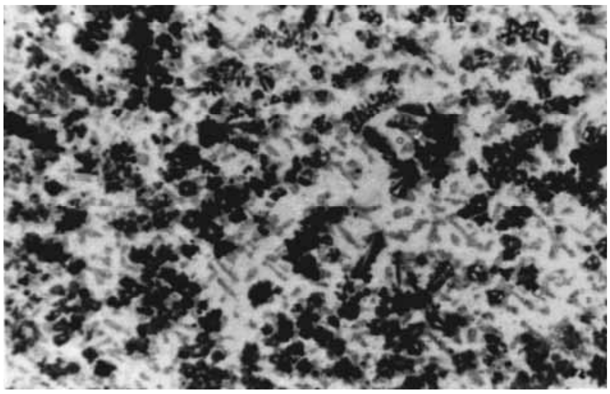
The aim of the work is to obtain an alloy 50 at. % Ti - 50 at. % Ni, which means that all other registered elements in the composition that can get into alloy from the starting components or through the reaction of the charge with the linen are considered undesirable. From that point of view and from given data concerning the chemical composition of tested ingots it is visible that only ingot G3 has satisfactory ratio Ti and Ni, in other words it is closest to the required ratio, Figure 1. All other ingots had significant deviation in this regard.

The mass portion of the accompanied elements in the tested ingots is shown in the Table 1. As it can be seen, ingots G3 and C1 had the lowest content of accompanied elements.

Table 1. **The mass portion of the accompanied elements**
Tablica 1. **Maseni udjeli pratećih elemenata**

| Ingot | C | Fe | Mn | Zn | Pb | S |
|---|---|---|---|---|---|---|
| A1 | 0,03 | 0,50 | 0,030 | 0,030 | 0,040 | 0,006 |
| M1 | 0,04 | 1,62 | 0,910 | 0,001 | 0,002 | - |
| M2 | 0,02 | 0,96 | 0,590 | 0,001 | 0,002 | - |
| G1 | 0,14 | 0,38 | 0,190 | 0,001 | 0,001 | - |
| G2 | 0,55 | 0,13 | 0,005 | 0,005 | 0,005 | 0,004 |
| G3 | 0,21 | 0,10 | 0,004 | 0,006 | 0,001 | 0,003 |
| C1 | 0,18 | 0,09 | 0,030 | 0,001 | - | 0,004 |
| Ingot | Cu | Al | Mg | Cr | Si | |
| A1 | - | - | - | - | - | |
| M1 | 0,003 | 0,038 | 0,020 | 0,007 | 0,002 | |
| M2 | 0,001 | 0,016 | 0,007 | 0,004 | 0,005 | |
| G1 | 0,002 | 0,100 | 0,020 | 0,007 | 0,002 | |
| G2 | 0,005 | 0,033 | 0,005 | 0,005 | | |
| G3 | 0,001 | 0,018 | 0,004 | 0,001 | 0,01 | |
| C1 | 0,030 | 0,050 | 0,010 | - | - | |

The basic reasons for unsuccessful forging of six ingots are the high degree of pores inside the ingots and the prime microstructure or in other words incomplete transformation of the prime into secondary microstructure. The microstructure of the sample taken from ingots after forging is shown in the Figures 2. - 6.

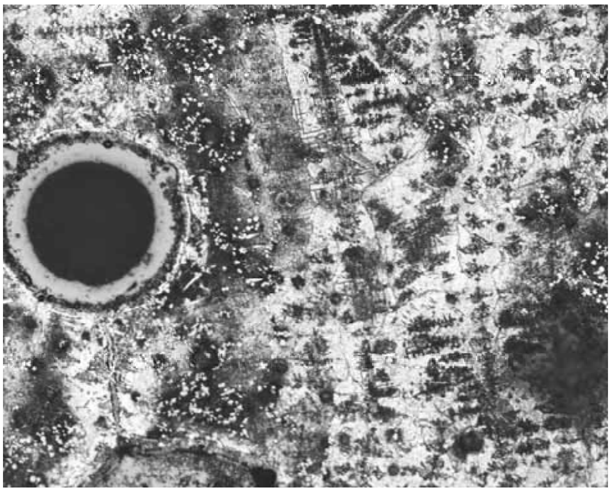


1:4:5 = HF:$HNO_3$:$H_2O$ 100 ×

Figure 2. **Microstructure of sample taken from ingot A1**
Slika 2. **Mikrostruktura uzorka uzetog iz ingota A1**

The ingot G3 only passed successfully through the phase of hot plastic working by forging and rolling. The basic features of this ingot are:

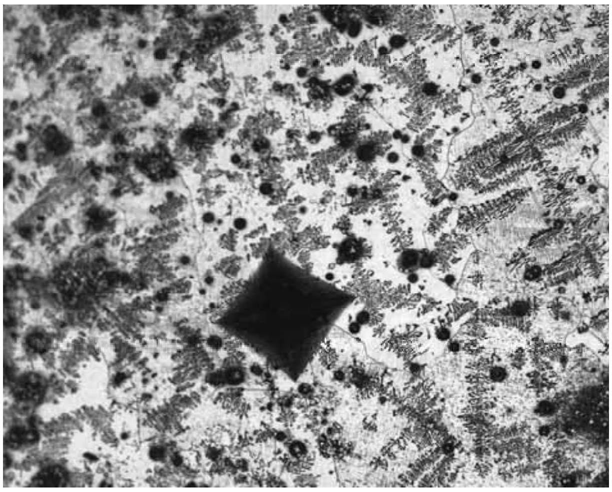
- higher level of purity in regard to its chemical composition and the ratio Ti / Ni = 49, 16 / 49, 74 at. %,
- complete transformation of the prime into secondary microstructure; ingot was without surface and internal pores after heat-treatment,
- the oxide scale formed during heat-treatment was stripped off before the forging,
- it was first preheated at 480 °C/1h, then transported into a furnace and heated at 850 °C/15 minutes.



1:4:5 = $HF:HNO_3:H_2O$ 100 ×

Figure 3. **Microstructure of sample taken from ingot M1**
Slika 3. **Mikrostruktura uzorka uzetog iz ingota M1**

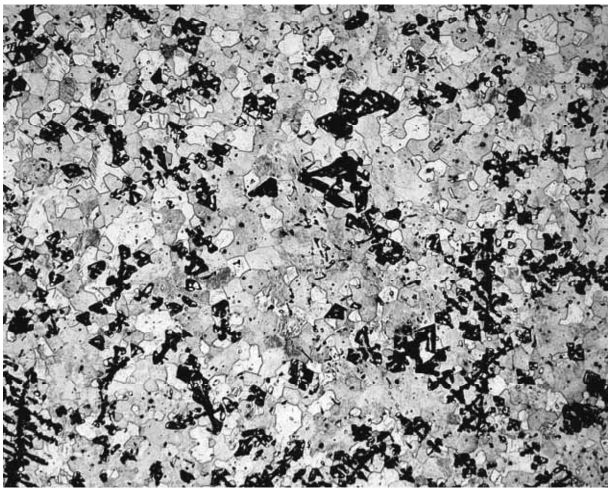
The rolling phase was carried out without any bigger problems. The alloy had a good machinability in



1:4:5 = $HF:HNO_3:H_2O$ 100 ×

Figure 4. **Microstructure of sample taken from ingot G1**
Slika 4. **Mikrostruktura uzorka uzetog iz ingota G1**

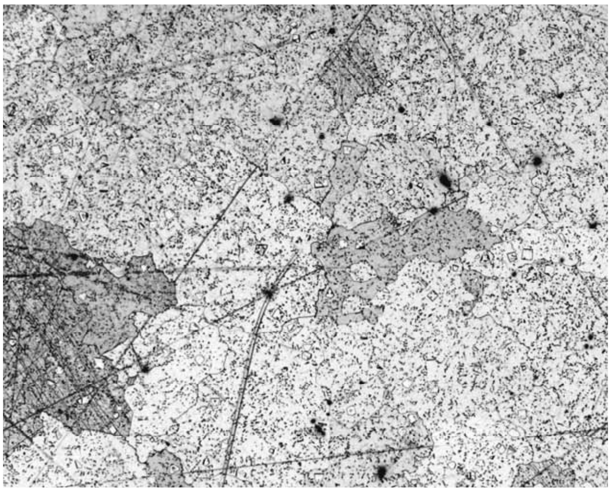
hot condition with regard that the realization of the both operation was a simulation of condition at which this



1:4:5 = $HF:HNO_3:H_2O$ 100 ×

Figure 5. **Microstructure of sample taken from ingot C1**
Slika 5. **Mikrostruktura uzorka uzetog iz ingota C1**

alloy needs to be successfully plastic worked. The cold drawing was an unsuccessful operation. The explanation for such behaviour of the alloy is given by the electron microscopy with EDS (Energy Dispersive Spectrometer).



1:4:5 = $HF:HNO_3:H_2O$ 100 ×

Figure 6. **Microstructure of sample taken from ingot G3 (electron microscope JEOL JSM-6500F - picture of second electrons, place 4, acceleration of electrons 20 kV)**
Slika 6. **Mikrostruktura uzorka uzetog iz ingota G3 (elektronski mikroskop JEOL JSM-6500F - slika sekundarnih elektrona, mjesto 4, ubrzanje elektrona 20 kV)**

The results of the electron microscopy confirmed that the matrix of the alloy is an intermetallic compound TiNi but in the microstructure there are phases of TiC and $Ti_2Ni$ [5], Figure 7. and 8. The carbide phase has dimensions of 1 and 10 μm and it is spherical while the phase $Ti_2Ni$ has polygonal shape, dimension between 15 and 40 μm and spherical shape dimension 1 μm. Both phases are brittle

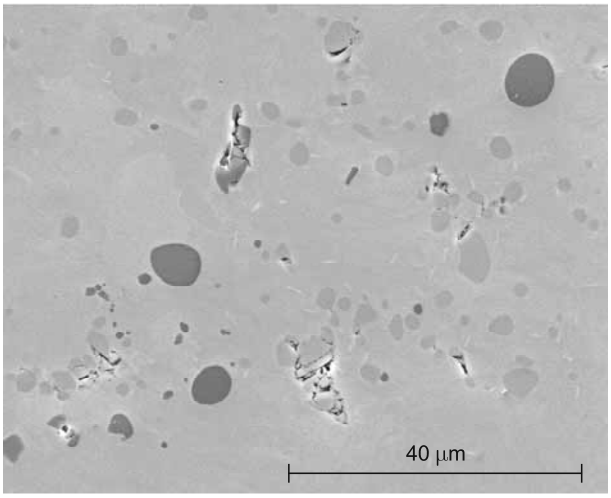



Figure 7. **TiC and $Ti_2Ni$ phase (electron microscope JEOL JSM-6500F)**
Slika 7. **TiC i $Ti_2Ni$ faza (elektronski mikroskop JEOL JSM-6500F)**

and hard and their dimension and amount are the reason for inferior mach inability in the cold condition.

Factors which had negative impact on the alloy's cold deformation capability can be sum up as follows:

- higher content of carbon and iron and inherent content of oxygen caused the reduction of the TTR (Transformation Temperature) value,
- brittle and hard secondary phases with bigger dimensions, uneven distributed.

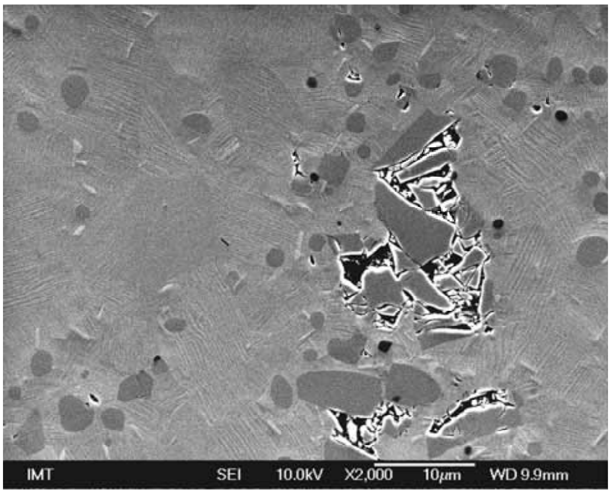



Figure 8. **$Ti_2Ni$ phase**
Slika 8. **$Ti_2Ni$ faza**

The phase transformation points austenite → martensite → austenite were determined by DSC (Differential Scanning Calorimetry) analyse of the sample (diameter 6 mm, taken from the bar of G3 ingot; the bar was in annealing condition after rolling), Figure 9. The transformation in both directions is carried out at the temperature below zero. The formation of martensite begins at –92 °C and ends at –106 °C, while the formation of austenite is carried out in a temperature interval from –44 to –26 °C. The negative temperatures of the transformation points are consequences of chemical composition, first of all of the content of carbon, oxygen and iron.

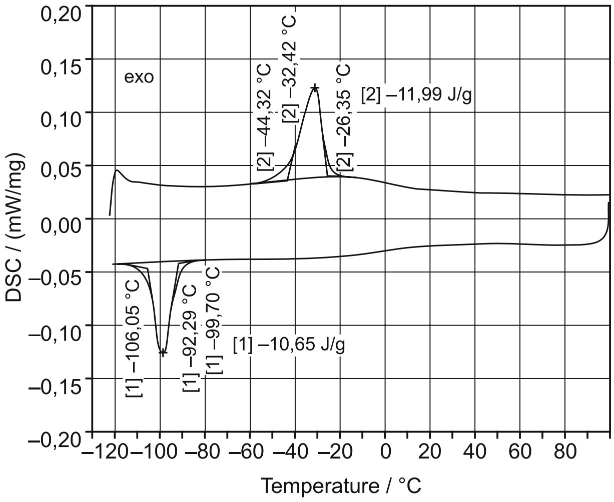



Figure 9. **Determination of the temperature points of phase transformation austenite - martensite - austenite**
Slika 9. **Određivanja temperaturnih točaka fazne transformacije austenit - martenzit - austenit**

The values of the mechanical properties given in the Table 2. are the average value of three measurements on a test bar with dimensions given in the Figure 10. The results of mechanical test on tensile strength coincide with the data

Table 2. **Mechanical properties of the NiTi rod**
Tablica 2. **Mehanička svojstva Nitinol šipke**

| Phase | Tensile yield strength $R_{p0,2}$ /MPa | Ultimate tensile strength $R_m$ /MPa | Elongation $A$ / % | Young's modulus $E$ / GPa |
|---|---|---|---|---|
| Austenite | 655,50 | 840,73 | 9,6 | 71,73 |
| Austenite / Martensite | 327,23 | 398,9 | 3,5 | 43,86 |
| Martensite | 473,73 | 677 | 5,8 | 58,53 |

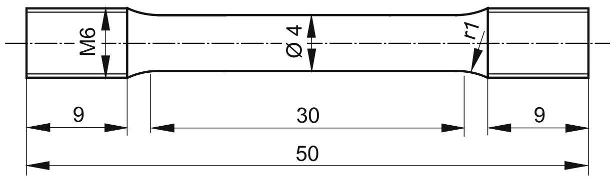



Figure 10. **Test bar for tensile testing at temperature below 0 °C**
Slika 10. **Epruveta za ispitivanje na istezanje na temperaturama ispod 0 °C**

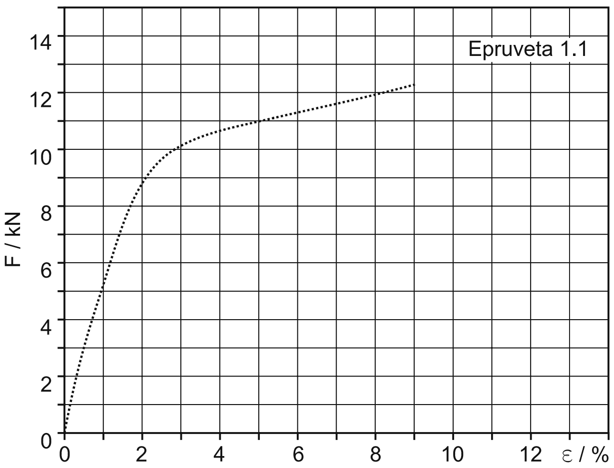



Figure 11. **Tensile testing of Nitinol test bar at 20 °C**
Slika 11. **Ispitivanje na istezanje epruvete od Nitinola na 20 °C**

from literary sources [2, 6, 7]. Diagram in the Figure 11. was obtained by tensile testing of the test bar (the test bar was made of the same bar taken from the ingot G3) at 20 °C and diagram in the Figure 12. is tensile testing at –15 °C. The curve on the Figure 11. is typical curve of elastic-plastic materials. Diagram on the Figure 12. shows the curve with plato deformation, what indicates stress induced transformation austenite to martensite. Higher values for tensile strength and flow stress at –115 °C are logic, as well as lower value for elongation at –60 °C because there are martenise and austenite phase at the same time, Figure 13.

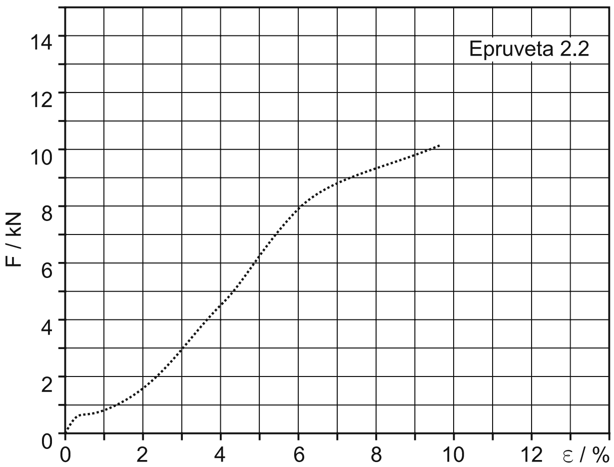



Figure 12. **Tensile testing of Nitinol test bar at –15 °C**
Slika 12. **Ispitivanje na istezanje epruvete od Nitinola na –15 °C**

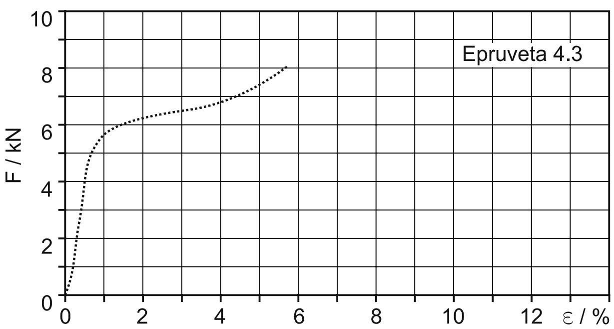



Figure 13. **Tensile testing of Nitinol test bar at –115 °C**
Slika 13. **Ispitivanje na istezanje epruvete od Nitinola na –115 °C**

Diagrams a, b and c on the Figure 14. were obtained by cycles of load - unload - load until fracture of the test bar. As can see on the Figure 14.a, the curve of tensile testing at 0 °C did not show a loop, other words the curve of unloading had linear flow. The curves of the tensile testing at –5 °C and –15 °C, Figure 14.b and 14.c, showed loops, what could means that $M_d$ temperature lies between –5 °C and 0 °C.

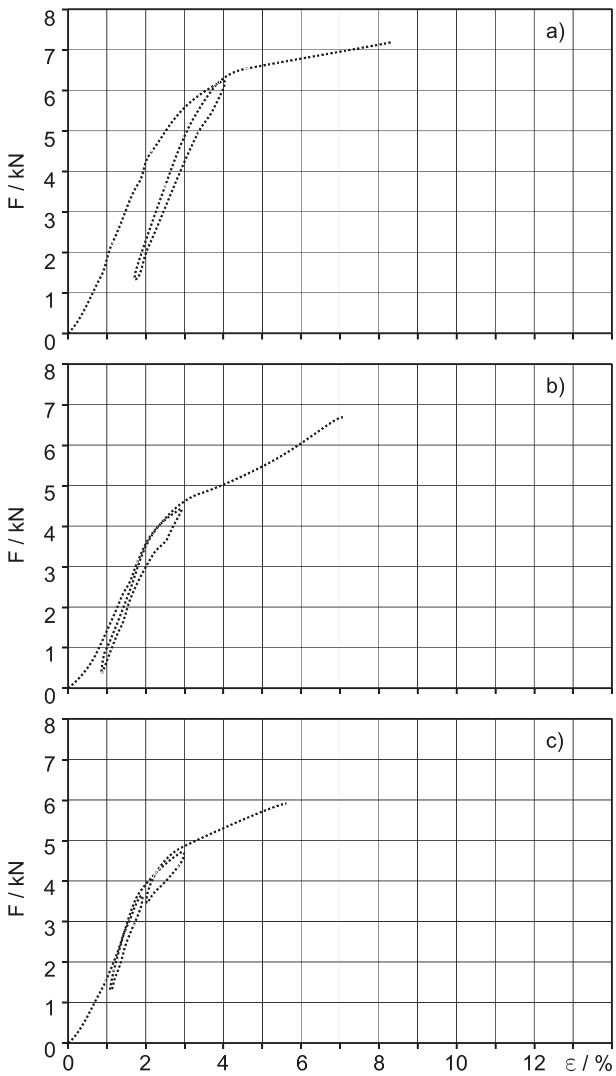



Figure 14. **Tensile testing of Nitinol test bar; a) at 0 °C, b) at –5 °C, c) at –15 °C**
Slika 14. **Ispitivanje na istezanje epruvete od Nitinola; a) na 0 °C, b) na –5 °C, c) na –15 °C**

Diagram on the Figure 15. shows an alloy behaviour in martensite phase, what is in accordance with literature[8]. The martensite had significantly lower modulus of elasticity and yield stress and return strain was 1,2 %.

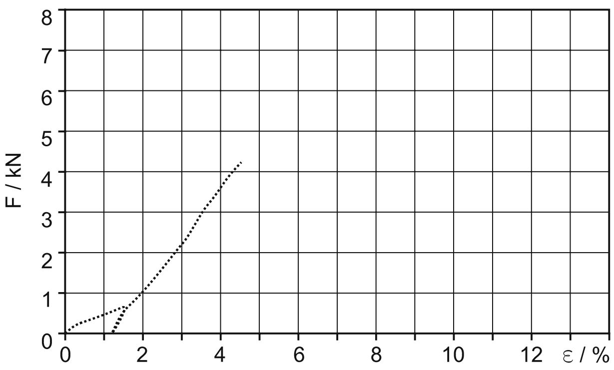



Figure 15. **Tensile testing of Nitinol test bar at –115 °C**
Slika 15. **Ispitivanje na istezanje epruvete od Nitinola na –115 °C**

## CONCLUSIONS

The results of electron microscopy, DSC analyse as well as the results of mechanical testing confirmed that it was obtained Nitinol alloy with superelasticity and shape memory but the values of these properties are modest in respect with the literature data.

The next phase is making new ingots according to technology for ingot G3. Particular attention will be pay to control chemical composition and carbon content trough temperature melt and to casting condition.

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