Effect of multi-axial deformation on the structure and properties of a nickel-enriched Ti-Ni shape memory alloy

V Komarov$^{1,2,3}$*, I Khmelevskaya$^2$, R Karelina$^{1,2}$, V Yusupov$^1$, R Kawalla$^3$, G Korpala$^3$, U Prahl$^3$ and S Prokoshkin$^2$

1 Baikov Institute of Metallurgy and Materials Science RAS, Moscow, Russia

2 National University of Science and Technology MISIS, Moscow, Russia

3 TU Bergakademie Freiberg, Germany

*Corresponding author: vickomarov@gmail.com

Abstract. In the present study, multi-axial severe plastic deformation of a nickel-enriched Ti-Ni shape memory alloy for medical applications was performed using the MaxStrain module of the Gleeble system at 350 °C with a high accumulated true strain of $e = 6.5$. The martensitic transformations and structure were studied using DSC and TEM analysis. The maximum completely recoverable strain was determined by a thermomechanical method. An ultrafine-grained structure with a grain/subgrain size below 100 nm was formed in a bulk nickel-enriched Ti-Ni alloy. The resulting structure provides a completely recoverable strain of 10.5%, which is much higher in comparison with the recrystallized structure (4%).

1. Introduction

Ti-Ni-based shape memory alloys (SMA) are widely used functional materials. Nickel-enriched Ti-Ni SMA, due to the unique combination of their functional and mechanical properties, is one of the most suitable materials for medical applications [1-4].

Severe plastic deformation (SPD) is one of the most effective methods of thermomechanical treatment for the formation of an ultrafine-grained (UFG) structure [4-5]. The best combination of functional and mechanical properties of Ti-Ni SMA can be achieved after formation of a UFG structure. However, this structure was obtained only in thin Ti-Ni samples with a thickness of about 0.1-0.2 mm [6-7]. The development of SPD methods is aimed at searching for new deformation modes, which would allow manufacturing bulk samples containing the UFG structure. The use of equal-channel angular pressing and warm forging allows obtaining only a submicroncrystalline structure in a Ti-Ni SMA [8-9].

It was shown in previous studies that SPD of an equiatomic Ti-Ni SMA in isothermal conditions using the MaxStrain module of the Gleeble system with multi-axial deformation results in the formation of the UFG structure with the average grain/subgrain size down to 55 nm, and in the realization of high functional properties [10-12].

The present work continues previous investigations and is a preliminary study aimed at investigation of the MaxStrain deformation effect on the structure and properties of bulk nickel-enriched Ti-Ni SMA for medical applications.

2. Experimental
In the present work, the nickel-enriched Ti-Ni SMA plate (about 55.9 mass.% Ni) was hot rolled at 900 °C and defined as a reference treatment (RT). Then the specimens were cut and their central part (1 cm³) was deformed by compression with two strikers, then the sample was rotated by 90° around its longitudinal axis and compressed again in the direction perpendicular to the previous compression direction [10]. This cycle was repeated 10 times at an anvil speed of 0.5 mm/s and a constant temperature of 350 °C. The accumulated true strain was e = 6.5.

The characteristic temperatures of martensitic transformations (MT) M_s, M_f (start and finish of forward MT), A_s, A_f (start and finish of reverse MT) were estimated by a Mettler-Toledo DSC at a cooling-heating rate of 10 K/min. The structure was studied using a JEM-2100 transmission electron microscope. The completely recoverable strain ε_r was determined by a thermomechanical method using a bending mode for strain inducing in cold water.

3. Results and Discussion

After RT, the structure can be characterized as a low-defect recrystallized structure with an average grain size of 30-40 microns (Figure 1). The rather large grain size can be explained by the high heating temperature of 900 °C. This structure is homogeneous and mainly consists of uniaxial grains. Black inclusions in Figure 1 are the Ti_2Ni phase, which always remains after smelting in an amount of up to 5% and does not participate in the MT.

The study of the structure and phase composition by transmission electron microscopy was performed after MaxStrain deformation at 350 °C with the accumulated strain e = 6.5. According to the previous experience [10-12], at these low temperatures in such an alloy the process of dynamic polygonization of B2-austenite should develop. Analysis of the bright field of TEM images in Figure 2 reveals that after MaxStrain deformation at 350 °C, the structure consists of equiaxed and elongated nano-sized (70-120 nm) grains and subgrains with a high density of free dislocations (not less than 10¹¹ cm⁻²). At the same time, a cellular substructure and submicroscale areas with a uniform distribution of dislocations are observed as well.

The observed martensite-like parallel plates are crystals of the R-phase, formed upon cooling to room temperature after MaxStrain deformation. The TEM study does not reliably reveal reflexes or images of
the Ti$_3$Ni$_4$ phase due to the very high defectness of the lattice and the extremely small size of the Ti$_3$Ni$_4$ particles. Thus, under this deformation condition as well as at 350 °C, $e = 6.5$, the formation of an UFG structure of B2-austenite is possible.

![Figure 2](image_url)  
Figure 2 – Structure of the nickel-enriched Ti-Ni alloy after MaxStrain deformation at 350 °C, $e = 6.5$. Bright field image and electron diffraction pattern.

The presence of the R-phase after MaxStrain deformation is confirmed by calorimetry (Figure 3). After the RT, only single calorimetric peaks are observed, indicating one-stage of forward and reverse B2$\leftrightarrow$B19$'$ MT. MaxStrain deformation leads to broadening and multiplication of peaks, indicating a two-stage B2$\leftrightarrow$R$\leftrightarrow$B19$'$ transformation. The deformation also shifts the peaks of forward and reverse MT to lower temperatures: from -17 to -70 °C and 13 to -10 °C, respectively, the MT hysteresis becomes larger. The finish temperature of the forward MT is not measured as it is below minus 100 °C.

![Figure 3](image_url)  
Figure 3. DSC curves of nickel-enriched Ti-Ni alloy after RT (a) and MaxStrain deformation (b).

The effect of MaxStrain deformation at 350 °C on the MT sequence and temperatures is defined by two main factors: strong strain hardening and strain aging. Strain hardening suppresses the formation of B19'-martensite while facilitates the formation of the R-phase from B2-austenite. The formation of the Ti$_3$Ni$_4$ phase as a result of strain aging is also favorable for the formation of the R-phase.

The characteristic temperatures can be regulated over a wide range by aging at different temperatures and heating times. The effect of post-deformation annealing after MaxStrain deformation on the structure and properties of a nickel-enriched Ti-Ni alloy needs to be studied in the future.

The completely recoverable strain is an important functional property of Ti-Ni SMA. A calorimetric study reveals that MaxStrain deformation leads to the appearance of B2$\leftrightarrow$R transformation and significant widening of the range of existence of the R-phase (Figure 3). The strain inducing has been started in the R-phase and has an advantage as compared to strain inducing in the B19'-martensite state, because the critical stress for B19'-martensite formation from R-phase (transformation yield stress) is lower than the reorientation stress of thermal B19'-martensite [2].
The results show that after the RT, the value of completely recoverable strain is about 4%. The MaxStrain deformation leads to realization of completely recoverable strain of 10.5%. This result is comparable with the highest values of completely recoverable strain, obtained in previous studies, and much higher than after the RT.

4. Conclusions
The possibility of conduction of the MaxStrain deformation for the nickel-enriched Ti-Ni shape memory alloy was studied. The MaxStrain deformation at a temperature of 350 °C with an accumulated true strain of \( e = 6.5 \) leads to the formation of an ultrafine-grained structure with an average size of structural elements below 100 nm and provides a significant advantage in completely recoverable strain in comparison with the recrystallized structure: 10.5% against 4 %, respectively. The obtained results of preliminary studies indicate that the use of the MaxStrain deformation is promising in terms of the formation of a nanocrystalline structure in bulk samples of a nickel-enriched Ti-Ni shape memory alloy and a corresponding improvement in functional properties.

Acknowledgements
The reported study was funded by RFBR, project number 19-33-60090.

References
[1] Otsuka K, Ren X 1999 Intermetallics 7 5 511-528
[2] Brailovski V, Prokoshkin S, Terriault P, Trochu P 2003 Shape memory alloys: fundamentals, modeling and applications (Montreal: ETS Publ.) p 851
[3] Jani J M, Leary M, Subic A, Gibson M A 2014 Mater. & Des. 56 1078-1113
[4] Resnina N, Rubanik V 2015 Shape memory alloys: properties, technologies, opportunities (Pfäffikon: Trans Tech Publications)
[5] Valiev R Z, Aleksandrov I V 2000 Nanostructural Materials Obtained by Severe Plastic Deformation (Integratsiya, Moscow)
[6] Brailovski V, Prokoshkin S, Inaekyan K and Demers V 2011 J. Alloys Compd. 509 2066-2075
[7] Sundeev R V, Shalimova A V, Glezer A M, Pechina E A, Gorshenkov M V 2018 Phys. Solid State 60 6 1168-1172
[8] Khmelevskaya I Y, Karelin R D, Prokoshkin S D, Isaenkova M G, Perlovich Y A, Fesenko V A, Komarov V S, Zaripova M M 2019 IOP Conf. Ser.: Mater. Sci. Eng. 503 1 012024
[9] Prokoshkin S, Khmelevskaya I, Andreev V, Karelin R, Komarov V., Kazakbiev A. 2018 Mater. Sci. Forum. 918 71-76.
[10] Khmelevskaya I, Komarov V, Kawalla R, Prokoshkin S, Korpala G 2017 J. Mater. Eng. Perform. 26 8 4011-4019.
[11] Khmelevskaya I, Komarov V, Kawalla R, Prokoshkin S, Korpala G 2017 Mater. Today: Proc. 4 3 4830-4835
[12] Komarov V, Khmelevskaya I, Karelin R, Korpala G, Kawalla R, Prokoshkin S 2019 J. Alloys Compd. 797 842-848
[13] Rykлина E P, Polyakova K A, Tabachkova N Y, Resnina N N, Prokoshkin S D 2018 J. Alloys Compd. 764 626-638