Low-temperature processing of Ti-Ni shape memory alloy by E.C.A.P. in shells

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Abstract. The possibility of Ti-50.1 at.% Ni SMA processing by the equal-channel angular pressing (ECAP) in core-shell mode at low deformation temperatures was studied in the present work. The ECAP was performed in steel and iron shells in a temperature range from room temperature to 350 °C. Ti-Ni samples with a diameter of 12 mm were successfully subjected to ECAP for one pass at 200 °C in iron shell with a diameter of 20 mm. Lowering of the deformation temperature both to the 100 °C and to the room temperature leads to the samples distraction during the first ECAP pass. Significant deformation hardening of the sample after one pass of the ECAP in core-shell mode at 200 °C is observed. Increase of the structure defectiveness confirmed by the noticeable broadening of forward (from 26 to 103 °C) and reverse (from 20 to 46 °C) martensitic transformations hysteresis. Values of hardness, distortion yield stress, and ultimate tensile strength after one pass of the ECAP in core-shell mode at 200 °C equals respectively, 275 HV, 1045 and 1200 MPa, that is noticeably higher than the same properties after reference treatment (annealing at 750 °C, 30 min): 176 HV, 520 and 945 MPa.

1. Introduction

Ti-Ni-based shape memory alloys (SMA) are advanced functional materials. They allow implementing performance characteristics that are unachievable using other materials [1-3]. Application of severe plastic deformation (SPD) by equal-channel angular pressing (ECAP) in a process of thermomechanical treatment (TMT) allow considerably improving mechanical and functional properties of Ti-Ni SMA due to formation of an ultrafine-grained (UFG) structure [4-6]. In the study [6] the possibilities of the ECAP application with channel intersection angle of 90° in special shells at the room deformation temperature was shown. ECAP of the sample with a diameter of 3 mm and a length of 40 mm allow noticeably increasing the hardness value of Ti-50.2 at.% Ni alloy from 210 HV before ECAP to 306 HV after one ECAP pass [7-9]. These results reveal perspectives of the ECAP in a core-shell mode for improvement of Ti-Ni SMA properties, particularly strength characteristics. For the further development of the implementation of this ECAP mode it is necessary to increase both the length and the diameter of the sample. For example, it is necessary for implementation of the ECAP in a core-shell mode as a primary operation before the production of long-length rods by the rotary forging, or for application of sample after ECAP in a core-shell mode as a semi-finished product for the manufacturing of small shape memory devices for technical or medical purposes. However, the increase of the core size may have a significant influence on the process of the ECAP. Therefore, in this work, the possibility of ECAP of Ti-Ni SMA bulk samples with the increased diameter of 12 mm in core-shell mode is studied.
2. Materials and methods
In the present work, Ti-50.1 at.% Ni SMA, supplied by Industrial Center MATEK-SMA Ltd., was studied. The billets for ECAP, rods 12 mm in diameter were produced by screw rolling at 850 °C to the diameter of 20 mm and subsequent hot rotary forging at 850 °C to the diameter of 12 mm. Before ECAP samples were annealed at 750 °C for 30 min with cooling in water. This state was also served as a reference treatment (RT). ECAP was carried out with a channel intersection angle of 120°. Low-carbon steel and pure iron were used as a material for shells production. The schematic representation of core-shell samples appearance is shown in Figure 1.

![Schematic representation of core-shell samples](image)

**Figure 1.** Schematic representation of core-shell samples I: steel shell with Ti-Ni core (a), pure iron shell with Ti-Ni core (b), dimensions in mm.

The applied regimes of the ECAP in core-shell mode are shown in Table 1.

| No. | Heating temperature, °C | Container temperature, °C | Number of passes | Shell material | Notation |
|-----|-------------------------|----------------------------|------------------|----------------|----------|
| 1   | 350                     | 350                        | 1                | steel          | S-350-350 |
| 2   | -                       | 330                        | 1                | steel          | S-/-350   |
| 3   | -                       | RT                         | 1                | steel          | S-/-RT    |
| 4   | -                       | RT                         | 1                | pure iron      | I-/-RT    |
| 5   | 100                      | 100                        | 1                | pure iron      | I-100-100 |
| 6   | 200                      | 200                        | 1                | pure iron      | I-200-200 |

The Vickers hardness measurements were carried out at a room temperature using the LECOM 400-A tester under load of 1 N. The mechanical properties were determined at a room temperature by the uniaxial tensile tests using the universal tensile machine INSTRON 3382 with a deformation rate of 2 mm/min. The following mechanical parameters were determined: critical stress for martensite reorientation (transformation yield stress) \( \sigma_{cr} \), dislocation yield stress \( \sigma_d \), ultimate tensile strength \( \sigma_u \), elongation to failure \( \delta \). Temperature ranges of martensitic transformations (MT) were studied using the Mettler Toledo calorimeter. Starting and finishing temperatures of forward MT \( M_s \) and \( M_f \), starting temperature of B2 to R transformation \( T_h \), starting and finishing temperatures of reverse MT \( A_s \) and \( A_f \)
were determined. The error limits of the reported values are as follows: ±15 MPa for $\sigma$, ± 9 for HV, ± 1.4 % for $\delta$, ± 3.0 °C for temperatures of martensitic transformations.

3. Results and discussion

3.1 ECAP Procedure

ECAP in core-shell mode, at the first stage, was carried out in the carbon steel shells with a diameter of 20 mm and a length of 115 mm. The length of the Ti-Ni sample, used as a core, was 100 mm. ECAP was carried out in three regimes, indicated above in table 1. Only one pass was conducted for each of the studied regimes. After regimes S-350-350 and S-//-350 samples of Ti-Ni SMA was successfully pressed, while steel shells were destructed. After regime S-//-RT both the Ti-Ni sample and the steel shell were destructed. Images of Ti-Ni cores and shells appearance after ECAP are shown in Figure 2.

![Figure 2](image.png)

**Figure 2.** Image of Samples of Ti-50.1 at.% Ni subjected to ECAP in core-shell mode in steel shells.

These experiments showed that it is necessary to apply another shell material, since low-carbon steel has insufficient plasticity at used deformation temperatures, because after all investigated ECAP regimes, the shell was destroyed during the first pass. Therefore, at the second stage, ECAP was carried out with the appliance of pure iron shells with a diameter of 20 mm and a length of 95 mm. The length of the Ti-Ni sample was also decreased to the 80 mm. The size of a shell and a core was decreased based on the previous experiment to minimize the probability of top die damage. Conduction of the ECAP in core shell mode at a room temperature without preliminary heating (I-//-RT) and at a temperature of 100 °C (I-100-100) led to the destruction of Ti-Ni core, while the integrity of the shells was preserved. Successful processing of the Ti-Ni sample was carried out at a temperature of 200 °C for 1 pass (I-200-200). Images of the sample and the iron shell before pressing and after partial shell removing after ECAP are shown in Figure 3.
3.2 Vickers hardness tests results
Results of Vickers hardness test are performed as a diagram in Figure 4.

Figure 4. Vickers hardness test results for Ti-50.1 at. % Ni SMA after studied regimes of the ECAP in core-shell mode.

Analyses of the obtained results reveals that maximum hardness value is observed after ECAP regime I-200-200. Pressing at the room temperature is accompanied with the core destruction, that does not allow to completely reinforce the core along the full length. Deformation in steel shells at higher deformation temperatures does not allow to achieve higher hardness value due to development of dynamic softening processes. Accordingly, the lowest deformation temperature for ECAP of Ti-Ni SMA core with a diameter of 12 mm in core-shell mode, that does not lead to core distraction and allow significantly improving hardness value after only one ECAP pass, is 200 °C. Hardness value increases from 176 HV to 275 HV as compared to RT. The closed hardness values for near-equiaxotic Ti-Ni...
SMA were previously obtained in samples with ultrafine grained structure and high values of properties after MS-deformation [10], quasi-continuous ECAP [11, 12] and rotary forging [13]. Therefore, further studies were carried out only for the I-200-200 ECAP regime.

3.3 Differential scanning calorimetry
DSC curves of samples after RT and I-200-200 ECAP regime are shown in Figure 5. Defined temperatures of forward and reverse martensitic transformation are shown in Table 2.

![DSC curves](image)

**Figure 5.** Results of differential scanning calorimetry of Ti-50.1 at.% Ni SMA subjected RT (a) and ECAP in core-shell mode at the temperature of 200 °C for 1 pass (b).

**Table 2** Temperature range of martensitic transformation of samples after RT and ECAP in core-shell mode.

| Treatment | $T_r$, °C | $T_{f\text{Peak}}$, °C | $M_s$, °C | $M_{Peak}$, °C | $M_f$, °C | $A_s$, °C | $A_{Peak}$, °C | $A_f$, °C | Hysteresis of forward MT, °C | Hysteresis of reverse MT, °C |
|-----------|----------|-----------------------|-----------|----------------|-----------|----------|--------------|----------|--------------------------|--------------------------|
| Reference | -        | -                     | 40        | 32             | 24        | 52       | 68           | 72       | 26                        | 20                       |
| ECAP in core-shell mode, 200 °C, 1 pass | 65       | 28                    | 10        | -18            | -38       | 16       | 47           | 62       | 103                      | 46                       |

After the RT the typical for the defect-free recrystallized near-equiatomic Ti-Ni SMA DSC curves are observed: the single-stage forward and reverse MTs with sufficiently narrow transformation hysteresis are occurred. The ECAP in core-shell mode is accompanied with the sharp increase of structure defectiveness, that confirmed by the noticeable broadening of forward (from 26 to 103 °C) and reverse (from 20 to 46 °C) hysteresis of MT. The staging of the forward MT changes, it occurs through an intermediate R-phase, which also correlates with the high structure defectiveness due to deformation hardening after ECAP.

3.4 Tensile test results
Mechanical properties of near-equiatomic Ti-Ni SMA samples after I-200-200 ECAP and RT regimes, obtained by tensile tests, are shown in Table 3. Representative stress-strain diagrams after ECAP and RT are shown in Figure 6.
Figure 6. Typical tensile diagrams of Ti-Ni near-equiatomic SMA after RT, ECAP in core-shell mode at 200 °C for 1 pass and ECAP + PDA at 200 °C, 1h.

Table 3. Mechanical properties of Ti-Ni near-equiatomic SMA after RT, ECAP in core-shell mode at 200 °C for 1 pass and ECAP + PDA at 200 °C, 1h.

| Treatment                                           | \( \sigma_{cr} \) (MPa) | \( \sigma_y \) (MPa) | \( \sigma_u \) (MPa) | \( \delta \) (%) |
|-----------------------------------------------------|--------------------------|----------------------|----------------------|------------------|
| Reference                                           | -                        | 520                  | 945                  | 105              |
| ECAP in core-shell mode, 200 °C, 1 pass              | -                        | 1045                 | 1200                 | 23               |
| ECAP in core-shell mode, 200 °C, 1 pass + PDA at 200 °C, 1 h | 150                      | 995                  | 1290                 | 34               |

Based on the obtained results, a considerable increase in the strength characteristics should be noted: the dislocation yield stress \( \sigma_y \) and ultimate tensile strength \( \sigma_u \) increases from 520 MPa and 945 MPa after RT to 1045 MPa and 1200 MPa, respectively, after I-200-200 ECAP regime. The obtained values exceed the strength characteristics, formed after quasi-continuous ECAP with a channel intersection angle of 120° at a temperature of 400 °C in 7 passes without using a shell, previously studied in [11]. Therefore, it can be concluded that ECAP in core-shell mode is a promising regime of TMT in case of possibilities to improve mechanical and functional properties of the Ti-Ni SMA.

4. Summary

Ti-Ni samples with a diameter of 12 mm were successfully subjected to ECAP for one pass at 200 °C in iron shell with a diameter of 20 mm. Lowering of the deformation temperature both to the 100 °C and to the room temperature leads to the sample distraction during the first ECAP pass. Studies of the temperature range of martensitic transformations, mechanical and functional properties, reveals significant deformation hardening of the sample after one pass of the ECAP in core-shell mode at 200 °C. Increase of the structure defectiveness confirmed by the noticeable broadening of forward (from 26 to 103 °C) and reverse (from 20 to 46 °C) hysteresis of martensitic transformations. Values of hardness, dislocation yield stress, and ultimate tensile strength after one pass of the ECAP in core-shell mode at 200 °C equals respectively, 275 HV, 1045 and 1200 MPa, that is noticeably higher than the same properties after reference treatment: 176 HV, 520 and 945 MPa.
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