Effect of True Strains in Isothermal \textit{abc} Pressing on Mechanical Properties of Ti$_{49.8}$Ni$_{50.2}$ Alloy

Oleg Kashin*, Konstantin Krukovskii, Aleksandr Lotkov and Victor Grishkov

Institute of Strength Physics and Materials Science of the Siberian Branch of the Russian Academy of Sciences, 634055 Tomsk, Russia; kvk@ispms.tsc.ru (K.K.); lotkov@ispms.ru (A.L.); grish@ispms.tsc.ru (V.G.)

* Correspondence: okashin@ispms.ru; Tel.: +7-3822-286-920

Received: 14 August 2020; Accepted: 28 September 2020; Published: 30 September 2020

Abstract: The paper analyzes the microstructure and mechanical properties of Ti$_{49.8}$Ni$_{50.2}$ alloy (at.-%) under uniaxial tension at room temperature after isothermal \textit{abc} pressing to true strains $e = 0.29 - 8.44$ at $T = 723$ K. The analysis shows that as the true strain $e$ is increased, the grain–subgrain structure of the alloy is gradually refined. This leads to an increase in its yield stress $\sigma_y$ and strain hardening coefficient $\theta = d\sigma/d\varepsilon$ at linear stage III of its tensile stress–strain curve according to the Hall–Petch relation. However, the ultimate tensile strength remains invariant to such refinement. The possible mechanism is proposed to explain why the ultimate tensile strength can remain invariant to the average grains size $(d_{av})$. It is assumed that the sharp increase of the ultimate tensile strength $\sigma_{UTS}$ begins when $(d_{av})$ is less than the critical average grain size $(d_{av})_{cr}$. In our opinion, for the investigated alloy $(d_{av})_{cr} \approx 0.5 \mu$m. In our study, the attained average grain size is larger the critical one. The main idea of the mechanism is next. In alloys with an average grain size $(d_{av})$ less than the critical one, a higher external stress is required for the nucleation and propagation of the main crack.

Keywords: TiNi; isothermal \textit{abc} pressing; mechanical properties; average grain–subgrain size

1. Introduction

The capability of TiNi-based alloys for thermoelastic martensite transformations, which lie behind their superelasticity and shape memory, makes them beneficial for use in engineering and medicine [1–4]. In practical terms, it is often required that such alloys be mechanically strong. One of the ways of increasing the yield stress and ultimate strength of these alloys is to refine their grain structure down to submicro- and nanoscales with no change of chemical composition. Such refinement is possible by conventional forming (hot and cold rolling, extrusion, rotary forging) and by severe plastic deformation (equal channel angular pressing [5–7], high pressure torsion [5,8,9], \textit{abc} pressing [10–16]), of which the former can provide a nanocrystalline and even an amorphous structure in the alloys while the latter with its constrained conditions allows more efficient transformations of their grain–subgrain and dislocation structures. However, to take full advantage of TiNi-based alloys, we should understand the mechanisms of their grain–subgrain transformation by severe plastic deformation (SPD) and the SPD effect on their functional and mechanical properties. After SPD transformation, TiNi-based alloys normally show a certain increase in their yield stress and ultimate tensile strength, but for attaining the record-breaking strength characteristics at the least cost, we should know what SPD modes (strain temperature, total true strain) can impart a desired grain structure to one or another type of this material.

Despite abundant research data [5–31], it is still unclear what threshold holds for the average grain size below which the ultimate tensile strength of TiNi-based alloys shows an efficient increase and how this increase is contributed by grain size distributions. In many of the works cited above, it is shown that a grain structure in which regions with different average grain sizes $(d_{av})$ (coarse-
grained, submicrocrystalline, nanocrystalline) coexist after SPD of TiNi-based alloys. The different volume fraction of such areas, as well as the uniformity of the distribution of such areas over the volume of the material can significantly affect its mechanical properties. The study of this influence is one of the tasks of this work. Some TiNi-based alloys still need a study to clarify their strain characteristics in relation with average grain sizes. All the foregoing is true for \( \text{abc} \) pressed TiNi-based alloys, among which only two have been examined in terms of the above issues: non-aging Ti\(_{50.2}\)Ni\(_{50.2}\) at 423 K and Ti\(_{50.8}\)Ni\(_{50.2}\) [10]. Hereinafter the alloy composition is given in at.\%.

In particular, Ti\(_{50.8}\)Ni\(_{50.2}\) with an initial grain size of 20–70 µm was \( \text{abc} \) pressed in steps, each at a true strain \( \varepsilon = 3.6 \) but at a different temperature in order of its gradual decrease from 873 to 573 K [11], such that each pressing event could be considered as transforming a different grain–subgrain structure. When \( \text{abc} \) pressed at 873 and 773 K, the alloy remained coarse-grained (5–10 µm), and when the temperature was decreased to below 673 K, its bulk was represented by submicrocrystalline grains sized to 100–700 nm with a small amount of nanograins sized to 20–100 nm. In the alloy \( \text{abc} \) pressed in the same way at \( \varepsilon = 7.7 \) and 573 K, the volume fraction of its nanostructural elements of size 20–50 nm was about 30\% [12,13].

At \( \varepsilon = 8.44 \), was reached after \( \text{abc} \) pressing at 723 K [14–16], the alloy was dominated by a submicrocrystalline structure with a noticeable nanograin fraction, residing mainly around coarse precipitation of the TiNi type, and at this temperature (723 K), intensive recovery processes occurred.

In Ti\(_{50.8}\)Ni\(_{50.2}\) \( \text{abc} \) pressed at 423 K and 673 K [10], tangled dislocations whose density increased with increasing the true strain were found after \( \text{abc} \) pressing at 423 K but no quantitative estimates of the dislocation density were presented. No estimates were also taken of the average size and volume fraction of grains sized to \( ~20 \) nm found in the alloy microstructure after \( \text{abc} \) pressing at 423 K. It was reported that the \( \text{abc} \) pressing temperature 673 K provided a dynamic recovery in the alloy by rearrangement and lowering of high density dislocations, the formation of dislocation-free recrystallized grains with a random grain size distribution, whose pattern was not given.

In Ti\(_{50.8}\)Ni\(_{50.2}\) \( \text{abc} \) pressed to grain–subgrain sizes of 2–40 µm at 873 K, the true ultimate tensile strength under uniaxial tension at room temperature measured 1560 MPa [13] and decreased to 1450 MPa when the alloy was further pressed to grain–subgrain sizes of 100–700 nm at 723 K. It was concluded that the ultimate tensile strength of the alloy was little influenced by the grain–subgrain size varying from coarse-crystalline to submicrocrystalline [13].

In Ti\(_{50.8}\)Ni\(_{50.2}\) \( \text{abc} \) pressed at 673 K, the true ultimate tensile strength \( \sigma_{\text{UTS}} \) increased from 1320 to 1490 MPa as the strain \( \varepsilon \) was increased from 1.5 to 6 [10]. Decreasing the \( \text{abc} \) pressing temperature to 423 K increased the true ultimate tensile strength \( \sigma_{\text{UTS}} \) to 1550 MPa at \( \varepsilon = 2.2 \) and to 1700 MPa at \( \varepsilon = 9.0 \). It was concluded that the high strength and the small elongation to fracture in the \( \text{abc} \) pressed material was governed by strain hardening through the formation of a tangled substructure with a high dislocation density and that the lower values of \( \sigma_{\text{UTS}} \) after \( \text{abc} \) pressing at 673 K was due to recovery processes [10].

Thus, the available experimental data give only an idea of the main trends of structural transformations in \( \text{abc} \) pressed non-aging TiNi alloys with a near-equiatomic composition but the relation between their structure and mechanical properties remains unclear.

In this context, our aim here is in providing systematic experimental data from which to judge the effect of isothermal \( \text{abc} \) pressing at 723 K on the grain size in Ti\(_{50.8}\)Ni\(_{50.2}\) at different true strains \( \varepsilon \) and the effect of its grain–subgrain structure on its yield stress, ultimate tensile strength, and deformation behavior at room temperature. As shown in [11–16], at room temperature an alloy of this composition contains a high temperature phase B2, an intermediate martensitic R-phase with a rhombohedral crystal lattice, and a martensitic B19′ phase with a monoclinic crystal lattice.

Typically, the Ti\(_{50.8}\)Ni\(_{50.2}\) alloy is considered as non-aging one. The probability formation of TiNi phase precipitates in this alloy during thermomechanical treatments is small. We suggest that the volume fraction of these precipitates is small and will not affect the properties of the alloy. The temperature 723 K, being much higher than \( \text{M}_s \) (\( \text{M}_s \) is the maximum temperature at which a martensitic transformation of B2(R)→B19′ induced by an external applied stress is possible), provides
pressing in the B2 phase of the alloy, its recovery processes, and a substantial decrease in its internal stresses.

Note that studying the structure and properties of TiNi-based alloys after abc pressing not only extends our knowledge of the capabilities of SPD processes but it can also identify proper technological modes of manufacturing various TiNi products, the more so as abc pressing is applicable to large-sized billets.

2. Materials and Methods

The test material was Ti_{49.8}Ni_{50.2} alloy (hereinafter the alloy composition is given in at.%) supplied as bars of diameter 20 mm (MATEK-SMA Ltd., Moscow, Russia). The bars were cut into cylindrical segments of length 25 mm which were then forged in three mutually perpendicular directions at 1123 K to obtain cubic specimens sized to about 20 × 20 × 20 mm³. The cubic specimens, hereinafter referred to as initial, were abc pressed in a die at 723 K (0.46 T_mel). A hydraulic press MIS-6000 K (MISIS, Moskow, Russia) with a force of 600 tons was used to perform deformation during abc pressing. At this temperature, the B2 phase of the alloy has a low plastic strain resistance such that the die after abc pressing remains intact. As has been shown [16,21,22], equal channel angular pressing at 723 K provides an ultrafine-grained structure in Ti_{49.8}Ni_{50.2} and a substantial increase in its mechanical properties. Applying abc pressing at 723 K to Ti_{49.8}Ni_{50.2} allows us to compare the different SPD methods in terms of the effect on the grain–subgrain structure of the alloy and on its yield stress and ultimate tensile strength.

The initial specimens placed in dies were kept in a furnace at 723 K for 10 min and were then hydraulically pressed with a rate of 0.16–0.18 s⁻¹. Each pressing cycle was a sequence of three mutually perpendicular compression events. Once compressed in one direction, the specimens were removed from the dies and were again placed in them without cooling so that the next compression event would be perpendicular to the previous one. At the end of each compression event, the specimen temperature decreased by no more than 10 K. Before each event, the dies with the specimens were heated to 723 K. The true strain in the specimens singly pressed in one direction was from ε = 0.15 to ε = 0.30. Its values 0.29, 0.62, 1.82, 4.15, 6.44, and 8.44 were attained by repeating the cycle of abc pressing.

For tensile tests, the abc pressed specimens were shaped as a dumbbell with a gage area of 7 × 1 × 1 mm² on an electrical discharge machine (Del'ta-test Ltd., Moscow, Russia), hand polished with silicon carbide abrasives gradually decreasing in roughness to 1200, and electrolytically polished in a mixture of acetic (Reahim Ltd., Moscow, Russia) and perchloric acids (Reahim Ltd., Moscow, Russia) with a ratio of 70:30. The tensile tests were performed at room temperature on a Walter + Bai AG LFM-125 testing machine (Walter + Bai AG, Löningen, Switzerland) with Dionpro software (Version 7, Walter + Bai AG, Löningen, Switzerland). The rate of movement of the mobile gripper of testing machine was constant and was 0.007 mm/s. For a sample with a working base length of 7 mm, this corresponds to an initial relative strain rate of 10⁻³ s⁻¹. For each true strain after abc pressing, four to six specimens were tested.

The temperature of martensite transformations were determined by an experimental setup (ISPMS SB RAS, Tomsk, City, Russia). The measurement method is described in details in [15].

The microstructure of the alloy was examined by light optical microscopy (Zeiss Axiovert-200M, (Carl Zeiss AG, Oberkochen, Germany) and by scanning and transmission electron microscopy (Zeiss LEO EVO 50 XVP (Carl Zeiss AG, Oberkochen, Germany) and JEM-2100 (JEOL Ltd., Tokyo, Japan) provided by Tomsk Regional Center for Collective Use TSC SB RAS).

The specimens for optical and SEM microstructure studying were cut using an electric discharge machine along the plane passing through the specimen center and parallel to any two arbitrary opposite edges of the specimen. Such cross section provided analysis of the specimen microstructure in its overall bulk. After cutting, the specimen surfaces were mechanically polished using a Saphir 350 (Audit Diagnostics, Bussiness & Technology Park, Carrigtwohill. Co. Cork, Ireland) grinder, and then they were chemically etched and electrolytically polished.
Transmission electron microscopy TEM microstructure studying was performed using thin foils. Thin plates with a thickness of 0.2 mm were cut from the blanks obtained after abc pressing in the selected section using an electric discharge machine. Finally, the specimen thinned electrolytically.

3. Results

3.1. Martensite Transformation Temperatures and Phase States

Figure 1 illustrates the martensitic transformations temperatures after abc pressing with various true strain. Here \( M_s \) and \( M_f \) are the start and finish temperatures of the direct martensitic transformation \( B2(R) \rightarrow B19' \) at cooling, respectively; \( A_s \) and \( A_f \) are the start and finish temperatures of the reverse martensitic transformation at heating, respectively; \( T_R \) is the start temperature of the martensitic transformation \( B2 \rightarrow R \) at cooling. The dotted line on Figure 1 shows the tensile test temperature \( T_{\text{test}} \).

![Figure 1. Martensite transformation temperatures versus true strain in Ti\textsubscript{49.8}Ni\textsubscript{50.2} after abc pressing.](image)

As can be seen from Figure 1, the temperatures of direct (at cooling) and reverse (at heating) martensite transformations in Ti\textsubscript{49.8}Ni\textsubscript{50.2} are almost independent of its true strain after abc pressing (as in Ref. [15]). Its direct martensite transformation, irrespective of the true strain, proceeds as \( B2 \rightarrow R \rightarrow B19' \). It is also seen that the state of all specimens at room temperature corresponds to the interval between the martensite start and finish temperatures \( M_s \) and \( M_f \).

3.2. Microstructure

Figures 2 and 3 present the microstructures for Ti\textsubscript{49.8}Ni\textsubscript{50.2} before and after abc pressing to \( e = 8.44 \). The data exemplify that the bulk of all specimens is occupied by B19’ martensite (Figures 2c and 3b) with a small (5–10 vol.\%) amount of R (Figure 2f) and B2 phases (Figures 2f and 3b) which fail to transform to B19’ on cooling to room temperature.
When shaped at 1123 K, the specimens acquire an inhomogeneous grain–subgrain structure (Figure 2). At room temperature, their bulk is represented by grains with an average size of about 40 µm which contain twinned B19′ domains with an average size of about 1.5 µm.

Increasing the true strain in abc pressed Ti49.8Ni50.2 gradually decreases the average grain size. However, up to $e = 4.15$, the material bulk reveals coarse grains of up to 40 µm with a developed dislocation substructure. At $e = 4.15$, its structure is represented by coarse and fine grains. The volume fraction of submicrocrystalline grains with $d \leq 1$ µm is no greater than 5 vol.%.

At $e = 8.44$, the material bulk has a submicrocrystalline structure with a grain–subgrain size of 0.1–1.5 µm which shows up as quasi-ring microdiffraction patterns (Figure 3). At the same time, there are individual grains of up to 5 µm. At $e = 8.44$, the volume fraction of submicrocrystalline grains with $d \leq 1$ µm, including nanograins, increases to ~20 vol.%. The estimated average grain size is $\approx 1.0$ µm.
3.3. Mechanical Properties

Figure 4 shows the typical engineering tensile stress–strain curves of Ti$_{49.8}$Ni$_{50.2}$ before and after abc pressing to different true strains. There are four stages of the strain–stress curve (as in Ref. [32]), the length of which was determined graphically. The initial stage I corresponds to quasi-elastic loading, stage II—pseudo-yield plateau, stage III—quasi-linear stage of strain hardening, ending with a yield stress, stage IV corresponds to parabolic hardening up to the ultimate tensile strength. There is some transition area between the stages.

![Figure 3](image1.png)

**Figure 3.** Structure of Ti$_{49.8}$Ni$_{50.2}$ abc pressed to $\varepsilon = 8.44$: (a) TEM image, (b) diffraction pattern.

![Figure 4](image2.png)

**Figure 4.** Engineering tensile stress–strain curves of Ti$_{49.8}$Ni$_{50.2}$ before abc pressing (1) and after abc pressing to $\varepsilon = 0.29$ (2), 0.62 (3), 1.82 (4), 4.15 (5), 6.44 (6), and 8.44 (7).

It is seen that at early quasi-elastic stage I, the curves are almost coincident. Figure 5 show the average mechanical properties of Ti$_{49.8}$Ni$_{50.2}$ estimated from its respective stress–strain curves. Within the spread of values, the pseudo-yield stress $\sigma_{m}$ (martensite shear stress) depends little on the true strain set for abc pressing and measures about 180 MPa (Figure 5a, curve 4). The extent of the pseudo-yield plateau (Figure 4, stage II) varies from 3 to 8%, showing no correlation with the true strain.
The average ultimate strength of *abc* pressed Ti<sub>49.8</sub>Ni<sub>50.2</sub> depends weakly on the true strain and measures $\sigma_{UTS} \approx 1000$ MPa (Figure 5a, curve 1), which is about 10% higher than its value before *abc* pressing.

The uniform elongation $\delta_{UTS}$ and the elongation to fracture $\delta_{total}$ vary slightly up to $\varepsilon = 4.15$ (Figure 5a curves 2, 3), and as the true strain is increased to $\varepsilon = 8.44$, these characteristics decrease steeply (2.5 and 1.5 times, respectively).

The pseudo-yield plateau is followed by a gradual transition to quasi-linear stage III (Figure 4) at which the strain hardening coefficient $\theta = \delta e / \delta \varepsilon$ increases with the true strain set for *abc* pressing (Figure 5b, curve 2). The stress at which linear stage III ends also increases, which corresponds to the yield stress $\sigma_y$ in Ti<sub>49.8</sub>Ni<sub>50.2</sub> in its martensite state (Figure 5b, curve 1).

**Figure 5.** Mechanical characteristics of Ti<sub>49.8</sub>Ni<sub>50.2</sub> versus true strain after *abc* pressing: (a) 1—ultimate tensile strength, 2—elongation to fracture, 3—uniform elongation, 4—pseudo-yield stress; (b) 1—yield stress $\sigma_y$, 2—strain hardening coefficient $\theta$.

Linear stage III is followed by parabolic hardening stage IV (Figure 4). This deformation stage for all test specimens, except for those *abc* pressed to $\varepsilon = 8.44$, is rather long, measuring several tens of percent. In Ti<sub>49.8</sub>Ni<sub>50.2</sub> *abc* pressed to $\varepsilon = 8.44$, the parabolic stage is very short: about 2%.

Once the test specimens reach their maximum stress (ultimate tensile strength $\sigma_{UTS}$), they are involved in strain localization with necking such that their tensile stress–strain curves reveal a steep decrease in the stress which culminates in fracture. In Ti<sub>49.8</sub>Ni<sub>50.2</sub> *abc* pressed to $\varepsilon = 8.44$, the final deformation stage differs from what is observed in the other specimens: the stress first decreases noticeably, then weakly and slowly, and then again rapidly up to eventual fracture.

### 4. Discussion

Our experiments show that increasing the true strain up to $\varepsilon = 8.44$ in Ti<sub>49.8</sub>Ni<sub>50.2</sub> *abc* pressed at 723 K weakly influences the temperatures of its martensite transformations, martensite shear stress $\sigma_m$, and ultimate tensile strength $\sigma_{UTS}$. At the same time, the true strain in *abc* pressed Ti<sub>49.8</sub>Ni<sub>50.2</sub> greatly influences its yield stress $\sigma_y$, strain hardening coefficient $\theta$ at the third stage of its tensile stress–stress curve (Figure 4, stage III), uniform elongation $\delta_{UTS}$, and elongation to fracture $\delta_{total}$.

The same martensite shear stress $\sigma_m$ irrespective of the true strain is expectable because $\sigma_m$ depends on the difference between $T_{\text{od}}$ and $M_s$ and these temperatures remain the same at all true strains used in *abc* pressing (Figure 1). Analysis of our studies and others available suggests that when deformed by SPD methods to large strains at a temperature of 673–723 K, non-aging binary TiNi alloys with a Ni content of 50.0–50.2 at.% assume mostly a submicrocrystalline grain–subgrain structure [10–16]. At these temperatures, their deformation is accompanied by efficient relaxation which makes them free of any appreciable internal stress [10,15]. For an average grain–subgrain size of 0.5–1.0 µm, the martensite shear stress $\sigma_m$ lies in the range 180–200 MPa, and for 0.1–0.3 µm, its value increases to about 300 MPa. It is significant that such features are observed not only after *abc* pressing [10,13] but after equal channel angular pressing as well [19–22]. Unfortunately, we have not found any data on the formation of a nanocrystalline structure in Ti<sub>49.8</sub>Ni<sub>50.2</sub> by one or another SPD
method. However, such a structure with an average grain size of 16 nm has been obtained in Ti\textsubscript{50.2}Ni\textsubscript{49.8} wires after cold drawing and annealing at 623 K [33,34], with the result that the material on its stress–strain dependence at room temperature reveals an increase in the pseudo-yield stress to $\sigma_m = 515$ MPa. The increase in $\sigma_m$ can be explained by substantial hardening during the so appreciable grain–subgrain refinement, which should inevitably decrease the B2--B19’ start temperature and increase $\sigma_m$ at room temperature.

From the results presented [10–16,19–22,33,34] it follows that in Ti\textsubscript{50.2}Ni\textsubscript{49.8} free of appreciable internal stress, the average grain–subgrain size has a critical value ($d_{av}$)$_c$ = 0.5 $\mu$m with respect to the pseudo-yield stress $\sigma_m$. When the material structure is refined to an average grain–subgrain size $d_{av}$ $\geq$ 0.5 $\mu$m, the pseudo-yield stress $\sigma_m$ remains almost unchanged, and when the average grain–subgrain size goes down to $d_{av} < 0.5$ $\mu$m, the pseudo-yield stress $\sigma_m$ increases such that the lower the size $d_{av}$, the higher the value of $\sigma_m$.

When the pseudo-yield stage ends, all processes associated with martensite transformations to B19 and martensite domain reorientation under external load are mostly completed, showing no effect on the further deformation of the alloy. Each true strain in abc pressing provides the alloy with a specific structure which naturally evolves as the true strain is increased. However, if another external load with another temperature and rate is applied to the alloy after abc pressing, e.g., uniaxial tension at room temperature (like in our case), the earlier formed structure becomes initial such that those dislocations which participate in its deformation during abc pressing are ineffective under further uniaxial tension. After induced phase transformations, the tensile deformation of the alloy at stage III is provided by new dislocations whose nucleation and motion depend on the structure formed by abc pressing: on the size of its grains, subgrains, and fragments, on the spatial location and density of dislocations inside its elements and boundaries, and on the state of its interfaces [35]. Our experiments suggest that these characteristics, excepting the average grain–subgrain size, vary little with true strains in abc pressing due to recovery processes. Thus, the new dislocation substructure in the abc pressed alloy under tension develops against the background of about the same grain–subgrain microstructure at all trues strains used.

For many metals and alloys, including SPD ones, the yield stress $\sigma_y$ obeys the empirical Hall–Petch relation [36–38]:

$$\sigma_y = \sigma_0 + k \; d_{av}^{-1/2},$$

(1)

where $\sigma_0$ is the lattice friction stress of a material (its constant), $k$ is the Hall–Petch coefficient, and $d_{av}$ is the average grain–subgrain size.

If roughly the same grain–subgrain microstructure is formed by abc pressing irrespective of the true strain, the dependence of the yield stress on the average grain–subgrain size $d_{av}$ should follow the Hall–Petch relation. The assumption can be verified by estimating $d_{av}$ from our data obtained by different types of microscopy (optical, TEM, SEM, electron back scatter diffraction). The estimates show that for the initial specimens before abc pressing, $d_{av} = 40$ $\mu$m, and for those abc pressed to $e = 8.44$, $d_{av} = 1.0$ $\mu$m. Figure 6a demonstrates how the average grain–subgrain size $d_{av}$ depends on the true strain $e$ in abc pressing, which agrees well with data reported elsewhere [19]. Figure 6b shows the $d_{av}^{-1/2}$ dependence of $\sigma_y$ plotted from the estimates of $d_{av}$. As can be seen, the dependence is well approximated by a straight line, except for $\sigma_y$ in the initial specimens and specimens with $e = 0.29$, and this dependence is fitted well by data reported for Ti\textsubscript{50.2}Ni\textsubscript{49.8} with $d_{av} = 0.19$ $\mu$m and $\sigma_y = 1270$ MPa after six cycles of equal channel angular pressing at 723 K [22].
It is considered that behind the main grain size effect on the yield stress of metals and alloys lies dislocation retardation by internal interfaces: the finer the grain size, the larger the number of interfaces and the shorter the free path of mobile dislocations [39]. In our study, the Hall–Petch relation holds for grain refinement in abc pressed Ti$_{49.8}$Ni$_{50.2}$, suggesting that the main deformation mechanism at stage III is the nucleation and motion of new dislocations and that the yield stress $\sigma_y$ is determined mainly by the average grain–subgrain size.

The $d_{av}^{-1/2}$ dependence of the strain hardening coefficient $\theta$ is also well approximated by a straight line, except for $\theta$ at the initial true strains in abc pressing (Figure 6b). The same behavior of $\theta$ in relation to $\epsilon$ is observed in submicrocrystalline Ti$_{49.8}$Ni$_{50.2}$ after equal channel angular pressing [19] and in nanocrystalline Ti$_{49.8}$Ni$_{50.2}$ with a maximum grain size no greater than 40 nm after cold drawing and annealing [33,34]. In the former case, the strain hardening coefficient is close to our values, and in the latter, it is 3-4 times higher.

In all test specimens of Ti$_{49.8}$Ni$_{50.2}$, the ultimate strength $\sigma_{UTS}$ is scarcely affected by the true strain in abc pressing. In other words, it remains constant as $d_{av}$ decreases from $\approx 40 \mu m$ to $\approx (1.0 \pm 0.5) \mu m$. Figure 7 shows the ultimate tensile strength $\sigma_{UTS}$ versus the average grain–subgrain size $d_{av}$ in Ti$_{49.8}$Ni$_{50.2}$ abc pressed in our study (open circles) and in Ti$_{49.8}$Ni$_{50.2}$ exposed to other types of large plastic deformation with attendant recovery processes (solid symbols) [19,22,33,34]. In the cited studies, the average grain sizes were much smaller than those reported here, and in view of their experimental conditions [19,22,33,34], it may be considered that the respective data were obtained for alloy microstructures similar to the one formed by abc pressing or for alloy specimens of the very approximate composition but with different average grain–subgrain sizes.

In view of the above assumptions, the $d_{av}$ dependences of $\sigma_{UTS}$ suggest the existence of a critical value $(d_{av})_{cr} \approx 0.5 \mu m$, which is more evident from the inset in Figure 7 at higher magnification. On engineering tensile diagrams, $\sigma_{UTS}$ means a maximum external stress responsible either for instantaneous failure (brittle fracture) or for macroscale strain localization with necking and eventual failure (ductile fracture). In both cases, the fracture surface of materials may show brittle elements (cleavages, quasi-cleavages) and ductile elements (dimple rupture) but their fracture, irrespective of this, is preceded by the formation of a critical crack which becomes a main one. The nucleation of cracks is due to local internal stresses which result from incompatibilities induced by plastic deformation under external stresses [35]. At a certain level of external stresses, such cracks can merge into a main one. If grains-subgrains of size larger than critical are present in a material, internal stresses sufficient for stable crack nucleation can arise at a certain external stress. Apparently, the critical grain–subgrain size in our case lies between 1 to 5 $\mu m$ and the external stress measures about 1000 MPa. It is not improbable that the volume fraction of grains-subgrains larger than critical can also be a contributor.
Figure 7. Ultimate strength versus average grain–subgrain size in Ti49.8Ni50.2 exposed to different types of large plastic deformation.

When the size of grains-subgrains become smaller than critical, higher external stresses are needed to provide internal stresses sufficient for stable crack nucleation. The question of why this happens so is a separate research issue.

5. Conclusions

The results of our study into the mechanical properties of Ti49.8Ni50.2 at room temperature after abc pressing to true strains $e = 0.29-8.44$ at $T = 723$ K and their comparison with other related data suggest the following.

1. As the true strain $e$ is increased, the grain–subgrain structure is gradually refined. At $e = 8.44$, being maximal in our study, the material assumes a microstructure with an average grain size $d_{av} = 1 \mu m$ in which the main fraction is submicrocrystalline and the volume fraction of fine-grained and nanocrystalline elements is small (about 20% in total).

2. Refining the grain–subgrain structure of the material to the average size $d_{av} = 1 \mu m$ increases its yield stress $\sigma_y$ and strain hardening coefficient $\theta = d\sigma / de$ at linear stage III of its tensile stress–strain curve, and the dependence of these characteristics on the grain–subgrain size is well described by the Hall–Petch relation.

3. Refining the grain–subgrain structure to the average size $d_{av} = 1 \mu m$ does not change the temperatures of martensite transformations, martensite shear stress $\sigma_m$, and ultimate strength $\sigma_{UTS}$. It is supposed that this is due to the existence of a critical average grain–subgrain size whose value ($d_{av}$)$_{cr} = 0.5 \mu m$ has not been attained at the strains used in abc pressing.

Author Contributions: Conceptualization, O.A. and A.L.; writing—original draft preparation, O.A.; writing—review and editing, A.L. and V.G.; software, K.K.; investigations, O.A., K.K., and V.G.; project administration, A.L.; funding acquisition, A.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Fundamental Research Program of the State Academies of Science for 2013–2020 (priority direct № III.23.2.2).

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.
References

1. Duerig, T.; Pelton, A.; Stoeckel, D. An overview of nitinol medical applications. Mater. Sci. Eng. A 1999, 273–275, 149–160, doi:10.1016/S0921-5093(99)00294-4.

2. Saadat, S.; Salichs, J.; Noori, M.; Hou, Z.; Davoodi, H.; Bar-on, I.; Suzuki, Y.; Masuda, A. An overview of vibration and seismic applications of NiTi shape memory alloy. Smart Mater. Struct. 2002, 11, 218–229.

3. Predki, W.; Knopik, A.; Bauer, B. Engineering applications of NiTi shape memory alloys. Mater. Sci. Eng. A 2008, 481, 598–601, doi:10.1016/j.msea.2006.12.195.

4. Wadood, A. Brief Overview on Nitinol as Biomaterial. Adv. Mater. Sci. Eng. 2016, Article ID 4173138, doi:10.1155/2016/4173138.

5. Valiyev, R.Z.; Aleksandrov, I.A. Bulk Nanostructure Metal Materials: Obtaining, Structure and Properties; Akademkniga: Moscow, Russian, 2007; p. 398.

6. Khmelevskaya, I.Y.; Prokoshkin, S.D.; Trubitsyna, I.B.; Belousov, M.N.; Dobatkin, S.V.; Tatyanin, E.V.; Korotitskiy, A.V.; Baturin, A.A.; Stolyarov, V.V.; Prokofiev, E.A. Structure and properties of Ti–Ni-based alloys after equal-channel angular pressing and high-pressure torsion. Mater. Sci. Eng. A 2008, 481–482, 119–122, doi:10.1016/j.msea.2007.02.157.

7. Shahmir, H.; Nili-Ahmadabadi, M.; Mansouri-Arani, M.; Langdon, T.G. The processing of NiTi shape memory alloys by equal-channel angular pressing at room temperature, Mater. Sci. Eng. A 2013, 576, 178–184, doi:10.1016/j.msea.2013.04.001.

8. Shri, D.N.A.; Tsuchiya, K.; Yamamoto, A. Surface characterization of TiNi deformed by high-pressure torsion. Appl. Surf. Sci. 2014, 289, 338–344, doi:10.1016/j.apsusc.2013.10.161.

9. Gundersov, D.; Lukyanov, A.; Prokofiev, E.; Kilmametov, A.; Pushin, V.; Valiev, R. Mechanical properties and martensitic transformations in nanocrystalline Ti$_{50}$Ni$_{50}$ alloy produced by high-pressure torsion. Mater. Sci. Eng. A 2009, 503, 75–77, doi:10.1016/j.msea.2008.08.044.

10. Shamsolhodaei, A.; Zarei-Hanzaki, A.; Moghaddam, M. Structural and functional properties of a semi-equiatomic NiTi shape memory alloy processed by multi-axial forging. Mater. Sci. Eng. A 2017, 700, 1–9, doi:10.1016/j.msea.2017.04.011.

11. Lotkov, A.I.; Grishkov, V.N.; Dudarev, Y.F.; Girsova, N.V.; Tabachenko, A.N. Formation of ultrafine grain structure, martensitic transformations and uniaxial properties of titanium nickelide after abc-pressing. Vopr. Materialoved. 2008, 1, 161–165.

12. Lotkov, A.I.; Grishkov, V.N.; Dudarev, E.F.; Koval, Y.N.; Girsova, N.V.; Kashin, O.A.; Tabachenko, A.N.; Firstov, G.S.; Timkin, V.N.; Zhopa, D.Y. Ultrafine Structure and Martensitic Transformation in Titanium Nickelide after Warm abc Pressing. Inorg. Mater. Appl. Res. 2011, 2, 548–555, doi:10.1134/S2075113310050145.

13. Lotkov, A.I.; Grishkov, V.N.; Baturin, A.A.; Dudarev, E.F.; Zhopa, D.Y.; Timkin, V.N. The effect of warm deformation by abc-pressing method on mechanical properties of titanium nickelide. Lett. Mater. 2015, 5–2, 170–174.

14. Lotkov, A.; Grishkov, V.; Zhopa, D.; Timkin, V.; Baturin, A.; Kashin, O. Superelasticity and shape memory effect after warm abc-pressing of TiNi-based alloy. Mater. Today Proc. 2017, 4, 4814–4818, doi:10.1016/j.matpr.2017.04.045.

15. Lotkov, A.I.; Kashin, O.A.; Grishkov, V.N.; Krukovskii, K.V. The influence of degree of deformation under isothermal abc pressing on evolution of structure and temperature of phase transformations of alloy based on titanium nickelide. Inorg. Mater. Appl. Res. 2015, 6, 96–104.

16. Zhopa, D.Y.; Lotkov, A.I.; Grishkov, V.N.; Timkin, V.N.; Rodionov, I.S.; Kolevatov, A.S.; Beloslutseva, A.A. Inelastic properties of titanium nickelide after warm abc-pressing. Izv. Vyssh. Uchebn. Zaved., Fiz. 2016, 59, 60–63.

17. Kreitcberg, A.; Brailovski, V.; Prokoshkin, S.; Gundersov, D.; Khomutov, M.; Inaekyan, K. Effect of the grain/subgrain size on the strain-rate sensitivity and deformability of Ti–50 at %Ni alloy. Mater. Sci. Eng. A 2015, 622, 21–29, doi:10.1016/j.msea.2014.10.069.

18. Prokoshkin, S.D.; Khmelevskaya, I.Yi.; Dobatkin, S.V.; Trubitsyna, I.B.; Tatyanin, E.V.; Stolyarov, V.V.; Prokofiev, E.A. Structure evolution upon severe plastic deformation of TiNi-based shape-memory alloys. Phys. Metals Metallogr. 2004, 97, 619–625.

19. Prokofiev, V.A. Structure and properties of ultra-low grain TiNi alloy obtained by intensive plastic deformation. Vestnik UGATU 2006, 8, 169–174.
20. Yurchenko, L.I.; Dyupin, A.P.; Gunderov, D.V.; Valiev, R.Z.; Kuranova, N.N.; Pushin, V.G.; Uksusnikov, A.N. Mechanical properties and structure of high-strength nanostructured nickel-titanium alloys subjected to ECAP and rolling. *Fiz. Perekh. Uporyad. Sost. Noveye Mater.* Available online: http://www.ptosnm.ru (accessed on 4 October 2006).

21. Dudarev, E.F.; Bakach, G.P.; Kolobov, Y.R.; Ivanov, K.V.; Lotkov, A.I.; Grishkov, V.N.; Valiyev, R.Z.; Ivanov, M.B. Localization of martensitic deformation on meso- and macroscopic levels in large grain and sub-micro grain alloys with shape memory. *Fiz. Mezomekh.* 2004, 7, 127–130.

22. Churakova, A.A.; Gunderov, D.V.; Lukyanov, A.V.; Lebedev, Y.A. Effect of thermal cycling in the range of phase transformation B2–B19° on the microstructure and mechanical properties of UFG alloy Ti_{30}Ni_{50}. *Lett. Mater.* 2013, 3, 166–168.

23. Valiev, R.; Gunderov, D.; Prokofiev, E.; Pushin, V.; Zhu, Y. Nanostructuring of TiNi alloy by SPD processing for advanced properties. *Mater. Trans.* 2008, 49, 97–101, doi:10.2320/matertrans.ME200722.

24. Waitz, T.; Kazykhanov, V.; Karnthaler, H.P. Martensitic phase transformations in nanocrystalline NiTi studied by TEM. *Acta Mater.* 2004, 52, 137–147, doi:10.1016/j.actamat.2003.08.036.

25. Pushin, V.G.; Lotkov, A.I.; Kolobov, Y.R.; Valiev, R.Z.; Dudarev, E.F.; Kuranova, N.N.; Dyupin, A.P.; Gunderov, D.V.; Bakach, G.P. On the nature of anomalously high plasticity of high-strength titanium nickelide alloys with shape-memory effects: I. Initial structure and mechanical properties. *Phys. Metals Metallogr.* 2008, 106, 520–530, doi:10.1134/S0030918X08110124.

26. Dudarev, E.F.; Valiev, R.Z.; Kolobov, Y.R.; Lotkov, A.I.; Pushin, V.G.; Bakach, G.P.; Gunderov, D.V.; Dyupin, A.P.; Kuranova, N.N. On the nature of anomalously high plasticity in high-strength titanium nickelide alloys with shape-memory effects: II. Mechanisms of plastic deformation upon isothermal loading. *Phys. Metals Metallogr.* 2009, 107, 298–311, doi:10.1134/S0030918X09030120.

27. Amirkhanova, N.A.; Valiev, R.Z.; Adasheva, S.L.; Prokofiev, E.A. The investigation of corrosion and electrochemical properties of Ni-Ti alloys in large and ultra-fine grained states. *Vestnik UGATU* 2006, 7, 143–146.

28. Kuranova, N.N.; Gunderov, D.V.; Uksusnikov, A.N.; Luk’yanov, A.V.; Yurchenko, L.I.; Prokof’ev, E.A.; Pushin, V.G.; Valiev, R.Z. Effect of heat treatment on the structural and phase transformations and mechanical properties of TiNi alloys subjected to severe plastic deformation. *Phys. Metals Metallogr.* 2009, 108, 556–568, doi:10.1134/S0030918X09120060.

29. Tong, Y.X.; Chen, F.; Guo, B.; Tian, B.; Li, L.; Zheng, Y.F.; Gunderov, D.V.; Valiev, R.Z. Superelasticity and its stability of an ultrafine-grained Ti_{30}Ni_{50} shape memory alloy processed by equal channel angular pressing. *Mater. Sci. Eng. A* 2013, 587, 61–64, doi:10.1016/j.msea.2013.08.049.

30. Tong, Y.X.; Hu, K.P.; Chen, F.; Tian, B.; Li, L.; Zheng, Y.F. Multiple-stage transformation behavior of Ti_{30}Ni_{50} alloy with different initial microstructure processed by equal channel angular pressing. *Intermetallics* 2017, 85, 163–169, doi:10.1016/j.intermet.2017.01.017.

31. Zhang, X.; Song, J.; Huang, C.; Xia, B.; Chen, B.; Sun, X.; Xie, C. Microstructures evolution and phase transformation behaviors of Ni-rich TiNi shape memory alloys after equal channel angular extrusion. *J. Alloys Compd.* 2011, 509, 3006–3012, doi:10.1016/j.jallcom.2010.11.189.

32. Pushin, V.G. *Nickel-Titanium Shape Memory Alloys. Part 1. Structure, Phase Transformations and Properties.* UrB RAS: Yekaterinburg, Russia, 2006; p.438.

33. Shi, X.B.; Hu, Z.C.; Hu, X.W.; Zhang, J.S.; Cui, L.S. Effect of plastic deformation on stress-induced martensitic transformation of nanocrystalline NiTi alloy. *Mater. Charact.* 2017, 128, 184–188, doi:10.1016/j.matchar.2017.04.002.

34. Shi, X.; Yu, M.; Guo, F.; Liu, Z.; Jiang, D.; Han, X.; Cui, L. Effect of deformation on the stability of stress-induced martensite in nanocrystalline NiTi shape memory alloy. *Mater. Lett.* 2014, 131, 233–235, doi:10.1016/j.matlet.2014.06.001.

35. Rybin, V.V. *Large Plastic Deformation and Fracture of Metals; Metallurgia:* Moscow, Russian, 1986; p. 224.

36. Petch, N.J. The Cleavage Strength of Polycrystals. *Iron Steel Inst.* 1953, 174, 25–28.

37. Nokhrin, A.V.; Chuvileev, V.N.; Kopylov, V.I.; Lopatin, Y.G.; Pirozhnikova, O.E.; Sakharov, N.V.; Piskunov, A.V.; Kozlova, N.A. Hall–Petch relation for nano- and microcrystalline metals produced by severe plastic deformation. *Vestn. Lobachevsky State Univ. Nizhni Novgorod* 2010, 5, 142–146.
38. Estrin, Y.; Vinogradov, A. Extreme grain refinement by severe plastic deformation: A wealth of challenging science. *Acta Mater.* **2013**, *61*, 782–817, doi:10.1016/j.actamat.2012.10.038.

39. Malygin, G.A. Plasticity and strength of micro- and nanocrystalline materials. *Phys. Solid State* **2007**, *49*, 1013–1033.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).