Optimization of the Mechanical Performance of Titanium for Biomedical Applications by Advanced, High-Gain SPD Technology

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Received: 27 April 2020; Accepted: 22 May 2020; Published: 26 May 2020

Abstract: This recent study deals with the optimization of the mechanical performance of Grade 2 and Grade 4 titanium with Conform severe plastic deformation (SPD) processing and subsequent rotary swaging. A comprehensive study of the materials behaviour and characterisation during and after processing is given by (finite element method - FEM) numerical simulation, microscopy methods and mechanical testing. The mechanical and fatigue properties are discussed in terms of texture and microstructure evolution. It is shown that the combination of Conform SPD and rotary swaging is a promising technique for economically reliable, high-gain production of titanium alloys fulfilling requirements for biomedical applications. Such a processing can improve the mechanical properties of the unalloyed titanium to the level of the commonly used Ti-6Al-4V.

Keywords: pure titanium; Conform SPD; severe plastic deformation

1. Introduction

The investigated materials, titanium alloys Grade 2 and Grade 4, have been used for biomaterials for many years, thanks to their very good biocompatibility. Titanium Grade 4 is known as the strongest of the four Grades of commercially pure titanium, with a minimum yield strength of 480 MPa. Titanium Grade 4 exhibits the highest content of oxygen and iron out of all commercially pure titanium grades. This grade is well-known for its good balance of biological and mechanical properties. However, commercially pure (CP) titanium alloys exhibit lower mechanical properties in comparison with titanium Grade 5 (TiAl6V4 alloy). The mechanical properties are a critical issue in the case of dental implants and orthopaedic screws. Therefore, in order to meet high requirements for specific surgical applications, improved processing paths are necessary to allow the use of high strength CP grades not containing potentially harmful elements V and Al [1–4].

These days, great effort goes into developing useful forming processes based on severe plastic deformation (SPD). Processes of this kind reduce the grain size in the material, and therefore improve its properties, particularly the mechanical ones. One attractive process variant involves mechanical working of pure titanium and leads to markedly (twice or three times) higher mechanical properties...
The resulting material can be used for making dental implants and other products [11]. The majority of dental implants are now made of an Al and V-based titanium alloy (Ti6Al4V), as it provides better mechanical characteristics than pure titanium. It has been reported that Ti6Al4V makes up almost 50% of the total production of titanium alloys. Most implants in human bodies are therefore made of this particular alloy. However, some recent studies have pointed out the risk of aluminium and vanadium being released into the human body. Elements released in this manner may be toxic and the presence of aluminium may even lead to Alzheimer’s disease [5,12–15]. In response to these findings, medical researchers seek a substitute material which can reduce these risks. Promising candidates are high-strength commercially pure titanium alloys Grade 2 and 4 with ultrafine-grained or nano-grained structures. SPD-processed titanium shows better mechanical properties than the conventional Ti6Al4V alloy [16]. In addition, commercially pure (CP) titanium alloys are approved for use in the human body. Commercialisation of SPD materials is also hindered by low productivity of their manufacturing processes. Most of them are laboratory-based forming techniques (such as ECAP - Equal Channel Angular Pressing) which are more appropriate for studies into materials characteristics. The challenge is to create an end-to-end robust manufacturing system for continuous production of ultrafine-grained materials and nanomaterials [16–19].

V.M. Segal was the first to suggest that ultrafine-grained materials and nanomaterials could be prepared by the ECAP technique with a modified die chamber [20]. Further development of this concept was investigated by a group led by R.Z. Valiev. They altered the configuration of the ECAP die chamber and named the process Conform SPD [21,22]. In this process, the feedstock was bottom fed at the angle φ of 120°. The feedstock had a square cross-section. Processing of CP titanium by this technique was successful, leading to substantial improvement in mechanical properties. Yet, the researchers continue to point out the instability of the process and the still unsatisfactory quality of the products, mainly due to seizing. The process is discontinuous as the Titanium feedstock was subjected to up to eight multiple passes in order to achieve the desired material state. The length of the products was about 6 metres. Discontinuous processing is problematic for high volume production and therefore a continuous process was developed at the company COMTES FHT a.s. that was entitled Conform SPD. A very similar principle is applied in this case, a round stock is fed from the top at the φ angle of 90°. The focus is now on making both processes more stable, designing heavy-duty tools for long-term operation and developing a process chain for routine production of materials for dental implants, which is the ultimate goal. The principle of Conform SPD for producing ultrafine-grained products is shown in Figure 1. The coining roll guides the feedstock to the gap between the driving wheel and the shoe. High friction forces cause the feedstock to move along the groove in the driving wheel, all the way to the abutment. Once the material hits the abutment, it changes its direction and exits the Conform SPD machine through the chamber die [16,22–24].

The implants are provided in various lengths and diameters combinations, depending on the patients. Threaded cylindrical dental implants are available in diameters ranging from 3.25 to 6.0 mm and lengths ranging from 5 to 18 mm [25,26]. Therefore, the present work investigates pure titanium after mechanical processing up to a true strain of 1.6 (representing 80% cross section reduction by rotary swaging) into a 5 mm wire.

This paper gives a description of the processing of titanium Grade 2 and Grade 4 by Conform SPD and cold rotary swaging. Furthermore, it discusses the differences between these two materials after SPD processing. This paper summarises the development of tools for SPD processing with the use of FEM, microstructure investigation including electron-backscatter diffraction technique (EBSD) and fractography, as well as the tensile and fatigue performance of both considered materials. These findings should support the use of nano-grained titanium for testing and production of dental implants.
Figure 1. Schematic illustration of Conform severe plastic deformation (SPD) technique (coordinate system: ND-normal direction, RD-rolling direction, TD-transverse direction).

2. Materials and Methods

Commercially available titanium Grade 2 and Grade 4 (ASTM B348) (Shaanxi Lasting Titanium Industry Co., Ltd., Xi’an, China) were the objects of investigations in this article. Their chemical compositions are given in Table 1. These compositions were determined with the use of the Bruker Q4 Tasman optical emission spectrometer. The as-received rod diameter was 10 mm for both materials.

| Material/Element  | Fe   | O    | C    | H    | N    | Ti   |
|-------------------|------|------|------|------|------|------|
| Titanium Grade 2  | 0.046| 0.12 | 0.023| 0.0026| 0.0076| Balance|
| Titanium Grade 4  | 0.5  | 0.4  | 0.1  | 0.0125| 0.05 | Balance|

2.1. Numerical Simulations

Optimization of tool for material SPD processing was performed using FEM (Scientific Forming Technologies Corporation, Columbus, OH, USA). A schematic illustration of the SPD process is shown in Figure 1. Axial symmetry of the processing chamber allows task reduction and just one-half of the equipment and feedstock can be considered for the simulation. Feedstock material was considered as plastic, while the rest of the processing equipment was considered as a rigid. The friction between the driving wheel and the titanium bar is a crucial parameter for the whole process simulation. The friction was modelled using Shear and Coulomb models. The Coulomb friction coefficient was set to $\mu = 10$ as a constant value with the compression separation criterion assuring that the workpiece could not slip in the forming groove. A pin on disc experiment was performed to verify these parameters. Temperature fields in the course of processing were investigated for the titanium feedstock only. Temperatures change rates made it possible to neglect the environmental impacts on the process. The feedstock model consisted of about 80,000 elements. The die chamber and its neighbourhood were fine meshed. For more information on the FEM model, see [8,27,28]. Temperature-dependent materials characteristics were obtained from JMatPro based on the material’s chemical composition [8,27,28]. The numerical simulation model was refined based on real experiments. The results of the numerical simulation were directly compared with a real experiment under equivalent conditions. The model of numerical simulation was thus refined and enabled to predict the whole process before the actual production of tools. A comparison of the initial model of the numerical simulation and the real forming process is shown in Figure 2. The numerical model reflects the velocity distribution (Figure 2b). The sample was taken directly from the forming chamber after processing and etched in its symmetrical half (Figure 2a). The etching of the workpiece allowed partial illustration of the material flow. The flow lines in the upper and lower corner of the chamber...
can be observed. There are dead zones in the corners where the material does not flow substantially. Shear zones arise between flowing and static material. This comparison of real results was applied for all calculations.

Figure 2. Comparison of (a) real workpiece flow and (b) numerical simulation in the forming chamber.

2.2. Materials Processing

Two types of processing were carried out using Conform SPD and rotary swaging of a cold rod. Severe plastic deformation was the only source of heat, i.e., no additional heating was applied during the Conform SPD process. During the Conform SPD processing, the die chamber temperature was monitored by a sheathed thermocouple. The output diameter of the Conform SPD-processed rod was 10 mm (the same as the diameter of the processed rods). The wheel speed was 0.5 rpm. The channel angle was 90° at the point where the material flow direction changes in this Conform SPD machine. As-received materials were rotary swages as well as rods after one Conform SPD pass in order to enhance their mechanical behaviour. Rotary swaging was carried out at ambient temperature. The aim was to explore work hardening development for ultrafine to nanocrystalline materials. The material feeding rate was approximately 0.5 m/s. The cross-sectional area reduction was 20% in a single pass. The maximum final cross-section area reduction was 90%, corresponding with a true strain of 2.2.

2.3. Tensile and Fatigue Tests

The additional work hardening provided by rotary swaging was conducted to a true strain 2.2, that is a maximal rotary swaging of pure titanium which provided good surface properties. Two results are shown in the section with tensile results; rotary swaging at a true strain 1.6 (diameter of the wire 5 mm) and at a true strain 2.2 (maximal value of rotary swaging for pure titanium).

Tensile testing was performed at ambient temperature. Quasi-static loading was applied. The tests were conducted on an electromechanical testing machine (Zwick Roell, Ulm, Germany). Three valid measurements for each batch were averaged for summary. Extension was measured using a mechanical extensometer. The following parameters were determined from the executed tensile tests: yield stress at 0.2% deformation (OYS), ultimate tensile strength (UTS), elongation (A) and reduction of area (RA).

Fatigue tests were conducted under the tension-tension mode at room temperature. Cyclic loading was performed at a stress ratio of $R = 0.1$ and, at frequencies up to 50 Hz. The temperature during tests was measured by thermovision (FLIR systems, Wilsonville, OR, USA) to avoid sample heating. The tests were carried out with the use of a servo-hydraulic testing system INOVA of loading capacity 15 kN. Tests were performed either up to specimen rupture or up to 10 million cycles. The
fatigue endurance limit, $\sigma_c$, was determined based on the three non-broken specimens tested at the same stress amplitude.

2.4. Microscopy

Observation of the microstructures of as-received and processed specimens was carried out after grinding and subsequent polishing of their cross-sections and etching in Kroll reagent. The images were captured using a Carl Zeiss—Observer.Z1m light optical microscope (Carl Zeiss Ag, Oberkochen, Germany) in the mode of bright-field illumination.

For the purpose of the microstructure observations with electron-backscatter diffraction technique (EBSD), specimens were cut from the Conform processed rods perpendicular to the processing direction. Specimen surfaces were ground on SiC papers (from 500 to 4000 grit) and subsequently polished with the use of a LectroPol-5 electrolytic polishing machine for 55 s, using a solution of 300 mL CH$_3$OH + 175 mL 2-butanol + 30 mL HClO$_4$ at −20 °C and voltage of 45 V. EBSD measurements were performed using a scanning electron microscope (SEM) FEI Quanta 200 FX (Thermo Fisher Scientific, Brno, Czech Republic) equipped by EDAX EBSD/EDS camera, at a working distance of 13 mm and with step size 50 nm.

Thin foils for transmission electron microscopy (TEM) bright field mode were electrolytically thinned in a Tenupol 5 device, using a solution of 30 mL HClO$_4$ + 175 mL 2-butanol + 300 mL CH$_3$OH at −10 °C and a voltage of 40 V. JEOL 200CX (JOEL, Tokyo, Japan) TEM with an acceleration voltage of 200 kV was employed. The linear intercept method was used for evaluating the subgrain size from the TEM images. The samples were oriented in the transverse direction to the processing route.

For ultra-fine grained materials which exhibit a grain size of few tens to hundreds of nanometres, conventional EBSD technique is not sufficient anymore since the grains have similar size as the interaction volume of the electron beam. Therefore, thin foils were also prepared for Automatic Crystal Orientation Mapping in Transmission Electron Microscopy (ACOM-TEM) investigations of the rotary swaged samples. In this method, a selected area is scanned with a focused primary electron beam. Concurrently, electron diffraction patterns are captured by a camera and compared to the pre-calculated templates (for a pre-defined phase, lattice parameters and orientation). The best match is selected as the orientation/phase for a given point. For a detailed explanation of the method, refer to [29–31]. Thin foils were prepared by mechanical thinning followed by electrolytic thinning with the use of a Tenupol 5 device, using a solution of 300 mL CH$_3$OH + 175 mL 2-butanol + 30 mL HClO$_4$ at −20 °C and a voltage of 40 V. The ACOM-TEM investigations were performed in a JEOL 2200FS HRTEM transmission electron microscope (JOEL, Tokyo, Japan) at accelerating voltage 200 kV.

Fracture analysis of the specimens broken during the fatigue tests was performed using a Tescan LYRA 3 XMU FEG/SEMxFIB SEM scanning electron microscope (TESCAN, Brno, Czech Republic). The analysis was performed to investigate the fatigue crack initiation site and mechanism of fatigue fracture.

3. Results

3.1. Numerical Simulation

The FE software DEFORM was used for in-depth investigation of the Conform SPD process. The re-designed die chamber (Figure 3a) is based on the original ECAP configuration, where the feedstock diameter (10 mm) is equal to the product diameter (10 mm). Figure 3b illustrates the distribution of strain rate. Figures with computed contours show the regions of shear deformation with an angle of approximately 45°. The strain rate is not homogeneous across the wire diameter. In the lower area, the strain rate reaches higher intensity than in the upper area. The distribution of true strain is shown in Figure 3c. Strain is non-uniform across the cross-section of the material. The largest strain is found in the lower part. This is consistent with the strain rate distribution, where the highest values are at the bottom of the shear deformation zone. Strain levels are also increased by friction and by the reduced cross-section of the channel. Along the axis of the feedstock, the strain magnitude is smaller, whereas the upper portion of the cross section shows higher values. This is due to friction and the
reduced cross-sectional area of the die. In Figure 4, the hardness value over the cross-section of titanium after one Conform SPD pass is showed. In the centre of the material cross-section, the hardness significantly increased at some points. Hardness decreases near to the surface of the processed material. Figure 3d presents the distribution of the material velocity within the die chamber. In the shear deformation zone, the material flow is slower. On the periphery of the shear deformation zone, the flow is particularly slow. The flow then becomes faster again in the die. The blue zones of shear deformation can be called dead zones. The material does not move at all or very slowly in these areas. Temperature distribution is illustrated in Figure 3e. Rapid heating due to deformation is readily visible. The highest temperature in the material is 650 °C, which falls within the hot forming zone. In the continuous Conform SPD technique, an increase in temperature to levels used in hot forming is common. Under steady-state conditions (leading to dynamic recrystallization), no additional heating is necessary. The temperature of the process depends on thermodynamic parameters (reduction and deformation rate). Figure 3f shows the results of damage analysis. With this information, damage in the product can be predicted. The data from this analysis does not represent any physical quantity. The amount of damage depends primarily on the stress state. The 0.4 threshold was chosen by estimate. The damage analysis helped to predict damage in the material and thereby to optimize the process geometry to mitigate the risk of damage. As a result, the design of the die chamber was modified to increase the pressure in the upper portion of the die chamber, to reduce the risk of defects in the product. Although the tensile stress component in the upper portion of the chamber was reduced, it was not eliminated completely, see Figure 3g. The assumption of the numerical simulation corresponded to real experiments see Figure 5. In the upper part of the semi-finished product, laps were found, which reached up to one millimetre below the surface. Their formation was predicted by the prevailing tensile strain in the upper part of the chamber. Due to the high degree of deformation, it is necessary to optimize the forming tools so that the tension strain is completely eliminated. In the case of conventional ECAP technology, backpressure is used for this purpose.
Figure 3. Results of numerical modelling of the Conform SPD process: (a) finite element model of the Conform SPD process, (b) effective strain rate field, (c) effective strain field, (d) total velocity field, (e) temperature field, (f) damage area and (g) maximal stress during processing.

Figure 4. Distribution of the hardness on the transverse cross-section through the workpiece (one Conform SPD pass).
3.2. Point Tracking Analysis

Point tracking analysis was performed. In Figure 6, three stages of the forming process are given: the area before entering the forming chamber, the shear deformation zone, and the exit area of the workpiece. The aim was to track the development of forming parameters in relation to time and position in the deformed workpiece. The tracked parameters were effective strain, temperature, stress and strain rate.

Figure 7a shows the development of the actual strain. The figure indicates that the highest deformation was reached at point 1 (strain value of 4.9 [-]). The lowest strain was reached at the middle point number 2. The actual strain on the cross-section ranges from 2 to 5 and is not homogeneous, as mentioned in the previous chapter. The uneven distribution is because the process is not symmetric. The temperature was approximately 600 °C and this temperature was obtained over the entire cross-section after the shear deformation zone (Figure 7b,c); this shows the evolution of the stress over time in the shear region (3.5 sec). It can be seen that the compressive stress prevails in the lower part. Towards to the upper part of the chamber the stress approaches zero. Figure 7d shows the evolution of the strain rate. The individual peaks of the graph reflect the entry of points into the area of shear deformation. Point 3 further shows a second peak, which is caused by deformation in the upper die region. The results suggest that deformation conditions are not homogeneous during the forming process.
3.3. Microstructure

The microstructure of as-received titanium Grade 2 is shown in Figure 8. Annealing twins can be observed in the recrystallised, equiaxed grains, which is characteristic for materials having low crystal symmetry [32]. The mean grain size was estimated as 29 µm (including twins). The microstructure of the titanium Grade 4 sample exhibits similar features (Figure 9). However, the mean grain size is slightly smaller (22 µm). The grain morphology and size is the same for both longitudinal and transverse directions (Figures 8 and 9).

As it is obvious from TEM investigations (Figure 10a,b—Grade 2) and (Figure 11a,b—Grade 4), that already one pass Conform SPD processing leads to a significant grain refinement. The micrograph shows a heavily deformed structure. The grain size is below 1 µm and in the larger grains formation of subgrain structure can be observed. After the single pass through Conform SPD, the average/mean grain size (including subgrains), estimated by the linear interception method, was 320 nm in the traverse and 340 nm in the longitudinal direction for titanium Grade 2. The subgrain size for titanium Grade 4 was 364 nm in the traverse and 374 nm in the longitudinal direction.

Further grain refinement was achieved by rotary swaging. In the rotary swaging process, the reduction of the cross sectional area was 80% (true strain of 1.6). Micrographs of specimens after one pass through the Conform SPD machine and subsequent rotary swaging are shown in Figure 10c,d and Figure 11c,d. The micrograph clearly shows that the grains have become much finer (fragmented into smaller subgrains). The non-uniform dislocation density distribution was developed. The size of subgrains was between 200 and 500 nm for both alloys (Table 2). Some subgrains in titanium Grade 2, however, were smaller than 100 nm. The mean subgrain sizes estimated from TEM observations are summarized in Table 2.
Figure 8. Microstructure of as-received titanium Grade 2: (a) longitudinal cross-section, (b) transverse cross-section—optical light microscopy.

Figure 9. Microstructure of as-received titanium Grade 4: (a) longitudinal cross-section, (b) transverse cross-section—optical light microscopy.
Figure 10. TEM micrographs of mechanically-worked titanium Grade 2: (a) after one Conform SPD pass, longitudinal cross-section, (b) after one Conform SPD pass, transverse cross-section, (c) after one Conform SPD pass and rotary swaging (1.6 true strain—80% area reduction), longitudinal cross-section, (d) after one Conform SPD pass and rotary swaging (1.6 true strain—80% area reduction), transverse cross-section.

Figure 11. TEM micrographs of mechanically-worked titanium Grade 4: (a) after one Conform SPD pass, longitudinal cross-section, (b) after one Conform SPD pass, transverse cross-section, (c) after one Conform SPD pass and rotary swaging (1.6 true strain—80% area reduction), longitudinal cross-section, (d) after one Conform SPD pass and rotary swaging (1.6 true strain—80% area reduction), transverse cross-section.

Table 2. Subgrain sizes in the materials as estimated from TEM micrographs.

| Material/Subgrain Size (nm) | Transverse Cross-Section | Longitudinal Cross-Section |
|-----------------------------|--------------------------|-----------------------------|
| Titanium Grade 2—as-received condition | 2895 ± 1448 | |
| Titanium Grade 2—after one Conform SPD pass | 320 ± 160 | 340 ± 170 |
| Titanium Grade 2—after one Conform SPD pass + rotary swaging (true strain of 1.6) | 370 ± 185 | 120–250* |
| Titanium Grade 4—as-received condition | 2200 ± 1100 | |
| Titanium Grade 4—after one Conform SPD pass | 364 ± 182 | 374 ± 187 |
| Titanium Grade 4—after one Conform SPD pass + rotary swaging (true strain of 1.6) | 405 ± 203 | 200–310* |

* Owing to the large statistical scatter in length of elongated grains, the shorter dimension of the elliptical grains was evaluated.

Micrographs of specimens which were subjected only to rotary swaging are shown in Figure 12. The grains were arranged in fibres, oriented in the direction of flow and elongated grains in the longitudinal direction can be observed. Relatively large numbers of deformation twins were nucleated.
Figure 12. Optical micrographs after rotary swaging (1.6 true strain—80% area reduction): longitudinal cross-section (a) for titanium Grade 2, (b) for titanium Grade 4.

3.4. EBSD Analysis

The orientation image maps (OIM) of single Conform SPD processed samples are shown in Figure 13a–f. It is obvious that the microstructure is very heterogeneous for both materials. They consist of larger grains (a few μm) and grains having submicron sizes. This feature can also be seen in grain size distribution histograms. There are two local maxima, at ~0.6 μm and at ~4.2 μm in the case of titanium Grade 2 and at ~0.6 μm and ~2.8 μm in the case of titanium Grade 4.

The calculated pole figures show a slightly stronger texture for titanium Grade 4. On the (0001) pole figure for titanium Grade 2, several distinct maxima can be seen which are inclined by ~50°—75° from the RD-processing direction. In contrast, for Grade 4, the maximum on the (0001) pole figure is inclined by ~50°—70° and forms a continuous area. The same holds for the (101̅0) pole figures: several distinct maxima inclined by ~15°—40° from the processing direction are present in the case of titanium Grade 2. Titanium Grade 4 specimens exhibit rather a continuous area with a maximum inclined by ~25° from the processing direction.
Figure 13. Orientation image maps of titanium Grade 2 (a) and Grade 4 (b), grain size distribution histograms of titanium Grade 2 (c) and Grade 4 (d), corresponding (0001), (101\textbar 0), (101\textbar 1) pole figures with the scale of intensities is shown as multiples of the random density (m.r.d.) from 0 to 8.000 for Conform SPD-ed titanium Grade 2 (e) and Grade 4 (f), respectively. High-angle grain boundary (HAGBs) (15°–100°) are indicated by black lines, low-angle grain boundary (LAGBs) (4°–15°) by white lines in Figure 13a,b (Rolling direction, “RD” perpendicular to the plane of sheet).

In Figure 14a–d, the results of the ACOM-TEM measurements conducted on the Conform SPD and Rotary Swaged samples are shown. As can be seen in the grain orientation maps Figure 14a,b, samples show, similarly to Conform SPD samples, heterogeneous microstructure. However, the overall grain structure is finer in this case. The “larger” grains have grain size around 1 μm, while the “refined” grains are below 0.5 μm. The titanium Grade 2 sample exhibits a higher fraction of low angle grain boundaries than the titanium Grade 4 sample. Both samples show intensive fibre texture where the normal of prismatic (101\textbar 0) plane is parallel with RS-processing direction. There is no significant difference in the texture between the two samples.
Figure 14. (a,b) Grain orientation maps and (c,d) corresponding (0001), (101\(\bar{1}\)), (10\(\bar{1}\)1) pole figures for Conform SPD + rotary swaged (true strain of 1.6) titanium Grade 2 and Grade 4, respectively (direction of rotary swaging indicated as “RS”, perpendicular to the plane of the sheet).

3.5. Mechanical Properties

In this section, two sample conditions are discussed: Conform SPD + rotary swaged and only rotary swaged samples. In addition, two results are mentioned: rotary swaging to a true strain 1.6 (diameter of the wire 5 mm) and the true strain 2.2 (maximal value of rotary swaging for pure titanium).

Figure 15 shows the mechanical performance for single pass Conform SPD processed titanium Grade 2 sample as a function of true strain induced by rotary swaging for titanium Grade 2. The single Conform SPD pass itself increases the ultimate tensile strength (UTS) from 103 MPa to 583 ± 6.1 MPa in comparison to the as-received condition. After a complete rotary swaging process, the cross-sectional area of the feedstock is reduced by 90% and true strain of 2.2 is induced in the specimen. It is obvious from Figure 15 that the offset yield strength (OYS) and the UTS monotonically increase as rotary swaging progresses. In the final condition, UTS = 1023 ± 4.5 MPa was measured,
which indicates a significant work hardening during the rotary swaging process. In contrast to strength values, the elongation monotonically decreases until reaching a value of 12% ± 1.3% in the final condition. Reduction of area (RA) decreases with respect to the as-Conform SPD condition, but the course of the RA—true strain curve, is relatively wavy. At 2.2 true strain, the RA is the same as in the as-received condition.

Similar results were obtained for titanium Grade 4 (Figure 16). After one Conform SPD pass and rotary swaging, the ultimate tensile strength reached 1250 ± 7.7 MPa; the cross-sectional area of the material was reduced by 90% (which corresponds to a true strain of 2.2), elongation (A) decreased to 9.8% ± 1.2%. The course of the OYS, UTS and A vs. true strain curves are monotonic, whereas the RA curve has some local minima.

Figure 17 shows the tensile test data for only rotary-swaged titanium Grade 2. As explained above, the purpose was to evaluate the effects of rotary swaging separately. After 90% reduction of cross-section, the ultimate tensile strength was 964 ± 5.8 MPa (Figure 17). In the case of titanium Grade 4 (Figure 18), the terminal condition of UTS and elongation were 1040 ± 6.2 MPa and 7.2% ± 1.2%, respectively.

After one Conform SPD pass and rotary swaging to a true strain of 1.6 (80% cross-sectional area reduction), elongation was no less than 10% in either material. The ultimate tensile strengths were 955 ± 5.8 MPa and 1140 ± 4.4 MPa for titanium Grade 2 (Figure 15) and titanium Grade 4 (Figure 16), respectively.

In summary, the Conform SPD, when applied before rotary swaging, adds 200 to 250 MPa to the UTS for titanium Grade 4 and 100 MPa to the UTS for titanium Grade 2.

Figure 15. Results of tensile testing of titanium Grade 2 after one Conform SPD pass and rotary swaging as a function of the true strain induced by rotary swaging.
Figure 16. Results of tensile testing for titanium Grade 4 after one Conform SPD pass and rotary swaging as a function of the true strain induced by rotary swaging.

Figure 17. Results of tensile testing for titanium Grade 2 after rotary swaging as a function of the true strain induced by rotary swaging.
3.6. Fatigue Performance

The fatigue tests were performed on specimens that had undergone a single pass Conform SPD and rotary swaging up to 80% area reduction (induced true strain 1.6). In this case, the UTS was 1060 MPa and 1140 MPa for titanium Grade 2 and titanium Grade 4, respectively, and the elongations were not less than 10% (c.f. Figures 15 and 16). Results of fatigue testing are listed in Table 3. The as-received titanium Grade 2 and titanium Grade 4 materials had fatigue strengths of $\sigma_C = 245$ MPa and $\sigma_C = 523$ MPa, respectively. The as-processed specimens had fatigue strengths of $\sigma_C = 396$ MPa (titanium Grade 2) and 698 MPa (titanium Grade 4). The increase in the fatigue strength of as-processed titanium Grade 2 and Grade 4 is therefore 151 and 175 MPa, respectively, when compared to the as-received condition.

Table 3. Results of fatigue testing for pure titanium in as-received and mechanically-worked conditions.

| Material                                         | $\sigma_C$ (MPa) |
|--------------------------------------------------|-----------------|
| Titanium Grade 2—as-received condition           | 245             |
| Titanium Grade 2—after one pass + rotary swaging (true strain of 1.6) | 396             |
| Titanium Grade 4—as-received condition           | 523             |
| Titanium Grade 4—after one pass + rotary swaging (true strain of 1.6) | 698             |

Single site fatigue crack initiation from the specimen surface was characteristic for all the specimens broken during fatigue tests. Typical morphology and character of the fatigue fracture surfaces of the titanium Grade 4 specimens are shown in Figures 19 and 20. The results of fractography for titanium Grade 2 are similar to the results of titanium Grade 4.

A combination of the transcrystalline with the intercrystalline fracture mechanism was characteristic for as-received titanium Grade 4 specimens (Figure 19b). In some failed grains, typical quasi-cleavage river like (Figure 19c) morphology was observed. Striations were a typical feature observed in grains of the material. In addition, secondary cracks were observed in the fatigue fracture region of the broken specimens. The intensity of the typical fractographic features characteristic of the material was more pronounced with increasing distance from the fatigue fracture origin. More fatigue cracks and larger striations were observed close to the final fracture region. The final fracture region was characteristic of dimple morphology.
Figure 19. Fractographic analysis of the as-received titanium Grade 4 specimen after fatigue testing: (a) fatigue crack initiation site, (b) striations, (c) quasi-cleavage, (d) final fracture region.

The fatigue fracture surface of the nanograined titanium Grade 4 specimens exhibited a transcrysalline fracture mechanism (Figure 20b). Striations (Figure 20c) were characteristic features for the fatigue fracture region of the material. Localised plane areas were observed on the fatigue fracture region of the fine-grained material. The typical character of the final fracture region is shown in Figure 20d.
4. Discussion

Previous reports [2,3,16,28] suggest that multiple Conform SPD passes do not lead to any additional appreciable grain refinement or improvement in mechanical properties. Thus, this investigation was focused on materials processing by a single pass through the Conform SPD machine. By contrast, it was found that no fewer than six to eight passes in the Conform ECAP process developed by the group of Prof. Valiev [21] are required to obtain the properties of titanium required for subsequent processing. The processing of the semi-finished products involves warm drawing further to improve their mechanical properties.

In terms of thermodynamic parameters, it is important to find the temperature of the sample during the process by means of numerical modelling. As mentioned above, temperatures in the range of 500–600 °C can be expected, despite the feedstock being at ambient temperature. In the similar ECAP technique, the temperatures are notably lower, which is caused by the intermittent nature of the process. In contrast, the continuous manner of Conform SPD can ensure temperatures within the above-mentioned range. Experimentally, we measured by a thermocouple only 200–250 °C, but for the space limitations, the point of measurement was 40 mm away from the die chamber. The temperatures found using the FE software varied across the cross-section of the material. In FE software, 90% of the energy input is considered to be converted to heat and the rest consumed in plastic deformation of the metal [33].

The actual true strain was not uniform across the cross section of the material. It ranged from 2.1 to 10.5. The highest values were obtained on the periphery of the cross section, i.e., near the surface of the material. This was due to higher strain rates on the periphery of the shear deformation zone, due to friction and due to the reduced cross section of the die. In the centre of the cross section, the strain values were lower. Experimentally, as Figure 4 shows, the hardness reaches higher values in the central region of the blank and it is lowest in the surface area. This observation contradicts the simulated distribution of the actual deformation. This issue can be explained by the stress relieving on the surface. Due to the higher degree of deformation achieved in this area (Figure 3c) and to the deformation heat, which reaches up to 650 °C (Figure 3e), slight surface hardening can be expected. This phenomenon can be observed for example in the conventional extrusion of aluminium alloys.

In both materials, the initial grain size was between 7 and 30 µm. After a single Conform SPD pass, the majority of the microstructure consisted of fragmented grains with a relatively high, non-uniformly distributed dislocation density. The mean subgrain sizes in titanium Grade 2 and Grade 4 were estimated as 320 nm and 374 nm, respectively. Authors of the report [34] suggest that in cold-rolled material, twinning only occurs at true strains below 0.5. Figure 3c shows that the amount of true strain in the first pass was larger than 2.5. Therefore, it appears that the role of twinning in Conform SPD processing of titanium is not substantial. Above a true strain of 0.5, shear deformation dominates. This means that even those slip systems, which are not favourably oriented with respect
to the principal stress are activated, despite their higher critical resolved shear stress for activation. Numerical modelling also confirmed that the thermodynamic conditions in Conform SPD are somewhat non-uniform. True strain reaches the highest values on the periphery of the cross-section of the round feedstock. Lower values of strain were found in the centre of the cross section. These appear to be the factors which lead to variation in the microstructure across the material. The Conform ECAP technique developed by Prof. Valiev’s group [35] involves a different type of microstructural evolution than Conform SPD developed by the authors of this paper. The microstructure produced by Conform ECAP initially consists of elongated grains with high dislocation density and deformation twins [35]. Grain boundaries are usually of the low-angle type. By contrast, the grain boundaries after Conform SPD are mostly high-angle ones. Despite similarities between these processes, their mechanisms of grain refinement differ.

Pole figures Figure 13e,f indicate that the deformation mechanism during the Conform SPD process is complex in both materials, involving mainly dislocation slips in the basal (0002) and prismatic (101̅0) planes. At elevated temperatures, it was shown by Paton et al [36] that the basal (112̅0) (0002) and prismatic (112̅0)(101̅0) slip systems have almost the same critical resolved shear stress. Our simulations showed that the temperature can even reach 650 °C inside the chamber. Thus, the activation of the dominant slip system during the deformation depends on the texture of the initial state. Evidence for mechanical twinning was not found by EBSD investigation. The same results were found in our previous studies [16,37] on Conform SPD-ed titanium Grade 2. After Conform SPD and rotary swaging process, both materials exhibited fibre texture and the prismatic (101̅0) planes were perpendicular to the processing direction. There is no significant difference in the texture between processed titanium Grade 2 and 4.

After only rotary swaging alone, more significant strengthening occurred in titanium Grade 2 than in titanium Grade 4. Its lower levels of interstitial elements facilitate greater accumulation of dislocations in the solid solution. However, higher strength values were found in titanium Grade 4. The initial work-hardening stage occurs due to the presence of interstitial elements. A decrease in ductility is seen with the progress of cold rotary swaging. This effect was also reported in [4,16,17,28]. On the other hand, a single Conform SPD pass and rotary swaging of both titanium Grades led to higher strengthening behaviour and a smaller decrease in ductility in comparison to only rotary swaged samples. This corresponds with the different mechanisms of deformation. In the Conform SPD process, twinning is not the dominant mechanism, whereas in simple rotary swaging, deformation by twinning is likely to prevail.

Comparison between the properties of as-received and mechanically-worked materials reveals higher fatigue strength in the nano structured materials and illustrates the impact of the grain size on fatigue performance. Similar results were reported by other authors [38,39]. The fatigue strength of ultra-fine to nano-grained titanium Grade 2 does not exceed the fatigue strength of the Ti-6Al-4V alloy (530 MPa) [6,16]. On the other hand, the fatigue strength of titanium Grade 4 exceeds almost 700 MPa.

Our study serves as an overview for understanding of the processing of titanium Grade 2 and Grade 4 by Conform SPD and cold rotary swaging, and discusses the differences between these two materials. Nano-grained titanium Grade 2 reached lower mechanical and fatigue properties in comparison to nano-grained titanium Grade 4. Further studies will focus in detail on fatigue properties and biocompatibility tests of these processed materials. The materials will be treated as actual human dental implants. These results will provide further information for potential serial production of new dental implants.

5. Conclusions

Titanium Grade 2 and Grade 4 were processed by Conform SPD and a subsequent rotary swaging process. The FEM numerical analysis predicted the material behaviour during the Conform SPD process and optimized the processing parameters. Significant grain refinement was observed by microscopy methods after the processing of the material which led to enhanced mechanical properties. Specifically, the UTS, OYS and fatigue strength was improved remarkably in every case.
It is shown that in the case of titanium Grade 4, the fatigue strength significantly exceeds the most popular Ti-6Al-4V alloy. The fracture analysis after fatigue tests showed that in the case of unprocessed titanium, the combination of the trans- and inter-crystalline fracture mechanisms was responsible for sample failure, while in the case of processed titanium, the transcrysalline fracture mechanism was dominant.

**Author Contributions:** Conceptualization, K.M. (Kateřina Mertová) and J.P.; methodology, K.M. (Kateřina Mertová) and J.P.; validation, K.M. (Kateřina Mertová), M.D.; investigation, K.M. (Kateřina Mertová), M.D., T.S., G.N., J.V. and S.F.; writing—original draft preparation, K.M. (Kateřina Mertová), T.S., G.N., S.F.; writing—review and editing, K.M. (Kateřina Mertová), G.N., K.M. (Kristián Máthis) and J.D.; visualization, K.M. (Kateřina Mertová), J.P., K.M. (Kristián Máthis) an M.D.; supervision, K.M. (Kateřina Mertová), J.D. and Z.T.; project administration, J.D.; funding acquisition, J.D., Z.T. All authors have read and agreed to the published version of the manuscript.

**Funding:** This paper was developed under the project entitled Development of West-Bohemian Centre of Materials and Metallurgy No.: LO1412, which is financed by the Ministry of Education of the Czech Republic. This research was partly funded by Ministry of Trade and Industry of the Czech Republic within the frame of institutional funding of Long term development of research organizations. G.N., K.M. (Kristián Máthis), J.V. and Z.T. acknowledge the support of the Operational Programme Research, Development and Education, The Ministry of Education, Youth and Sports (OP RDE, MEYS) [CZ.02.1.01/0.0/0.0/16_013/0001794].

**Conflicts of Interest:** The authors declare no conflict of interest.

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