International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:11, No:6, 2017

The High Strength Biocompatible Wires of Commercially Pure Titanium

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***Abstract*—**COMTES FHT has been active in a field of research and development of high-strength wires for quite some time. The main material was pure titanium. The primary goal of this effort is to develop a continuous production process for ultrafine and nanostructured materials with the aid of severe plastic deformation (SPD). This article outlines mechanical and microstructural properties of the materials and the options available for testing the components made of these materials. Ti Grade 2 and Grade 4 wires are the key products of interest. Ti Grade 2 with ultrafine to nano-sized grain shows ultimate strength of up to 1050 MPa. Ti Grade 4 reaches ultimate strengths of up to 1250 MPa. These values are twice or three times as higher as those found in the unprocessed material. For those fields of medicine where implantable metallic materials are used, bulk ultrafine to nanostructured titanium is available. It is manufactured by SPD techniques. These processes leave the chemical properties of the initial material unchanged but markedly improve its final mechanical properties, in particular, the strength. Ultrafine to nanostructured titanium retains all the significant and, from the biological viewpoint, desirable properties that are important for its use in medicine, i.e. those properties which made pure titanium the preferred material also for dental implants.

***Keywords*—**CONFORM SPD, ECAP, titanium, rotary swaging.

I. Introduction

The past decade has seen intensive research into forming processes in relation to SPD. SPD is an umbrella term for a group of forming techniques that impart ultra-large plastic strain to the material being formed [1]-[3]. The forming process changes the material's mechanical properties (increases its strength while maintaining its ductility) and refines its microstructure [2]. This fact is behind the research into ultrafine-grained materials.

Today's most widely used SPD processes include HPT (High-Pressure Torsion), ARB (Accumulative Roll-Bonding), ECAP (Equal-Channel Angular Pressing), CONFORM (Continuous Forming) and their modified variants [2]. A large number of studies have been devoted to these processes [2], [4]. However, most of them have focused on easy-to-form metals (Al, Cu), or on exploring exclusively the geometric aspects of the process [5]. Only a handful was dealing with the processing of titanium using SPD [6]-[8].

Making of ultrafine-grained metals is often associated with the ECAP (equal channel angular processing) method [1]-[3]. However, this method is not suitable for processing large volumes of metals, since it is based on repeated pressing of a small specimen through a special extrusion die. Thus, the recent research efforts are focused on the development of continuous processes based on ECAP [4], [7], [8]. The below described experiments were performed on the CONFORM machine which is often used for continuous extrusion of aluminium and copper profile in industrial scale, Fig. 2. In COMTES FHT, the device has been modified in order refine the structure during the forming process [4], [6]-[8]. The refinement is achieved thanks to the shear deformation and high hydrostatic pressure inside the chamber die which was designed based on the ECAP method [3].

Dental implants are made of commercially pure titanium (CP Ti) whose chemical composition meets technical designations of Grade 1 through Grade 4. Chemical compositions of these CP Ti grades are given in Table I. CP Ti grades differ predominantly in their iron and oxygen levels. Atoms of these elements occupy interstitial positions in titanium lattice. With increasing levels of these elements, the strength of the material increases whereas the ductility decreases [6]. CP Ti is widely used in dentistry, particularly for its excellent biocompatibility, as it does not contain the potentially toxic aluminium and vanadium, unlike the below-mentioned Ti6Al4V alloy [9]. The present study, therefore, attempts to expand the knowledge in this area. When compared to other metals and alloys used in dentistry, titanium shows the most favourable ratio of cost price and material properties (corrosion resistance, biocompatibility and others).

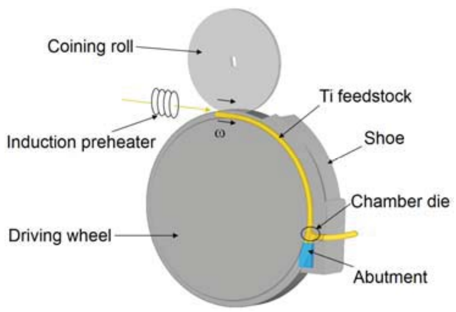

Fig. 1 CONFORM SPD device

II. Characterization of Material and Process

The experimental materials were in the form of 10 mm-diameter bars of commercial-purity titanium grade 2 and grade 4. The stock had not been heat-treated in any way prior to the forming experiments. Both of these grades are commercially pure and the chemical composition is defined by the ASTM standard. The exact chemical composition, for both grades, is

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shown in Table I. The composition was measured by means of a Bruker Q4 Tasman optical emission spectrometer, and a Bruker G8 Galileo gas analyser.

TABLE I
CHEMICAL COMPOSITION OF FEEDSTOCK IN WEIGHT PERCENT (WT. %)

Material	Fe [%]	O [%]	C [%]	H [%]	N [%]	Ti[%]
Ti Grade 2	0,046	0,12	0,023	0,0026	0,0076	balance
Ti Grade 4	0,05	0,4	0,1	0,0125	0,05	balance

The processing of materials was done in two single steps for both materials under the same technological parameters (temperature, true deformation, deformation rate). At the first stage, bars (diameter = 10 mm) were extruded with a help of the CONFORM SPD device. The extrusion temperature was hold in a range from 180 °C to 220 °C. Nevertheless, the real temperature is probably even higher as the deformation heat is generated during the forming process, Fig. 2. Totally, three passes, through the CONFORM SPD device, were achieved. The product cross-section was identical to that of the feedstock (10 mm). Cold working, the subsequent process, was carried out at ambient temperature. In this operation, the cross-section area was reduced by 20% in each pass. The total area reduction was 80%.

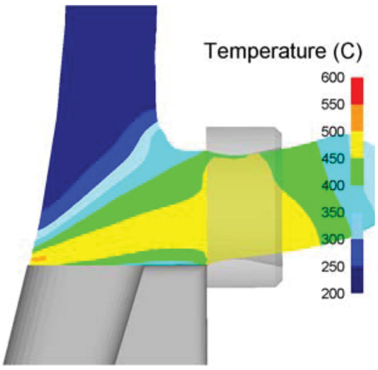

Fig. 2 Numerical model of the temperature distribution during the CONFORM SPD process

The material's mechanical properties at room temperature were determined with cylindrical tensile test specimens with a gauge length of 25 mm and a diameter of 5 mm.

Longitudinal and transverse metallographic sections were prepared by mechanical grinding and polishing. In the final polishing step, 10% hydrogen peroxide solution with colloidal silica of 50 nm mean grain size was used. The microstructure was revealed by etching with Kroll's reagent. Micrographs were taken using Nikon Eclipse MA 200 optical microscope.

For the purposes of observation in the transmission electron microscope (TEM), thin foils were prepared with final electrolytic thinning in a Tenupol 5 device, using a solution of 300 mL CH_3OH + 175 mL 2-butanol + 30 mL $HClO_4$ at –10 °C and a voltage of 40 V. The TEM analysis was performed in a JEOL 200CX instrument with an acceleration voltage of 200 kV.

III. MICROSTRUCTURE OBSERVATIONS

The microstructure of the feedstock consisted of equiaxed recrystallized grains with annealing twins (as shown in Figs. 3 and 4), which are characteristic for the hexagonal lattice. The same characteristic was observed for both grades difference. The smaller grain size, 32 µm, was measured for the Ti Grade 4. The initial grain size of 62 µm was measured for the Ti Grade 4. The lower value, for the Ti Grade 4, was probably caused because of to the higher content of oxygen which slows down the grain growth during the processing.

Fig. 3 The initial structure of Ti Grade 2 with the mean grain size of 62 µm

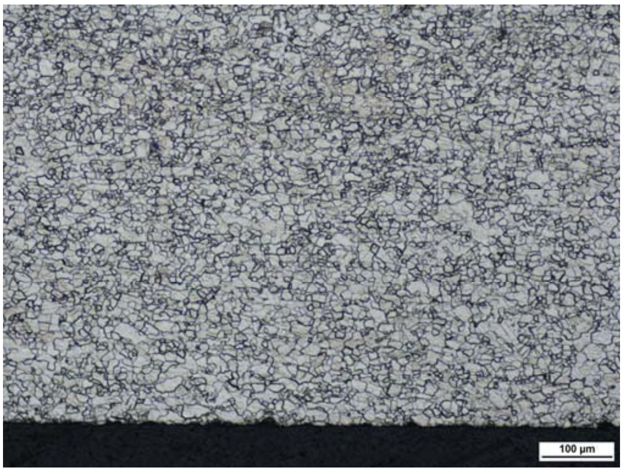

Fig. 4 The initial structure of Ti Grade 4 with the mean grain size of 32 µm

The first pass, through the CONFORM SPD device, led to intensive grain refinement for both grades (Table II). The mean grain size was 325 nm for Ti Grade 2. The higher value of mean grain size, compared to Ti Grade 2, was achieved for Ti Grade 4, as the value reached 374 nm. Subsequent passes produced equiaxed grains, nevertheless the further refinement did not occur. The mean grain size was even higher after the third pass for both grades (Table II). This phenomenon would have been probably caused by the dynamic or post-dynamic recrystallization. As seen from Fig. 2, the deformation could increase the temperature up to 500 °C which is sufficient for softening processes. The generation and effects of deformation heat are often ignored in SPD applications. The substructure upon three passes, for both grades, is consisted from polyhedral grains with non-uniform dislocation density. The variations in grain morphology are an indication of non-uniform deformation conditions (temperature distribution, stress state, strain rate) within the material. There was non-uniformity in not only grain morphology but in grain size as well, as shown in Figs. 6 and 9. Figs. 9 and 10 show the microstructure upon 3 passes through CONFORM SPD and after cold working with a cross section area reduction of 35%. Microstructural changes were visible: higher dislocation density and grains elongated in the direction of material flow. The mean grain size was not further refined, equiaxed grains were just elongated. The width of elongated grains, after three passes through the CONFORM SPD device and cold working with 30% of the area reduction, was 370 nm for Ti Grade 2 and 410 nm for Ti Grade 4. These factors are characteristic for the work hardening.

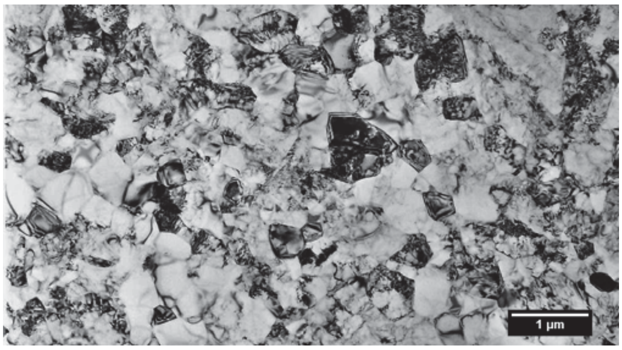

Fig. 5 The structure of Ti Grade 2 upon three passes through CONFORM SPD; the mean grain size is 390 ±150 nm

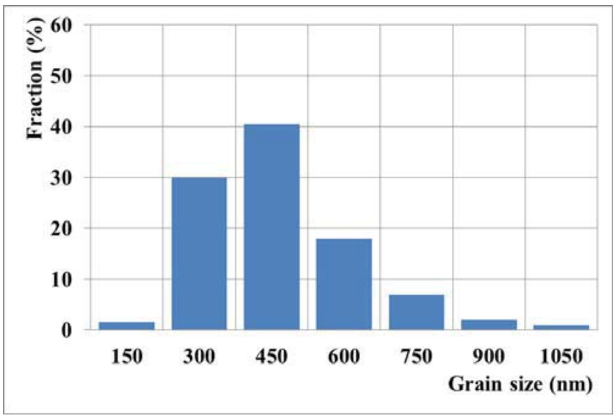

Fig. 6 Grain size histogram in the direction after the third pass

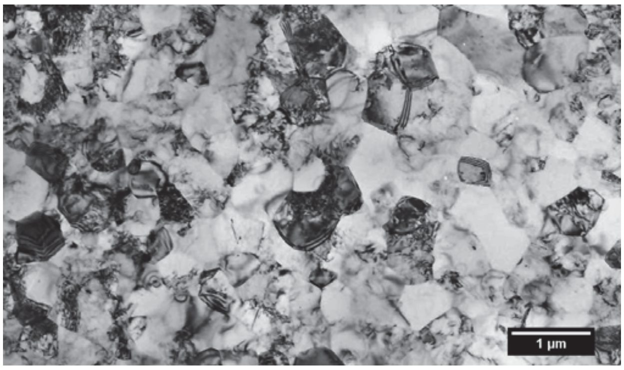

Fig. 7 The structure of Ti Grade 4 upon three passes through CONFORM SPD; the mean grain size is 435 ±195 nm

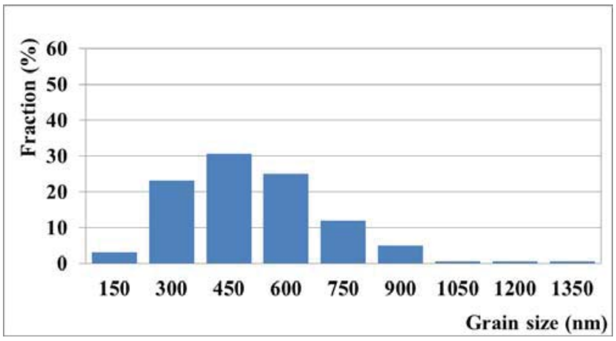

Fig. 8 Grain size histogram in the direction after the third pass

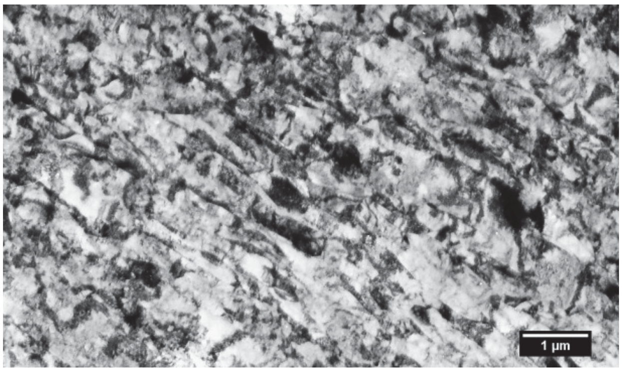

Fig. 9 Microstructure of Ti Grade 2 upon 3 passes through CONFORM SPD and after cold working (cross section area reduction of 35%)

TABLE II
MEAN GRAIN SIZE IN THE TRANSVERSE DIRECTION

Condition	Ti Grade 2 [nm]	Ti Grade 4 [nm]
As - received	62000	32000
1 pass	325 ± 180	374 ± 150
2 pass	330 ± 170	338 ± 178
3 pass	390 ± 150	435 ± 195
3 pass + cold area reduction 35%	370 ± 150	410 ± 150

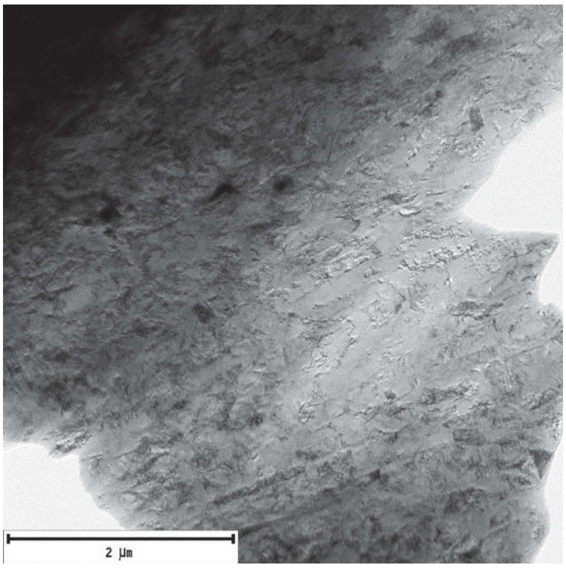

Fig. 10 Microstructure of Ti Grade 4 upon 3 passes through CONFORM SPD and after cold working (cross section area reduction of 35%)

TABLE III
MECHANICAL PROPERTIES AFTER CONFORM SPD PROCESSING AND AFTER CONFORM SPD + ROTARY SWAGING

Condition	Ti Grade 2			Ti Grade 4		
	0.2 OYS [MPa]	UTS [MPa]	A_5 [%]	0.2 OYS [MPa]	UTS [MPa]	A_5 [%]
As - received	370	480	25	563	650	24
1 pass	540	582	22	707	748	22
2 pass	560	601	22	740	760	22
3 pass	570	624	21	756	773	21,5
3 pass + cold area reduction 80%	960	1050	11	1240	1250	9

Ultimate tensile strength (UTS); offset yield (OYS); Elongation (A5).

IV. Mechanical Properties

Mechanical properties of workpieces in various conditions are given in Table III. Clearly, the largest increment in mechanical properties was attained upon the first pass. The ultimate strength rose from 480 MPa to 582 MPa for Ti Garde and from 650 MPa to 748 MPa for Ti Grade. This increment is given mainly by fragmentation of initial grains and by increased dislocation density. Subsequent passes led to smaller increments in ultimate strength and yield stress. This effect is in agreement with the grain sizes obtained (Table II) which did not decrease with additional passes. The final ultimate strength upon three passes was 624 MPa for Ti Grade 2 and 773 MPa for Ti Grade 4. Another important finding was the constant ultimate elongation A5, irrespective of the number of subsequent passes. The material therefore exhibited excellent ductility. Fig. 10 then shows the example of stress-strain curve for Ti Grade 4 for each pass through the CONFORM SPD device.

A further increase in mechanical properties was obtained by cold working applied after the three passes through the CONFORM SPD machine (Table III). As a consequence of the work hardening, the ultimate strength and the yield strength rapidly increased, nevertheless the elongation dropped down. The ultimate stress, after three passes though the CONFORM SPD machine and cold working with the reduction of 80%, reached 1050 MPa for Ti Grade 2 and 1250 MPa for Ti Grade 4. These values are roughly more than two times higher compared to the initial state.

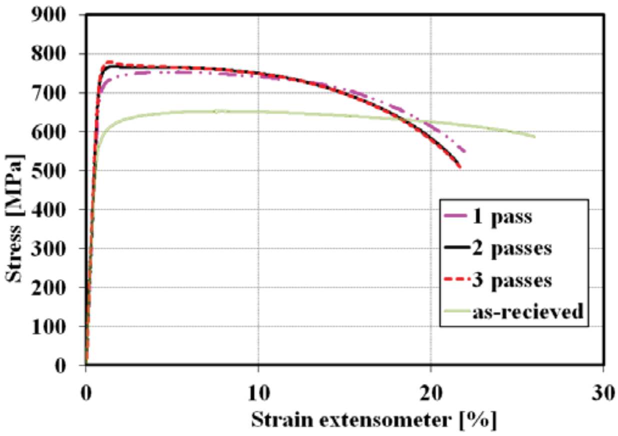

Fig. 11 Engineering stress-strain curves in different structural states for Ti Grade 4

V. Conclusions

The purpose of this study was to analyze the effect of SPD and cold working on mechanical and microstructural properties of ultrafine-grained Grade 2 and Grade 4 titanium.

Forming by CONFORM SPD led to considerable refinement of the initial microstructure. The resulting grains were equiaxed and the dislocation density in them was non-uniform. The first pass through the machine led to a notable reduction in grain size. The mean grain size after the first pass was in the range of 325 nm for Ti Grade 2 and 374 nm for Ti Grade 4. Subsequent passes did not result in further grain size reductions. The mean grain size, after three passes through the CONFORM SPD device, was 390 nm for Ti Grade 2 and 435 nm for Ti Grade 4. The increased grain size, after third pass, was probably caused due to dynamic or post-dynamic recrystallization. Subsequent work hardening resulted in grain elongation and increased dislocation density. The width of elongated grains, after three passes through the CONFORM SPD device and cold working with 30% of the area reduction, was 370 nm for Ti Grade 2 and 410 nm for Ti Grade 4. Generally, the grain refinement was more pronounced for Ti Grade 2.

The largest increase in ultimate strength occurred after the first pass through the CONFORM SPD machine. The value rose from 480 MPa to 582 MPa for Ti Grade 2 and from 650 MPa to 748 MPa for Ti Grade 4 without any significant reduction in ductility for both materials. Subsequent passes led to only slight increases in ultimate strength. After three passes through the CONFORM SPD device, the specimens were cold worked, which brought strength to 1050 MPa for Ti Grade 2 and to 1250 MPa for Ti Grade 4. The increase of the ultimate strength was accompanied by the decrease of ductility as a consequence of the work hardening effect.

ACKNOWLEDGMENT

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.

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