The effect of annealing on mechanical and structural properties of UFG titanium grade 2

J Palán¹, T Kubina¹, P Motyčka¹,  
¹ COMTES FHT a.s., Dobřany, Czech Republic, EU

E-mail: jan.palan@comtesfht.cz, tomas.kubina@comtesfht.cz, petr.motycka@comtesfht.cz

Abstract. The present paper explores the effect of annealing on mechanical and structural properties of ultrafine-grained (UFG) Ti Grade 2 after it was mechanically worked in either CONFORM SPD or rotary swaging (RS) machine. The main objective of this study was to optimize the annealing schedule in order to achieve recovery in the severely deformed structure and at the same time retain the mechanical properties of the worked material. The temperatures of the recovery processes were determined by means of dilatometry. It was found that in an ultrafine-grained material the temperatures of the recovery processes are shifted towards lower values. Based on dilatometric analysis, annealing schedules were developed and mechanical and structural properties were evaluated.

1 Introduction
Technologies which make use of severe plastic deformation (SPD) have been receiving major attention. SPD leads to considerable grain refinement and therefore to improved mechanical properties. The relationship between mechanical properties and grain size is described by the Hall-Petch equation. The best-known SPD technique is equal channel angular pressing (ECAP) where material is forced through two channels which connect at an angle. High hydrostatic pressure, shear deformation and sufficiently low temperature lead to intensive grain refinement [1]. Research into processing of pure titanium by SPD techniques has been pursued for quite some time [2]. Today, ultrafine-grained materials can even be produced using the CONFORM ECAP (CONFORM SPD) method [3]. The main advantage of this method is its continuous process [4]. As proven in the early study [2,4], processing of Ti by CONFORM ECAP provides higher strength without any substantial decrease in elongation. The strengthening effect is however limited by a certain number of passes, or more accurately, by certain grain refinement achieved [5]. After this number of passes, mechanical properties cease to rise. This can be explained by the fact that beyond a certain limit of grain refinement, equiaxed grains merely rotate without becoming finer [6]. Nevertheless, ultimate strength and yield stress can still be improved through classical work hardening. Process routes that involved working in the CONFORM ECAP machine and subsequent drawing in a wire-drawing machine have already been tested [5]. It should be noted that subsequent working causes changes in the microstructural characteristics of the material, and reduces its ductility. What is meant by the changes in microstructural characteristics is substantially higher dislocation density. The material that had been worked in this manner then exhibits reduced toughness and high residual stresses due to non-uniform deformation. These negatively affect its behaviour, for instance during machining. Workpiece fracture may occur due to superposition of machining-induced stresses and the residual stresses caused by
previous working (work hardening). Figure 1 shows a fractured implant. It was manufactured from a material that had been worked by CONFORM SPD and rotary swaging. Residual stresses may also compromise the shape stability of the product and cause the Bauschinger effect. In addition, they may have impact on the fatigue strength of the material. Nevertheless, one can improve all these properties by appropriate heat treatment which relieves residual stresses and provides recovery of the structure. Its temperature must be optimal to ensure that these desirable effects are not accompanied by a decrease in strength. An important factor which plays a role in choosing the annealing temperature is the accumulated strain. Generally, accumulated strain energy introduced by severe deformation causes recovery processes to start at lower temperatures. The present work studied this shift of recovery temperatures, and the effect of temperature on mechanical properties of commercial-purity Grade 2 titanium in various heat-treated conditions.

Figure 1. Fractured implant. The implant material was treated as follows: CONFORM SPD (3 passes) + rotary swaging (cross section area reduction=80 %). A detail of the failure location is shown on the right.

2 Material and experiment description

The material used was CP Grade 2 titanium with the chemical composition given in Table 1. This composition was measured by means of a Bruker Q4 Tasman optical emission spectrometer, and a Bruker G8 Galileo gas analyser. The diameter of the Ti rods was 10 mm.

|       | Fe   | O    | C    | H    | N    | Ti    |
|-------|------|------|------|------|------|-------|
| wt. % | 0.046| 0.12 | 0.023| 0.0026| 0.0076| 99.822|

The processing was carried out in CONFORM SPD machine (Figure 2 – left), type 315i, with a modified die chamber, and in the HMP R4-4 rotary swaging machine. In the CONFORM SPD process, the temperature was 220 °C, the wheel speed was 0.5 rpm, and the angle of the die chamber was 90°. Three passes through the CONFORM SPD machine were completed. The product cross-section was identical to that of the feedstock. Rotary swaging (Figure 2 – right), 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 %.
Figure 2. 3D model of the CONFORM SPD process (left) and the detail of the shear deformation zone inside the die chamber (middle). On the right picture, the principle of rotary swaging is shown.

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 CH3OH + 175 ml 2-butanol + 30 ml HClO4 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. Selective electron diffraction was used for the determination of the phases. Grain size was measured using the linear intercept method.

The effect of deformation on the thermal expansion of titanium, and the temperature range for recovery were explored using a Linseis L75 Platinum horizontal dilatometer with an Al2O3 specimen chamber and a pull bar. The temperature changes were monitored with a thermocouple on specimens of 5 mm diameter and with lengths of approximately 20 mm. Nitrogen (N2) was used as the protective gas. After heating to 950 °C at a rate of 3 K/min, the specimen was cooled at 20 K/min to 600 °C. Then the specimen was left to cool in air to the ambient temperature.

The specimens were annealed at various temperatures in a range between 150–500 °C for various times in a box furnace. The specimens were placed into a heated furnace. Cooling took place in air. Prior to annealing, the material was subjected to three passes through the CONFORM SPD machine and to rotary swaging with an overall cross section area reduction of 80 %. Hardness was measured on specimens annealed according to the initially proposed annealing sequences. Based on their values, new annealing sequences were developed. Specimens annealed using these sequences were then tensile-tested.

3 Microstructure
CONFORM SPD passes led to considerable refinement of the initial microstructure. The initial mean grain size was 5390 nm (Figure 3 left). After three passes, it dropped to 390 nm (Figure 4 right). After three passes, the resulting grains were equiaxed and the dislocation density in them was non-uniform. Figure 4 shows the microstructure upon 3 passes through CONFORM SPD and after rotary swaging with a cross section area reduction of 35 %. Microstructural changes were visible: higher dislocation density and grains elongated in the direction of material flow.
Figure 3. The micrograph on the left shows the initial structure with the mean grain size of 5390 nm. The micrograph on the right shows the structure upon three passes through CONFORM SPD; the mean grain size is 390 nm. Both micrographs are of the transverse section through the wire.

Figure 4. Microstructure upon 3 passes through CONFORM SPD and after rotary swaging (cross section area reduction of 35 %). Detail of microstructure on a longitudinal section through the wire.

4 Dilatometric measurement
The changes in length during heating is shown in Figure 5. The length change of the undeformed specimen (as-received condition) does not change significantly, and is in a good agreement with literature data [17]. The length of the deformed specimen increases more rapidly and then somewhat more slowly again twice – within two temperature intervals. The increase is assumed to be linked with stress relief but the shape of the peak suggests that several processes might operate concurrently. The minor decrease in the expansion rated is assumed to be linked either with the recovery and recrystallization or rearrangement of the atoms of alloying elements into lattice defects. The temperature ranges of these phenomena are listed in Table 2.

Figure 5. Length change during the heating for as received state and for state after three passes through the CONFORM SPD device and after rotary swaging with the area reduction of 80%.
Table 2. Peak start and end temperatures for changes in length during heating.

| Condition         | Peak 1 start /°C | Peak 1 end /°C | Peak 2 start /°C | Peak 2 end /°C |
|-------------------|------------------|----------------|------------------|----------------|
| CONFORM SPD + RS  | 175              | 350            | 430              | 535            |

5 Mechanical properties

Hardness measurement

The hardness measurement was provided for the sample after CONFORM SPD and rotary swaging for different annealing temperatures and times. Figure 6 indicates that annealing in the 150–300 °C interval caused no substantial decrease in hardness. Where hardness became lower, the decrease was only slight. One can assume that the structure becomes rearranged in order to reduce the total energy stored, and that residual stresses are relieved, which is evidenced by dilatometric measurement. At temperatures of 350–500 °C, the decrease in hardness is substantial because recrystallization sets in.

Figure 6. Hardness vs. annealing temperature and time for sample after CONFORM SPD (3 passes)+RS (Area reduction of 80%).

Tensile testing

Tensile properties found by testing are given in Table 3. Table 3 indicates that the largest increase in mechanical properties was obtained by the first pass through the CONFORM SPD machine. The subsequent passes led to smaller increments. It is important to note that the increase in ultimate strength and yield stress upon CONFORM SPD is not offset by a decrease in ductility. The improvement in mechanical properties is mainly due to grain refinement. A further increase in mechanical properties was obtained by rotary swaging applied after the three passes through the CONFORM SPD machine.

Table 3. Mechanical properties after CONFORM SPD processing and after CONFORM SPD + rotary swaging. Ultimate tensile strength (UTS); offset yield (OYS); reduction of area (RA); Elongation (A5).

| Condition                                      | 0.2 OYS [MPa] | UTS [MPa] | A5 [%] | RA [%] |
|-----------------------------------------------|---------------|-----------|--------|--------|
| as received                                   | 370           | 480       | 25     | 52     |
| CONFORM SPD – 1 pass                          | 540           | 580       | 23     | 62     |
| CONFORM SPD – 2 passes                        | 560           | 600       | 23     | 62     |
| CONFORM SPD – 3 passes                        | 570           | 623       | 20     | 64     |
| CONFORM SPD – 3 passes + RS (80 % area reduction) | 980           | 1057      | 12     | 56     |

Tensile testing after annealing

Figure 7 and Figure 8 show the evolution of mechanical properties with annealing temperature and time for sample after three passes on the CONFORM SPD device and rotary swaging with the area...
reduction of 80%. Figure 7 shows the response at 250 °C. It is clear that annealing for one hour causes a slight decrease in ultimate strength but a more pronounced decrease in yield stress. At annealing times between one hour and four hours, the values of mechanical properties do not change and the structure exhibits good thermal stability. Mechanical properties decrease slightly again after annealing for five hours. Similar behaviour was found at the temperature of 300 °C (Figure 8). The only difference is that mechanical properties decrease more steeply at the higher temperature. The annealing had no effect on the A5 elongation value. Another finding was that the ratio of ultimate strength and yield stress increased after only one-hour annealing. One can therefore conclude that annealing improves the toughness of the material.

6 Conclusion

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

Forming by CONFORM SPD led to considerable refinement of the initial microstructure. The mean grain size was 390 nm. The resulting grains were equiaxed and the dislocation density in them was non-uniform. Thanks to the grain refinement, the yield stress and ultimate strength increased without the ductility of the material being reduced. After that, the material was rotary-swaged. The grains in the microstructure produced by rotary swaging were not equiaxed any more: they were elongated in the forming direction, with higher dislocation density. Working led to a large amount of work hardening. It was reflected in the increased ultimate strength and yield stress and in the reduced A5 elongation.

Dilatometric analysis revealed that the temperatures of recovery in the deformed specimen had decreased. The reason is that the activation energy for recovery processes was reduced by the deformation applied in CONFORM SPD and rotary swaging. Dilatometry also showed that the amount of residual stresses from forming had been relieved.

The effect of annealing in the temperature interval of 150–500 °C on hardness was explored. In the 150–300 °C range, hardness did not decrease substantially. The structure showed a good thermal stability.

The materials annealed at 250 °C and 300 °C were tested in tension. As short annealing as one hour caused a slight decrease in ultimate strength and a more pronounced decrease in yield stress. The decrease was steeper after annealing at 300 °C. On one hand, annealing led to a slight decrease in ultimate strength but on the other hand, the ratio of ultimate strength and yield stress increased, which suggests better toughness. Future research will focus on microstructural evolution after annealing.
Acknowledgement
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.

References
[1] Valiev R.Z et al. 2000 Bulk nanostructured materials from severe plastic deformation. Progress in Materials Science. 45 103-189.
[2] Kubina T et al. 2015 Preparation and thermal stability of ultra-fine and nano-grained commercially pure titanium wires using CONFORM equipment. Materiali in Technologije. 49 213-217.
[3] Raab G et al. 2004 Continuous processing of ultrafine grained Al by ECAP–Conform. Materials Science and Engineering: A. 382 30-34.
[4] Duchek M et al. 2013 Development of the production of ultrafine-grained titanium with the Conform equipment. Materiali in Technologije. 47 515-518.
[5] Gunderov D.V et al. 2013 Evolution of microstructure, macrotexture and mechanical properties of commercially pure Ti during ECAP-conform processing and drawing. Materials Science and Engineering: A. 562 128-136.
[6] Mishra A et al. 2007 Microstructural evolution in copper subjected to severe plastic deformation: Experiments and analysis. Acta Materialia. 55 13-28.
[7] Wei Q, Cheng S et al. 2004 Effect of nanocrystalline and ultrafine grain sizes on the strain rate sensitivity and activation volume: fcc versus bcc metals. Materials Science and Engineering: A. 381 71-79.
[8] Ostrovská L, Vistejnova L et al. 2016 Biological evaluation of ultra-fine titanium with improved mechanical strength for dental implant engineering. Journal of Materials Science. 51 3097-3110.
[9] Zrník J. et al. 2007 Evropská strategie výrobních procesů (Ostrava: Repronis)
[10] Raab G et al. 2004 Continuous processing of ultrafine grained Al by ECAP–Conform. Materials Science and Engineering: A. 382 30-34.
[11] Zemko M et al. 2014 Technological aspects of preparation of nanostructured titanium wire using a CONFORM machine. IOP Conference Series: Materials Science and Engineering. 63 p ??.
[12] Gunderov D.V et al. 2013 Evolution of microstructure, macrotexture and mechanical properties of commercially pure Ti during ECAP-conform processing and drawing. Materials Science and Engineering: A. 562 128-136.
[13] Semenova I.P et al. 2008 Strength and fatigue properties enhancement in ultrafine-grained Ti produced by severe plastic deformation. Journal of Materials Science. 43 7354-7359.
[14] Palán J et al. 2015 Continuous extrusion of commercially pure titanium GRADE. 4. Journal of Achievements in Materials and Manufacturing Engineering. 69 33-37.
[15] Humphreys F.J et al. 2004 Recrystallization and related annealing phenomena (Boston: Elsevier) p 574.
[16] Eivani A.R. et al. 2016 Mechanism of the formation of peripheral coarse grain structure in hot extrusion of Al-4.5Zn-1Mg. Philosophical Magazine. 96 1188-1196.
[17] Hindert P 1943 Thermal expansion of titanium. Journal of Research of the nationa Bureau of Standards. 30 101-105.
[18] Reglitz G et al. 2015 Combined volumetric, energetic and microstructural defect analysis of ECAP-processed nickel. Acta Materialia. 103 396-406.