Archives of Materials Science and Engineering

Volume 88
Issue 1
November 2017
Pages 5-11

International Scientific Journal published monthly by the World Academy of Materials and Manufacturing Engineering

Possibilities of biocompatible material production using conform SPD technology

J. Palán *, L. Maleček, J. Hodek, M. Zemko, J. Dzugan
COMTES FHT a.s., Průmyslová 995, Dobřany 334 41, Czech Republic
* Corresponding e-mail address: jan.palan@comtesfht.cz

ABSTRACT

Purpose: At present, materials research in the area of SPD (severe plastic deformation) processes is very intensive. Materials processed by these techniques show better mechanical properties and have finer grain when compared to the input feedstock. The refined microstructure may be ultrafine-grained or nanostructured, where the grain size becomes less than 100 nm. One of the materials used for such processes is CP (commercially pure) titanium of various grades, which is widely used for manufacturing dental implants. The article deals with one of the technologies available for the production of ultrafine-grained titanium: Conform technology. CP titanium processed by CONFORM technology exhibits improved mechanical properties and very favourable biocompatibility, due to its fine-grained structure. The article presents the current experience in the production of ultrafine CP titanium using this technology. The main objective of this article is describing the behaviour of CP titanium during forming in the Conform device and its subsequent use in dental implantology.

Design/methodology/approach: In the present study, commercially pure Grade 2 titanium was processed using the CONFORM machine. The numerical simulation of the process was done using FEM method with DEFORM^{TM} software. The evaluation was performed by simple tensile testing and transmission electron microscopy. The first conclusions were derived from the determined mechanical properties and based on analogies in available publications on a similar topic.

Findings: This study confirmed that the SPD process improves mechanical properties and does not impair the ductility of the material. The CONFORM process enables the continuous production of ultrafine-grained or nanostructured materials.

Research limitations/implications: At the present work, the results show the possible way of continuous production of ultrafine-grained or nanostructured materials. Nevertheless, the further optimization is needed in order to improve the final quality of wires and stabilize the process. As these factors will be solved, the technology will be ready for the industry.

Practical implications: The article gives the practical information about the continuous production of ultrafine-grained pure titanium Grade 2 and the possibility of use this material for dental implants.

Originality/value: The present paper gives information about the influence of the CONFORM technology on final mechanical and structural properties with the emphasis on technological aspects.

Keywords: CONFORM, ECAP, Titanium, Dental implants

Reference to this paper should be given in the following way:

J. Palán, L. Maleček, J. Hodek, M. Zemko, J. Dzugan, Possibilities of biocompatible material production using conform SPD technology, Archives of Materials Science and Engineering 88/1 (2017) 5-11.

BIOMEDICAL AND DENTAL MATERIALS AND ENGINEERING

1. Introduction

The past decade has seen intensive research into forming processes in relation to severe plastic deformation (SPD). SPD is an umbrella term for a group of forming techniques that impart ultra-large plastic strain to the material being formed in order to refine the initial structure. The occurrence of ultrafine structure or nanostructure is conditional on high hydrostatic pressure (P >1 GPa), and large shear deformation applied at relatively low temperatures. Temperatures of SPD processes should meet the condition of T (SPD) <0.4 T (melting). Another aspect is the strain magnitude, defined as e(true strain) >6-8 [1]. When the above conditions are met, the forming process leads to a high density of lattice defects, predominantly dislocations, and to formation of subgrains, which reduces the stored energy. This fact is behind the research into ultrafine-grained materials.

Today's most widely used SPD processes include High-Pressure Torsion (HPT), Accumulative Roll-Bonding (ARB), Equal-Channel Angular Pressing (ECAP), Continuous Forming (CONFORM) and their modified variants. A large number of studies have been devoted to these processes [1-10]. However, most of them have focused on easy-to-form metals (Al, Cu) [1-4], or on exploring exclusively the geometric aspects of the process [5-7]. Only a handful was dealing with the processing of titanium using SPD [8-10].

The present study, therefore, attempts to expand the knowledge in this area. It focuses on studying ultrafine-grained titanium for dental implants. 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) [11]. Another reason for aiming at these products (used for dental implants) is the fact that the diameter of the Ti rods produced (10 mm) is particularly suitable for this type of application.

2. Characterization of material and process

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 1. 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. 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.

The biocompatibility of metals for dental applications is important for ensuring that dental implants are not harmful to health. A number of studies have been devoted to the biocompatibility of titanium alloys [11-16]. Some of them [13], [16] pointed out the effect of grain size on the biological behaviour of CP Ti. In these studies, authors indicate that the biological behaviour is more favourable when nanostructured Ti is obtained.

Table1.
Chemical compositions of CP Ti Grade 1 through Grade 4 and Ti6Al4V alloy (according to ASTM F67) in wt. %

ASTM Grade	Fe max.	O max.	N max.	C max.	Al	V	Ti
Grade 1	0.20	0.18	0.03	0.08	–	–	balance
Grade 2	0.30	0.25	0.03	0.08	–	–	balance
Grade 3	0.30	0.35	0.05	0.08	–	–	balance
Grade 4	0.30	0.40	0.05	0.08	–	–	balance
Ti6Al4V (Grade 5)	0.40	0.20	0.05	0.08	5.5-6.5	3.5-4.5	balance

CP Ti shows poorer mechanical properties than Ti6Al4V in terms of tensile strength and fatigue resistance. Nevertheless, these can be improved by employing SPD processes which refine the grain and thus enhance the mechanical properties of the material. In medical applications, Young's modulus is very significant, as it plays an important role in the implant's contact with the bone. The mechanical properties which are required of the above-named CP Ti grades are specified in Table 2.

Table 2.
The required mechanical properties of CP Ti Grade 1 through Grade 4 and Ti6Al4V alloy (according to ASTM F67) at room temperature

ASTM Grade	Tensile strength R_m, MPa	Yield strength $R_{p0.2}$, MPa	Elongation A_5, %
Grade 1	min. 240	170-310	24
Grade 2	min. 345	275-450	20
Grade 3	min. 450	380-550	18
Grade 4	min. 550	483-655	15
Ti 6Al4V (Grade 5)	min. 895	min. 828	10

The principle of forming CP Ti in CONFORM machine to obtain ultrafine-grained products is shown below (Fig. 1). The feedstock is guided by the coining roll 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 machine through the chamber die.

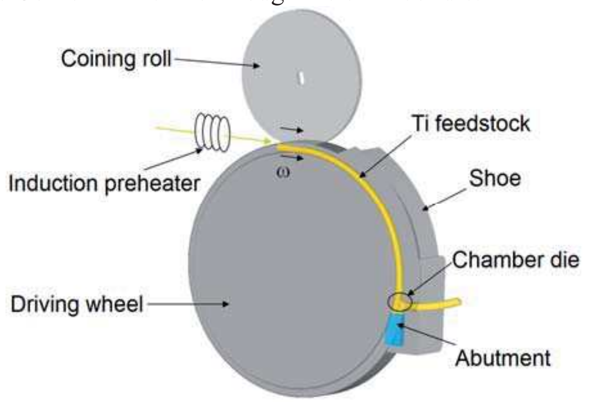


Fig. 1. CONFORM machine

3. Computer simulation of process

An FEM model of the Conform process has been developed using DEFORM-3D v.10.1.2 software. With the aid of the model, the forming process can be analysed in detail and with emphasis on optimum geometry of the tooling. The material flow and the effects of the equipment modification can be studied without conducting extensive experiments. In addition, one can evaluate the loading on individual tools.

The FEM model was developed using several simplifying assumptions. The tooling was assumed to undergo no deformation (i.e. rigid bodies). A Ti feedstock was considered to be plastic. Thanks to the plane symmetry of the entire process, only one half of the equipment and the Ti feedstock were used for a computation.

The temperature transfer between the Ti feedstock and the driving wheel has been examined. No other parts (tools) were considered. The heat transfer coefficient between the Ti feedstock and the driving wheel was $\alpha = 1000$ W/(m^2·K). The impact of the environment was neglected due to the rate of temperature changes.

The value of the heat transfer coefficient α at the interface between the Ti feedstock and the driving wheel was determined as follows. First, the Ti feedstock heated to 700°C was introduced into the cold driving wheel groove. The decrease in the temperature of the Ti feedstock was measured. The measured data was compared with simulated data for several heat transfer coefficient values. Figure 2 shows the comparison between the measured and the calculated data. As this graphical comparison confirms, a good agreement between the measured and the calculated values was found at $\alpha = 1000$ W/(m^2·K). The heat transfer coefficient between all other tools of $\alpha = 1000$ W/(m^2·K) was determined by estimation (the first approach).

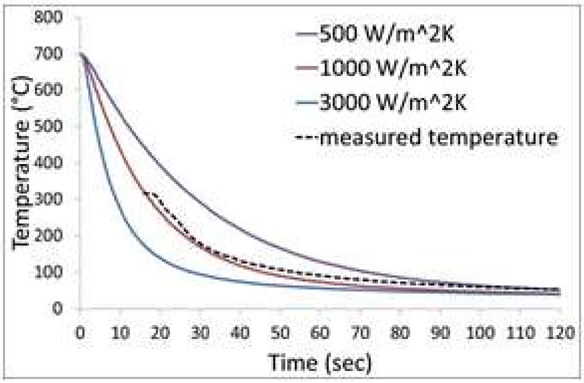


Fig. 2. Measured and calculated decreases in temperature used in determining the heat transfer coefficient between the Ti feedstock and the driving wheel

Friction between the Ti feedstock and the driving wheel plays a significant role in the numerical model, as the friction between these two parts ensure the forming force which push the feedstock through the chamber die. Shear and Coulomb types of friction were tested in the model. The best results were achieved using Coulomb friction with $\mu = 10$ and a constant value with the compression separation criterion. In other cases (values) considered the contact between the titanium feedstock and the driving wheel was insufficient.

Another important characteristic was the friction coefficient between the Ti feedstock and the chamber die which was found by tribometric measurement. At the temperature of $t = 350°C$, the friction coefficient value was $\mu_f = 0.58$. In order to confirm this value, two simulations involving the values of $\mu_f = 0.2$ and $\mu_f = 0.7$ were carried out. Using a visual comparison of the appearance of the

Fig. 3. Metallographic investigation – macro of the Ti feedstock section in the chamber die

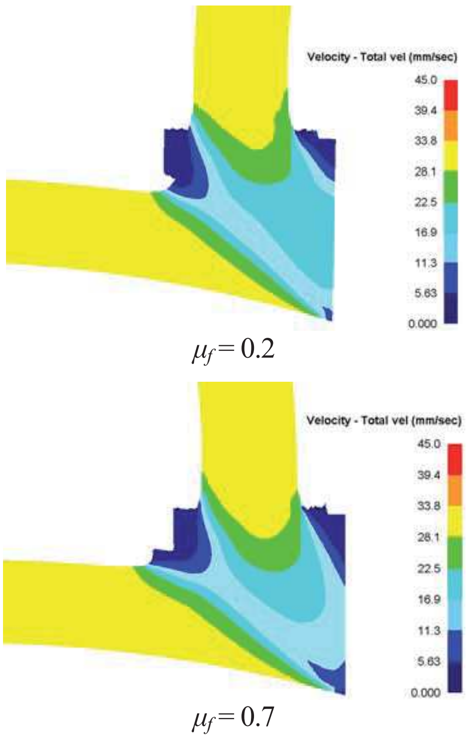


Fig. 4. Illustration of the velocity fields at two friction coefficient levels

titanium feedstock cross-section in the chamber die (Fig. 3) and the simulated velocity field within the feedstock (Fig. 4), the friction coefficient value was determined as $\mu_f = 0.6$ (rounded from 0.58). The friction coefficient between all other tools of $\mu_f = 0.6$ was determined by estimation (the first approach).

4. Process trials

Based on the numerical simulations, a geometry of the tools for titanium extrusion was developed. The materials and heat treatment schedules for the individual parts were selected with respect to the extreme loads under the trial conditions.

The driving wheel was made of nickel-chromium superalloy Inconel 718. AISI H13 and Vanadis 4 alloys were used for making the abutment. The shoe and chamber die were manufactured from AISI H13. All these tooling parts are used for prototype production at COMTES FHT a.s.

The SPD process taking place in Conform equipment involves extreme loads which act predominantly on the abutment. In the CP Ti Grade 2 forming trials, these materials were able to sustain high loads and the desired microstructures have been obtained. However, when the CP Ti Grade 4 feedstock was formed, the abutments sustained damage caused by higher temperatures and loads (Fig. 5). Creep processes dominated among the mechanisms involved.

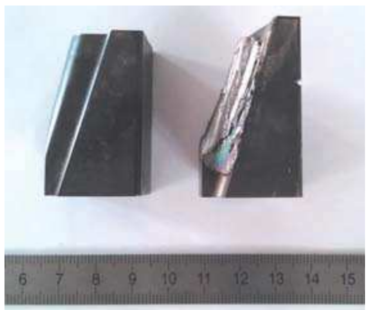


Fig. 5. Abutment damage (a new abutment on the left and the damaged one on the right)

These tooling parts continue to be developed (geometry, surface coatings) in order to optimise the material flow for effective grain refinement and extended life.

The trials are illustrated in Figure 6 which shows plots for the parameters. The first part on the left-hand side of the diagram (which ends approx. 38 minutes into the process) shows the start of the trial where high heating temperatures for the Ti feedstock and tools are required. It is followed by the stage of production of ultrafine-grained titanium characterised by a relatively stable profile of the parameters. The parameter with more significant variations is the current because the feedstock material tends to harden during multiple extrusion process which leads to higher power inputs.

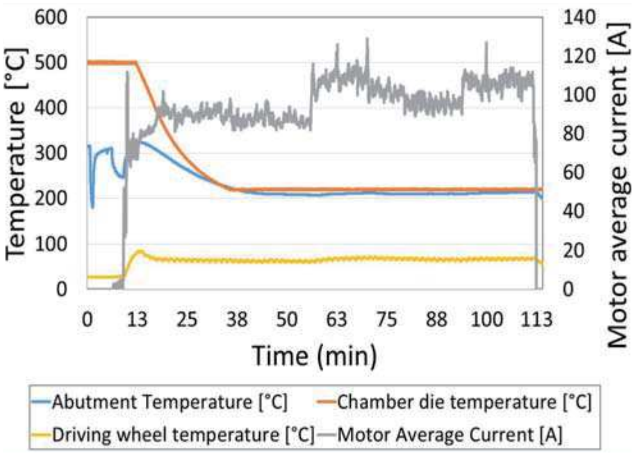


Fig. 6. Parameter plots during trial

5. Resulting properties

The material produced according to a particular schedule in Conform machine was tension-teste. Given values represent average values from at least three specimens. Engineering stress-engineering strain curves for CP Ti Grade 2 after one, two and three passes are shown in Figure 7. The significant improvement in mechanical

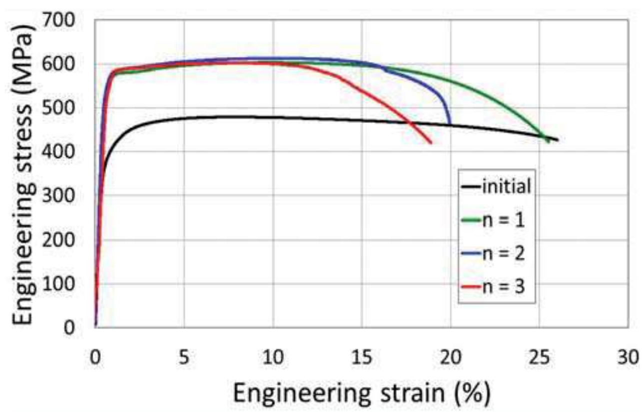


Fig. 7. Engineering stress versus engineering strain for CP Ti Grade 2 in different structural states (n = number of passes)

properties was achieved after first pass, as the ultimate strength raised from the value 479.5 MPa to 602.8 MPa, moreover the elongation was retained almost at the same level. Further passes did not raise the ultimate strength.

Table 3 gives a summary of the resulting mechanical properties.

Table 3.
Mechanical properties of CP Ti Grade 2 after SPD processing in CONFORM equipment (n = number of passes)

State	Tensile strength R_m, MPa	Yield strength $R_{p0.2}$, MPa	Elongation A_5, %	Reduction of area Z, %
initial	479.5	370.6	25.2	51.7
$n = 1$	602.8	540.5	24.6	64.6
$n = 2$	612.5	545.1	20.9	50.2
$n = 3$	601.9	552.8	24.2	64.3

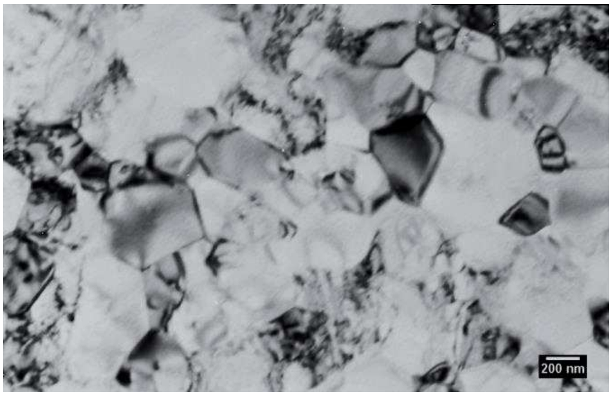
For the purpose of observation in the transmission electron microscope (TEM), thin foils were prepared with final electrolytic thinning in a Tenupol 5 device, using a solution of 300 ml CH_3OH + 175 ml 2-butanol + 30 ml $HClO_4$ at -10°C and a voltage of 40 V. The TEM analysis was performed in a JEOL 200CX instrument with an acceleration voltage of 200 kV. Selective electron diffraction was used for determination of the phases. Grain size was measured using the linear intercept method. The technique which has proven to be the best for evaluating the microstructures of ultrafine-grained materials is transmission electron microscopy (TEM). Using TEM, it was possible to determine phase composition, grain size and strain distribution. Examples of evaluation of substructures of Ti rods are shown in Figure 8.

TEM analysis of samples taken from Ti rods which had underwent one, two and three passes revealed the following facts.

In all cases, the microstructure was ultrafine-grained with mean grain sizes of d_{avg} ~ 320 nm (upon first pass), d_{avg} ~ 250 nm (second pass) and d_{avg} ~ 330 nm (third pass). In all specimens, there were regions with polyhedral grains and regions with heavily-deformed microstructure. Electron diffraction analysis showed that the matrix consisted of αTi.

6. Conclusions

The results of development of ultrafine-grained titanium production process by means of SPD-based Conform



n=1

n=2

n=3

Fig. 8. Titanium substructures after three passes through Conform equipment (*n* = number of passes)

technique have been presented. The input feedstock for the forming process was Grade 2 CP Ti.

Numerical simulations and experimental trials have been used for the development. The simulations enabled the effects of the tooling geometry on the SPD process to be analysed (strain distribution, strain rate and material flow). Thanks to the experimental trials, the operating conditions of the Ti rod production process could be explored (temperature profiles, tooling material behaviour).

As all experiments took place in pilot operation conditions, future development efforts will focus on optimising the process primarily in the following areas:

- Use of numerical simulations for analysing changes in friction conditions and for designing a chamber die with an optimum geometry;
- Conducting trials in order to explore the effects of changes in tooling parameters (geometry, material composition);
- Testing other titanium grades for the purpose of obtainning nanostructure throughout the workpiece volume.

Acknowledgements

This paper was created by project Development of West-Bohemian Centre of Materials and Metallurgy No.: LO1412, financed by the MEYS of the Czech Republic.

References

[1] R.Z. Valiev, T.G. Langdon, Achieving Exceptional Grain Refinement through Severe Plastic Deformation: New Approaches for Improving the Processing Technology, Metallurgical and Materials Transactions A 42/10 (2011) 2942-2951.

[2] A. Azushima, R. Kopp, A. Korhonen, D.Y. Yang, F. Micari, G.D. Lahoti, P. Groche, J. Yanagimoto, N. Tsuji, A. Rosochowski, A. Yanagida, Severe plastic deformation (SPD) processes for metals, CIRP Annals - Manufacturing Technology 57/2 (2008) 716-735, DOI: 10.1016/j.cirp.2008.09.005.

[3] M. Zemko, T. Kubina, J. Dlouhý, J. Hodek, Technological aspects of preparation of nanostructured titanium wire using a CONFORM machine, IOP Conference Series: Materials Science and Engineering 63 (2014) 012049, DOI: 10.1088/1757-899X/63/1/012049.

[4] M. Duchek, T. Kubina, J. Hodek, J. Dlouhý, Development of the production of ultrafine-grained titanium with the conform equipment, Materials and Technology 47/4 (2013) 515-518.

[5] S. Xu, G. Zhao, X. Ren, Y. Guan, Numerical investigation of aluminium deformation behaviour in three-dimensional continuous confined strip shearing process, Materials Science and Engineering A 476/1-2 (2008) 281-289, DOI: 10.1016/j.msea.2007.05.003.

[6] J.R. Cho, H.S. Jeong, Parametric investigation on the curling phenomenon in CONFORM process by three-

dimensional finite element analysis, Journal of Materials Processing Technology 110/1 (2001) 53-60, DOI: 10.1016/S0924-0136(00)00658-0.
[7] J. Hodek, T. Kubina et al, FEM Model of Continuous Extrusion of Titanium in Deform Software, "COMAT 2012", Pilsen, 2012.
[8] G.I. Raab, A.W. Polyakov et al, Formation of a nanostructure and properties of titanium rods during equal-channel angular pressing CONFORM followed by drawing, Russian Metallurgy 5 (2009) 416-420.
[9] D.V. Gunderov, A.W. Polyakov et al, Evolution of microstructure, macrotexture and mechanical properties of commercially pure Ti during ECAP-conform processing and drawing, Materials Science and Engineering A 562 (2013) 128-136, DOI: 10.1016/j.msea.2012.11.007.
[10] A.W. Polyakov, I.P. Semenova G.I. Raab, V.D. Sitdikov, R.Z. Valie, Peculiarities of ultrafine grained structure formation in Ti Grade-4 using ECAP-Conform, Reviews on Advanced Materials Science 31 (2012) 78-84.
[11] L. Ostrovska, L. Vistejnova, J. Dzugan, P. Slama, T. Kubina, E. Ukraintsev, D. Kubies, M. Kralickova, M. Kalbacova, Biological evaluation of ultra-fine titanium with improved mechanical strength for dental implant engineering, Journal of Materals Science 23/6 (2015) 3097-3110, DOI: 10.1007/s10853-015-9619-3.
[12] D.M. Brunette, P. Tengval, M. Textor, P. Thomsen, Titanium in Medicine, Springer-Verlag, Berlin, Heidelberg, 2001, ISBN 978-3-642-63119-1.
[13] J. Petruželka, L. Dluhoš et al, Nanostrukturní titan – nový material pro dentální implantáty, Česká Stomatologie 106/3 (2006) 72-77.
[14] R.Z. Valiev, I.P. Semenova et al, Nanostructured Titanium for Biomedical Applications, Advanced Engineering Materials 10/8 (2008) 1-4.
[15] L. Dluhoš et al, Nanostrukturní titan v detální implantologii, 1. KONGRES biomedicíny v oromaxilofaciálnej oblasti, Zborník referátov, EQUILIBRIA, s.r.o. Kosice, Slovakia, 2009, 299-304, ISBN 978-80-89284-37-5.
[16] D. Hrušák, M. Zemko et al, Usage of nanostructured titanium for endosteal implants, NANOCON 2009, TANGER Ltd., Roznov pod Radhostem, The Czech Republic, 2009, ISBN 978-80-87294.
[17] T. Kubina, J. Dlouhý, M. Köver, M. Dománková, J. Hodek, Preparation and thermal stability of ultra-fine and nano-grained commercially pure titanium wires using conform equipment, Materials and Technology 49/2 (2015) 213-217, DOI: 10.17222/mit.2013.226.