TECHNICAL UNIVERSITY OF CLUJ-NAPOCA

ACTA TECHNICA NAPOCENSIS

Series: Applied Mathematics, Mechanics, and Engineering
Vol. 64, Issue I, March, 2021

RESEARCH ABOUT THE TRIBOLOGICAL PROPERTIES IMPROVEMENT OF AN ALLOY BASED ON TITANIUM HYDRIDE POWDER FOR AUTOMOTIVE COMPONENTS

Cristina Ileana PASCU, Stefan GHEORGHE, Claudiu NICOLICESCU,
Ioan VIDA-SIMITI

Abstract: *In this study it was proposed to obtain an alloy based on titanium but which would allow to reduce the cost price of its elaboration and, on the other hand to have improved wear properties and work hardening ability. For these reasons, titanium hydride was used as based material, which has a lower cost price than pure titanium and, due to the dehydrogenation property during sintering treatment, which allows the intensification of densification. For the same reasons it was considered opportune using PM techniques as a cost-effective way. Thus, for this comparative research, a classic sintering process was chosen, on a single level and a sintering regime in two steps. In order to improve the wear behavior of the material, small amounts of metal were added: 8%wt. Mn, 6%wt. Alumix321, 3%wt. Sn, 2%wt. Zr, and 1%wt. graphite. Final microhardness, microstructural aspects and the wear behavior of the titanium hydride-based alloy have been studied. It was found that the hardness of the sintered samples in two steps was increased, the wear resistance improved and the relative constancy of the values of the friction coefficients.*

Key words: *titanium hydride, sintering, two-step sintering, microstructure, hardness, wear behavior.*

1. INTRODUCTION

In the last half century, titanium and titanium alloys have gained increasingly wider use in various industries, especially in the fields of aerospace, marine and biomedical [1]. Titanium (Ti), as a pure metal is characterized by three special properties: it is the most biocompatible metal [2], being the most used material for biomedical implants [3], has the highest corrosion resistance being the ideal choice in the maritime field [4] and has a high specific resistance and the same magnitude of strength as steel being considered an ideal structural metal to replace steel in automotive industry [5].

Structural applications of titanium and its alloys are limited because of the high cost of production despite the fact that titanium exhibits admirable combined properties such as high strength-to-weight ratio and excellent corrosion resistance [6]. Titanium has been for a long time rare and expensive material [7]. The reason is that conventional metallurgical methods are ineffective in the case of Ti due to its tendency to react at elevated temperatures with broad range of elements [8]. Titanium and titanium alloys processed by traditional methods such as casting [9] and/or forging [10] normally produce an average material utilization factor of only 10%-15 % for finished components [11, 12].

There has been a growing interest in the last decade in Ti powder metallurgy (PM) as a cost-effective way of direct production of complex parts from Ti and its alloys [13, 14]. The PM approach has additional benefits like significantly improving the chemical and microstructural homogeneity of components [15]. Titanium parts may be produced by a wide range of PM techniques. These, depending on the complexity and size of the final components include standard compaction procedure followed by sintering (the press-and-sinter) [16], sintering followed by compacting using hot plastic deformation [17], by direct rolling and extruding of loose powders [18], method of hot isostatic pressing (HIP) [19] and MIM (metal injection molding). [20]. A large spectrum of PM processing routes provides advantages of the elaborated Ti-products: classical sintering, laser forming, spark plasma sintering [21], spraying, rapid solidification [22], mechanical alloying and vapor deposition [23]. However, there are still many issues to be addressed for the wider development of powder metallurgy of titanium such as in-depth identification of impurities arising from raw materials and sintering atmosphere, development of novel sintering methods and new alloy design.

In the automotive field, one of the greatest applications of titanium-based materials is for components belonging to the internal combustion engine area that equip the vehicle (pistons, valves, connecting rod, crank caps, bolts, etc.) [24, 25]. According to [26] among the materials used in the automotive field, titanium-based alloys have a 30% preponderance in modern jet turbine engines, mainly in the front area of the engine.

Nevertheless, according to [27] the high price of pure titanium is its main disadvantage, as well as its relatively low tribological properties [28].

Recent research has revealed the benefits of titanium hydride powder (TiH_2) used as precursor material for Ti powders obtaining. Various comparative studies between the sintering of titanium hydrides and pure titanium have highlighted the advantages of using titanium hydrides not only in terms of significantly lower cost but also due to their dehydrogenation properties. This process appears due to a process of self-reduction by hydrogen atoms and intensifies the sintering process [29, 30].

This paper presents a comparative study on the final mechanical, microstructural and tribological characteristics for an alloy based on titanium hydride obtained through Powder Metallurgy by classical sintering (CS) and sintering in two steps sintering (TTS).

2. EXPERIMENTAL PROCEDURE

As basic material, micrometric titanium hydride, water atomized, with a purity of over 99.7%, was used, Figure 1. In order to obtain a titanium-based alloy with superior physical-mechanical and tribological characteristics, the following components were added to the initial powder by mixing and homogenization: 6% wt. Alumix321, 8% wt. Mn, 3% wt. Sn, 2% wt. Zr and 1% wt. C.

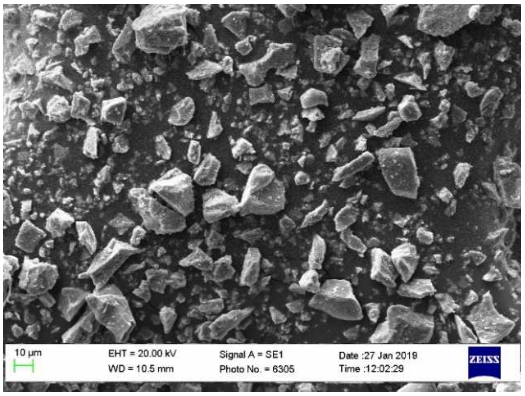

Fig. 1. The SEM image of the TiH_2 powder

The homogenization of the mixture was performed for 90 minutes in a Planetary Mono Mill PULVERISETTE 6 from Fritsch, in an argon atmosphere, having the following characteristics: balls material stainless steel – 1.3541 ISO/EN/DIN codeX47Cr14, B50, powders ratio 1:1, 200 rpm rotational speed of main disk, 250 ml grinding bowl.

The SEM image of the homogenised mixture is presented in Figure 2.

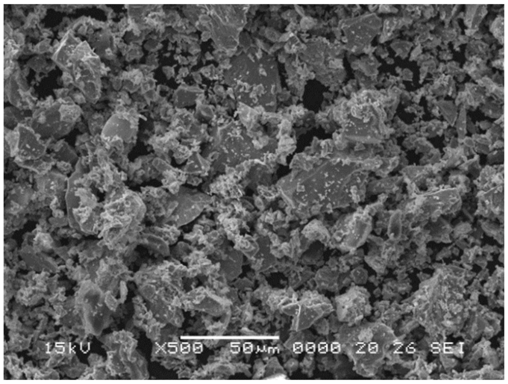

Fig. 2. The SEM image of the mixture

The elemental composition and morphology of the mixture were determined with a scanning electron microscope (SEM) model PHENOM PRO X which has an integrated spectrometer EDS built in and performs highly in imaging and analysis. The chemical composition analysis of mixture is presented in Figure 3, the EDS spectrum is also shown with peaks for the identified elements.

Next, the homogenized mixture was uniaxially cold pressed, on a computerized electromechanical type A009 testing machine.

The applied compaction pressure was 600 MPa with integrated TCSoft2004Plus software.

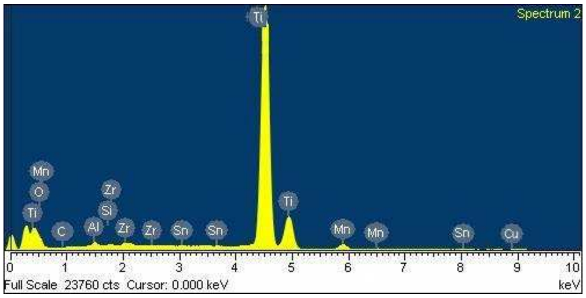

Fig. 3. EDS spectrum of the mixture

The parts were packed into a cylindrical die, with the diameter of the green compacts being 12.05mm.

In the next stage, in order to achieve the densification, techniques specific to powder metallurgy were applied to the green compacts. Thus, a classical sintering process (CS) was applied, Figure 4 and two-step sintering (TSS), Figure 5.

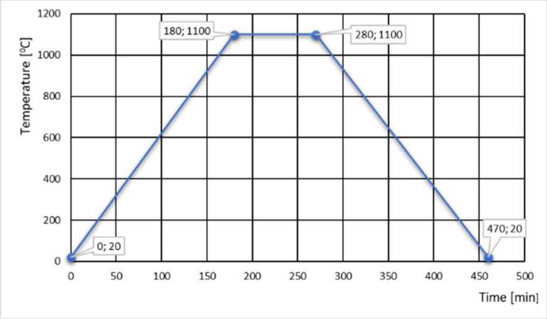

Fig. 4. Classic sintering cycle

The green compacted have been sintered into a Nabertherm furnace, in argon atmosphere, with a heating rate of 6^0C/min for both cycles.

Classic sintering cycle, Figure 4, was performed in one step, at 1100^0C for 100 minutes dwell time.

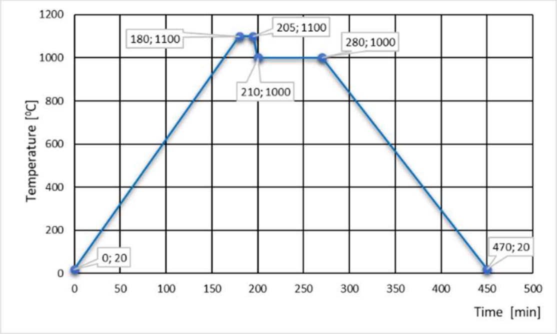

Fig. 5. TSS cycle

For TSS cycle, Figure 5, the green parts were sintered in two-steps. First, they were heated until 1100^0C for 25 minutes dwell time, and then, at 1000^0C with maintenance on the temperature level for 75 minutes dwell time.

3. RESULTS AND DISCUSSIONS

For the pieces of Ti-based powders obtained by classic sintering (CS), the SEM microstructural aspects (Figure 6) and the energy-dispersive X-ray spectroscopy analysis (EDS), Figure 7, are shown by using a scanning electron microscope PHENOM PRO X with integrated spectrometer EDS.

From the Figure 6.a it can be observed a higher porosity that may be explained by the presence of the ceramic carbides into the Ti-based composite.

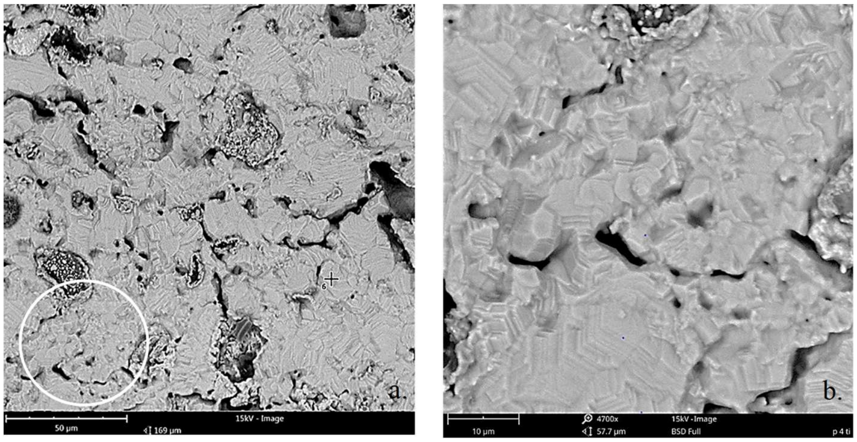

Fig. 6. SEM images of the sample obtained after CS cycle: a – x1600; b – x4700

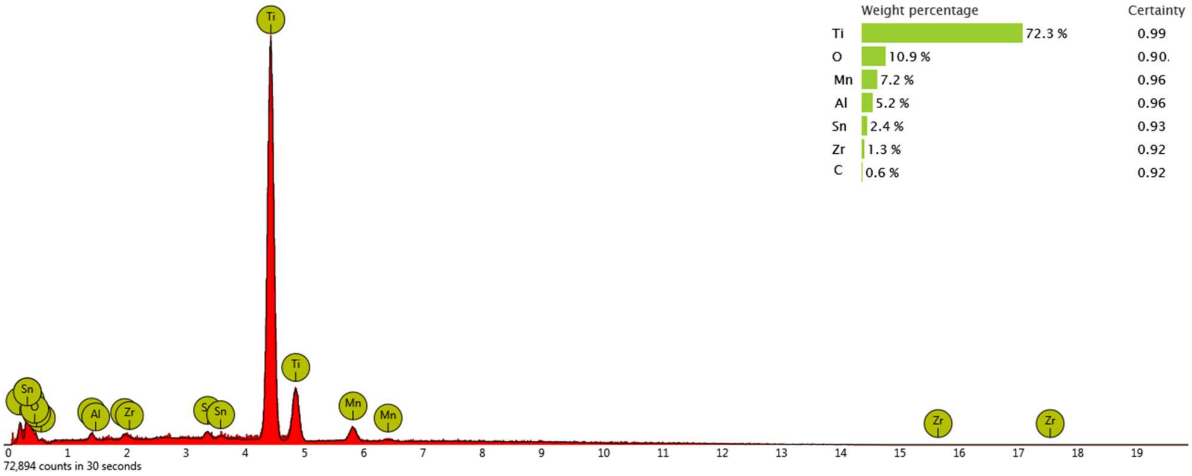

Fig. 7. EDS Graphical identification of site compositions of the sample obtained after CS cycle

Also, the samples contain inclusions of amorphous material which represents the non-homogeneities of the alloy, because of different composition, as will be seen in Figure 7, represented in the EDS analysis. Figure 6.b shows the detailed surface topography for an area of the SEM from the Figure 6.a for a titanium-based part obtained by classical sintering. There are strong bonds between the crystals, which give the alloy a high mechanical strength.

In Figure 6.b it is observed that the sample it is largely crystallized, presented with a fairly homogeneous composition on the samples surface area.

The EDS analysis in Figure 7 shows a relatively high percentage of oxygen, due to oxidation in the surface layers of the parts because of their exposure on the ambient atmosphere after classic sintering in argon [16].

Next, Figure 8 the SEM microstructural aspects for the samples obtained by two-steps sintering (TSS) are presented. Figure 8.b shows the detailed surface topography of an area of the SEM from the Figure 8.a for a titanium-based part obtained by TSS treatment.

In Figure 9 the EDS graphical identification of site compositions for the sample obtained by TSS is shown.

From the Figure 8 it can be noted that the samples obtained by TSS are well sintered, revealing stark connection between the crystals (as seen in the Figure 8.b), and a lower porosity than for the pieces obtained by classical sintering, presented in Figure 6, which ensures a high mechanical strength.

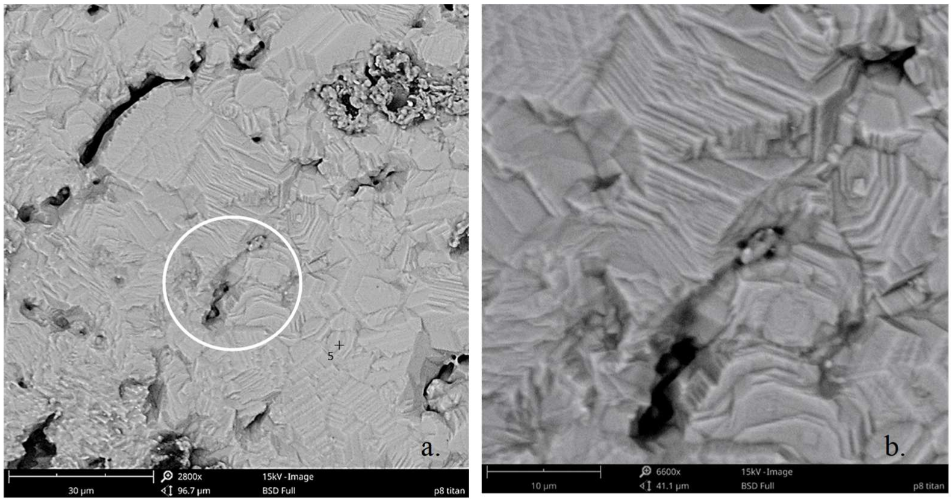

Fig. 8. SEM images of the sample obtained after TSS cycle: a – x2800; b – x6600

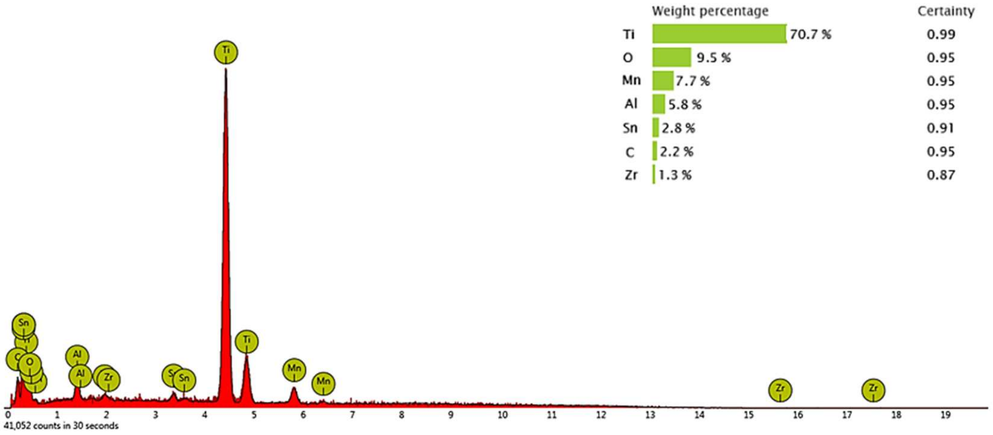

Fig. 9. EDS Graphical identification of site compositions of the sample obtained after TSS cycle

The EDS analysis presented in Figure 9 relieves a homogeneous distribution of metal components in the mass of Ti-based alloy. However, a significant concentration of oxygen, 9.5% and a slight increasing in carbon percentage can be observed, due to oxidation and carburization of the surface layer of the parts during their exposure on the circumambience.

Further, the microhardness Vickers (HV) was performed for both sample sets obtained by both classical sintering and two-step sintering, by using a micro-Vickers hardness tester Namicon CV-400DTS, with a load of 100g and 15 sec time pressing.

In Figure 10 the micro-hardness HV1 average value for sample sets of Ti-based alloy obtained by CS and TSS is presented.

From figure 10 it can be observed that the values of the final microhardness HV average of the samples obtained by TSS are clearly superior to those obtained by CS.

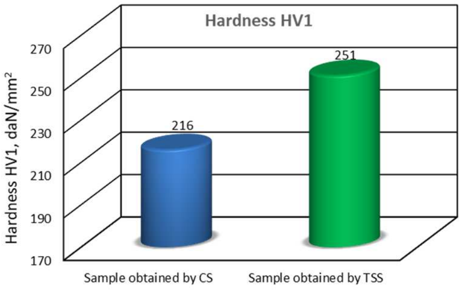

Fig.10. The microhardness HV average versus sintering treatment

In order to compare the specific porosity of the samples obtained by CS and TSS treatments, an analysis of the surface layer was accomplished, using the 5th generation Phenom desktop SEM platform. Thus, in figure 11 the 3D roughness of both types of Ti-based composites obtained by CS and TSS are presented.

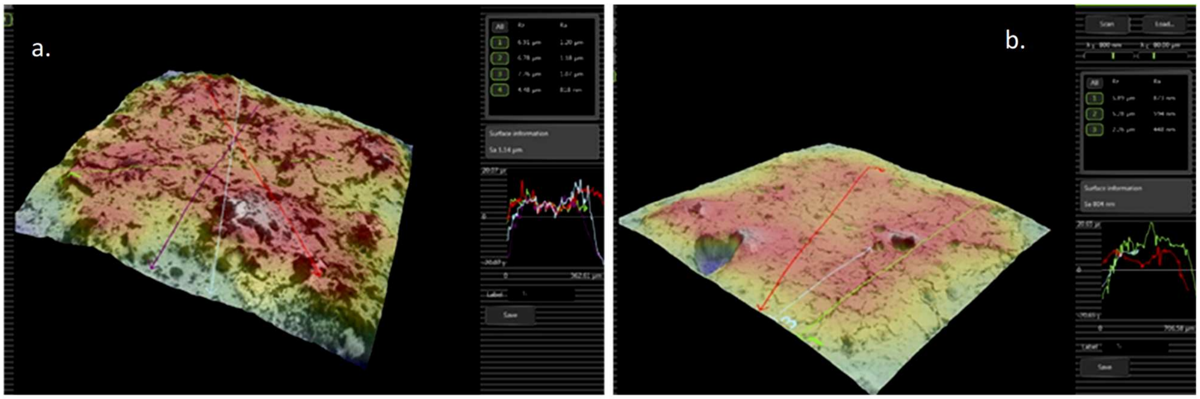

Fig.11. Surface roughness of samples based on Ti powders obtained by CS (a) and TSS (b)

Fig.12. Tribological dependents for the samples based on Ti powders obtained by CS (a) and TSS (b)

There is a higher porosity in the samples made by CS (Figure 11.a) than in the samples obtained by TSS (Figure 11.b)

Figure 12 presents the tribological behavior of the samples based on TiH_2 powders obtained by the two sintering regimes.

The wear tests were performed with a TRB-0254 tribometer, a device that allows the determination of wear coefficients, friction forces and penetration depth. For wearing tests, the probe based on Ti powders were placed as the cylindrical shape and for the counterpart a ball made from stainless steel 440C with the diameter of 6 mm was used. A normal force of 3N was used to perform the test.

One can observe a relatively constant evolution of the studied parameters over time and, a classical behavior for such cycles. Thus, there is a start period (break-in period) with a sudden increase from a minimum value to a working value of the variables, after which one enters the normal operation period, in which the values remain practically constant.

For the classical sintering cycle, an average value of the wear coefficient of 0.636 is obtained, while for the two-steps sintering (TSS) cycle, the value of the same parameter is 0.514.

Although the samples obtained by TSS have a better value of the average wear coefficient than for the pieces based on Ti powder obtained by classical sintering (CS).

However, for the samples based on Ti powder obtained by classical sintering (CS) the evolution of wear coefficient is more constant on the level. $\mu_{\max CS} = 0.727$ versus $\mu_{\max TSS} = 0.753$.

The graphs show that, in proportion, the penetration depth follows the evolution of the coefficient of friction and the friction force.

4. CONCLUSIONS

In this research, a comparative study between the mechanical, microstructural and wear properties for samples made from titanium hydride powder obtained after two different sintering cycles: classical sintering and two-step sintering was performed.

Following this analysis, it was found that:

- regarding the microstructural and mechanical aspects, the samples obtained by TSS showed a more homogeneous distribution of the components in the basic Ti metal matrix, a lower porosity and strong bonds appeared between the crystals, which produced a high mechanical strength compared to the CS ones. Thus, the values of the final micro-hardness of the specimens obtained by TSS were obviously higher than those obtained by CS.
- from the point of view of the tribological behavior of the samples based on TiH_2 powders, it was observed that the value of the average friction coefficient is lower for the parts obtained by TSS based on titanium, but for those obtained by CS the evolution was constant on the level, which means that lower friction coefficients can be obtained and that the manufacturing technology is perfectible at TSS.

Following the considerations presented above, it is considered that obtaining this alloy based on titanium hydride by sintering in two steps is a perfectible and successful option.

5. REFERENCES

[1] C. Veiga, C., Davim, J., Pand, J., Loureiro, A.J.R., *Properties and applications of titanium alloys: A brief review*, Reviews on Advanced Materials Science 32, pp. 133–148, 2012.

[2] Ratner, B.D., *A Perspective on Titanium Biocompatibility*. In: Titanium in Medicine. Engineering Materials. pp.1-12, Springer, Berlin, Heidelberg, 2001,

[3] Elias, C.N., Meyers, M.A., Valiev, R. Z., Monteiro, S., *Ultrafine grained titanium for biomedical applications: An overview of performance*, Journal of Materials Research and Technology 2(4), pp.340–350, 2013.

[4] Golaz, B., Michaud, V., Lavanchy, S., Månson, J.-A.E, *Design and durability of titanium adhesive joints for marine applications*, International Journal of Adhesion and Adhesives 45, pp. 150-157, 2013.

[5] Sachdev, A., Kulkarni, K.N., Fang, Z.Z., Girshov, V., *Titanium for Automotive Applications: Challenges and Opportunities in Materials and Processing*, JOM: the journal of the Minerals, Metals & Materials Society 64, pp.1.2-114, 2012.

[6] Yu, C., Peng Cao, P., Jones, M.I., *Titanium Powder Sintering in a Graphite Furnace and Mechanical Properties of Sintered Parts*, Metals 7, 67-81, 2017.

[7] Donald F. Heaney, D.F., German, R.M., *Advances in the Sintering of Titanium Powders*, In Proceedings: Euro PM2004, Powder Metallurgy World Congress & Exhibition, Ed. European Powder Metallurgy Association, pp.327-345, Austria, October 2004, Viena.

[8] Wang, B., Peng Le, P., Ma, G. Li, D., D. Savvakin, D., Ivasishin, O., *Microstructure and Properties of Ti80 Alloy Fabricated by Hydrogen-Assisted Blended Elemental Powder Metallurgy*, Frontiers on Materials 7, pp.1-10, 2020 https://doi.org/10.3389/fmats.2020.00291.

[9] Cotton, J.D., L. P. Clark, L.P., Phelps, H., *Titanium investment casting defects: A metallographic overview*, JOM: the journal of the Minerals, Metals & Materials Society 58, pp. 13-16, 2006.

[10] Kumar, A. Gupta, R.K. Chauthai, A., Ram Kumar, P., *Development of Titanium Alloy Hemispherical Forging for Pressure Vessel of Launch Vehicle*, Materials Science Forum 3, pp.830-833, 2015

[11] Banerjee, D., Williams, J.C., *Perspectives on titanium science and technology*, Acta Materials 61, pp. 844-879, 2013.

[12] Léopold, G., Nadot, Y., Billaudeau, T., Mendez, J., *Influence of artificial and casting defects on fatigue strength of moulded components in Ti-6Al-4V alloy*, Fatigue & Fracture of Engineering Materials & Structures 38, pp. 1026-1041, 2015.

[13] Ivasishin, O. M., and Moxson, V. S. *Low-cost titanium hydride powder metallurgy. Titanium,* Powder Metallurgy, pp. 117–148, 2015.

[14] Fang, Z.Z., Paramore, J.D., Sun, P., Chandran, K. S. R., Zhang, Y., Xia, Y., Cao, F., Koopman M., Free, M., *Powder metallurgy of titanium – past, present, and future*, International Materials Reviews 63, pp. 407-459,2018.

[15] Zhao, Q., Yang, F., Torrens, R., Bolzoni, L., *Comparison of hot deformation behaviour and microstructural evolution for Ti-5Al-5V-5Mo-3Cr alloys prepared by powder metallurgy and ingot metallurgy approaches*, Materials & Design 169, 107682, 2019,

[16] Pascu, C.I., Gheorghe, S., Rotaru, A., Nicolicescu, C., Cioateră, N., Roşca, A.S., Rotaru, P., *Ti-based composite materials with enhanced thermal and mechanical properties*, Ceramics International 46, pp. 29358-29372, 2020.

[17] Matsumoto, H., Kitamura, M., Li, Y., Koizumi, Y., Chiba, A., *Hot forging characteristic of Ti–5Al–5V–5Mo–3Cr alloy with single metastable β microstructure*, Materials Science and Engineering: A 611, pp 337–344, 2014.

[18] Zhang, Y., *A study of direct powder rolling route for CP-Titanium*, PhD. Thesis, Centre for Material Engineering, University of Cape Town, 2015.

[19] Samarov, V, Seliverstov D, Froes FHS., *Fabrication of near-net-shape cost-effective titanium components by use of prealloyed powders and hot isostatic pressing*, In: Qian M, et al., editor. Titanium powder metallurgy, Oxford (UK): Butterworth-Heinemann, pp. 313–336, 2015.

[20] German, R.M., *Progress in Titanium Metal Powder Injection Molding*, Materials 6, pp.3641-3662, 2013.

[21] Sharma, B., Sanjay, D.I, Vajpai, K., Ameyama, K., *An Efficient Powder Metallurgy Processing Route to Prepare High-Performance β-Ti–Nb Alloys Using Pure Titanium and Titanium Hydride Powders,* Metals 8, pp.516-532, 2018.

[22] Sastry, S. M. L, Peng, T. C., Meschter, P.J., O'Neal, J.E., *Rapid Solidification Processing of Titanium Alloys*, Rapid Solidification Processing of Titanium Alloys, JOM 35, pp.21-28, 1983.

[23] Liu, H., Ruying, Z., Cai, M., Sun, X., *A facile route to synthesize titanium oxide nanowires via*

water-assisted chemical vapor deposition, Journal of Nanoparticle Research 13, pp. 385–391, 2011.

[24] Froes, F.H., Iman, M.A., *Cost Affordable Developments in Titanium Technology and Applications, Affordable Titanium III*, Trans Tech Publications, Zurich, 2010.

[25] Schauerte, O., *Titanium in Automotive Production,* Advanced Engineering Materials 5, pp. 411-418, 2013.

[26] Fuji,H., Takahashi, K., Yamashita, Y., *Application of Titanium and Its Alloys for Automobile Parts*, Nippon Steel Technical Report 38, pp. 70-75, 2003.

[27] Boyer, R.B., *Attributes, Characteristics, and Applications of Titanium and Its Alloys*, JOM 62, pp. 35-43, 2010.

[28] Chen, K.M., Zhou, Y., Li, X. X., Zhang, Q. Y., Wang, L., *Investigation on wear characteristics of a titanium alloy/steel tribo-pair*, Materials & Design 65, pp. 65-73, 2015.

[29] Lee, D-W, Lee, H-S, Park, J-H, Shin, S-M, Wang, J-P, *Sintering of Titanium Hydride Powder Compaction*, Procedia Manufacturing 2, pp. 550 – 557, 2015.

[30] Ivanova, I.I., Podrezov, Y. N., Krylova, N. A., Danylenko, V. I., Demidyk, Barabash, V. A., *Effect of Process and Structural Factors on the Mechanical Properties of Titanium Sintered from Titanium Hydrides*, Powder Metallurgy and Metal Ceramics 58, pp. 270–277, 2019.

Cercetări privind îmbunătățirea proprietăților tribologice ale unui aliaj pe bază de hidrură de titan cu aplicabilitate în domeniul auto

Rezumat: Datorita proprietăților deosebite pe care le posedă, titanul și aliajele de titan își găsesc aplicabilitate cu interes mărit în domeniul auto. In lucrare se prezintă cercetări asupra obținerii unui aliaj pe bază de titan cu preţ de cost redus și proprietăți de uzură îmbunătățite. S-a utilizat ca material de bază hidrura de titan, care, datorită posibilității de dehidrogenare în timpul procesului de sinterizare, permite intensificarea densificării. Din aceleași motive, s-a considerat oportun utilizarea procedeelor specifice metalurgiei pulberilor ca o posibilitate de reducere a prețului de cost al aliajului. Pentru acest studiu comparativ, s-a ales un regim de sinterizare clasic, pe un singur palier și un regim de sinterizare în doi pași. În vederea îmbunătățirii comportării la uzare a materialului, s-au adăugat cantități mici de: 8%wt. Mn, 6%wt. Alumix321, 3%wt. Sn, 2%wt. Zr și 1%wt. grafit. S-au determinat duritățile, aspecte microstructurale și comportarea la uzare a aliajului pe baza de hidrură de titan. Se constată creşterea durităţii la probele sinterizate în doi paşi, îmbunătăţirea rezistenţei la uzare şi constanţa relativă a valorilor coeficienţilor de frecare.

Cristina Ileana PASCU, Assoc. Prof., PhD., Eng., University of Craiova, Faculty of Mechanics, Calea Bucuresti str., no.107, Craiova, Romania, Tel: 0744931172, E-mail: ileana.pascu@edu.ucv.ro

Ştefan GHEORGHE, Prof., PhD., Eng., University of Craiova, Faculty of Mechanics, Calea Bucuresti str., no.107, Craiova, Romania, Tel:0741057963, E-mail: stefan.gheorghe@edu.ucv.ro

Claudiu NICOLICESCU, Assoc. Prof., PhD., Eng., University of Craiova, Faculty of Mechanics, Calea Bucuresti str., no.107, Craiova, Romania, Tel: 0740231587, E-mail: claudiu.nicolicescu@edu.ucv.ro

Ioan VIDA-SIMITI, Prof., PhD., Eng., Technical University of Cluj-Napoca, Member of Technical Sciences Academy of Romania, Str. Memorandumului nr. 28. Cluj-Napoca, România, Tel:0745525294, E-mail: Vida.Simiti@stm.utcluj.ro