

## The Influence of Powder Particle and Grain Size on Parts Manufacturing by Powder Bed Fusion

Ioana GHIUTA<sup>1,a\*</sup>, Andrea GATTO<sup>2,b</sup>, Elena BASSOLI<sup>2,c</sup>,  
Sorin Ion MUNTEANU<sup>1,d</sup>, Tibor BEDO<sup>1,e</sup>, Mihai Alin POP<sup>1,f</sup>,  
Camelia GABOR<sup>1,g</sup>, Maria COVEI<sup>3,h</sup>, Mihaela COSNITA<sup>3,i</sup>, Daniel CRISTEA<sup>1,j</sup>,  
Bela VARGA<sup>1,k</sup> and Daniel MUNTEANU<sup>1,l</sup>

<sup>1</sup>Transilvania University, Materials Science Department, Romania

<sup>2</sup> University of Modena & Reggio Emilia, Department of engineering "Enzo Ferrari", Italy

<sup>3</sup>Transilvania University, Product Design and Environment Department, Romania

<sup>a</sup>ioana.ghiuta@unitbv.ro, <sup>b</sup>andrea.gatto@unimore.it, <sup>c</sup>elena.bassoli@unimore.it,  
<sup>d</sup>muntean.s@unitbv.ro, <sup>e</sup>bedo.tibor@unitbv.ro, <sup>f</sup>mihai.pop@unitbv.ro, <sup>g</sup>camelia.gabor@unitbv.ro,  
<sup>h</sup>maria\_covei@yahoo.com, <sup>i</sup>mihaela.cosnita@unitbv.ro, <sup>j</sup>daniel.cristea@unitbv.ro,  
<sup>k</sup>varga.b@unitbv.ro, <sup>l</sup>danielmunteanu@unitbv.ro

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**Abstract.** Nanostructured powder materials, or powders with increased amorphous ratio, can potentially lead to increased productivity during powder bed fusion, due to the hypothesis that nanostructured raw materials can be layer-sintered with lower specific energy, and consequently lower processing times when compared to commercial powders. Sintering of such materials can potentially be done faster, as compared to conventional powders. In addition, using nanostructured powders, or powders with high amorphous content, or even nanometric (nano-sized particles) powders, can result in higher density and hardness values of the sintered part, using the same process parameters. The main issue with nano-sized particles is their loss of flowability, which could be overcome by controlling the particle shape during manufacturing. This work presents our results concerning the manufacturing and characterization of titanium alloy powders, with potential use in additive manufacturing. The powders were manufactured using severe plastic deformation by mechanical milling from commercially available powders, with various rotation speeds, ball diameters, and milling periods, in order to obtain micrometric particles, but with nanometric or high amorphous content structures. The powders were further analyzed in terms of morphology, structure, and chemical composition.

### Introduction

Titanium alloys have been broadly used due to their attractive properties, such as, high corrosion resistance, low density, low elastic modulus and good biocompatibility [1,2], excellent high strength to weight ratio, high-temperature stability and good machinability [3,4]. The automotive, aerospace and marine fields are the major industries where titanium alloys are used, due to their special physical, chemical and mechanical properties [5,6]. They are also used widely for medical implants [7,8].

Unalloyed, pure titanium ( $\alpha$ -Ti), has a tendency to stick, fret or cold weld during processing. Because the properties of commercially pure titanium are affected by the presence of octahedral interstitial elements such as oxygen and nitrogen, a common industry practice, in order to avoid the previously mentioned conditions, is to use titanium alloys with  $\beta$ -stabilizing elements, which include molybdenum, vanadium and manganese, as well as  $\alpha$ -stabilizing elements (ex: aluminum) [9]. The Ti6Al4V, an  $\alpha$ - $\beta$  alloy, is the most commonly used titanium alloy, due to a combination of strength and ductility when properly processed and heat treated [3,9].

In order to obtain structures with enhanced properties for powders of this alloy, different processing methods have been developed, including both top-down and bottom-up approaches [3,10, 11]. The most successful top-down approach involves the application of severe plastic

deformation, in which materials are subjected to the imposition of very large strains without the introduction of any concomitant changes in the cross-sectional dimensions of the samples [12]. Mechanical milling is one of the severe plastic deformation processes [10,12]. Through mechanical milling processes, nano-crystalline materials can be obtained with relatively simple equipment at a low-cost. Yan Long et al. pointed out the influence of ball milling time on the microstructure and alloy properties [3,13]. Ultrafine-grained Ti6Al4V were obtained by high energy ball milling and spark plasma sintering [3]. Fujiwara et al. have also presented results on the Ti6Al4V alloy, subjected to severe plastic deformation, followed by sintering using the Hot Roll Sintering process, in order to improve the mechanical properties. They have accomplished the production of powder particles consisting of a shell and core hybrid microstructure, meaning a shell structure with nano-grains and a core structure with work-hardened coarse grains [12].

This paper presents our findings concerning the influence of processing parameters on the powder microstructural characteristics, including crystallite size, phase fractions, and chemical composition, after severe plastic deformation of Ti6Al4V powders in a planetary mill.

## Materials and Methods

Ti6Al4V powders, supplied by EOS – Electro Optical Systems (the global technology and quality leader for high-end solutions in the field of additive manufacturing), was milled, with various parameters. In order to obtain materials with internal structures with nanometer-size crystallites, or with increased amorphous content, without significant volume alteration, a planetary ball mill was used (Fritsch Pulverisette 7). The Ti6Al4V powder was added to the stainless-steel milling bowls, mixed with stainless steel balls. The milling balls were selected in a ratio of 1:3:1 depending on the ball diameter, namely 6, 10 and 15 mm, as in the work mentioned elsewhere [3]. After sealing the milling bowls, these were purged with argon, in order to avoid powder oxidation. The experiments were conducted at two rotation speeds, namely 300 rpm and 400 rpm. During the milling process sample collection was carried out every 4 hours, until the experiment reached 50 hours.

The morphology of the samples was investigated using scanning electron microscopy, (Hitachi, S3400N, type II), while the quantitative elemental analysis of the samples was performed using EDX (Thermo, Ultra Dry, Noran System 7, NSS Model).

The X-ray diffraction studies were carried out using a Bruker D8 Discover Advanced Diffractometer locked coupled continuous scan, a scintillation counter with 12800 steps, 2 seconds/step and a radiation with 1.5406 Å wavelength -  $\text{Cu}\alpha_1$ , at 40kV, 20mA).

Differential Scanning Calorimetry was performed on selected samples, in order to observe possible phase transformations during heating, which would translate in released energy during the heating process, with beneficial consequences during additive manufacturing processes (lower energy input, necessary for melting/particle fusion). A Netzsch DSC 200 F3 Maia differential scanning calorimeter was used, with a 10 K/min heating/cooling rate, using aluminum crucibles, purged with  $\text{N}_2$ , heated up to 590 °C.

## Results and Discussion

As observed in figure 1, the initial titanium alloy powder is spherical in shape, with an average granule size of 40  $\mu\text{m}$ . The chemical composition is listed in table 1.

Table 1 Unaltered powder chemical composition, obtained by EDX.

Elements	Point 1	Point 2	Point 3
Ti	87.92	88.53	87.02
Al	9.49	8.61	10.53
V	2.54	2.71	2.45
Cr	0.05	0.14	0.00

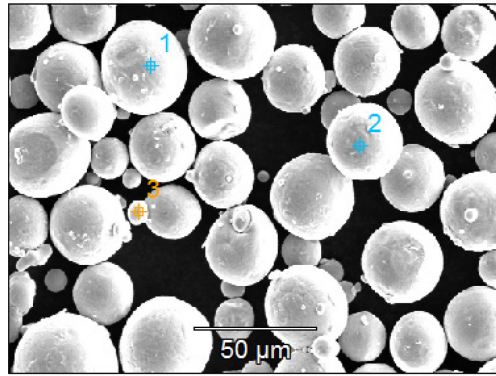


Fig. 1 SEM micrograph of the unaltered Ti6Al4V powder.

After the milling/severe plastic deformation process, selected samples were analyzed in terms of chemical composition and morphology. One can observe in figure 2 that the granule average size decreases drastically, and a certain degree of agglomeration occurs. This phenomenon would negatively impact the use of these powders in additive manufacturing, due to potential clumping at the surface of the powder bed. The chemical composition is altered, as well, noticed on the EDX spectra presented in figure 3. Apart from the desired elements, one can notice the presence of oxygen, which means, even if the milling bowls were purged with argon, a certain degree of oxidation occurs.

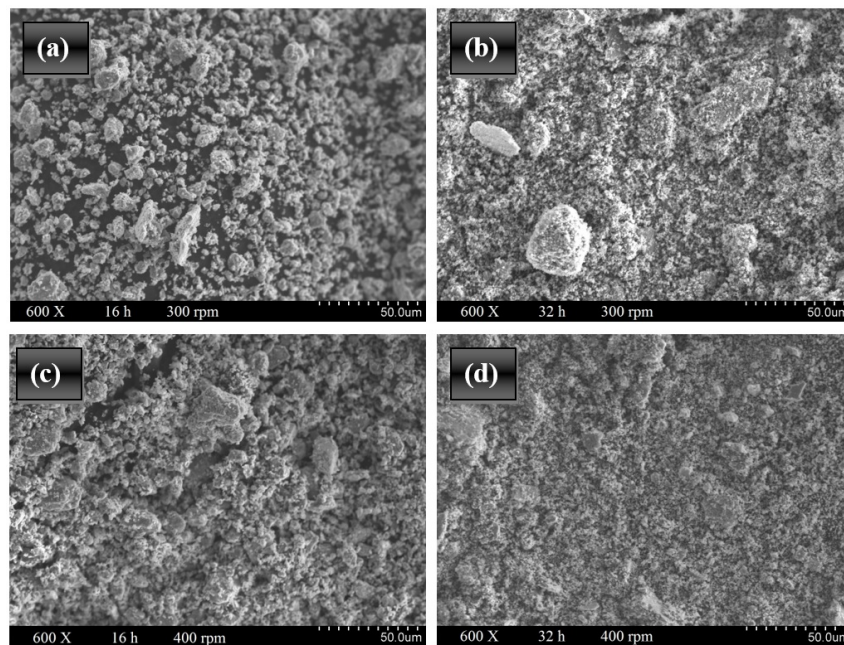


Fig. 2 SEM micrograph of the mechanically milled Ti6Al4V powder, after 16 and 32 hours, and 300 and 400 rpm.

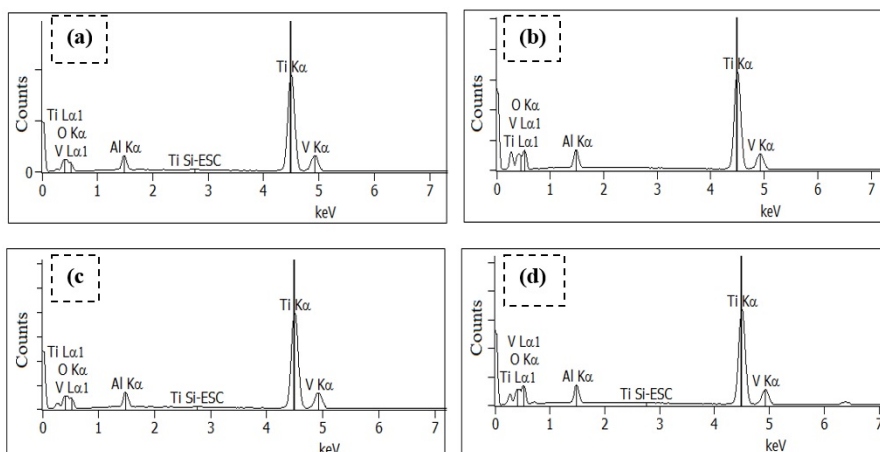


Fig. 3 EDX spectra of the mechanically milled powders. The peaks for oxygen are clearly noticeable.

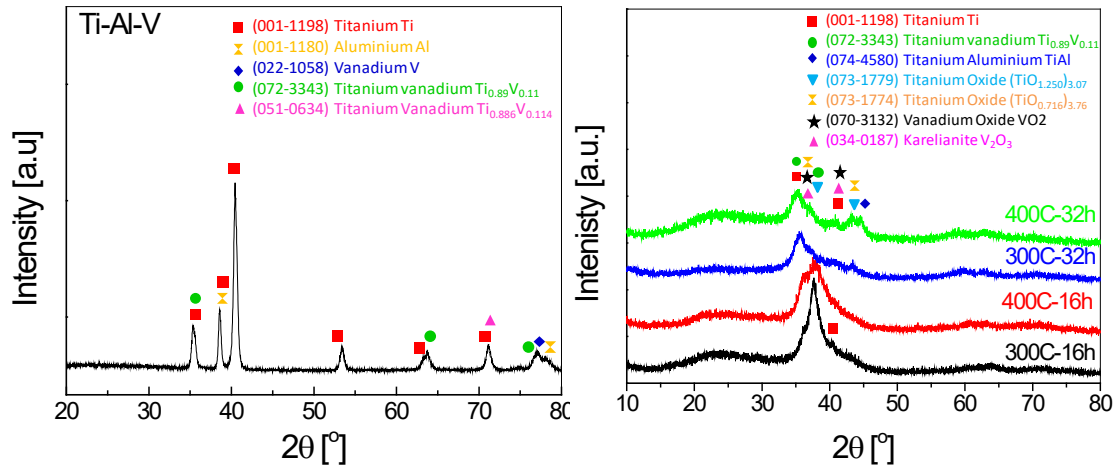


Fig. 4 XRD patterns of Ti6Al4V  
a) initial powder; b) after 16 h, respectively 32 h of milling at 300/400 rpm

The diffraction patterns for the unaltered powder and the mechanically milled powders can be observed in figure 4. The amorphization of the mechanically milled powders is clearly noticed, extrapolated from the wide diffraction bands, which are replacing the sharp diffraction peaks from figure 4a. The degree of amorphization is presented in table 2, as well as the evolution of the crystallite size, as function of the milling period and rotation speed. The main factor contributing to the amorphization of the powders seems to be the milling period. At 16h milling time, the crystallinity percentage is relatively close, for both rotation speeds. However, at 32h milling period, the crystallinity percentage for the sample milled at 400 rpm decreases drastically. This may be the result of mechanical processing and / or the temperature of the material during milling. New crystalline phases, attributed to titanium oxides and vanadium oxides are noticed (which confirm the results of the chemical composition analysis). This observation highlights the effect of the milling medium, considering the increased reactivity of this particular powder with oxygen.

Table 2. The variation in crystallite size and crystallinity percentage, as function of the milling time and rotation speed.

Samples	Crystalline phase	D [nm]		Crystallinity [%]
		Scherrer on the representative diffraction line	Soft on all the diffraction lines assigned to that phase	
Initial sample	Ti	17.27	28.05	80.3
	Al	23.83	32.14	
	V	16.97	18.37	
	$Ti_{0.89}V_{0.11}$	15.86	22.33	
	$Ti_{0.886}V_{0.114}$	16.27	29.00	
300 rpm 16 h	$Ti_{0.89}V_{0.11}$	6.03	3.86	35.2
300 rpm 32 h	Ti	8.47	3.15	33.7
	$Ti_{0.89}V_{0.11}$	8.47	4.25	
400 rpm 16 h	Ti	7.63	2.89	37.9
	$Ti_{0.89}V_{0.11}$	7.63	3.99	
	<b>VO<sub>2</sub></b>	<b>34.67</b>	<b>3.12</b>	
	<b>V<sub>2</sub>O<sub>3</sub></b>	<b>68.20</b>	<b>3.07</b>	
400 rpm 32 h	Ti	7.21	3.15	25.6
	$Ti_{0.89}V_{0.11}$	7.21	4.39	
	TiAl	17.09	1.03	

For a few phases, there are rather large differences between the crystal size calculated with the Scherrer equation and the software, respectively. This is explained by the fact that the calculated peaks have relatively low intensity and can be distorted by noise, or are not representative peaks (they appear as "hops" besides larger peaks).

In order to test the hypothesis that a material in powder form, with an increased amorphous content, could be sintered using lower laser intensities, or could be sintered with a faster scanning speed during additive manufacturing, differential scanning calorimetry analyses were performed on selected samples. The potential phase transformations that should be desired are the ones that exhibit an exothermic effect, extrapolated from a positive peak. Figure 5 presents the variation of the energy per mass as function of the temperature, for the unaltered powder and the mechanically milled Ti6Al4V powder. One can notice that, for the heating regimen (up to 590 °C), the commercially available powder does not exhibit any phase transformations. The case is not the same for the powder which was milled for 50h (300rpm). A relatively high intensity peak is noticed, with a maximum intensity at around 356 °C. The calculated energy for this transformation, for this particular case, is 4681 J/g. This phenomenon can be explained by the possible rearrangement of the atoms, from the metastable quasi-amorphous structure exhibited by the milled powder, to the highly crystalline powder.

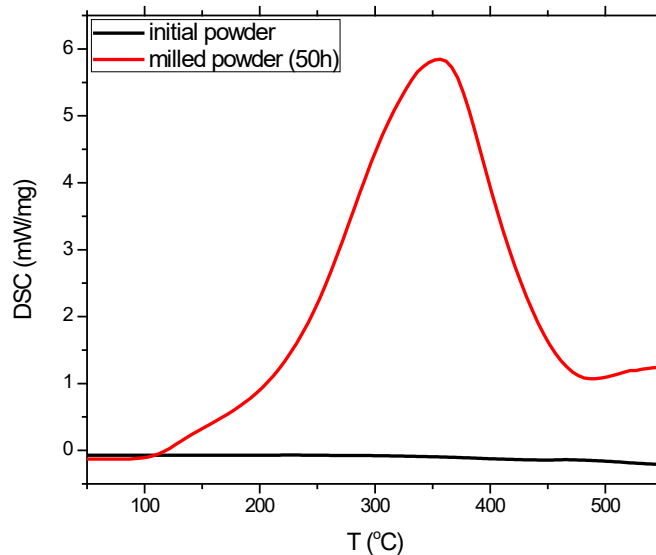


Fig. 5 The variation of the energy per mass as function of the heating temperature, for the initial and mechanically milled powders.

## Conclusions

Commercially available titanium alloy powders were mechanically milled, in order to change their structure, considering the assumption that for the sintering of quasi-amorphous powders the energy requirements would be lower. After the process of milling the Ti6Al4V powder, a double result was achieved, namely the reduction of the particle size from an average size of 40 $\mu$ m to about 15-20 $\mu$ m (by agglomeration), close to the acceptable limits for use in some of the additive manufacturing processes, as well as the transformation into a quasi-amorphous state, as demonstrated by the x-ray diffraction analysis.

With the increase of the milling time, an exothermic reaction was observed during heating, a phenomenon not noticed for the unaltered powder. Additional experiments are needed to determine the optimal number of milling hours after which the amorphous state with the maximum exothermic reaction is obtained translating this into lowering the energy required for melting/sintering. Moreover, the particle size and shape need to be kept in certain limits, in order to not hinder the additive manufacturing process.

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