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# Microstructural evolution and mechanical properties of the Ti–6Al–4V alloy produced by vacuum hot-pressing

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**Abstract:** In this work, the properties of the titanium industry workhorse, the Ti–6Al–4V alloy, processed by vacuum hot-pressing are studied. More in detail, relative density, microstructure characterisation and chemical analysis, precisely oxygen, nitrogen and carbon content, as well as flexural properties and hardness are considered. Components with relative density as high as 98% and mechanical properties similar to the wrought alloy, where these properties are affected by the formation of a reacted layer due to the interaction between titanium and the boron nitride (BN) coating, are obtained.

Keywords: Vacuum hot-pressing, Ti-6Al-4V, Prealloyed, Master alloy, BN-Ti interaction, Flexural properties.

#### 1. Introduction

The interest for titanium as engineering material started approximately 80 years ago thanks to the special attention paid by the aeronautic industry in this material due to its particular combination of properties: the highest specific strength (strength to density ratio), outstanding corrosion resistance and strength at temperature (up to approximately 500  $^{\circ}$ C) [1].

The first well developed and studied titanium alloy is the alphabeta Ti–6Al–4V alloy, which is still one of the most popu-lar and employed and represents the workhorse of the titanium industry. The aerospace industry accounts for a large percent-age of the total consumption and other sectors such as medical, automotive, marine and chemical share the rest of the market [2].

Titanium, as well as its alloys, can be produced by conventional processes, like casting, primary working and machining, and by powder metallurgy where powders are consolidated and sintered to produce near-net-shape products. There are two general approaches when working with powder metallurgy methods which differ by the way in which the alloying elements are added to titanium powder. In the first one, the blended elemental (BE), elemental titanium powder is mixed with alloying elements powders or with master alloy powders; meanwhile, in the prealloyed (PA) approach, each powder particle has already the final composition.

The conventional pressing and sintering method allows to produce powder metallurgy products with properties similar to wrought materials but, typically, they suffer from residual porosity [3]. In order to overcome or, at least, substantially reduce this disad-vantage, alternative processes, where the sintering step is carried out simultaneously with the application of high temperature and pressure, were developed. Within these methods, known as hot consolidation processes, four of them are normally employed in the industry: hot-pressing, hot isostatic pressing (HIP), hot powder extrusion and hot powder forging [4]. In the hotpressing process, which is the simplest of the previously mentioned, compaction and sintering take place simultaneously [3,4]. For temperatures higher than 600 °C, die tools made out of ceramics or graphite are normally used, where graphite is being used for temperatures up to 3000 °C. Industrially, there are different options to heat the compact: indi-rect heating using tubes and coils, direct resistance heating where the power is supplied through punches, direct heating of the die and inductive heating of the die. The compaction is usually done in an inert atmosphere, such as argon, or under vacuum and crucial parameters like the temperature, the pressure and the shrinkage of the samples in the direction of pressing are checked. Some early works had been done on hot-pressing of elemental titanium sponge powder [5-7] as well as on hydride-dehydride (HDH) Ti-6Al-4V [8].

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Fig. 1. Graph of the vacuum hot-pressing cycle used to sinter Ti-6Al-4V titanium alloy powders at 1100 °C where the delay between the programmed temperature and the measured temperature can be noticed.

This work focuses on the study of the influence of one of the main processing parameters, namely the pressing temperature, on the development of the microstructure and the correlated mechanical properties of both prealloyed and master alloy addition powder as well as prealloyed powder with different particle size distribution obtained by means of the hydride–dehydride process. Special attention is paid to the determination of oxygen, nitrogen and carbon content to discover possible reactions which can occur between the powders and the processing tools since small amount of interstitial elements affect significantly the properties of titanium and titanium alloys [9–11].

### 2. Experimental procedure

In this study, three Ti–6Al–4V powders with different particle size and dissimilar interstitials content, which are function of the powder production route, are processed. Two prealloyed powders bought from two suppliers (Phelly and Se-Jong Materials) and one powder produced by the blended elemental approach using an Al:V master alloy are vacuum hot-pressed. These materials will be identified along the discussion of the results as Ti64-Ph, Ti64-SJ and Ti64-MA, respectively. The production method and parameters employed to obtain the Ti64-MA powder can be found elsewhere [12]. Table 1 reports some physical and chemical characteristics of the powders used during the vacuum hotpressing study where oxygen (ASTM E1409) and nitrogen (ASTM E1937) are measured by means of inert gas fusion method and carbon (ASTM E1941) by combustion technique.

Regarding the data shown in Table 1, the selected powders allow to study the influence of the production method (PA versus MA) as well as the influence of the particle size (Ti64-Ph versus Ti64-SJ). Moreover, it is important to remark that the high car-bon content of the Ti64-MA alloy compared to the others is due to the production process but it should not influence the final results since it is not dissolved inside the titanium matrix [12]. It is worth mentioning that the three powders have in common the irregu-lar morphology due to the hydride–dehydride production process and that this type of powder is not normally used for hot-pressing, since spherical powders are preferred, even though they can be used [4].

Approximately 75 g of each powder are loaded into a 65 mm diameter graphite mould to obtain specimens of approximately 5mm in thickness. Before pouring the loose powder, the lower graphite punch is inserted into the mould and a graphite foil 0.75 mm thick is used to line the inner of the mould. This graphite

foil has low reactivity and it is employed to avoid the direct contact between the titanium powders and the graphite mould at high temperature and, thus, avoiding or limiting possible reactions such the formation of a titanium carbide layer. Furthermore, on the top of the lower punch a graphite foil coated with a high temperature ceramic boron nitride (BN) spray on its upper part is placed. This BN coating will be in contact with the powder during the entire vacuum hot-pressing cycle. Another BN coated graphite foil is put on the top of the powder to facilitate the mould release and to limit reactions. Afterwards, a second graphite disc is placed on the top of the upper graphite foil and the entire set is cold uniaxially pressed at approximately 18 MPa.

During the study, three temperatures are employed between 900 °C and 1300 °C (step of 200 °C), the dwell time at maximum temperature is 1 h for 900 °C and 1100 °C and 30 min for 1300 °C. The time selected for each temperature guarantees the complete densification of the specimens and corresponds to an effective dwell time of 30 min due to the delay induced by the inertia of the heating system as it can be seen in Fig. 1, which shows an example of cycle used during vacuum hot-pressing. The control of the temperature is done by means of thermocouples, placed directly in contact with the graphite mould, which guarantees a precision of  $\pm 5$  °C. During the experiments, the pressure is increased simultaneously with the temperature and the maximum temperature and the maximum pressure are reached at the same time. For the three processing temperatures, the maximum applied pressure is kept constant at 30 MPa as well as the heating rate of 10 °C/min and the vacuum level of 10<sup>-1</sup> mbar. Cooling of the samples is performed by switching off the heating elements (furnace cooling) with the simultaneous removing of the pressure.

Once pressed, the specimens are removed from the graphite mould and sandblasted to clean their surface. Subsequently, the specimens are characterised in terms of density by water displacement method and chemical analysis (oxygen, nitrogen and carbon). Moreover, hardness test and three-point bending test (ASTM B528) to obtain the maximum bending strength and flexural strain are carried out. For this purpose, specific flexion samples are cut off from the centre of the disc and half of them are also ground in order to remove the surfaces which have been in contact with the BN coating during consolidation. This allows to clarify if there has been some interaction between the titanium powders and the BN coating and to study the influence of an eventual contamination or interstitial elements pick up on the mechanical properties of titanium alloys. Finally, microstructural analysis by means of optical and electronic microscope is done on samples which have been ground with silicon carbide paper (320), polished with a 9µm

#### Table 1

Characteristics of the powders studied (particle size distribution and chemical analysis).

Material		Ti-6Al-4V		
Production method		PA <sup>a</sup> (Ph)	PA <sup>a</sup> (SJ)	MA <sup>b</sup>
Morphology		Irregular	Irregular	Irregular
D <sub>MAX</sub> [µm]		45 <sup>c</sup>	75	106
Chemical analysis	0	0.390 <sup>c</sup>	0.418	0.428
[wt.%]	Ν	0.0360 <sup>c</sup>	0.0072	0.0121
	С	0.0320 <sup>c</sup>	0.0124	0.1050

<sup>a</sup> Prealloyed.

<sup>b</sup> Master alloy.

<sup>c</sup> Supplier specifications.

alumina and then with a silica solution and, in the end, etched by typical Kroll's reactant.

# 3. Results and discussion

As previously mentioned, the specimens are characterised in terms of density by Archimedes' method (Fig. 2) and the relative density is calculated on the bases of the nominal value of the wrought alloy  $(4.43 \text{ g/cm}^3)$ .

Analysing Fig. 2, it can be seen that relative density values reached at each temperature are very similar for the different materials since they vary between 97% and 98%. Therefore, it seems that there is not a clear influence of the particle size (Ti64-Ph versus Ti64-SJ) or the amount of interstitials dissolved in the powder as well as the powder production route (Ti64-SJ versus Ti64-MA) on the final density of vacuum hot-pressed HDH Ti-6Al-4V powders. Moreover, it seems that the relative density increases continuously with the hot-pressing temperature for the master alloy addition Ti64-MA powder whereas the prealloyed powders reach their maximum at 1100 °C and starts to decrease. Nonetheless, considering the standard deviation of the value, it can be noticed that with the processing temperature considered the difference between the three powders is limited. The values shown in Fig. 2, which are comparable to that of other author when processing the Ti-6Al-4V alloy [13] or the Ti-6Al-7Nb alloy [14] by vacuum hot-pressing or by inductive hot-pressing [15], are higher that those obtained from conventional pressing and sintering process, approximately 95% of the theoretical density [12].

Fig. 3 shows the microstructural evolution with the processing temperature of the Ti–6Al–4V powders, whose characterisation was carried out by means of a scanning electron microscopy on the cross section of specimens previously mounted, ground, polished and etched with Kroll's reactant.

As it can be seen in Fig. 3, the micrographs of the specimens hot-pressed at 900  $^{\circ}$ C (Fig. 3a–c) indicate that this temperature is not high enough to guarantee the complete homogenisation of the



**Fig. 2.** Relative density results as a function of the temperature for Ti–6Al–4V powders sintered by vacuum hot-pressing.

microstructure, especially in the case of the master alloy addition powder, since some small particle of the master allov are still visible, due to the fact that the processing temperature is lower than the nominal beta transus of the Ti-6Al-4V alloy. Moreover, the residual porosity can be clearly distinguished and no significant differences in terms of grain size can be highlighted on the base of the particle size or powder production methods due to the features previously described. Moreover, it can also be seen that the microstructure of Ti64-SI resembles much more that of Ti64-MA instead that of Ti64-Ph which could indicate that Ti64-SJ is not a fully prealloyed powder. When the materials are processed at 1100 °C, a great difference between the microstructure of the three powders is visible. In particular, the microstructure of the prealloyed powders (Fig. 3d and e) is composed by approximately the same amount of  $\alpha$  grain and  $\alpha$  +  $\beta$  lamellae uniformly distributed throughout the microstructure, even though, generally, the  $\alpha$ grains of Ti64-Ph are much more equiaxed compared to Ti64-SJ. On the other side, Ti64-MA alloy (Fig. 3f) is characterised by a greater percentage of  $\alpha$  grains and small and concentrated Widmanstät-ten areas most probably located near former master alloy particles and, therefore, near zones where locally the percentage of alloying elements is higher. This indicates that the selected temperature does not guarantee the complete diffusion of the alloving elements towards the titanium matrix and, therefore, to obtain a fully homo-geneous microstructure. Based on these results, an influence of the particle size can be clearly evinced since the bigger the par-ticle size the bigger and more elongated  $\alpha$ grains. Nevertheless, the change of the geometry of the  $\alpha$  grains from equiaxed to elongated is most probably also influenced by the diffusion of the alloying ele-ments since some undiffused particle is also detected in the Ti64-SJ specimens.

At the highest temperature considered (1300 °C), the microstructure of all the Ti–6Al–4V powders (Fig. 3g–i) is homogeneous and composed by  $\alpha$  grains and  $\alpha + \beta$  lamellae. This is the typical laminar microstructure usually obtained by the slow cooling through the two-phase  $\alpha + \beta$  region of the  $\alpha + \beta$  titanium alloys from above the beta transus. Furthermore, it can also be noticed that Ti64-Ph and Ti64-SJ are characterised by a very uniform distribution of finer microconstituents in comparison to those of the Ti64-MA alloy which is composed by larger  $\alpha$  grains and finer  $\alpha + \beta$  lamellae resulting in a less homogeneous grain size distribution.

It is worth mentioning that from the microstructural evolution results (Fig. 3) it seems that the final relative density obtained is much higher than that shown in Fig. 2 since, apart from the specimens processing at 900 °C, very few and small isolated pores with a diameter lower than 10  $\mu$ m are found in the materials sintered at 1100 °C and 1300 °C which could correspond to a relative density close to fully dense materials.

Fig. 4 shows oxygen and carbon content results by inert gas fusion method and combustion technique for the three materials as a function of the hot-pressing temperature. As it has been said, half of the specimens are ground to remove to outer surface



**Fig. 3.** Microstructural evolution with the hot-pressing temperature for specimens consolidated at 900 °C: (a) Ti64-Ph, (b) Ti64-SJ and (c) Ti64-MA; at 1100 °C: (d) Ti64-Ph, (e) Ti64-SJ and (f) Ti64-MA and at 1300 °C: (g) Ti64-Ph, (h) Ti64-SJ and (i) Ti64-MA.



Fig. 4. Oxygen and carbon content as a function of the temperature for Ti-6Al-4V powders sintered by vacuum hot-pressing.

but since not significant differences between the ground and not ground specimens are found, a single value for each material in every processing condition is plotted in Fig. 4.

As it can be seen in Fig. 4. oxygen content remains constant with the increasing of the processing temperature and there is few oxy-gen pick up with respect to the initial content of the starting powder for both Ti64-SI and Ti64-MA and the maximum oxygen content is always approximately 0.42 wt.%. An exception is the Ti64-Ph pow-der where oxygen content increases when raising the sintering temperature most probably due to the oxygen adsorbed into the surface of the powder particle, being favoured compared to the other powders due to the higher specific area that correspond to a lower particle size. On the other side, carbon content (Fig. 4) follows the same trend of oxygen and, therefore, it remains constant with the processing temperature at 0.03 wt.% for Ti64-SJ and at 0.06 wt.% for Ti64-MA and it increases for Ti64-Ph, once again most probably due to the finer powder particle. Nonetheless, conversely to oxy-gen, there is always some carbon pick up most probably due to the interaction with the graphite tools or, most probably, with the car-bon rich atmosphere inside the hot-pressing chamber generated by the graphite tools at high temperature [4]. It is worth mentioning that the lower carbon percentage found in the Ti64-MA samples compared to the content of the starting powder is due to the fab-rication route of this alloy where some wax was added as process control agent during milling of the master alloy which is elimi-nated during heating [12]. Nevertheless, the final carbon content measured on the three vacuum hot-pressed Ti-6Al-4V powders is, generally, lower than the limit specified for this alloy, which is equal to 0.08 wt.% [16].

Fig. 5 shows nitrogen percentage results which have been split between ground and not ground specimens since nitrogen percent-age in the first ones is, in most of the cases, double than in the last ones.

Analysing the data shown in Fig. 5, it can be noticed that there is always some nitrogen pick up and the nitrogen content increases with the sintering temperature for the three powders. Moreover, the increment is much more important for the highest tempera-ture (1300 °C) reaching variable between 0.08 wt.% and 0.10 wt.%depending on the powder considered. On the other side, the nitro-gen content results to increase with respect to the percentage found in the starting powder indicating that nitrogen diffuses through the titanium matrix. Moreover, the removal of the surface of the speci-mens, at least, halves the final nitrogen content permitting to fulfil the limit of the chemical composition required for this alloy, which is 0.05 wt.% [16].

As the chemical analysis and, in particular, the nitrogen content reveals, there was some interaction between the processed powder and the BN coating used to cover the graphite mould. Thus, the surface of the specimens was analysed by means of SEM in backscattering mode and by XRD the micrographs of the Ti64-SJ alloy, which are representative for all the materials studied, are shown in Fig. 6.

As it can be seen in Fig. 6a, there is no interaction between the powder and the BN coating when using a processing tem-perature of 900  $^{\circ}$ C. However, since the chemical analysis reveals that there is some nitrogen pick up (Fig. 5), this could either be some diffused nitrogen from the BN coating or some contamination from the atmosphere of the processing chamber. When raising the



Fig. 5. Nitrogen percentage as a function of the temperature for ground and not ground Ti-6Al-4V powders sintered by vacuum hot-pressing.



**Fig. 6.** BSE-SEM images of the surfaces of the specimens made out of the Ti64-SJ powder which have been in contact with the BN coating: (a)  $900 \degree C$ , (b)  $1100 \degree C$  and (c)  $1300 \degree C$ .

temperature up to 1100 °C, it can be noticed the formation of some dark coloured interaction zones (Fig. 6b). With a hot-pressing temperature of 1300 °C, the Ti–6Al–4V powder strongly reacts with the BN coating forming a uniform layer variable between 15  $\mu$ m and 25  $\mu$ m in thickness, denser in the outer part and more porous in the inner (Fig. 6c). EDS analysis of the interaction zones indicates that the mean nitrogen content is about 5.8 wt.% (16.7 at.%). The same behaviour concerning the evolution of the reacted layer with the temperature described for the Ti64-SJ powder was found when analysing the surface of the elemental titanium and other titanium alloys fabricated by vacuum hot-pressing [14].

The surfaces of the specimens obtained by the vacuum hotpressing technique were also analysed by means of XRD. No significant differences between the diverse Ti–6Al–4V samples are found during this analysis since only titanium compounds are found due to the greater affinity of titanium, compared to aluminium or vanadium, for interstitial elements. As a representative example for all the materials processed, the XRD patterns of the surface of the Ti64-SJ alloy specimens are displayed in Fig. 7.

As already supposed on the bases of the chemical analysis results shown in Fig. 5, at 900 °C the Ti-6Al-4V powder picks up some nitrogen and, therefore, forms a nitrogen rich interstitial solid solution  $\alpha$  -Ti(N). Moreover, a very low intense peak of BN, most probably stuck from the BN coating not removed by sandblasting, is detected as well as some undiffused AI:V compound identified as  $Al_2V_3$  (Fig. 7). The presence of some master alloy added by the supplier to the, supposed, prealloyed powder (Ti64-SJ), which corresponds with the Al<sub>2</sub>V<sub>3</sub> found in the specimens vacuum hot-pressed at 900 °C indicates that the supplier added some alloying elements during the HDH process to adjust the final composi-tion. This was already supposed on the bases of the evolution of the microstructural features with the hotpressing temperature (Fig. 3b). Exactly the same results are obtained on the pattern of the Ti64-MA since an Al:V master alloy is added intentionally while no such compound is detected in the other prealloyed pow-der (Ti64-Ph). With the increment of the processing temperature at 1100 °C the amount of diffused nitrogen through the titanium matrix increases, in agreement with the nitrogen content mea-sured by inert gas fusion technique. Stoichiometric compounds like Ti<sub>2</sub>N and TiN are formed even if the peaks of the solid solution  $\alpha$ -Ti(N) can still be identified with their position slightly displaced towards lower diffraction angles in comparison to the peaks of  $\alpha$  titanium due to the increment of both the "a" and "c" parameters of the unit cell induced by the presence of interstitials dissolved into the titanium matrix [17,18]. Furthermore, the higher thermal energy available in the system promotes the formation of tita-nium borides, both TiB and TiB<sub>2</sub>, on the base of the reactions that normally take place between titanium and boron nitride such as Ti + 2BN  $\rightarrow$  TiB<sub>2</sub> + N<sub>2</sub> and Ti + BN  $\rightarrow$  TiB + 1/2N<sub>2</sub> [19]. The absence of boron or titanium boride at 900 °C is mainly due to the higher sol-ubility of nitrogen in beta titanium with respect to that of boron being as high as 22 at.% for nitrogen and lower than 0.2 at.% for boron, respectively [20].

The XRD pattern of the specimen vacuum hot-pressed at 1300 °C points out that the interaction of titanium with the BN coating becomes stronger with the increment of the temperature and, consequently, the relative intensity of titanium nitrides, especially TiN, and titanium borides peaks increase. The abnormally strong relative intensity of the TiB peak at 60.6°, which correspond to the (0 2 0) plane, is due to the [0 1 0] preferred growth direction of TiB [21]. The results shown in Fig. 7 agree with the study of the reactions that occurs at the BN-Ti interface where their interaction leads to the formation of titanium borides directly at the interface and titanium nitride further from the interface towards the material [22,23]. Therefore, the denser part of the reacted layer, whose magnification is shown in Fig. 8, is mainly composed by titanium borides whereas the inner part is more porous since it is composed by needlelike and preferentially oriented TiB grains and titanium nitrides [21].

Representative examples of the load-deflection curve for each of the material studied, in particular of the specimens hot-pressed at 1100 °C whose surface was removed, are shown in Fig. 9.

From the curves shown in Fig. 9 it can be seen that, with the relative density values obtained by means of the hot-pressing tech-niques (Fig. 2), the flexural modulus of the three materials is very similar. It is worth mentioning that, generally, the hot-pressed Ti–6Al–4V samples behave as brittle materials and the materials fail without any appreciable plastic deformation. Therefore, the val-ues of the maximum bending strength coincides with those of the transverse rupture strength (TRS) and can be calculated by means of the formula specified in the ASTM B528 standard.



Fig. 7. XRD patterns of the surface of the Ti64-SJ specimens obtained by vacuum hot-pressing.



**Fig. 8.** Detail of the reacted layer where the denser part in the outside and the porous part in the inside can be clearly distinguished.

Figs. 10 and 11 report, respectively, the results of maximum flexural strength ( $\sigma_f$ ) and flexural strain ( $\varepsilon_f$ ) obtained by means of the three-point bending tests done on the Ti–6Al–4V hot-pressed specimens. As for nitrogen results, maximum flexural strength and flexural strain are subdivided between machined and not machine



**Fig. 9.** Representative examples of load-deflection curve for ground and not ground Ti–6Al–4V hot-pressed specimens.

specimens and represented as a function of the processing temperature.

Generally, the maximum flexural strength (Fig. 10) presents the same behaviour in each material independently of the mechanical grinding of the outer layer: it increases from 900 °C to 1100 °C and then decreases when passing from 1100 °C to 1300 °C. The only exception in this trend is the Ti64-Ph material where the maximum flexural strength always decreases with the increment of the processing temperature for both ground and not ground samples. Moreover, the removal of the reacted layer always leads to, at least, an increment of 200 MPa. It is clear that the difference between ground and not ground samples gets higher with the processing temperature since a higher thermal energy permits a faster dif-fusion of nitrogen and boron towards titanium giving as a result the formation of a thicker layer (Fig. 6) which makes the material more brittle. From the data shown in Fig. 10, it could be seen that the prealloyed powders reach higher maximum bending strength than the master alloy addition either before or after the grinding process with the only exception of the not ground specimens pro-cessed at 1300 °C whose maximum strength is similar. Since the final relative density obtained is almost equal for the three materi-als, the higher values of Ti64-Ph and Ti64-SJ are most probably due to the combined effect of contamination by interstitials and finer microstructural features (Fig. 3). In the case of Ti64-SJ and Ti64-MA the increment of the strength from 900 °C to 1100 °C is favoured by the homogenisation of the alloying elements and of the microcon-stituents (Fig. 3b and c versus Fig. 3e and f). At 1300 °C, this effect is



**Fig. 10.** Maximum flexural strength results as a function of the temperature for Ti-6Al-4V powders sintered by vacuum hot-pressing.



Fig. 11. Flexural strain results as a function of the temperature for Ti-6Al-4V powders sintered by vacuum hot-pressing.

overcome by the embrittlement due to the formation of the reacted layer composed by titanium nitrides and borides (Fig. 7). It is worth mentioning that the maximum flexural strength values shown in Fig. 10 are, at least, comparable to those of the Ti–6Al–7Nb obtained by means of vacuum hot-pressing (822–1485 MPa) [14] or higher than the flexural strength of wrought Ti–6Al–4V (903–1090 MPa)[24].

As it can be seen in Fig. 11, the trend of the flexural strain with the temperature is exactly the same as that of the maximum flexural strength since it increases from 900 °C to 1100 °C favoured by the homogenisation of the microstructure, but then it decreases due to the combination of the small changes in terms of relative density, percentage of interstitials (oxygen, nitrogen and carbon) and microstructural features described for the three processing temperatures. Furthermore, this behaviour is applicable to both ground and not ground specimens but, despite the removal of the outer layer, the final flexural strain values are similar. Once again, the only exception is the Ti64-Ph powder, where the strain always decreases, which is also the only one where oxygen content clearly increases continuously with the processing temperature. No such big differences could be found between the Ti-6Al-4V materials obtained from powders with a different particle size or produced by a powder production route since the flexural strain values range between 1.5% and 2%.

Finally, Fig. 12 displays hardness test results, precisely HV30, as a function of the temperature. It should be specified that the hardness values were not influenced by the presence of the reacted layer since the measurements are taken in the cross-section of the specimens.

Analysing the hardness data shown in Fig. 12, it can be seen that the values measured on Ti64-Ph specimens slightly decreases when



**Fig. 12.** Hardness results as a function of the temperature for Ti-6Al-4V powders sintered by vacuum hot-pressing.

raising the hot-pressing temperature from 900 °C to 1100 °C and, then, stay almost constant. This could be due to the microstructural changes and, in particular, to the grain growth that the specimens suffer with the increment of the processing temperature which overcome the effect of the reduction of the residual porosity and the slight increment of the interstitials. In the case of Ti64-SJ and Ti64-MA, the hardness increases with the hot-pressing temperature from 900 °C to 1100 °C, due to the homogenisation of the microstructure, the increment of the relative density, and, afterwards, stabilises most probably due to the counterbalancing effect of the grain growth.

Concerning the comparison between the three Ti–6Al–4V powders, it can be noticed that Ti64-Ph always has the highest hardness, which is most probably correlated with the higher oxygen content of this material (Fig. 4) and the finer microstructural features.

On the other side, Ti64-SJ and Ti64-MA have more or less the same hardness which indicates that the slight differences in terms of relative density, interstitials content and microconstituents counterbalanced themselves permitting to obtain the same hardness values at the three hot-pressing temperatures studied. Finally, the hardness values shown in Fig. 12 are similar to those found in other work starting from prealloyed hydride–dehydride or PREP powders [13] or the  $\alpha + \beta$  Ti–6Al–7Nb alloy processed by means of vacuum hot-pressing under similar processing conditions [14]. Moreover, the final hardness of vacuum hot-pressed Ti–6Al–4V materials is generally higher than the nominal values of 321 HV of the wrought alloy [16], even though of some residual porosity, due to the greater amount of oxygen dissolved in the hot-pressed specimens (at least 0.42 wt.%) in comparison to the value specified for the wrought alloy (0.20 wt.%).

## 4. Conclusions

This study demonstrates that titanium alloys produced by both the typical titanium powder metallurgy approaches, prealloying or blending elemental routes, can be processed by hot-pressing using HDH powders and reaching high densities, 98% of the theoretical value, which is higher than the ones reachable using the conventional pressing and sintering route. Therefore, hot-pressing could be employed as an alternative way to produce relatively complexshaped products made out of titanium.

There is a significant interaction between the powders and the boron nitride coating which leads to the formation of a reacted layer which grows thicker and denser when raising the temperature and it is mainly formed by titanium compounds (titanium nitride and titanium boride) due to high affinity of titanium for interstitials. Maximum flexural strength and hardness values higher than that of the Ti–6Al–4V wrought alloys or the hot-pressed Ti–6Al–7Nb alloy are normally obtained and the elimination of the outer layer entails an improvement of the mechanical strength.

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