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Modification of Sintered Titanium Alloys by Hot Isostatic Pressing

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Abstract: Powder metallurgy (PM) permits to obtain titanium alloys with properties and microstructures close to ingot metallurgy products. However, residual porosity is normally present in the products produced by the PM route of powder pressing and sintering (P&S)\, and this needs to be reduced by using post-sintering process step such as hot isostatic pressing (HIP) and forging. In this study, the microstructural and mechanical property changes caused by HIP of samples of two alloys, near-α Ti-3Al-2.5V alloy and α+β Ti-6Al-4V, produced by P&S route were investigated. Two types of powders were utilised: prealloyed powders and blend of elemental titanium powder and master alloy powder. Four conditions defined by HIP temperature, pressure and time were used to HIP the sintered samples with two geometries. The results show that, independent of the HIP conditions used, HIP increased the relative density of the samples to approximately 97.5% and their hardness by 30-50 HV depending on the HIP condition. However, HIP at 1000ºC changes the fracture mode of the sintered samples from ductile to brittle.

Keywords: Ti alloys, Powder Metallurgy, Prealloyed, Master alloys, HIP

1. Introduction

Titanium and its alloys have an excellent combination of desirable properties including the highest specific strength of all metals and alloys, outstanding corrosion resistance and biocompatibility. However, their applications are restricted to mainly high technology industries such as aerospace and biomedical industries due to their high cost compared to other metals. The high cost arises from the high cost of extracting titanium metal due to its high affinity to oxygen and the high cost of making titanium and titanium alloy mill products and shaped parts due to their high reactivity with atmosphere at high temperatures and poor machinability associated with the relative low thermal conductivity of titanium alloys [1, 2]. One way to reduce the cost of titanium alloy products is to produce them by using near-net shape forming technologies [3] such as powder metallurgy (PM) and casting. PM is favourable due to the fact that titanium and titanium alloy powders can be directly obtained in the titanium metal extraction process. Among the PM techniques, powder pressing and sintering (P&S) process has the lowest cost, but also a drawback which is the presence of residual porosity in the sintered parts leading to relatively low mechanical properties. This drawback can be overcome by using post-sintering processing step such as hot isostatic pressing (HIP) which is typically used to consolidate titanium and titanium alloy powders with spherical powder particles making them difficult to compact by powder pressing [4, 5]. In a normal HIP process, the powders are encapsulated and degassed and the containers are evacuated, prior to applying heat and pressure to the sealed container, but for the purpose of this study, the pre-sintered samples can be HIPed directly without using containers, since the pores in the samples are closed pores.

The majority of research on HIP of titanium and titanium alloy powders was performed in the 1980's and focused on commercially pure titanium [6] and Ti-6Al-4V alloy [7-9], which is known as the "workhorse" alloy and most widely used. Typical HIP temperatures used for Ti-6Al-4V are in the range of 800-960ºC (below the alpha/beta transus); the typical applied pressure is 100 MPa; and the HIP time varies between 2 and 4 hours [10]. Ti-3Al-2.5V alloy, known as "half 6-4", was developed for making parts for aircraft hydraulic and fuel systems, but is nowadays also used in various non-aerospace applications such as making parts for sports equipment and medical and dental implants [11, 12]. As far as the authors are aware, no studies have been reported in the literature about PM processing of Ti-3Al.2.5V alloy apart from a recent study by some of the authors [13]. The purpose of this study is to determine the effects of HIP under four conditions defined by the HIP temperature, pressure and time on the microstructures and mechanical properties of Ti-6Al-4V and Ti-3Al-2.5V alloys produced using the P&S route.

2. Experimental Procedure

For the Ti-6Al-4V alloy, a prealloyed powder (called Ti64-PA powder) and a powder (called Ti64-MA powder) prepared by blending hydrogenation-dehydrogenation (HDH) titanium powder (0.27 wt.%O and 0.016 wt.%N) with an Al-V master alloy powder were used to study the possible differences due to the nature of the starting powder. For the Ti-3Al-2.5V alloy, a powder (called Ti32-PA powder) prepared by bending HDH titanium powder with prealloyed Ti-6Al-4V powder and a powder (called Ti32-MA powder) prepared by blending HDH titanium powder with an Al-V master alloy powder were used. The details of making the powders can be found elsewhere [14].The powders were uniaxially cold-pressed using a die-wall lubricated floating die and with a pressure below the critical pressure which causes delamination of powder compacts during ejection. The powder compacts were sintered at 1250ºC for 2 hours in a tube furnace with a high vacuum of approximately 10^{-5} mbar. Samples with two shapes were produced: rectangular strips with dimensions of 30 x 12 x 2 mm^3 and dog-bone shaped samples for tensile testing. The density of the sintered samples was measured using the Archimedes method, and the relative density of the samples was calculated by taking the theoretical density of Ti-6Al-4V as 4.43 g/cm^3 and that of Ti-3Al-2.5V as 4.48 g/cm^3 [12]. The mean values of the relative density of the pre-sintered samples from this calculation were 95.4(±1.2)% for Ti-6Al-4V alloy and 94.9(±0.2)% for Ti-3Al-2.5V alloy. Without using containers, the sintered samples were HIPed using four different conditions shown in Table 1. Prior to the HIP cycle, the HIP chamber was evacuated and purged with argon three times. The heating and cooling rates used were both 10ºC/min and the maximum temperature and pressure were reached simultaneously.

Table 1: The HIP conditions used in the study.

HIP cycle	Temperature [ºC]	Time [min]	Pressure [MPa]
HIP-1	1000	20	100
HIP-2	1000	120	100
HIP-3	850	20	100
HIP-4	850	20	200

The as-sintered and HIPed samples were characterised in terms of relative density, microstructure, mechanical properties, oxygen and nitrogen contents (by means of inert gas fusion technique, LECO) and fractography. The tensile tests were performed following the UNI-EN 10002-1 standard and with a crosshead speed of 1 mm/min. The Young's modului of the samples were measured using the long-wavelength method in which a piezoelectric transducer with a frequency range between 20 Hz and 100 KHz and accuracy of 0.005% supplied by Grindosonic was employed.

3. Results and Discussion

Figure 1 shows the relative density values of as-sintered samples and samples HIPed at 850ºC and 1000ºC, respectively. HIP causes an increase of the relative density by 1.5-2.5%. The maximum relative density achieved is 97.7%, not fully dense, due probably to the open porosity present in the sintered samples. Moreover, no significant differences were observed in terms of the relative density of samples made using different starting powders (i.e. PA vs. MA). This is why a single value is presented for each alloy and PM condition.
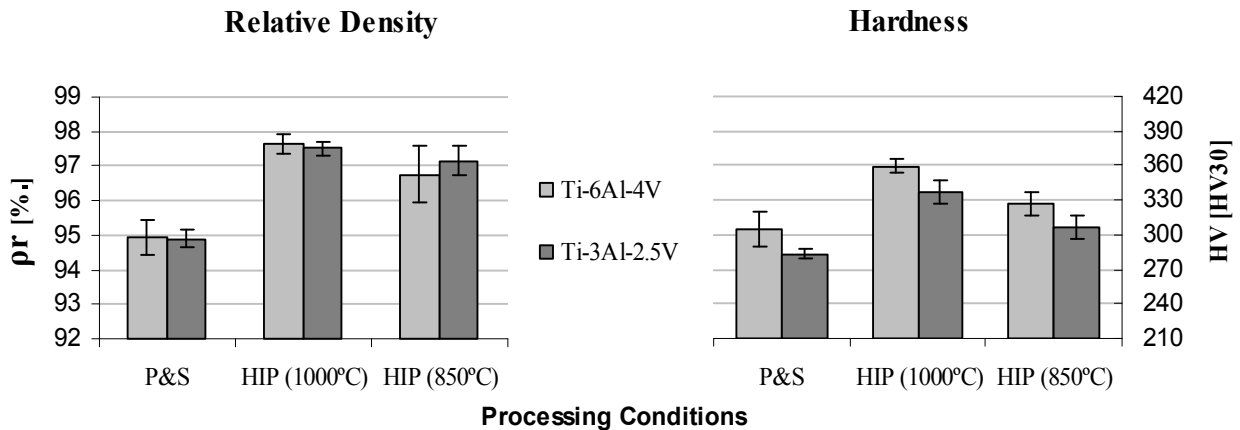
Relative Density **Hardness**

Figure 1. Relative density (left) and hardness (right) of Ti-6Al-4V and Ti-3Al-2.5V samples HIPed at 1000ºC and 850ºC, respectively in comparison with samples produced by P&S (1250ºC-2h).

An increase in the hardness of the sintered samples caused by HIP (Figure 1) was also observed, and the hardness increase was more significant with HIP at 1000ºC than with HIP at 850ºC. The hardness increase is likely due to the microstructural changes caused by HIP including reducing the porosity level. The microstructures of the as-sintered samples are shown in Figure 2. The typical microstructural features (α grains and α+β lamella) of the Ti-6Al-4V and Ti-3Al-2.5V alloys obtained by slow cooling of these alloys from above the β transus (996ºC and 935ºC, respectively, for the two alloy compositions) [12] were observed. Porosity is present in the microstructures of all as-sintered samples, and the complete chemical homogeneity of the samples was confirmed by energy dispersive X-ray spectrometry (EDS) analysis. The microstructures of the samples produced with the powder made by blending titanium and master alloy powders are very similar to those of the samples made with pre-alloyed powder. For this reason, it is only necessary to study the effect of HIP on sintered samples made with one type of powders.

   Figure 3 shows typical the microstructures of Ti-6Al-4V and Ti-3Al-2.5V samples HIPed at 1000ºC and 850ºC, respectively. A comparison of the microstructures of P&S and HIPed samples (Figures 2 and 3) indicate that the main microstructural change of the samples caused by HIP is the reduction of residual porosity, which is more significant with the higher HIP temperature, consistent with the change of the relative density of samples caused by HIP (Figure 1).
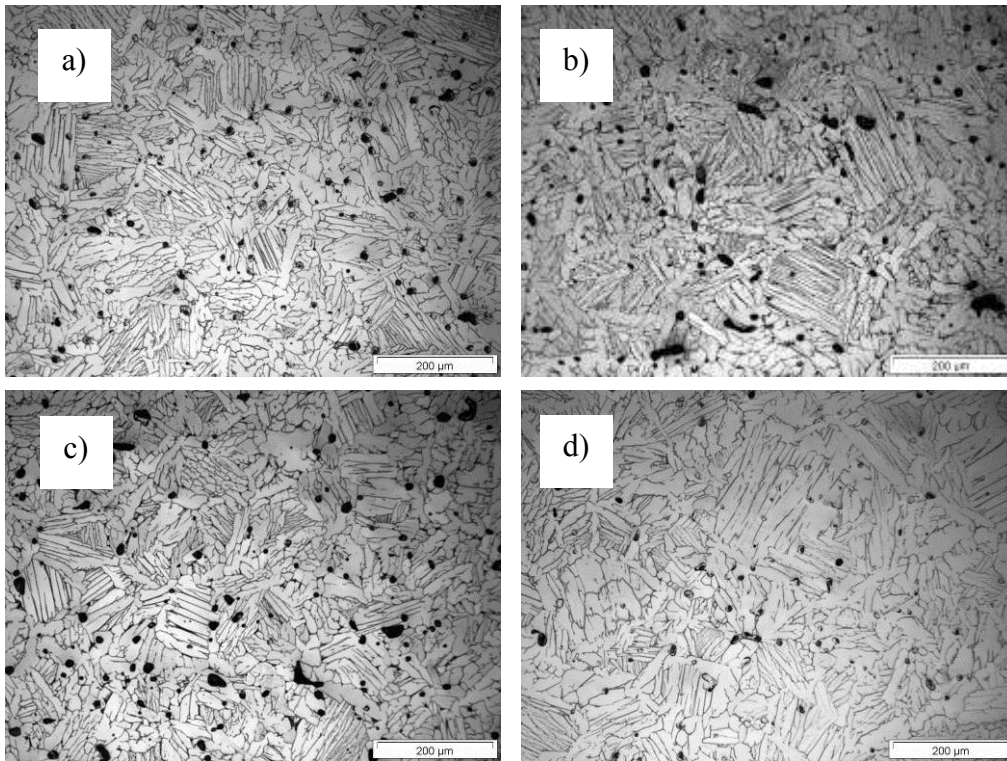
Figure 2. Optical micrographs of P&S (1250ºC-2h) samples: a) Ti64-PA, b) Ti64-MA, c) Ti32-PA and d) Ti32-MA.
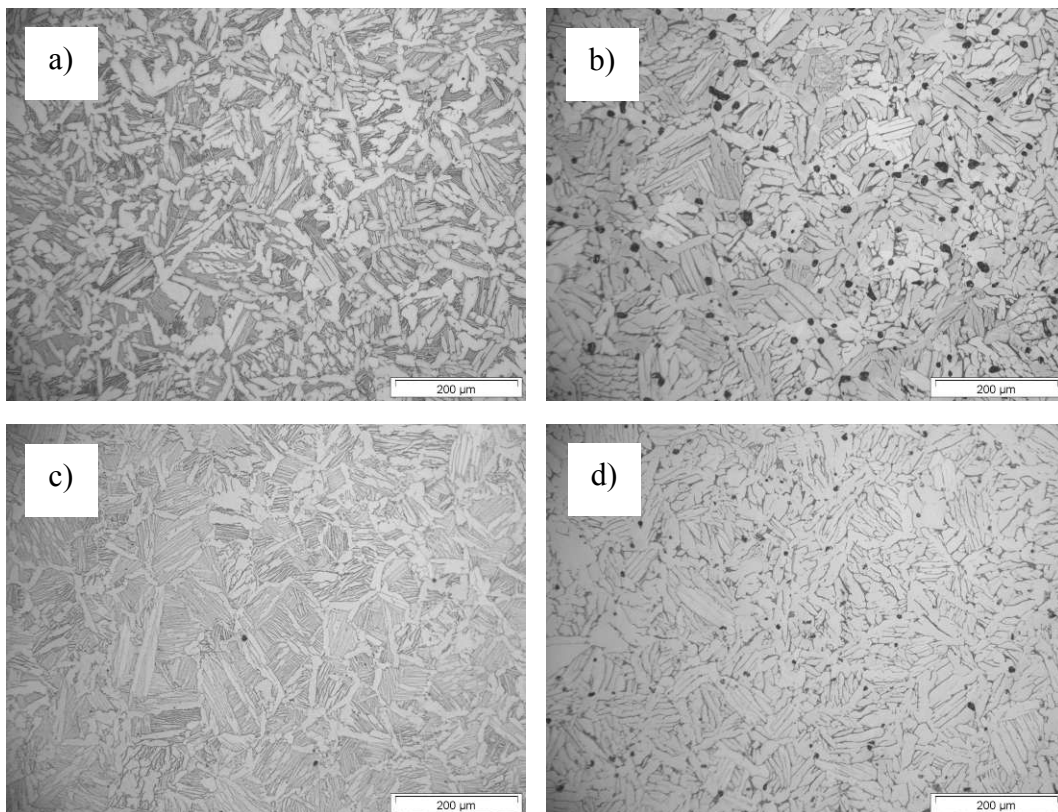

Figure 3. Optical micrographs of Ti64-PA samples HIPed at: a) 1000ºC and b) 850ºC; and Ti32-PA samples HIPed at: c) 1000ºC and d) 850ºC.

The microstructures of samples HIPed at 850ºC (Figures 3b and d) consist of α grains and α/β lamella, similar to those of the as-sintered samples (Figure 2). On the other hand, the microstructures of samples HIPed at 1000ºC consist of primary α grains in a matrix of α/β lamella formed by transformation of β phase. This kind of bimodal microstructure is normally obtained by annealing Ti-6Al-4V alloy at 955ºC for 1 hour followed by air cool [12], and it clearly reveals that the samples HIPed at 1000ºC were heat treated at a temperature inside the α+β region instead of above the β transus of the alloys which are supposed to be 996ºC and 935ºC, respectively, for the two alloy compositions. On the other hand, it is also clear that the samples HIPed at 850ºC were heat treated below the α+β region. This is most probably due to the fact that the region of coexistence of the α and β phases (α+β region) and, consequently, the β transus of the alloys is shifted towards higher temperatures due to the high oxygen content of these PM alloys in comparison with the values specified for the wrought alloy with low oxygen content (Table 2), considering that oxygen is a strong α phase stabiliser of titanium alloys. Thermal analysis of the sintered and HIPed are in progress to obtain the actual beta transus of the PM alloys covered in this study.

Table 2. Oxygen and nitrogen contents of P&S and HIPed samples and corresponding wrought alloys.

Alloy	Conditions	Chemical analysis	
		Oxygen [wt.%]	Nitrogen [wt.%]
Ti-6Al-4V	P&S	0.45 ± 0.03	0.020 ± 0.007
	HIP (1000ºC)	0.50 ± 0.09	0.034 ± 0.009
	HIP (850ºC)	0.45 ± 0.03	0.024 ± 0.001
	Wrought	0.20	0.050
Ti-3Al-2.5V	P&S	0.37 ± 0.05	0.024 ± 0.002
	HIP (1000ºC)	0.42 ± 0.01	0.036 ± 0.014
	HIP (850ºC)	0.39 ± 0.01	0.026 ± 0.003
	Wrought	0.15	0.030

Figure 4 shows the typical engineering stress-strain curves of the tensile test specimens cut from the as-sintered samples and samples HIPed at 1000ºC for 2 hours (HIP-2 condition). In comparison with the typical ultimate tensile strength (UTS) of wrought alloys, 900 MPa for Ti-6Al-4V and 620 MPa for Ti-3Al-2.5V [12], the as-sintered samples show higher UTS values for both alloys. The elongation to fracture of the tensile test specimens cut from the P&S Ti-6Al-4V samples are 3-4%, clearly lower than that of corresponding wrought alloy (10%), while those of the P&S samples made with Ti32-PA and Ti32-MA powders are similar to that of the corresponding wrought alloy (15%). Unfortunately, the tensile test specimens cut from the HIPed samples performed badly, showing little or no ductility and, in most cases, the fracture stresses of the specimens are clearly lower than the expected UTS values of the corresponding alloys. This is rather surprising, since the reduction of residual porosity of pre-sintered samples should lead to improvement of ductility and strength. This result may be due to the higher oxygen content of HIP samples (see Table 2) and the fact that HIP changes the shape of the pores in the as-sintered samples from mainly spherical to more irregular or highly elongated. High oxygen content in titanium alloys can significantly reduce their ductility since the interstitial oxygen atoms are very effective in resisting the movement of dislocations. In the meantime, the pores present in the PM samples act as stress concentration sites and the more irregular or elongated pores are more effective for this function, leading to the failure of the material at lower stresses.
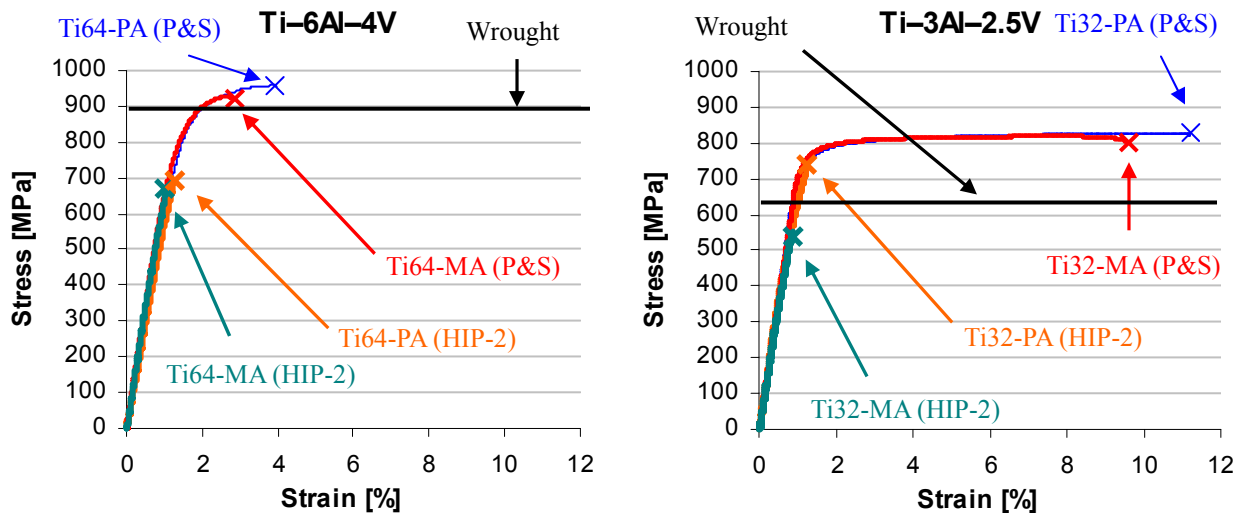
Figure 4. Typical engineering stress-strain curves of Ti-6Al-4V (left) and Ti-3Al-2.5V (right) tensile test specimens cut from samples HIPed at 1000ºC and 100 MPa for 2 hours in comparison with those of specimens cut from P&S samples (1250ºC-2h).

From the stress-strain curves shown in Figure 4, it can be noticed that the Young's modului are lower than the expected values. Nevertheless, dynamic Young's modulus measurements indicate that the actual elastic modului of the alloys are 110±6 GPa and 112±3 GPa for sintered Ti-3Al-2.5V and Ti-6Al-4V samples and 114±3 GPa and 118±2 GPa for HIP'ed Ti-3Al-2.5V and Ti-6Al-4V specimens.

From the fractographic analysis shown in Figure 5, it was observed that HIP at 1000ºC changed the fracture mode of the sintered samples from ductile to brittle. The fracture surface of the tensile test specimens cut from the P&S samples is composed of a uniform distribution of non-equiaxial dimples typical of the pore-assisted fracture of ductile metals whereas the fracture surface of the HIPed samples consists of cleavage facets typical of the fracture of brittle materials.
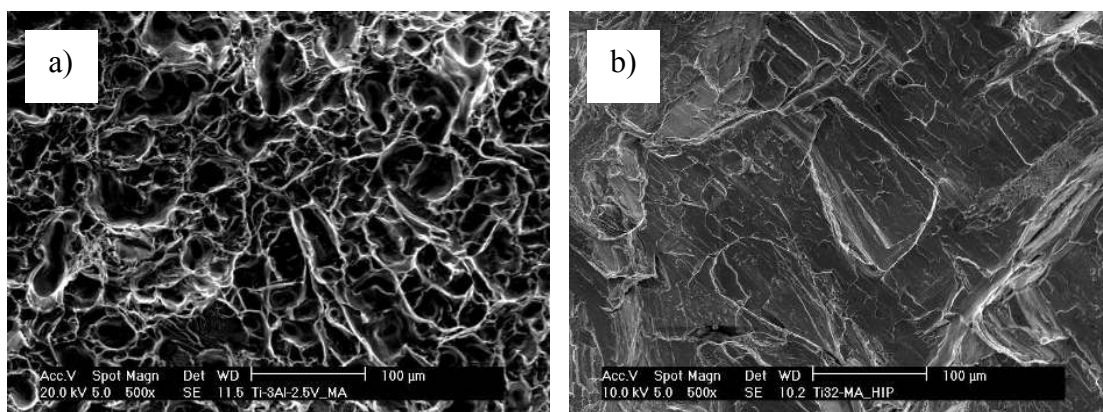

Figure 5. Typical fractographs of tensile test specimens cut from Ti-3Al-2.5V a) P&S and b) HIPed samples.

4. Conclusions

HIP (without using containers) of Ti-3Al-2.5V and Ti-6Al-4V alloys fabricated by the powder pressing and sintering route increases their relative density from 95% to approximately 97.5% and their Vickers hardness by 30-50 HV, depending on the HIP conditions, especially the HIP

temperature in relation to the beta transus of the alloy studied. HIP of pre-sintered samples slightly increases their oxygen and nitrogen contents, and leads to the formation of a bimodal microstructure composed of primary α grains and α+β lamella colonies. The as-sintered samples show similar or higher ultimate tensile strength to those of corresponding wrought alloys, but HIP causes the tensile properties of the as-sintered samples to deteriorate, due likely to the increase of oxygen and nitrogen contents and change of pore morphology.

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