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Colloidal approach for the design of Ti powders sinterable at low temperature

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Abstract

The colloid-chemistry control of metallic powders in aqueous slurries is proposed as a way to produce spherical granules of fine titanium particles able to be processed by powder metallurgy (PM) techniques. Significant improvement of sintering behaviour is achieved, leading to high dense parts at reduced sintering temperature and time. Consequently the control of grain growth during sintering was achieved, as well as the oxygen content. This approach can be extended to other strategies for Ti design, such as the homogeneous dispersion of second phases for further control of grain size and modification of properties.

Keywords

Powder technology, Colloidal processing, Titanium, Sintering, Microstructure, Hardness

1 Introduction

Aimed by reducing the total cost of products, powder metallurgy (PM) processing of Ti is a subject of high interest. However, using of conventional PM techniques presents difficulties due to the intrinsic characteristics of Ti, like low strain ability, and high reactivity [1,2], which lead to low compressibility. Other concerns have been identified [3,4] in which active research is being carried out: (1) grain growth during sintering step; (2) high influence of oxygen content on mechanical properties and (3) quality and cost of available powders. The grain growth during sintering is a consequence of the high temperatures (1250 ºC – 1350 ºC) and long times (2 h or 4 h) needed to achieve high densities [5,6], as in the case of elemental Ti and the main Ti alloys sintering proceeds in solid state. In addition, high sintering temperatures increase the content of interstitial elements (as oxygen and nitrogen), which are detrimental to mechanical properties. Those problems could be overcome by reducing the particle size of the starting powders and consequently the sintering temperature. However, powders with small particle size are difficult to process by conventional PM techniques as they present poor flowability and compressibility.

On the other hand, spray-dry permits to transform small particle powders into granules suitable to flow, fill a die and get pressed into green compacts. It requires the stable dispersions of powders in a liquid media, usually water that are sprayed through a nozzle and dried by a hot air current. The colloidal chemistry of the powders dispersed in water became so critical to achieve homogenous materials. In fact colloidal control of aqueous slurries has been used for long in ceramics to achieve complex shapes and microstructures [7,8], being less common its use for metals. Recently, by controlling the colloid-chemistry of the metallic particles in water, successful results have been obtained for pure Ni and Ni-ceramic composites with high solid contents for structural or energetic applications [9-11]. These results open the way to other metals like Ti, for which there are no published works so far to obtain dense materials, but only for foams [12].

This work describe for the first time a bottom up approach to reduce the grain size and sintering temperature for the fabrication of dense Ti parts profiting from the synergism of colloidal and powder metallurgy techniques. It frames into the innovative research for new processing strategies of Ti dense structures that keep the use of inexpensive conventional techniques and an easy-to-transfer assumption. It should be noted that colloidal approach is here explored for the tailoring of Ti granules able to be processed by PM. The manipulation of the colloidal-chemistry of the metallic powders into the aqueous suspension will determine afterwards the features of the Ti granules to face shaping solicitations like compressibility under pressure and low oxygen content.

2 Materials and methods

Starting materials were two elemental titanium spherical powders, with different particle size supplied by AP&C Inc (Canada): powder smaller than 45 µm (Ti45) and powder smaller than Ti 10 µm (Ti10) grade 1. Powders were characterized for processing control (see additional information).

A previous study [13] was made to obtain the optimal parameters for preparing stable aqueous suspensions of the Ti10 powder. Slurries of Ti10 with high solid contents (up to 50 vol %) were fabricated in water using ammonium polyacrilate (PAA) as dispersant and polyvinyl alcohol (PVA, Aldrich) as binder. Selected suspensions were spray-dried using an atomizer Labplant SD-05 with the main controlled operating parameters such as the temperature at the inlet (220 ºC) and at the exhaust (100 ºC), the slurry pump rate (2 l/h), the air flow rate (38 m^3/h), and the atomizing nozzle design set to provide spherical agglomerates.

Both the Ti45 powders and the agglomerates from suspensions of Ti10 powders were processed by pressing and sintering. Pressing was performed in a double-effect uniaxial press into cylinders of 16 mm diameter, using different pressures to obtain the compressibility curve. The green compacts were sintered in vacuum (10^{-5} mbar) at 1100 ºC for 30 minutes. The sintering temperature was selected from a dilatometry study using a dilatometer SETARAM Setsys 1700 (see additional information). The green density was measured using dimensions, and sintered density was measured using both dimensions and a Monosorb Multipycnometer (Quantachrome Co.), to obtain data of total, close and open porosity. The oxygen content of sintered samples was measured with a LECO TCH-600, and hardness was measured in Vickers scale using 10 kg load (HV10). The microstructure was examined with optical and scanning electron microscopy, grain size was measured by image analysis, and phase identification was carried out by X-ray diffraction (XRD) in a Philips X´PERT using Cu-Kα radiation.

3 Results and discussion

Fig.1a shows the particle size distribution of the processed dry granules and the starting powders. For granules, the cumulative curve indicates that only the 5% in volume of the granules (Dv5) are below 10 μm (mean particle size of Ti10) while the 95% (Dv95) is under 300 μm being the Dv50 of about 50μm. In the differential curve it can be seen a bimodal distribution of particle sizes with mean sizes at 25 μm and 160 μm respectively. If compared with the particle size distribution of the starting Ti10 powders, it can be clearly seen that the fine fraction was removed, while the Dv95 of Ti10 fits the lowest mean particle size of the bimodal distribution of the granules. This fact can be verified in Fig.1b where an overview of the powders after granulation is included. In this micrograph the coarse fraction of Ti10 powder are the only particles that can be observed isolated, while the fine fraction is forming spherical granules of different sizes. The absence of fine particles ensures a correct flowing and filling of pressing molds during common powder metallurgical processes. The Ti45 powder distribution is unimodal, similarly to the T10 distribution, being the curve slightly shifted to the right, meaning that a fraction of fine particles is present.

Moreover, Fig.1c and Fig.1d show the feature of the surface and the cross-section, respectively, of an isolated granule. Generally we can found in the literature that the granules processed by spray-dry from sub-micronic particles appears as hollow spheres or doughnuts-shaped [14,15], but it can be observed in Fig.1c that granules of Ti10 prepared in this work are completely dense, showing a homogenous and compact distribution of particles with different sizes within all the volume. Bimodal granule size distribution as well as the homogenous distribution of Ti10 particles inside the granule, will contribute to improve packing and compaction during cold pressing.

The compressibility curve of spray-dried powders and Ti45 powders are shown on Fig. 2. Green density achieved, expressed as percentage to the theoretical, is higher for pressed Ti10 granules than for Ti45 powder for all the studied pressures, thus proving that employment of agglomerates improves the pressing behavior of free powders. It is remarkable that the most of the work currently done in processing of Ti powders by cold pressing is carried out using irregularly-shaped powders [16], as spherical powders can only be pressed by more advanced processing, as hot pressing, hot isostatic pressing or powder injection molding. Results in this work demonstrate that spherical powders can be successfully processed by cold pressing through granules shaped in a previous colloidal step, achieving green density values even higher than those obtained by coarser and irregular-shaped powders [3,16,17]. It is worth mentioning that Ti10 powders before granulation could not be pressed in the uniaxial press, due to the small size and spherical shape of particles, and also Ti45 powders could not be granulated as it was not possible to produce stable suspensions due to the big particle size.

A key factor in Ti processing is the oxygen pick-up. The properties of Ti products are very sensitive to oxygen content, being necessary to keep it below the specified contents for each commercial Ti grade. However, the control of oxygen is hard, as the sources of oxygen are numerous [18]. Despite the preparation of granules in aqueous suspensions, experimental data do demonstrate that no oxygen pick up occurs under the conditions employed in this work. DTA-TG curves (Fig.3a) show that endothermic peak corresponding to the alpha-beta transition appears exactly at the same temperature (898 ºC) for the agglomerates and for the free powder. This transition temperature is especially sensitive to the presence of oxygen as an alpha stabilizer, what means that there is no oxygen peak-up in this step of the processing. Moreover, the TG curve indicates a different behavior for the two materials. Ti10 powders gain mass when increasing the temperature, due to the oxidation, whereas Ti10 granules show the decrease of mass up to 400 ºC due to the elimination of binder. At higher temperatures, the mass remain stable probably due to the reaction of oxygen with residual carbon present in the materials from the former binder. This can be the reason why sintered samples from spray-dried powders (Ti10) present lower oxygen content than samples from Ti45 powders (see Table 1), thus confirming that aqueous processing is not providing additional oxygen to the samples. Fig. 3b shows the XRD patterns of the sintered samples. All the diffraction peaks correspond to alpha titanium (JCPDS Nº 00-044-1294), and no other phases are identified. Correspondingly, the microstructure (Fig. 3c, d) of sintered samples is composed in both cases by only equiaxed grains of alpha phase and pores.

The main differences between the two materials are the reduction of both porosity and grain size in samples made out of Ti10 granules. The mean grain size was measured by image analysis, and a reduction of 40 % was observed in Ti10 with respect to Ti45 (Table 1). These results permit to confirm that the smaller particle size of the powder particles improves the sintering behavior. Regarding hardness (Table 1), values of Ti45 are higher than Ti10, which is related to the higher oxygen content that raises hardness, whereas the values of Ti10 corresponds to that of CP Ti grade 4 (commercially pure Ti with 0.4 wt.% oxygen).

4 Conclusions

- The combination of colloidal processing of powders in water and PM techniques has been successfully used to obtain bulk dense parts of Ti.
- Spherical agglomerates with homogenous distribution of Ti particles were obtained through atomization (spray-dry) of the optimized suspensions. These agglomerates improve the compressibility of Ti 10 µm powder, either with respect to 45 µm powder.
- The sintering behavior has been improved. Relative density values are around 96 % of the theoretical, with a sintering temperature of only 1100ºC, being lower than those reported in the literature for Ti alloys. Besides, the sintered Ti10 material presents smaller grain size, lower volume of open porosity and even lower oxygen content than for materials obtained from powder bigger in size.
- It is proved that water is a feasible carrier for titanium processing where no extra oxygen is provided to the final component.

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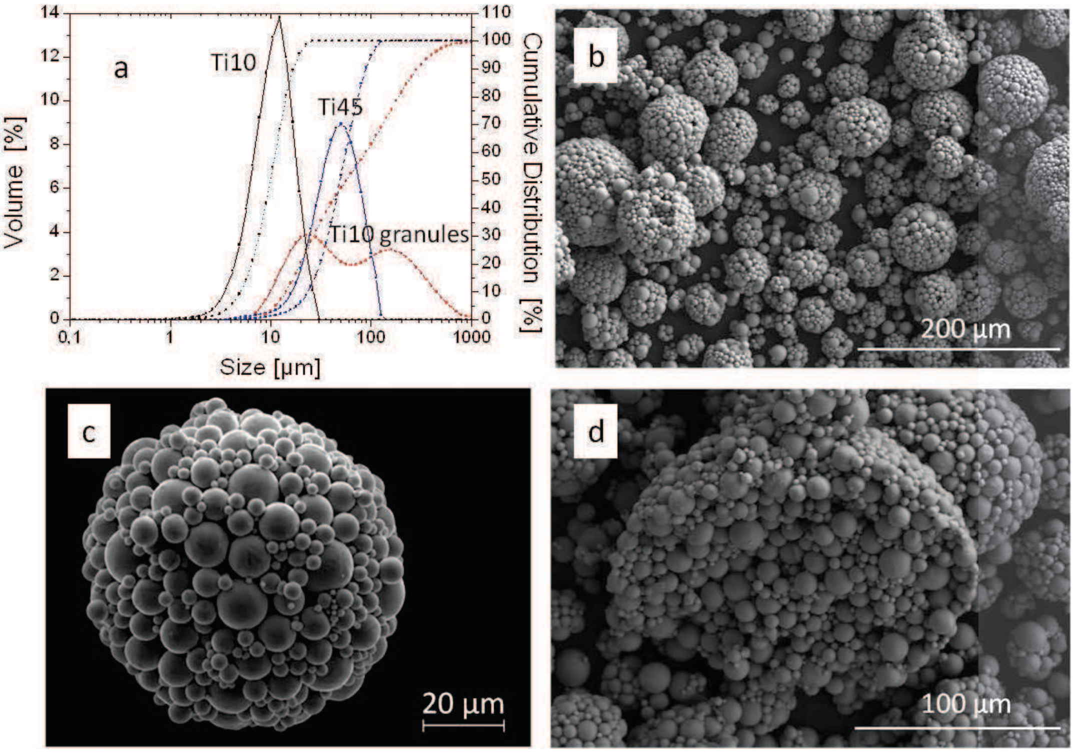

Figure 1. (a) Particle size distribution for the Ti10 and Ti45 starting powders and the Ti10 granules obtained by spray dry process from aqueous suspensions. (b) SEM micrograph showing a general view of the Ti10 spray-dried spherical granules with different sizes. (c) Close up to a granule showing its high packing density as well as the homogeneous particle size distribution. (d) Micrograph of a fractured granule proving that density and particles distribution is maintained all over the volume.

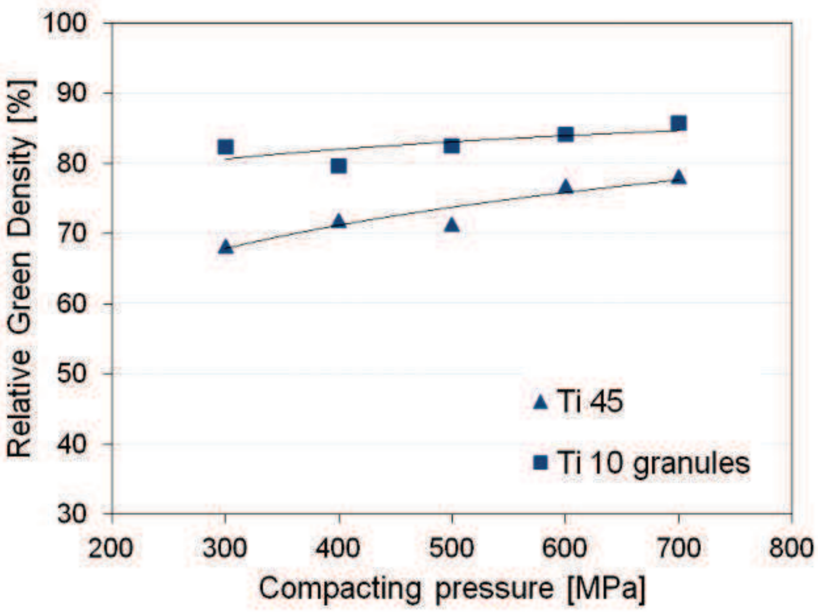

Figure 2. Compressibility curves of Ti45powder and Ti10 granules.

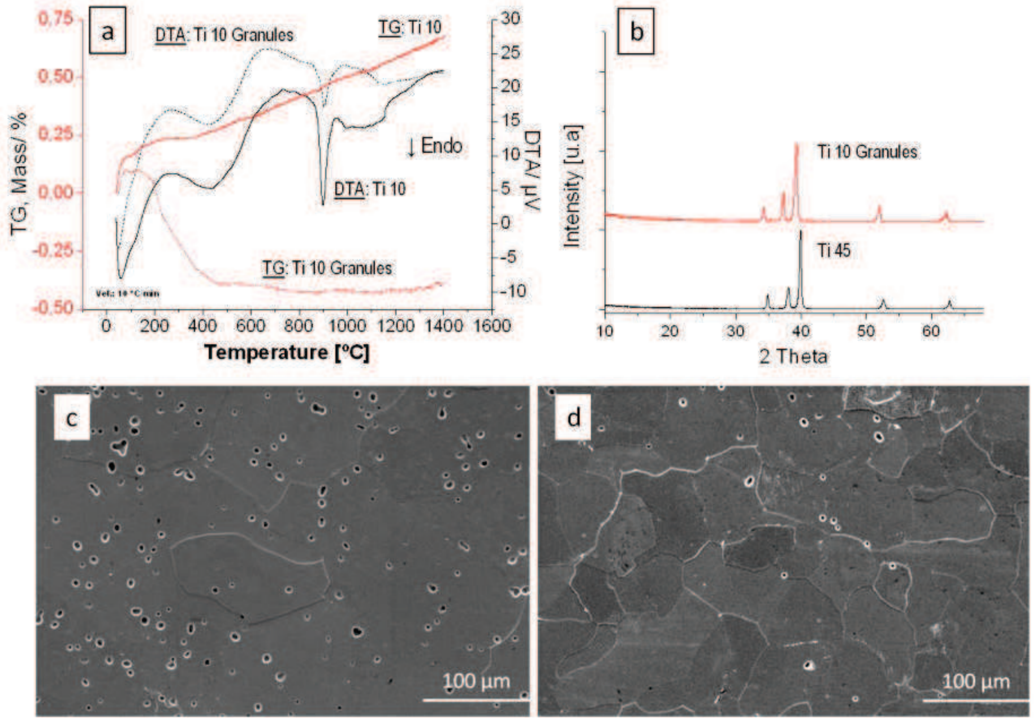

Figure 3. (a) DTA-TG curves of Ti10 initial powder and agglomerates obtained by spray-dry. (b) XRD patterns of sintered samples obtained from Ti45 as-received powder and Ti10 granules. (c) Microstructure of sintered samples obtained from Ti45 as-received powder. (d) Microstructure of sintered samples obtained from Ti10 spray-dried powders, pressed and sintered in the same conditions than (c) (1100 ºC, 30 min, vacuum).