*Abstract

Role of stabilisers in the design of Ti aqueous suspensions for pressure slip casting

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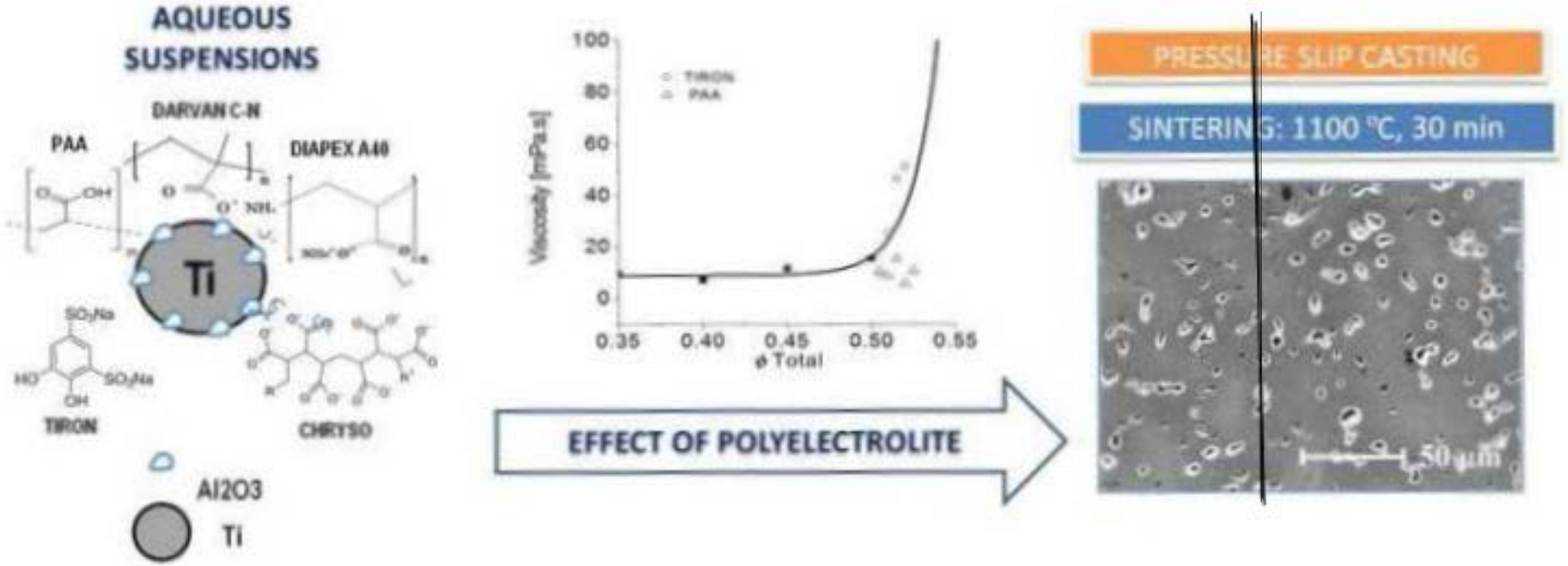
microstructure analysis by SEM. Ti bulk pieces with 97 % density and fine and homogeneous microstructure, of which the relationship between the oxygen content and hardness agrees with that measured for CPTi grade 4 (249±24 HV30), can be processed by PSC.

Keywords

Powder processing, Rheology, Composites, Titanium, Colloidal Processing

*Graphical Abstract (for review)



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1. Introduction

The titanium processing by powder metallurgy presents a number of difficulties derived from the low strain capacity due to the crystalline structure at room temperature and its high reactivity, which leads to low compressibility, as studied and described by Donachie [1], Lutjering [2] and Barnerjee and Williams [3]. In previous works related to processing of Ti by PM, Qian et al. [4] and Wang et al. [5] demonstrated that it is necessary to reach sintering temperatures in the range of 1250 ºC to 1350 ºC and times as long as 2 or 4 hours to achieve high densities. Those high sintering temperatures and times increase the grain growth and the content of interstitial elements (such as oxygen and nitrogen), which are detrimental to mechanical properties [6]. Those problems could be overcome by reducing the particle size of the starting powders and consequently the sintering temperature, but the use of fine particles makes the pressing step more difficult if uniaxial pressing is to be used [7]. Another strategy to avoid grain growth during sintering, in addition to reducing the sintering temperature, is the addition of small percentage of submicron or nanometric ceramic particles, such as Al_2O_3, ZrO_2 or Y_2O_3, to fix grain boundaries by particle pinning or by solution drag, as described by Manohar et al. [8]. The case of Al_2O_3 is well-known due to its high stability; it is economic and presents similar density to Ti.

The role of alumina is important to impede the grain growth of Ti by blocking the grain boundaries and thereby obtaining fine microstructures with suitable mechanical properties. This strategy

would provide better control of the mechanical properties, as well as modification of the elastic modulus and improvement of the wear resistance, as demonstrated Bolzoni et al. [7].

Colloidal processing is a versatile method for obtaining complex-shaped bodies with special characteristics for physical, chemical and mechanical requirements. Colloidal processing has been long used in ceramics to achieve green bodies with larger densities, complex structures, such as laminates, and more homogeneous microstructures with dispersed second phases. This processing method has allowed for the tailoring of new materials capable of facing the increasing need of technological development. One way to produce materials with enhanced properties is through formulations of two different phases. Regardless of their final application or use, a suitable control of the dispersion between phases is required because this controls the final properties of the material and its response under service.

For the proper dispersion of ceramic particles and to prepare the small Ti powders, colloidal processing has been considered as a processing route.

It implies the preparation of stable suspensions with dominating repulsive forces among particles capable of maintaining the dispersion even during consolidation. Colloidal processing is rarely used in metals because of its high density and high surface reactivity, but the possibility to process fine particles in tailored microstructures makes these techniques interesting for metals, such as titanium, with low density, high melting point and high reactivity.

Studies dealing with the colloidal behaviour of metal powders usually describe the surface behaviour of the dispersions, such as those conducted by Gavoille et al [9] and Zaitsev et al. [10]. By controlling the colloid-chemistry of the metallic particles in water, suspensions of pure nickel and nickel-ceramic composites with high solid contents have been obtained by Sanchez-Herencia et al. [11] and Hernandez et al. [12]. Currently, there are scarce studies concerning the rheological properties of concentrated suspensions of pure Ti and Ti alloys and its consolidation in colloidal methods. Most of the studies are focused on porous materials. Xu et al. [13] studied

the performance of some dispersants to produce aqueous Ti slurries for slip casting using Ti powder produced by a hydride-dehydride (HDH) process with particle size lower than 45 μm. Based on this study, Xu et al. [14] used a selected dispersant to create aqueous suspensions with up to 47 vol.% of pure HDH Ti powder with a mean particle size of 14 μm to be processed by slip casting. The cast bodies obtained were sintered at temperatures up to 1200ºC during 30 min to obtain sintered densities up to 83.2 $g \cdot cm^{-3}$ with an open porosity of 9.9±0.4 % and a 0.47 % oxygen content.

Neirinck et al. [15] studied the formation of stable emulsions to create porous titanium by electrophoretic deposition in Ti alloys (Ti6Al4V) as substrate material. To stabilise the emulsions of Ti, dispersants are used to provide on the Ti surfaces with sufficient positive charge at low pH to ensure the electrophoresis process. The optimal amount of polyelectrolyte for creating stable emulsions was determined by the yield of the electrophoretic deposition (EPD) experiments instead of the usual colloidal processing techniques, such as zeta potential and rheological measures. Erk et al. [16] used gelcasting and thermoreversible gelcasting process to create porous titanium structures. These methods can obtain controlled porosity up to 44 vol.% with low contamination. The thermoreversible gelcasting process is based on a non-aqueous system, such as the powder transport medium, to eliminate oxygen contamination.

Spray-drying is a technique widely employed in powder-related technologies to transform small powders into granules suitable to flow, fill a die and be pressed into green compacts. The spray-drying technique allows for the designing of Ti granules that are able to flow and to be processed by conventional PM techniques. Neves et al. [17, 18] reached a sintering density of approximately 96 % of the theoretical value through this method.

The aim of this work is to evaluate the role of different polyelectrolytes as stabilisers for the creation of concentrated Ti aqueous suspensions and the influence on the final properties of the bulk materials. The addition of a small percentage of alumina particles (1 wt.% up to 5 wt.%) as a

second phase to create homogeneous and stable suspensions is also considered. The stabilised and concentrated suspension with Ti and Al_2O_3 particles will permit the creation of dense Ti materials with alumina particles well-dispersed homogeneously on the Ti matrix or dissolved on it.

The role of stabilisers was evaluated according to their active functional groups, stereochemistry and their affinity for the Ti surface at the working pH. The study is focused on the dispersion optimisation to (i) achieve the lowest viscosity value that tolerates the addition of Al_2O_3 up to 5 wt.%, and (ii) improve particle packing and reduce the oxygen content of the final compact. Compacts were produced by pressureless slip casting (PLSC), pressure slip casting (PSC) and a combination of spray-drying and the conventional powder metallurgy route (SDP), where the preparation of a stable suspension is mandatory. In view of the final results, the specificity of the selected stabilisers was determined.

2. Experimental Procedure

2.1 Materials

Elemental titanium powder, grade 1, with spherical morphology and mean particle size of 10 µm (Ti10), supplied by AP&C Inc. (Canada), was used. The Al_2O_3 powder was provided by Condea HPA05, USA; it has a high purity (99.99 %) and is present as the alpha phase. The particle size was determined by dynamic light scattering (DLS) (Dv50) using a Mastersizer S, (Malvern instruments Ltd, Worcestershire, United Kingdom). The shape of the alumina powder is irregular, with a mean particle size of 0.5 µm. The powder density and specific surface area were measured by helium pycnometry (Monosorb Multipycnometer, Quantachrome Instruments Co., Florida, USA) and N_2 adsorption–desorption by the BET method (Monosorb Surface Area Analyzer MS-13, Quantachrome Instruments Co., Florida, USA), respectively. The oxygen

content was measured using an inert gas fusion technique using LECO TC-500 (Michigan, USA) equipment. These characteristics are summarised in Table 1 for Ti and alumina powder.

Table 1. Characteristics of Ti and alumina powders.

Powder type	**Particle Size [µm]**		**Specific surface area [$m^2 \cdot g^{-1}$]**	**Density (by He pycnometry) [$g \cdot cm^{-3}$]**	**O [wt.%]**
	D_v50	**D_{BET}**			
Ti	10	7.4 ± 0.1	0.17 ± 0.01	4.51 ± 0.01	0.216±0.001
Al_2O_3	0.40	0.16 ± 0.1	9.50± 0.01	3.97± 0.01	49.610±0.001

For the stabilisation of the slurry rheology, several dispersant agents were considered:

i) Polyacrylic acid (PAA, Mw=2000 g/mol, Acros Organics, USA), prepared in an tetramethylammonium hydroxide (HTMA) solution at pH 10, which was previously used in Neves et al. [17,18].

ii) An ammonium polymethacrylate aqueous solution (Darvan C-N g/mol, Vanderbilt Minerals, USA);

iii) A solution of an ammonium salt of an acrylic polymer in water (Diapex A40, Mw=10.000 g/mol, BASF, Germany);

iv) A 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt (Tiron, Mw=332.2, Sigma Aldrich);

v) A gypsum fluidiser based on a polycarboxylate copolymer (neomere®FLOW 530 V, Chryso, France).

2.2 Suspension preparation and processing.

Slurries of 50 vol.% of Ti (81,8 wt.%), and their mixtures with Al_2O_3 up to 5 wt.%, were prepared in water by adding the stabilisers mentioned above. Powders were added to a solution of the stabilisers in deionised water at 9<pH<10. The pH of the slurries was adjusted by adding HTMA,

whereas the stabilisers were added in concentrations between 0.6 from 1.4 wt.%. Slurries were homogenised with a mechanical mixer and then dispersed using an ultrasound probe (400W) (Bioblock Scientific vibra cell (TM) 75041, 750W)) for 1 minute to break soft agglomerates and were later kept under stirring for 1 hour.

The rheological characterisation was conducted using a rheometer AR-G2 (T.A. Instruments, USA) with a 40 mm parallel plate that requires a sample volume of 250 µl. The temperature was maintained constant at 25 ºC. The flow behaviour was measured by the controlled shear rate (CR).To obtain the high shear flow behaviour, CR experiments were conducted using a measuring program in three stages: first, a linear increase of the shear rate 0 to 450 s^{-1}; a plateau at 450 s^{-1} for 1 min; and finally a decrease to zero in 1 minute.

Ti slurries with 1 wt.% of Al_2O_3 particles (Ti + 1 wt.% Al_2O_3) and 1 wt.% of all the stabilisers were processed by pressure slip casting (PSC). The results were compared to suspensions prepared with 1 % PAA and processed by two techniques: pressureless slip casting (PLSC) and powder metallurgy processing (PM). The PM process consists of spray-drying the slurries to obtain granules of a mixture of Ti and Al_2O_3 particles of approximately 50-100 µm in size, followed by pressing (SDP). The slurries were spray-dried using a Labplant SD-05 spray-drier (North Yorkshire, United Kingdom) 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 atomising nozzle design, were set to provide spherical agglomerate. Pressing was performed at 600 MPa in a double-effect uniaxial die into cylinders of 16 mm in diameter. In PLSC, the Ti + 1 wt.% Al_2O_3 slurries were cast in a porous mould made on plaster of Paris; the duration of filtration was 24 hours. In PSC, the slurries were cast in a polymeric mould commonly used for slip casting under pressure. A paper filter with a very small size of pores was used on the upper face of the mould to avoid the loss of solid. The pressure applied was 2 bar for 10 seconds. Slip casting leads to suspension consolidation by the filtration of liquid; the duration

of filtration depends on the dispersion state of the suspension and the pressure in the mould. A short time of filtration prevents particle sedimentation and segregation, and it is expected to maintain the homogeneity of the starting suspension.

All the green bodies obtained were sintered in the same conditions for comparison: 1100 ºC for 30 minutes under high vacuum (<10^{-4} mbar).

The characterisation of the green bodies consisted in the measure of their density at room temperature by the Archimedes method in Hg and in the study of the microstructure of the compacts by a Philips Model XL30 scanning electron microscope (Philips, The Netherlands). Similarly, the characterisation of sintered parts consisted in the measurement of their density at room temperature by the Archimedes method using an analytical balance with a resolution of ± 0.1 mg and by He pycnometry (Monosorb Multipycnometer, Quantachrome Instruments Co., Florida, USA). The values of density are expressed as relative density, which is the measured density over the theoretical. The rule of mixtures was used to determine the theoretical density of the compounds. The oxygen content, which is an interstitial element and has the greatest effect on the mechanical properties of titanium, was measured using an inert gas fusion technique. For these measurements, a LECO TC-500 (Michigan, USA) calibrated with suitable standard samples was employed [22]. The hardness was also evaluated through a universal hardness tester (Wilson Wopert Universal Hardness Digital Testor 930, Illinois Tool Works Inc., USA), using the Vickers scale (HV30) with an indentation load of 30 kgf/mm^2 according to the ASTM –E-92 standard for metallic materials [23], and finally the microstructure was analysed with a Philips Model XL30 scanning electron microscope (Philips, The Netherlands).

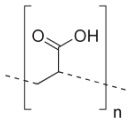
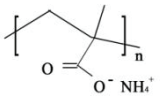
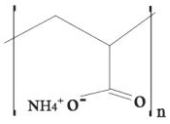
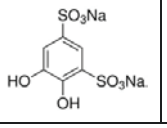
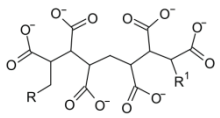
3. Results and Discussion

3.1 Rheological behaviour

The evolution of the viscosity with the solid content in Ti aqueous slurries was determined using the optimised amount of PAA established through electrokinetics tests [Neves et al [17]). In view of those results, 10 μm spherical powders were dispersed in an aqueous solution of PAA (1 wt.% relative to the final solid content of the slurry) where the pH was previously adjusted to 10 by the addition of HTMA. Fig. 1 (a) shows the evolution of the viscosity with the shear rate for the Ti slurries prepared with different volume fractions of solids, and Fig. 1 (b) shows the evolution of the viscosity values measured for a shear rate of 100 s^{-1}. The Ti slurry exhibits a strong thickening behaviour with increasing solid contents up to 50 vol.%. For a higher concentration of powders (such as 55 vol.%), the viscosity of the slurry increases significantly; however, the flow behaviour changes from dilatant to pseudoplastic. The flux behaviour of the Ti slurries suggests the formation of networks among particles when the shear rate increases and consequently demonstrates a lack of stability. The thickening and the flux complexity of the Ti slurries within the range of the volume fraction 50-55 vol.% lead to a narrow working gap for the addition of Al_2O_3.

Stabilisers can provide different effects on the slurry stability and later during the particles packing, strengthening electrostatic and/or steric mechanisms, according to their structures and capability of adsorption to the particle surface. Table 2 summarises the main characteristics (nomenclature, molecular weight and formula) of the additives used for the stabilisation of the Ti+1 wt.% Al_2O_3 slurries. The additives used as stabilisers in this study were: (i) dispersants, such as acrylic polymers (PAA, DARVAN C-N and DIAPEX A40) with similar functional groups (carbonyl) and a linear structure but different molecular weights, and (ii) fluxing agents, such as a polycarboxylate copolymer (CHRYSO), with similar functional groups to acrylates but with different stereochemistry and a rigid structure, such as the TIRON, with sulfonic functional groups.

Table 2. Additives for the stabilisation of Ti+1wt.% Al_2O_3 slurries

	Dispersants			**Fluxing agents**	
Additive (Mw)	*PAA (2000 g/mol)*	*DARVAN C-N*	*DIAPEX A40 (10.000 g/mol)*	TIRON (332.2 g/mol)	CHRYSO
Formula					

The rheology of Ti+1 wt.% Al_2O_3 slurries (formulated with 50 vol.% of Ti plus 1 wt.% of Al_2O_3 up to a final concentration of solids of 50.5 vol.%) was prepared by adding 1 wt.% of each stabiliser considered in Table 2. Fig. 2 shows the evolution of the slurry viscosity vs. the shear rate for all the stabilisers. The plotted data correspond to the values collected for the shear rate during the CR test. In general, the addition of stabilisers smothers the shear-thickening behaviour of the slurry. The Ti+1 wt.% Al_2O_3 slurry achieves a quasi-Newtonian behaviour with the addition of CHRYSO, a large polycarboxylate copolymer, whose plastic character compensates for the dilatant behaviour of the powder slurry prepared without additives. Linear chains with carbonyl groups provide a higher dispersion and lower viscosities than TIRON and CHRYSO additives because the latter form a cross-linked network by interactions between polymer chains. Those additives maintain a relatively high value of viscosity for lower shear rates, behaving as a worse dispersant but a better fluxing agent than polyacrylates.

The addition of TIRON and CHRYSO as stabilisers has been carefully considered. In Fig. 3, the plots (a) and (b) show the flow curves for the Ti+1 wt.% Al_2O_3 slurries for different additions of each stabiliser, TIRON and CHRYSO, respectively. The viscosity behaviour of the Ti+1 wt.% Al_2O_3 slurry dispersed with 1 wt.% of PAA (from Fig. 2) has also been plotted for comparative purposes. In all cases, most of the curves show dilatant behaviour because the viscosity increases with the shear rate (shear-thickening behaviour). Additions of TIRON under 1 wt.% reduce the dilatancy, but the viscosity remains over 10 mPa s. When TIRON is added as a

stabiliser, the viscosity increases considerably if it is compared with slurries dispersed with polyacrylates. For additions of TIRON ranging from 0.8-1 wt.%, the viscosity remains between 20-30 mPa s up to shear rates up to 500 s^{-1} (fig. 3). The addition of 1.2 wt.% of TIRON does not have a such strong effect over the slurry flux, and it again behaves as a low viscous dilatant fluid. Similarly, the addition of CHRYSO decreases the thickening trend of the slurries. Moreover, the viscosity remains especially low (< 20 mPa s) for additions ranging from 1-1.2 wt.% of CHRYSO, whereas higher amounts of CHRYSO make the viscosity increases drastically from 40 to 100 mPa s for shear rates up to 500 s^{-1}, evidencing the dilatant behaviour of the fluid.

The plot in fig. 4 shows a quick picture of the viscosity range for Ti + 1 wt.% Al_2O_3 slurries formulated with different stabilisers, as a summary of fig. 2 and 3. The values of viscosity for the slurries at a shear rate of 100 s^{-1} were denoted. In general, polyacrylates provides lower viscosities, as well as TIRON, when 1.2 wt.% is added. However, CHRYSO and lower additions of TIRON (≤1wt.%) provide higher viscosities but strongly smother the dilatant behaviour of the slurry [(Howard [19] and Moghadas et al. [20]]. Consequently, to compare the effect of a dispersant and a fluxing agent in the increase of the solid content of the slurry, when a larger volume fraction of Al_2O_3 is added, both PAA and TIRON have been selected.

According to the rheological measurements related to the increase of the solid content of pure Ti slurries (in Fig. 1), 1 wt.% of TIRON and 1 wt.% of PAA were added to facilitate the Al_2O_3 incorporation to the 50 vol.% Ti-based slurry. The amount of Al_2O_3 considered in these tests was 1-5 wt.%. The selection of the additives was based on the preservation of the fluidity and the homogeneity (i.e., dispersion) of the powder mixture. Fig. 5 shows the viscosity evolution of slurries formulated with different Al_2O_3 additions with TIRON and PAA. As expected from previous results, the addition of TIRON reduces the thickening behaviour of the slurry, whereas the addition of PAA provides lower values of viscosity.

PAA as a stabiliser allows the incorporation of Al_2O_3 up to 5 wt.%, maintaining the viscosity within the range of values of the Ti + 1 wt.% Al_2O_3 slurry, even considering that Al_2O_3 incorporation results in an increase of the total solid content up to 52.5 vol.%. Moreover, the addition of Al_2O_3 up to 4 wt.% decreases the viscosity, due to the presence of a well-dispersed bimodal population of particles in the suspension. The effect of the bimodal distribution of particle sizes over the flux behaviour of the Ti-based slurries evidences the active role of PAA as a dispersant.

The addition of TIRON allows the incorporation of 3 wt.% of Al_2O_3 without increasing the viscosity compared with the Ti + 1 wt.% Al_2O_3 slurry prepared with TIRON (Fig. 3a). However, the increase of viscosity for higher Al_2O_3 additions (over 4 wt.%) is accompanied by a change in the slurry flow. The thinning trend can be considered an advantage depending on the shaping technique selected for packing, when relatively high values of viscosity could be considered to avoid the segregation of particles with different sizes and/or densities, such as Ti and Al_2O_3. Consequently, we can conclude that TIRON has a predominant role as a thinning agent in the rheology optimisation because it is also found by other authors, such as Moghadas et al. [20]. However, it complicates the slurry flux when Al_2O_3 is added, whereas PAA promotes the incorporation of a second population of particles, even when that supposes an increase in the total amount of solids in the suspension.

3.2 Processing of compacts

Concentrated aqueous suspensions of Ti + 1 wt.% Al_2O_3 (50.5 vol.% of total solid concentration) using 1wt.% of the dispersants in Table 2 were processed by pressure slip casting (PSC). Cast bodies were dried for 24 h under room conditions and were then sintered in vacuum at 1100 ºC for 30 minutes. To evaluate the microstructural uniformity and density, shaped bodies prepared by PSC with different additives were compared with those fabricated by PLSC and SDP from a Ti + 1 wt.% Al_2O_3 slurry stabilised by the addition of 1wt.% PAA. The details of these two processes

(PLSC and SDP) were described in the experimental section. Green bodies were characterised by SEM to check the homogeneity of the dispersion of both phases, as well as the degree of particle packing. Fig. 6 shows an SEM image of the fracture surface of the green part obtained by PSC for the sample processed with PAA additive. As observed in the micrograph, the cast body presents a highly dense packing of the spherical Ti particles where the Al_2O_3 small particles were homogeneously distributed on the Ti surfaces. The rest of samples presented similar packing behaviour.

The relative green densities of the green bodies, as well as the relative densities determined by both the Archimedes method and He pycnometry for the sintered parts, are shown in Fig. 7. The inspection of the green densities shows that parts shaped by PSC exhibit a relative density between 61-65 % of the theoretical. In contrast, the samples processed by SDP present high density (>80 %), corresponding to the high pressure used in the pressing step (600 MPa), and the samples shaped by PLSC present density values lower than 60 %, as expected from a pressureless method. Samples fabricated using polyacrylates as stabilisers have similar green density values, but all of them have lower densities than the bulk parts shaped using TIRON and CHRYSO. This is a consequence of the dilatant behaviour of the suspension stabilised by the addition of dispersants. Those suspensions react against pressure during casting, forming disorganised microstructures that prevent the full packing of particles, as observed by Autier et al. [21]. Whereas shear-thinning additives, such as TIRON and CHRYSO, provide a well-defined particle network, which allows a smooth approach of particles and then offers re-organisation paths during packing under pressure.

On the other hand, the relative sintered density measured by the pycnometer and Archimedes methods shows differences depending on the processing used and the type of stabiliser. For a clearer explanation of these influences, the porosity data were obtained from the density values. The total porosity is the difference between the theoretical density calculated by the rule of

mixtures and the density measured by the Archimedes method. The closed porosity is the difference between the theoretical density calculated by the rule of mixtures and the density measured by the pycnometer, and the open porosity is the difference between the total and closed porosity. These data are collected in Table 3, together with the oxygen content and hardness of sintered materials. In this table, two columns are related to the oxygen content: the total oxygen content of the samples, measured with LECO equipment, as described in the experimental section, and (O in Ti) the result of subtracting the oxygen content of alumina from the total amount of oxygen. Supposing that the alumina is not dissolved in the titanium, the difference will be the oxygen dissolved in the Ti matrix, and it will be come from oxygen pick up during processing or from the additives.

Table 3. Data of the porosity, oxygen content and hardness of the Ti+1wt% Al_2O_3 sintered materials

Processing / additive	P_{Total} [%]	P_{Closed} [%]	P_{Open} [%]	O [wt.%]	O in Ti [wt.%]	Hardness [HV30]
SDP / PAA	**3.7**	**1.2**	**2.4**	**0.951±0.001**	**0.45**	**346±25**
PLSC / PAA	**9**	**3.5**	**5.5**	**1.052±0.001**	**0.55**	**280±22**
PSC / PAA	6.7	4.3	2.4	1.331±0.001	0.83	218±22
PSC / DARVAN C	13.2	6.5	6.7	1.475±0.001	0.98	204±46
PSC / DIAPEX40	**11.0**	**4.8**	**6.2**	**0.756±0.001**	**0.26**	**259±20**
PSC / TIRON	18.5	2.9	15.6	0.667±0.001	0.17	209±43
PSC / CHRYSO	8.9	3.0	5.9	0.897±0.001	0.40	249±24

In addition to the data in Fig. 7 and Table 3, the SEM microstructures of unetched materials are shown in Fig 8 to evaluate the porosity of sintered materials. All the materials present similar quantity and distribution of porosity, in accordance with the values of closed porosity in Table 3. Although it is not easy to distinguish between open and closed porosity from the SEM images, it

is clear that among the materials processed by PSC, the highest porosity is for DARVAN C dispersant, whereas PAA and DIAPEX40 present similar porosity.

From Fig. 7 and Table 3, comparing materials processed with the same technique (PSC) and different additives, it is clear that polyacrylates provide higher closed porosity (6.5 - 4.3 %) if they are compared with those of TIRON and CHRYSO (2.9 - 3.0 %), which have values in the range of parts shaped by SDP and PLSC. Closed porosity is a result of the packing degree achieved using different additives and depends on the rheology of the slurry. TIRON and CHRYSO provide a better fluidity of the suspension (Fig. 2) during the PSC and then a higher packing degree during shaping and a lower close porosity. Whereas the closed porosity for the five stabilisers used varies between 3 % and 6.5 %, the open porosity shows a wider variation, from 6.7 % to 18.5 %, depending on the additive used, which is believed to be related to the decomposition of the additive during sintering.

Porosity and oxygen content are two of the main factors affecting the mechanical properties of sintered titanium. One interesting observation from Table 3 is that there is no a relationship between the oxygen content and the porosity in materials processed by PSC, and thus, the oxygen content is more related to the type of stabiliser. For instance, TIRON provides the highest open porosity (15.6 %) and the lowest oxygen content (0.17 wt.%). Therefore, it is important to understand the role of additives in the oxygen content of sintered materials. The lowest values of oxygen among the materials processed by PSC are for samples using DIAPEX40, TIRON and CHRYSO as stabilisers. The reason is attributed to the steric conformation of these additives on the titanium particle surfaces, providing a higher volume of exclusion, keeping the suspension media away from the particle and avoiding contact to react with oxygen. In these cases, the values of hardness are in accordance with the values of the oxygen content for a similar closed porosity: the lower the oxygen content is, the lower is the hardness. In particular, the hardness and oxygen content of material processed with CRHYSO is in accordance with those values

reported for CPTi grade 4. In contrast, PAA and DARVAN C additives do not adequately protect the surface particles at the slurry, and the final oxygen pick up is much higher. Moreover, these additives do not provide an adequate rheology for PSC, resulting in lower packing and worse values of hardness.

It is also interesting to compare materials prepared using the same additive (PAA) and different processing routes (SDP, PLSC, PSC). From Fig. 7 and Table 3, it is clear that material processed by SPD presents the highest green density and the lowest porosity after sintering among all the prepared materials. Comparing this material with the others prepared with the same additive (PAA) and different processing methods, the SPD presents the lowest oxygen content and the highest hardness. However, the value of hardness is much higher than the value expected for Ti with 0.45 % oxygen, which is attributed to the dissolution of the alumina in the Ti, leading to an increment of hardness by a mechanism of solution hardening of both Al and O. Studies by transmission electron microscopy (TEM) are in progress to confirm this dissolution, but for the moment, there is no evidence of alumina particles in the microstructures analysed by SEM (Fig. 9 a). In contrast, materials with the same composition processed by PLSC (Fig. 9 b) and PSC show lower hardness than SDP and, in the case of PSC, lower than expected from the oxygen content (0.83 %). In these cases, hardness is influenced more by closed porosity, and the higher the closed porosity, the lower the hardness. Undissolved alumina particles can be found in sintered PSC materials independently of the stabiliser used, indicating that there is no or little dissolution of alumina and that the oxygen content is due to pick up during processing and from the additive. The easiest way to show the alumina particles is inside the pores, as shown in the SEM image and EDX analysis in Fig. 9c and 9d, respectively. The reason for the different dissolution behaviour of the alumina in the titanium is related to the energy available during the sintering process. The higher green density in the SDP samples provides a higher amount of diffusion paths and contact points for the atoms to migrate and allow densification. There is enough energy

for the alumina to dissolve at the same time as the self-diffusion of Ti. In the case of PSC, the green density is much lower, and the energy available during sintering is mainly invested in promoting self-diffusion of titanium for densification.

4. Conclusions

The influence of different stabilisers on the preparation of stable and concentrated aqueous suspensions has been studied.

The use of stabilisers, such as TIRON and CHRYSO, reduces the dilatant behaviour of Ti slurries, providing an adequate rheology for shaping by PSC. Moreover, those dispersants protect the Ti surfaces from the suspension media by reducing the oxygen pick up, leading to sintered materials with oxygen contents and hardness values in the range of commercial grades with low close porosity (approximately 3 %).

The addition of Al_2O_3 improves the rheology of the Ti slurries by providing better shaping conditions. Polyacrylate-based dispersants allow for the introduction of a higher quantity of alumina particles (up to 5 wt.% of Al_2O_3), extending the limits of processability in terms of the solid content determined for pure Ti slurries. The use of PAA as dispersant takes full advantage of the bimodality of the particle population when the mixtures of Ti and Al_2O_3 were considered.

The materials shaped by PSC reach high values of density, up to 97 %, with homogeneous microstructures. For a similar oxygen contribution to the process (0.4 wt.%), PSC pieces shaped with CRHYSO match the hardness of CPTi grade 4 (249±24 HV30), whereas SDP microstructures show a significant reinforcement (346±25 HV30). Bulk pieces shaped by SDP exhibit a higher grain size than similar compositions processed by PSC. For the 82 % green pieces shaped by SDP, the thermal energy was employed in phenomena that occur during sintering, such as Al diffusion and grain growth, whereas the energy was mainly employed in the self-diffusion of Ti in the densification of the green PSC pieces (65 % of density).

In general, the close porosity is due to the degree of packing and consequently depends on the suspension rheology, whereas open porosity depends on the stabiliser decomposition during sintering. Hardness is correlated with the oxygen content for media values of close porosity (4 %). The oxygen content is not related to the open porosity.

Acknowledgments

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Table(s)

Table 1. Characteristics of Ti and alumina powders.

Powder type	**Particle Size [µm]**		**Specific surface area [$m^2 \cdot g^{-1}$]**	**Density (by He pycnometry) [$g \cdot cm^{-3}$]**	**O [wt%]**
	D_v50	**D_{BET}**			
Ti	10	7.4 ± 0.1	0.17 ± 0.01	4.51 ± 0.01	0.216±0.001
Al_2O_3	0.40	0.16 ± 0.1	9.50± 0.01	3.97± 0.01	49.610±0.001

Table 2. Additives for the stabilization of Ti+1wt.% Al_2O_3 slurries

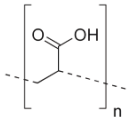
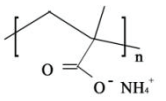
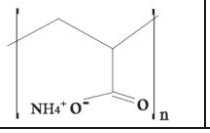
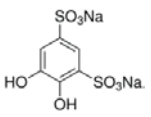
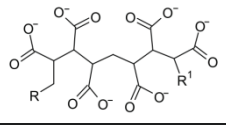
	Dispersants			**Fluxing agents**	
Additive (Mw)	*PAA (2000 g/mol)*	*DARVAN C-N*	*DIAPEX A40 (10.000 g/mol)*	TIRON (332.2 g/mol)	CHRYSO
Formula					

Table 3. Data of porosity, oxygen content and hardness of the Ti+1wt% Al_2O_3 sintered materials.

Processing / additive	P_{Total} [%]	P_{Closed} [%]	P_{Open} [%]	O [wt %]	O in Ti [wt %]	Hardness [HV30]
SDP / PAA	**3.7**	**1.2**	**2.4**	**0.951±0.001**	**0.45**	**346±25**
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PSC / TIRON	18.5	2.9	15.6	0.667±0.001	0.17	209±43
PSC / CHRYSO	8.9	3.0	5.9	0.897±0.001	0.40	249±24

Figure 1

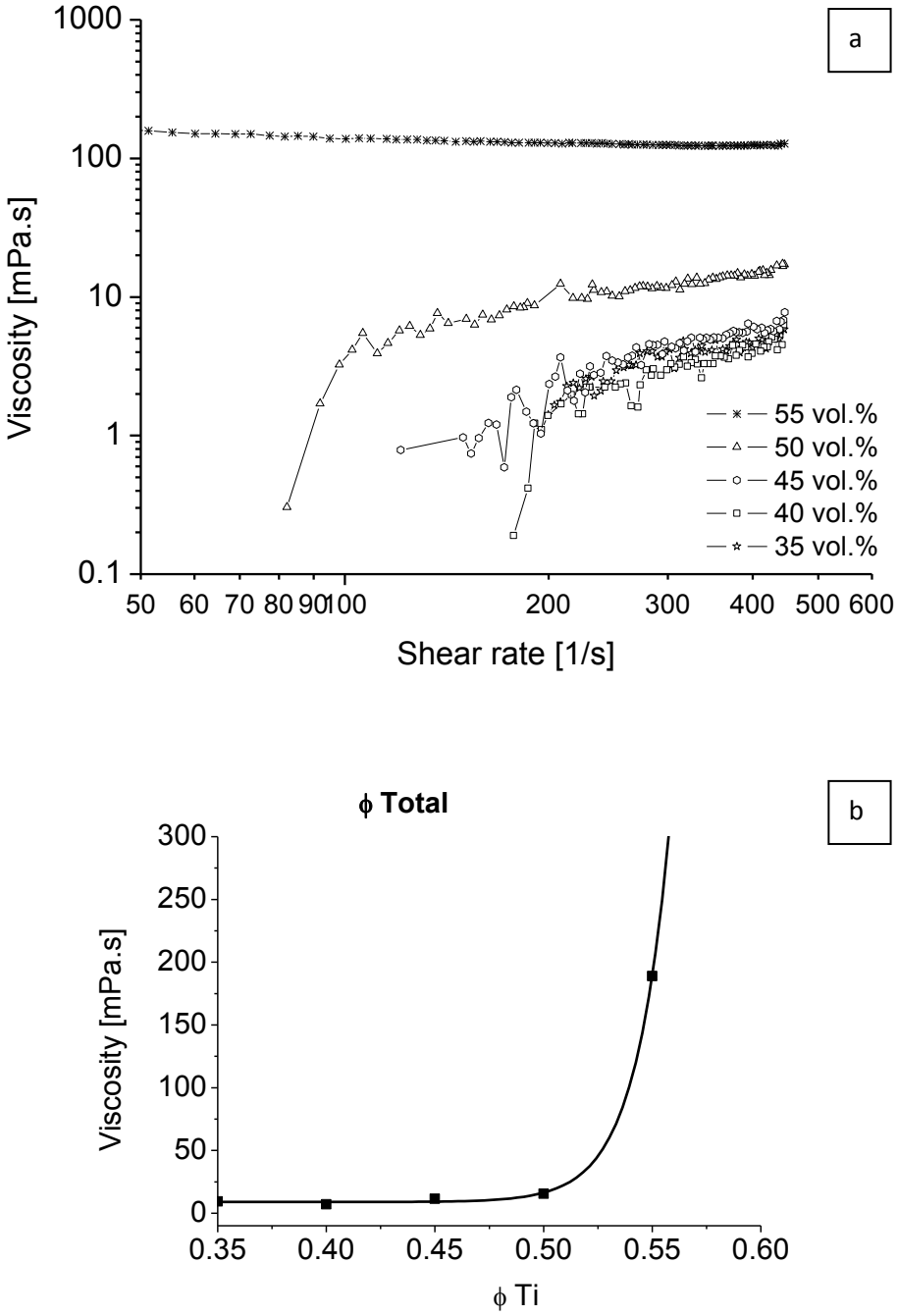

Figure 1. a) Viscosity evolution vs shear rate for Ti slurries with different solid contents and, b) viscosity values measured for a shear rate of 100 s^{-1} vs the volume fraction of Ti slurries

Figure 2

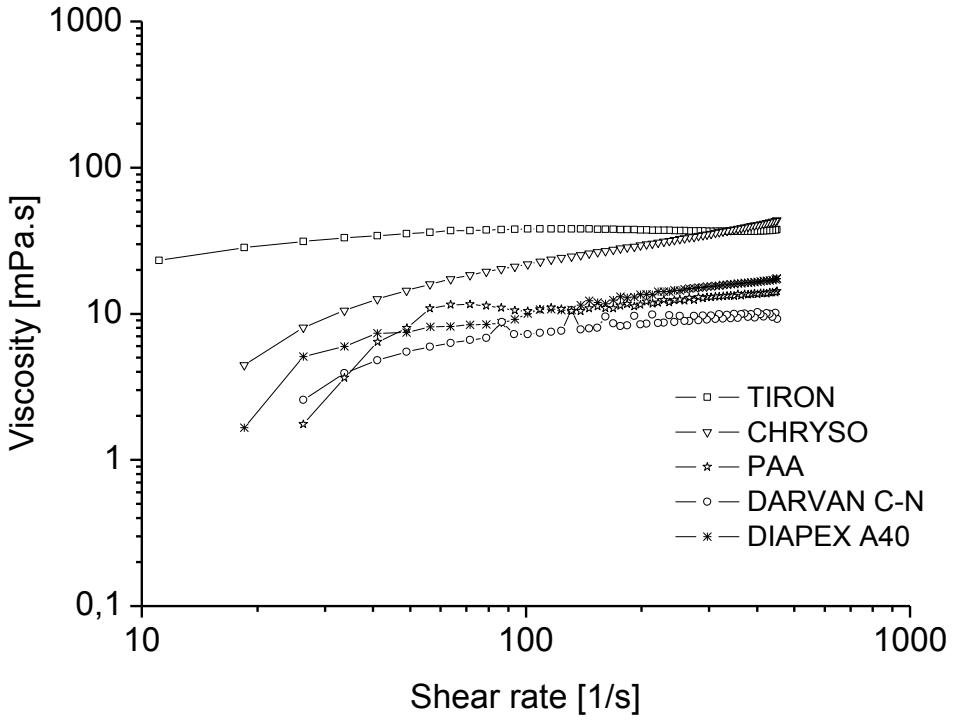

Figure 2. Viscosity evolution with the shear rate of flow curves of Ti+1 wt% Al_2O_3 slurries (50.5 vol.% of solid content) with 1 wt.% of different dispersants: PAA, DARVAN C-N and DIAPEX A40, TIRON and CHRYSO.

Figure 3

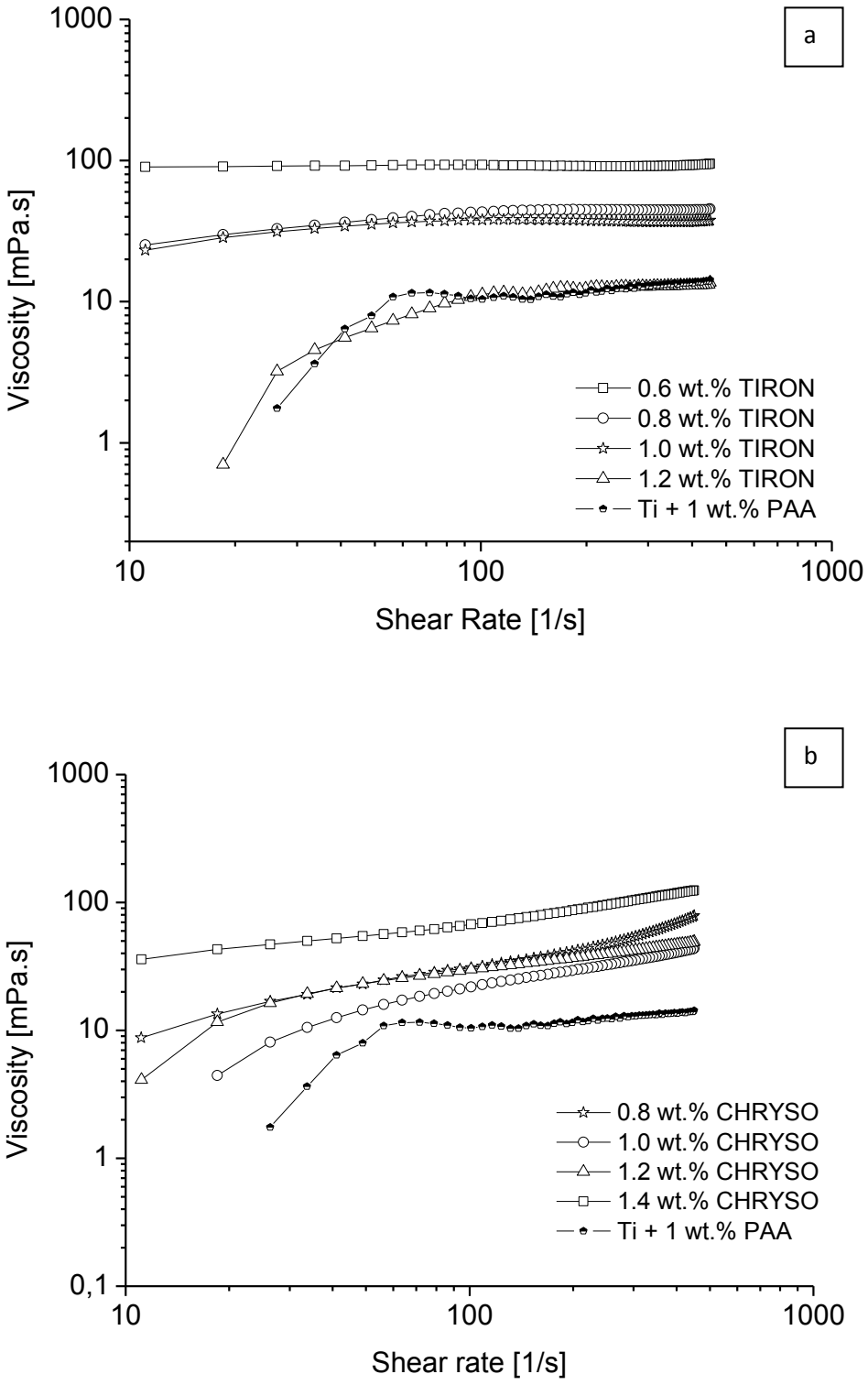

Figure 3. Evolution of the viscosity of Ti + 1 wt% Al_2O_3 slurries with different contents of (a)TIRON and (b) CHRYSO.

Figure 4

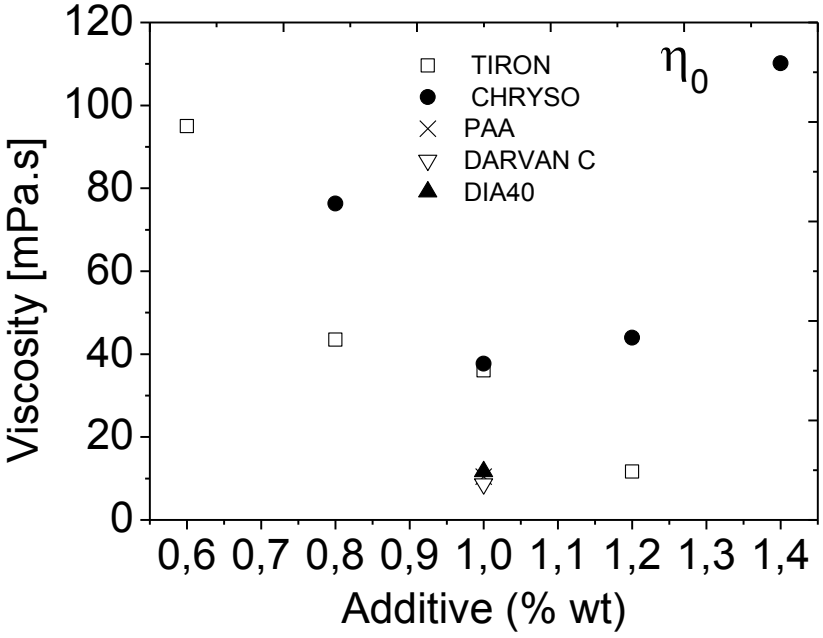

Figure 4. Values of viscosity at a shear rate of 100 s^{-1} for the slurries prepared with different kinds and amounts of stabilizers.

Figure 5

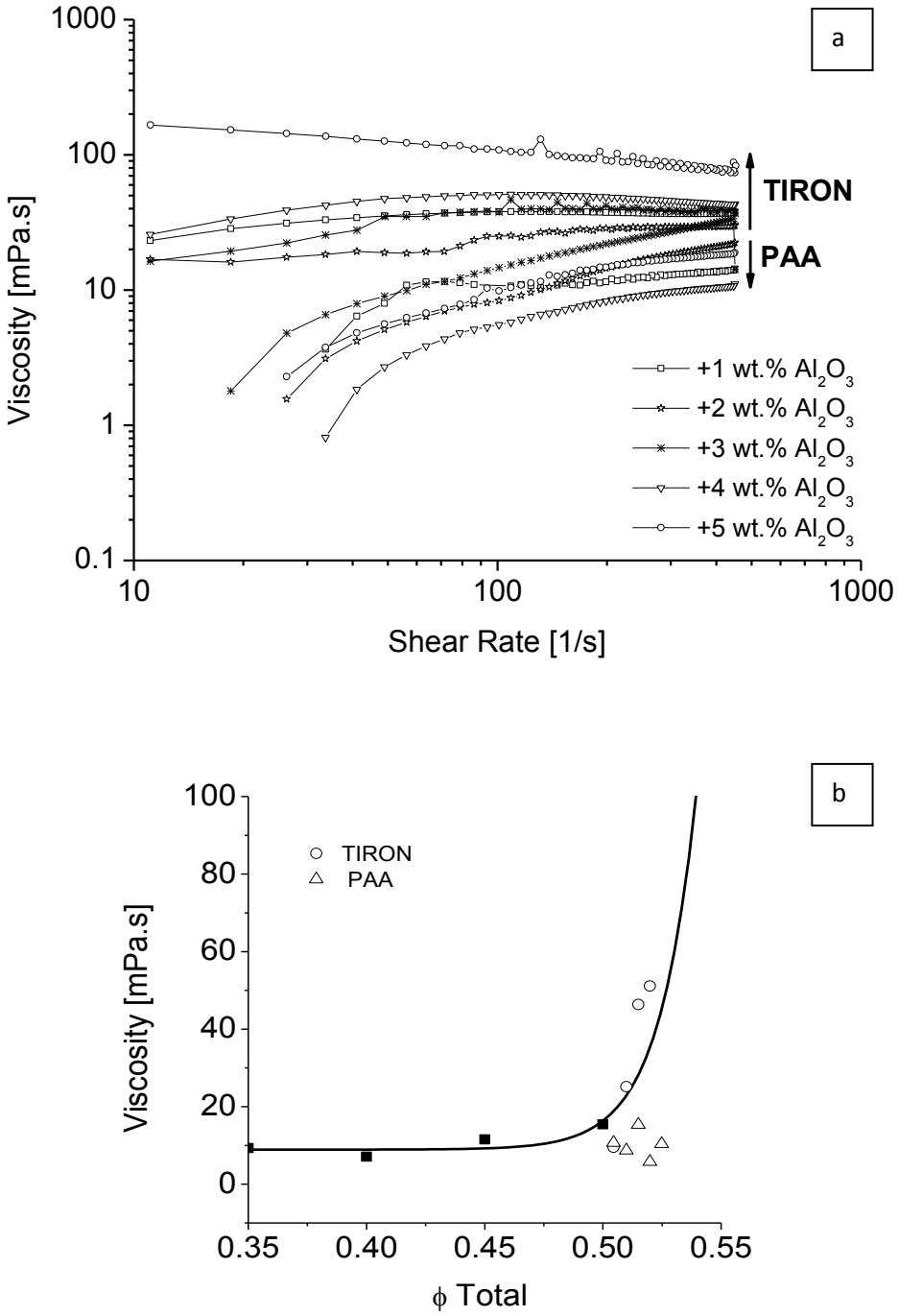

Figure 5. (a) Evolution of the viscosity with the shear rate for slurries with different contents of Al_2O_3 particles and for two stabilizers: 1 wt.% TIRON and 1 wt.% PAA. (b) Values of viscosity at a shear rate of 100 s^{-1} vs the total volume fraction of solids for the slurries prepared with different amounts of Al_2O_3 and both stabilizers.

Figure 6

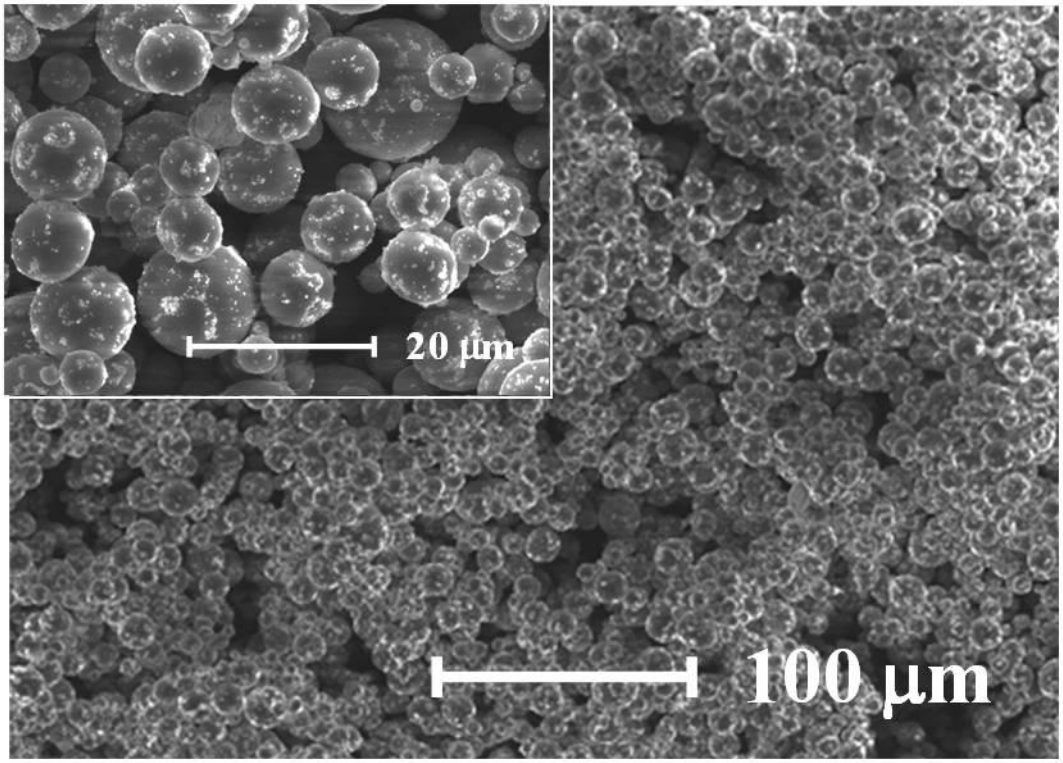

Figure 6. SEM micrograph showing the fracture surface of green sample with 50 vol.% Ti+ 1wt % alumina and 1% of PAA additive. Detail of the alumina particles disperse don Ti surface.

Figure 7

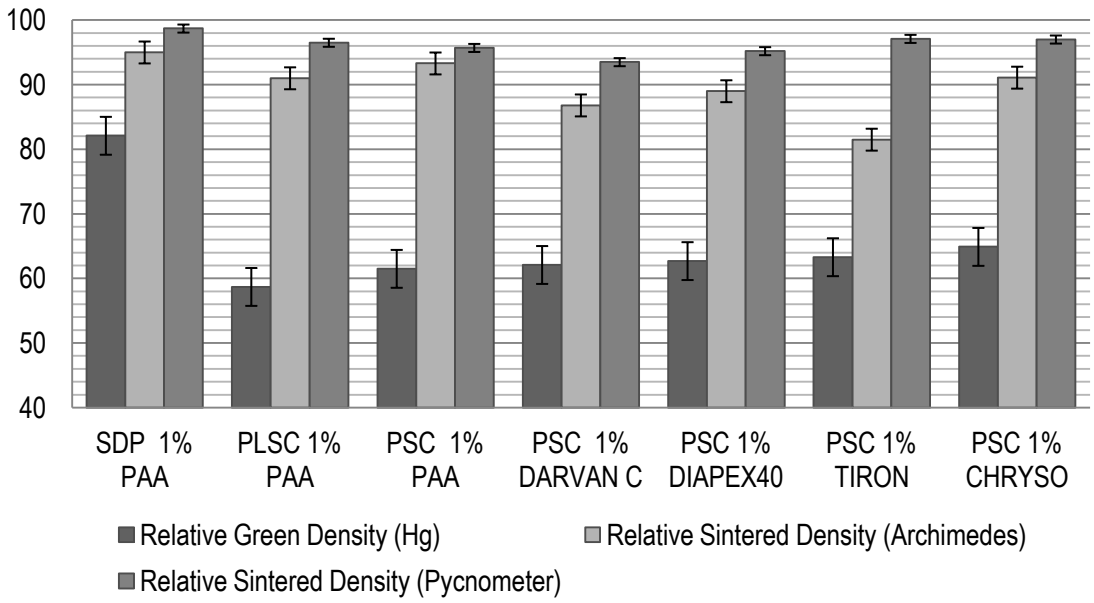

Figure 7. Relative green density and relative sintered density (Archimedes and Pycnometer) for Ti+1wt% Al_2O_3 samples with different additives.

Figure 8

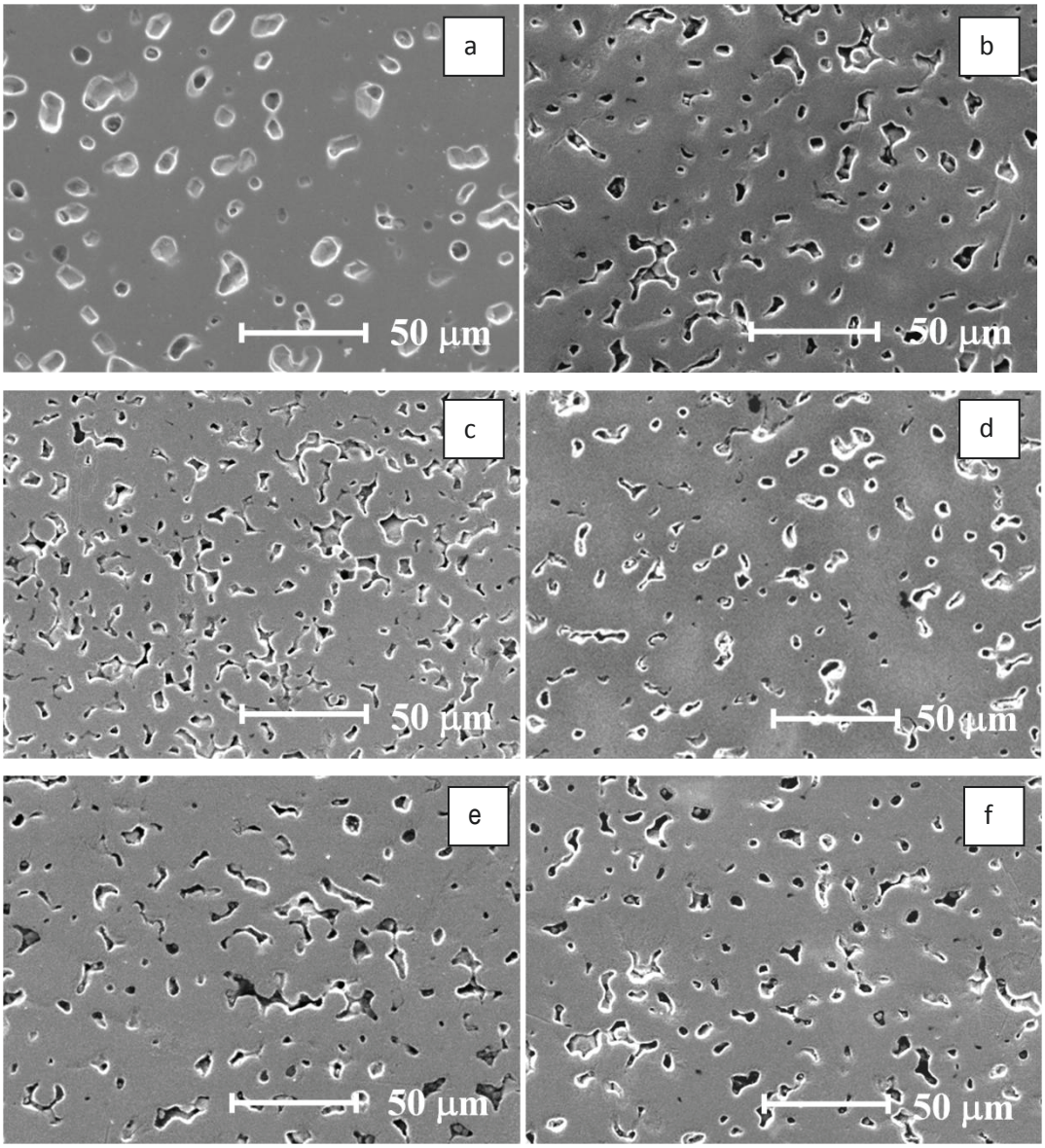

Figure 8. SEM images of microstructure of sintered samples with different additives and processing. a) PLSC/PAA , b) PSC / PAA, c) PSC / Darvan C, d) PSC / DIAPEX 40, e) PSC / Tiron, f) PSC / Chryso.

Figure 9

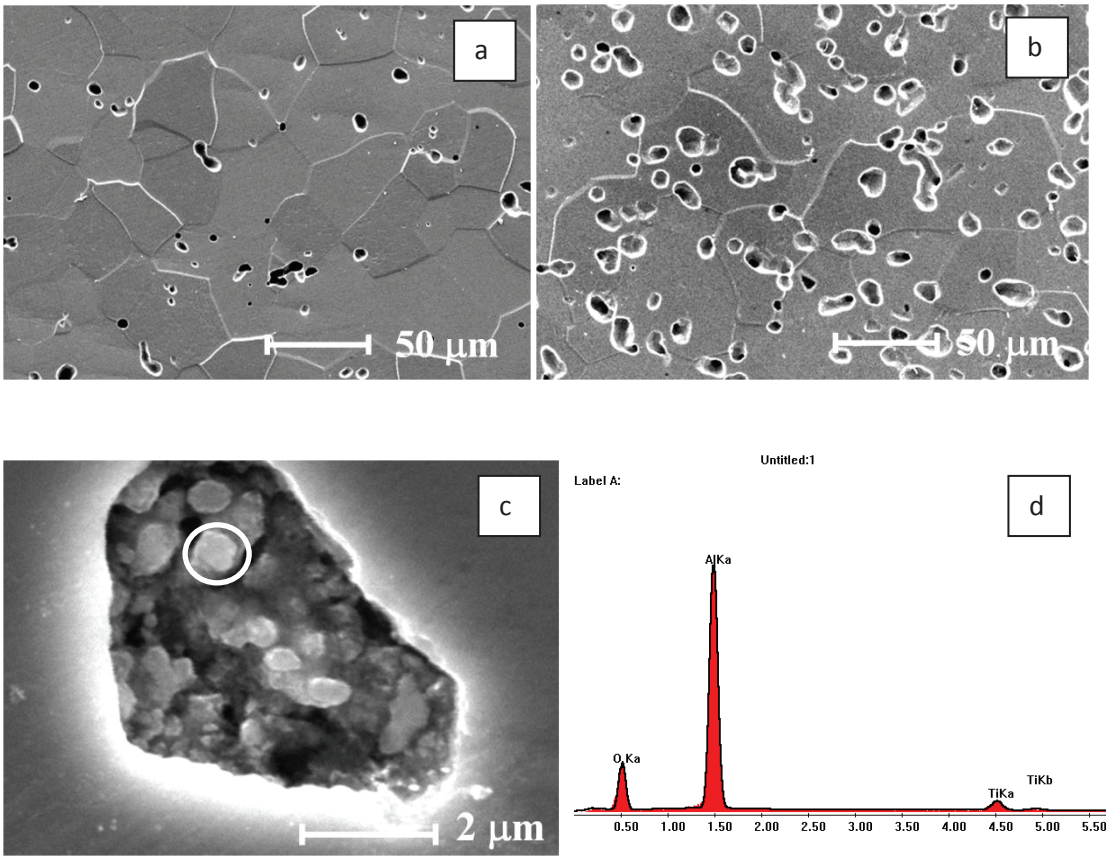

Figure 9. a) and b) SEM images of microstructure of sintered samples processed by SDP and PLSC. c) SEM image of a pore showing undissolved alumina particles after sintering, d) EDX analysis of alumina particle of image c).