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MANUFACTURING CERAMIC SHELLS FOR CASTING TITANIUM COMPONENTS

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ABSTRACT

Nowadays there is a tremendous pressure in the foundry area to produce titanium (Ti) parts for different industrial sectors due to the high strength/density ratio, high corrosion resistance, fatigue strength, biocompatibility, osteointegration behaviour and ability to be sterilized. To reach this objective, investment casting technique is the natural choice, however, casting these very reactive alloys in ceramic shells is a difficult task due to the reaction metal-ceramic, low metal fluidity and reactivity with melting atmospheres. These barriers have to be overcome to successfully obtain high quality parts. In this paper, some properties of ceramic shells developed for investment casting of Ti alloys are evaluated. The main purpose is to determine the influence of different face coat slurries and stuccos and sintering temperature in the mechanical strength, permeability, dimensional changes and microstructure of the ceramic shells, which are primordial characteristics for the quality of the castings.

Keywords: ceramic shells, titanium, foundry, investment casting

INTRODUCTION

Casting liquid metals to produce solid objects is a manufacturing process that has been practised for over 5000 years, with investment casting (production of metallic engineering castings using a consumable pattern inside a ceramic shell) being one of the oldest known metal shaping methods (Beeley and Smart, 1995). The technique itself has tremendous advantages in the production of quality components with the key benefits of accuracy, versatility and metallurgical integrity. As a result, the process is one of the most economic methods of forming a wide range of metal components. Environmental and economic pressures have, however, resulted in a need for the industry to improve current casting quality, reduce manufacturing costs and explore new markets for the process. Nowadays, the production of accurate and intricate metallic components suitable for aeronautical and aerospace applications, and more recently, in human parts, like dental crowns and customized prostheses that can be made in several metallic alloys, are the main concerns of many research groups (Niinomi and Williams, 2003). Fig. 1 shows some applications of Ti casted parts.

Production of the investment casting ceramic shell mould is a crucial part of the whole process, because its characteristics determine the quality of the metallic parts obtained. The key requirements of an investment casting mould are: sufficient green (unfired) strength to withstand wax removal without failure; sufficient fired strength to withstand the weight of cast metal and handling; sufficiently weak to prevent hot-tearing in susceptible alloys; high thermal shock resistance to prevent cracking during metal pouring; high chemical stability; low reactivity with the metals being cast to assure adequate surface finish; sufficient mould permeability and thermal conductivity to keep an adequate thermal transfer through the mould wall and hence allow the metal to cool, and low thermal expansion to limit dimensional changes within the mould wall and ultimately to the casting. This list is by no means exhaustive. The range of alloys to cast, size and complexity of castings and specific requirements of the cast components led to an array of mould properties and materials, all used for specific purposes within the casting industry. The underlying factor in all cases is the wide range of precise requirements to produce a successful casting (Jones and Yuan, 2003).

Fig. 1 Examples of applications of Ti and Ti alloys parts; from left to right: aeronautic component, medical implants, jewellery artefacts and accessories

Briefly, the process can be described as follow: a wax pattern is dipped into a slurry (ceramic flour and a colloidal binder), sprinkled with coarse refractory stucco and dried. After repeating these steps, the necessary number of times (typically, around seven) to produce a shell with adequate strength, the "lost" pattern is burned and the metallic alloy is poured into the ceramic shell. After knockout, the component can directly be used or have some finishing operations like machining and chemical milling (Lino et al., 2003). A complete scheme of this process is shown in Fig. 2.

Accordingly to the alloy to be poured, different ceramic flours and binders should be used to produce adequate slurries that allow low roughness on interior shell surface, with low reactivity with the molten metal (Duarte et al., 2007), adequate permeability to allow air diffusion during pouring, enough strength to withstand the liquid metal pressure without breaking and right thermal properties to support the thermal shock during pouring (Jones and Yuan, 2003).

Traditionally, the ceramic shells production uses water-based colloidal silica binders. These binders usually contain between 20 and 30 wt% amorphous SiO_2 particles, stabilised with Na^+ counter ions. Gellation of the colloid to produce a binding phase for the refractory particles within the shell mould is achieved by moisture removal (Jones and Marquis, 1995). Colloidal binders produce ceramic moulds with very low green strength, which are prone to crack during wax removal and handling (Jones, 1993). This can be overcome with liquid polymer additions; latex based, for alkaline systems, or PVA (polyvinyl alcohol) based for acidic binders.

Polymers increase the ceramic green strength and have a tendency to reduce the level of "wet-back" of moisture into previously dried coats when new layers are added (Jones and Leyland, 1995). The amorphous network crystallises during the sintering stage to form a strong ceramic bond. The use of sodium ions promotes crystallisation to cristobalite (Jones et al., 1991), producing a ceramic shell with enough strength to withstand the vigorous conditions of metal casting without failure or integrity loss. Unmodified colloid binders are exceptionally strong, leading to problems during casting of alloys susceptible to hot-tearing. The use of polymer-modified binders reduces fired strength due to burn out of the organic phase, but in turn increases the ceramic permeability, reducing the incidence of casting misrun or non-fill (Connolly et al., 1998).

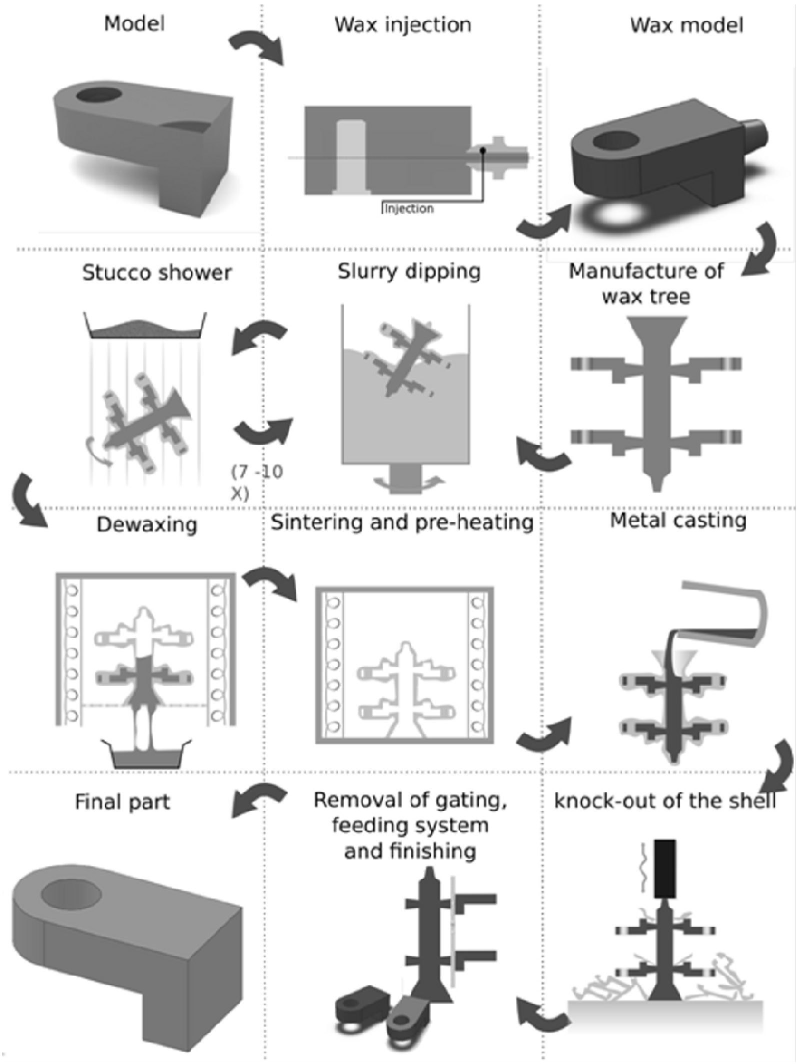


Fig. 2 Main stages from the model to the metallic part by the investment casting process

Filler materials for slurries tend to be −200 mesh (< 75 μm), or a combination of −200 and −325 mesh (< 45 μm) to achieve required primary surface finish and sufficient shell strength during casting. Oxides such as zircon, alumina, aluminosilicates, mullite and fused silica are predominant, although more exotic materials such as yttria and zirconia are used for reactive alloy casting (Jones and Marquis, 2000). Stucco particles are commonly aluminosilicate based due to economic questions. The purpose of the stucco is to minimise the drying stresses on the coatings by presenting a number of distributed stress concentration centres which reduce the magnitude of the local drying stress. The second main purpose of the stucco is to present a rough surface, thus facilitating a mechanical bond between the primary coating and the back-up or secondary investment. When the primary coat has set (air-dried until the binder gels), the assembly is systematically dipped into a second slurry and stuccoed until the required thickness of shell is built-up. The particle size of the stucco is increased as more coats are added, to maintain maximum mould permeability and to provide bulk to the mould. Each coating is thoroughly hardened between dippings. Thus, an investment casting mould consists of individual layers of fine and granular refractory materials held together by a binder that had been set to a rigid gel. There are some flexibility to change the composition of each layer.

Coating the pattern with the usual ceramic slurries (based on silica, zircon or aluminosilicates) generates a reaction with the Ti alloys during casting and solidification, forming a 0,3 – 0,6 mm very hard, cracked and weak reaction layer, called alpha-case (Sung and Kim, 2005). This surface layer, result of the Ti reaction with the metallic oxides of the ceramic shells, is composed by fragile intermetallics compounds that significantly reduce the mechanical properties of the casted parts (Ding et al., 2003). To overcome this problem, titanium alloys should be poured into special ceramic shells that avoid or significantly reduces this type of reaction. In this case, to select the most suitable ceramics one should take in account, as shown in Fig. 3, the standard free energy change of oxides formation (ΔGº). Expensive ceramics such as CaO, ZrO_2 and Y_2O_3 must be adopted as mould materials and binders because their standard free energy changes of oxides formation is more negative than that of TiO_2, preventing interface reactions (Kim et al., 2003).

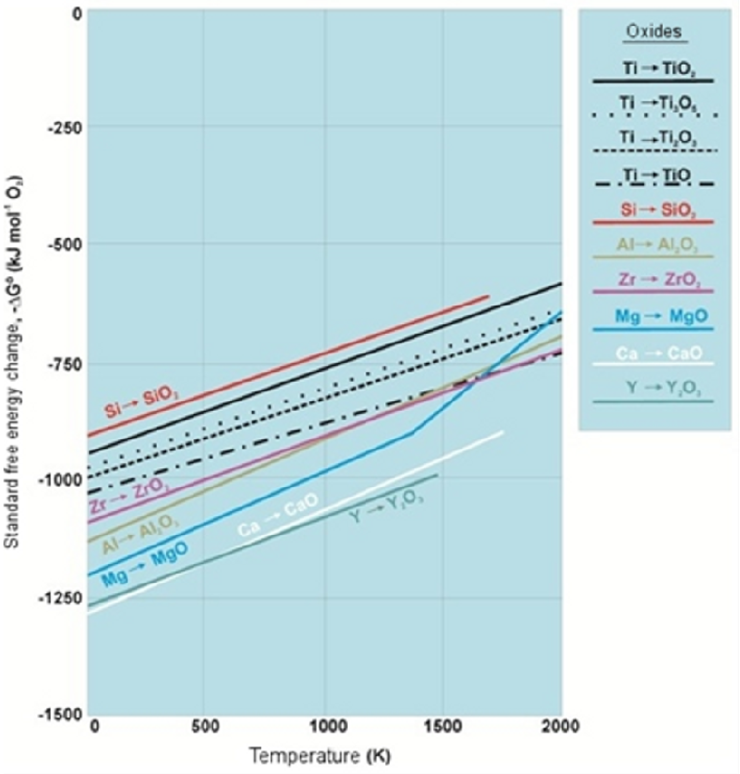


Fig. 3 Standard free energy variation of oxides formation (ΔGº) with the temperature (UC, 2008)

To produce ceramic shells with the previously presented characteristics, other ceramics properties should be considered, such as: softening temperature, thermal expansion coefficient and thermal conductivity.

As one can see in Table 1, the use of both Y_2O_3 and Al_2O_3 (accordingly with Fig 3, these are suitable materials for contact with Ti and its alloys), two ceramics with almost the same thermal expansion coefficient, seems recommendable to avoid shell cracking during dewaxing and sintering. Another important property of these ceramics is the high thermal conductivity values which reduce the solidification and cooling times.

Table 1 Properties of some ceramic materials used to produce ceramic shells to cast Ti and its alloys (Goodfellow, 2007; Carniglia and Barna, 1992)

Oxides	**-ΔG° at 1000K (kJ mol^{-1} O$_2$)**	**Softening Temperature (°C)**	**Thermal Expansion Coef. (x 10^{-6}K^{-1}) 20-1000 °C**	**Thermal Conductivity (Wm^{-1}K^{-1}) 20 °C**
Y_2O_3	1079,1	1811	8,1	8 - 12
ZrO_2	895,1	2036	10 (ZrO_2/6% CaO)	2,5 (ZrO_2/6% CaO)
CaO	1069,4	2195	-	-
MgO	997,2	2139	-	-
Al_2O_3	906,6	1541	8,0	28 - 35

So, it is therefore imperative to enlarge the research in this area in order to improve castings quality, reduce the manufacturing costs and explore new markets and applications for the process. Optimisation of the mechanical and physical properties of the ceramic shells will be fundamental to achieve these aims. Fig. 4 shows an example of a Ti part produced by investment casting.

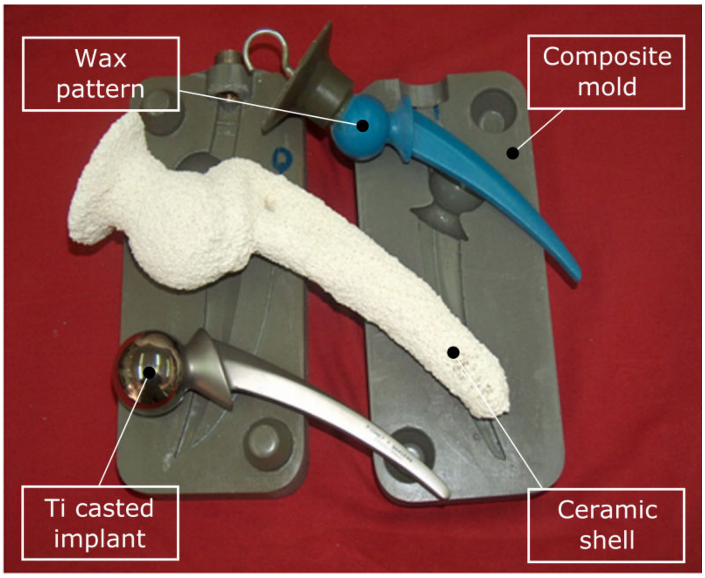


Fig. 4 From the top to down: wax pattern with the pouring system, ceramic shell and Ti casted part placed over the composite mould used to inject the wax pattern

EXPERIMENTAL WORK

In this paper, several samples with different slurries were manufactured and sintered at temperatures in the range 900-1400 ºC to achieve the most suitable mechanical strength, permeability and friability for casting Ti parts with adequate properties for different industrial sectors. To reach the proposed objectives, different tests were defined. Table 2 presents all the parameters that were studied; the face coat composition, sintering temperature and number of test samples produced for each type of test. In all the experiments the back-up used was colloidal silica based alumina slurry and alumina stucco. This experimental procedure was conducted considering the previous experience of the research team in the production of silica based ceramic shells to cast aluminum alloys (Lino et al., 2003). Some previous tests have shown that for the system organic binder/yttria, the sintering temperature must be higher than 1200ºC to avoid shell´s interior surface friability, which conducts to metallic parts with high roughness, due to the lack of adhesion between particles (Duarte et al., 2009).

Table 2 Experimental test conditions

Face coat systems (slurry+stucco)		**Sintering Temp. (ºC)/2h**	**Tests Number of specimens for each condition**			
Flour	**Binder**		**Flexural strength**	**Permeability**	**Dimensional variation**	**Microstructure: SEM/optical microscopy**
Yttria flour + Yttria stucco	Silica based	900, 950, 1000, 1050, 1100, 1150, 1200	4	2	1	1
Yttria flour + Yttria stucco	Organic binder	1200, 1250, 1300, 1350, 1400	4	2	1	1
Alumina flour + Alumina stucco	Silica based	900, 950, 1000, 1050, 1100, 1150, 1200	4	2	1	1

The samples for the flexural strength, permeability and dimensional variation tests are shown in Figs. 5 to 7, respectively. It should be stated that they were conceived to have a constant thickness; however, considering the precision capacity of the shells manufacturing process, this goal was impossible to reach and a thickness variation between 5 to 7 mm was obtained. The samples were produced using the procedure described in Fig. 2.

Fig. 5 Flexural test specimen (20x140 mm, with thickness varying from 5 to 7 mm) obtained in a wax mold

Fig. 6 Permeability test specimen (around 40 mm diameter with 5 to 7 mm thickness) obtained in a wax mold

Fig. 7 Dimensional variation test specimen (5x40 mm, with thickness varying from 5 to 7 mm) cut from flexural strength samples

The flexural strength tests were performed in a Instron 4802 universal testing machine (load speed 1mm/min, supports span distance 60 mm and 1 kN load), the permeability tests were conducted in an experimental equipment developed by Zollern & Comandita (1/time to re-establish atmospheric pressure after 0,1 bar vacuum) and the dimensional variation tests were obtained in a dilatometer Bach 810L model (heating speed 100 ºC/h until 1300 ºC, maximum equipment capacity).

The materialographic preparation of samples for SEM and optical microscopy analysis was done according to a procedure developed previously and briefly described in Table 3, using Struers consumables and equipment (Duarte et al., 1999). This procedure is very important to assure that the pull-out during sample preparation is minimized, allowing the correct interpretation of the microstructure. These observations were done to determine if the sintering temperature variation promotes significant diffusion and consequently bonding between ceramic particles of the binder/slurry/stucco.

Table 3 Grinding and polishing steps of ceramic samples vacuum infiltrated with epoxy resin

Grinding	**SiC Paper# 180**	**SiC Paper# 320**	**SiC Paper# 500**	**SiC Paper# 800**
Speed (rpm)	300	300	300	300
Force (N)	250	250	250	250
Time (min)	3	3	3	3
Polishing	**DP - Plan**	**DP - Plan**	**DP - Plan**	**DP - Plan**
Abrasive	DP spray 15 µm	DP spray 6 µm	DP spray 3 µm	OP-S
Lubricant	Blue	Blue	Blue	
Speed (rpm)	150	150	150	150
Force (N)	250	250	250	250
Time (min)	18	6	5	2

RESULTS AND DISCUSSION

The results of the flexural strength tests are shown in Fig. 8. As one can see, the flexural strength increases with the sintering temperature to all the systems, being almost the same for the silica binder/yttria or silica binder/alumina face coat systems. The values obtained with sintering temperatures of 1200 ºC (around 15MPa), are adequate to cast conditions (shells withstand pre-heating, vacuum atmosphere and pouring temperature) of Ti alloys, accordingly to authors previous experience. The flexural strength increase in the range 1200 - 1400 ºC for the system organic binder/yttria is half (around 5 MPa) of the one obtained with the other two systems from 1000 to 1200 ºC (10 MPa). The organic binder/yttria system was only tested for sintering temperatures higher than 1200 ºC because lower temperatures produce shells with high friability. The gaining of 5 MPa resistance obtained using sintering temperatures in the range 1200 - 1400 ºC should only be explored for production of very complex and intricate components.

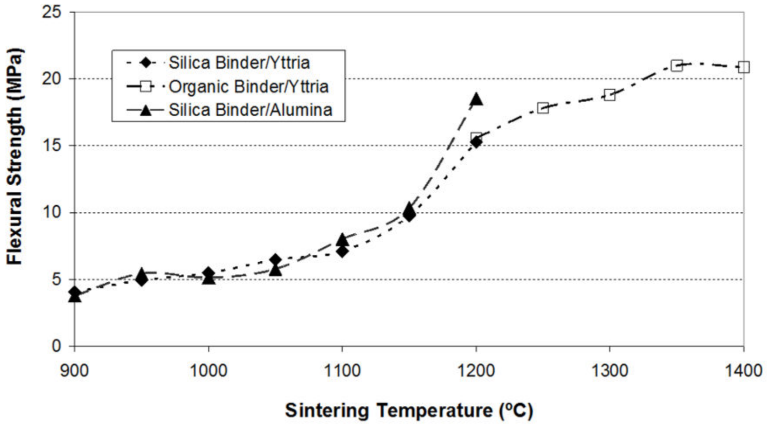


Fig. 8 Evolution of the flexural strength with the sintering temperature for different face coat systems (see Table 2)

The permeability tests results are shown in Fig. 9. The values obtained do not have yet a consistent progress due to experimental apparatus limitations; the time established to reach a specific pressure is recorded by an operator with a chronometer, which always has an error margin. In future work, more samples of each condition must be tested to reduce the relevance of this imprecision (for instance, 4 specimens of each condition). Another detected problem that can affect the results is the samples thickness variation, due to non-uniform runoff during ceramic shells construction. The bibliographic search was not very helpful in clarifying the typical values for ceramic shells permeability. The values indicated in Fig. 9, show a slight permeability increase with the temperature but with a considerable oscillation mainly in the system silica binder/yttria demanding more tests and some changes in apparatus to have an automatic record of time with pressure variation.

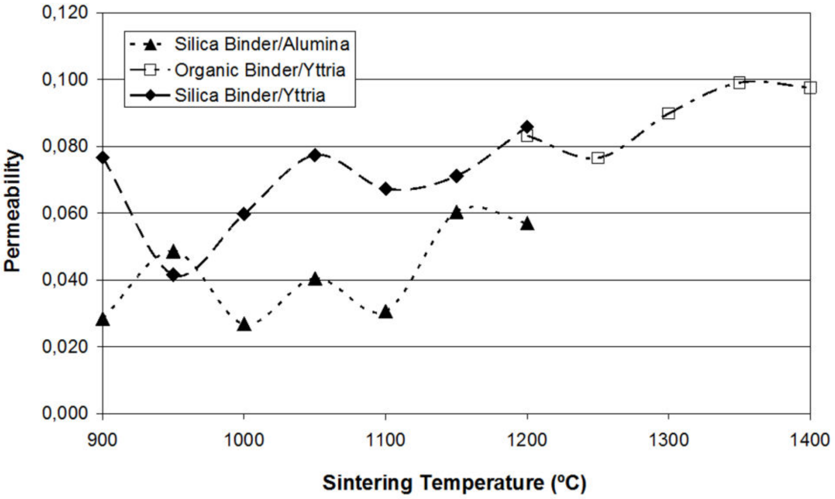


Fig. 9 Evolution of the permeability with the sintering temperature for the different face coat systems (see Table 2)

The results of dimensional variation are depicted in Fig. 10. One can see that they are almost the same for the three tested systems (see table 2), which means that the shells size is not controlled by the face coat, but essentially by the thermal expansion coefficient of the back-up, that in this work was the alumina slurry and stucco, with silica binder.

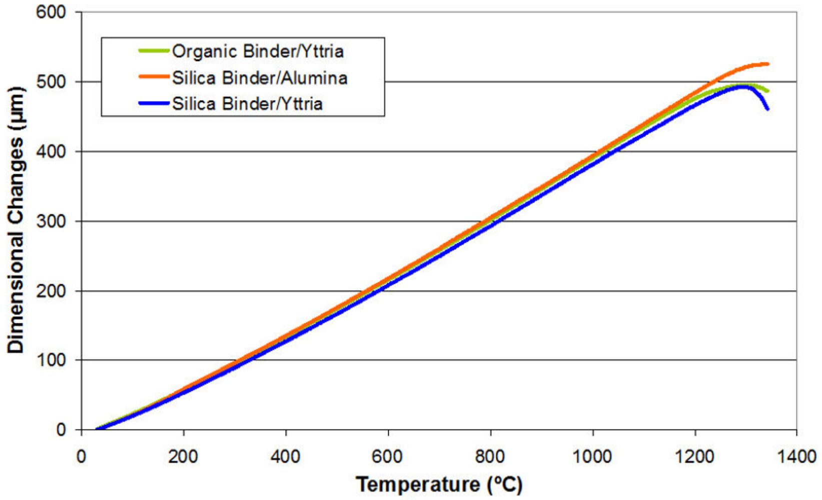
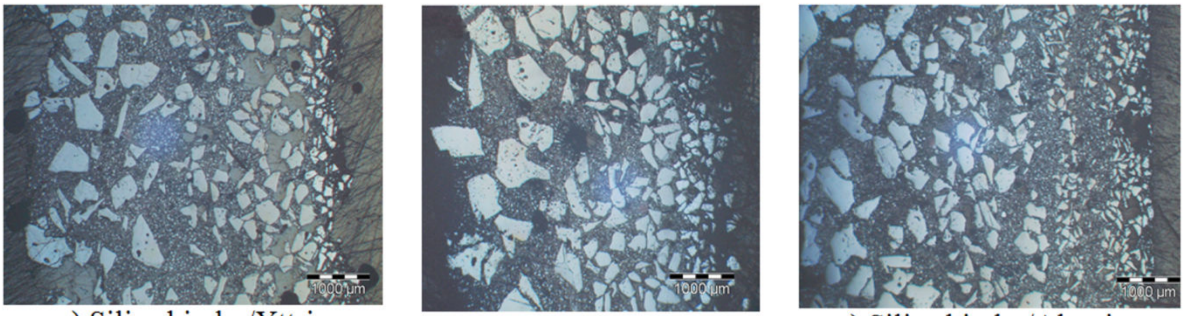


Fig. 10 Shells dimensional variation with the temperature for the different face coat systems (see Table 2)

All the samples microstructures described in Table 2 were analyzed by optical microscopy and SEM. However, only one result for each system (sintering temperature 1200 ºC) is presented because no significant differences were detected and the mechanical strength obtained with this sintering temperature is already adequate for the casting conditions. Fig. 11 shows the optical microstructures of the three systems. In all the samples the measured face coat thickness is around 800 µm.



a) Silica binder/Yttria b) Organic binder/Yttria c) Silica binder/Alumina

Fig. 11 Microstructures of the sintered shells. Each image shows: on left, the back-up composed by silica based binder and alumina slurry with alumina stucco. The right side shows the face coat of: a) yttria; b) yttria; c) alumina

The SEM/EDS analysis of the samples sintered at 1200 ºC is presented in Figs. 12 to 14. The EDS analysis was done to detect if any diffusion occurs during the sintering cycle, with new phases or compounds generation or necking formation between particles.

Any bonding between the particles was detected using SEM microstructural analysis. All the situations tested have enough strength to withstand the casting of the metallic alloy but not in excess, allowing an easy knockout. The chemical elements detected by EDS are in accordance to the initial chemical compositions of the different constituents (see Table 2), as shown in EDS profiles of Figs. 12 to 14.

Each Fig. (from 12 to 14) presents the microstructure (SEM) of the ceramic shell cross section enhancing the face coat (right side) and the stucco (left side) and also the regions (Z1 to Z3) where the EDS spectrums were obtained.

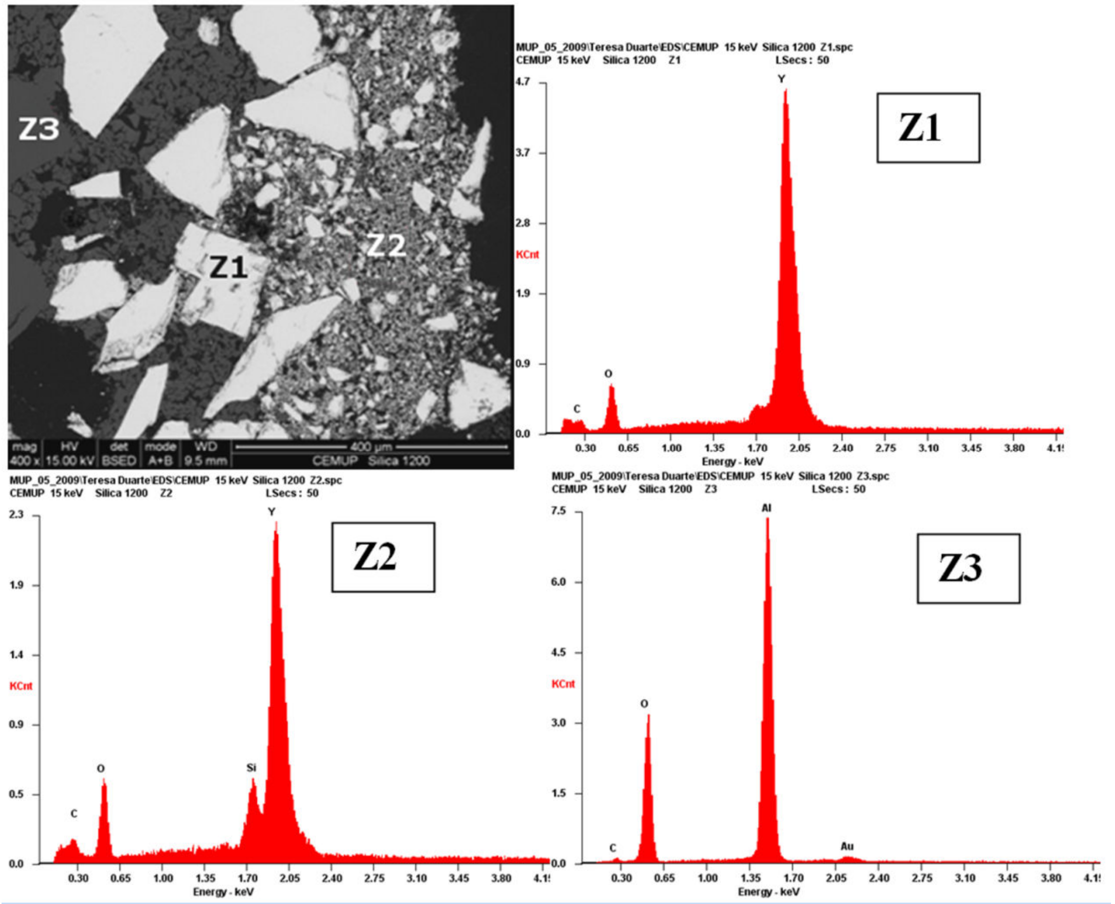


Fig. 12 From left to right: Back-up (Z3) and face coat - system silica binder/yttria (Z2) with yttria particles (Z1): Z1 - EDS profile - Y_2O_3 particles; Z2 - EDS profile - Slurry with silica and Y_2O_3; Z3 - EDS profile - Alumina back-up

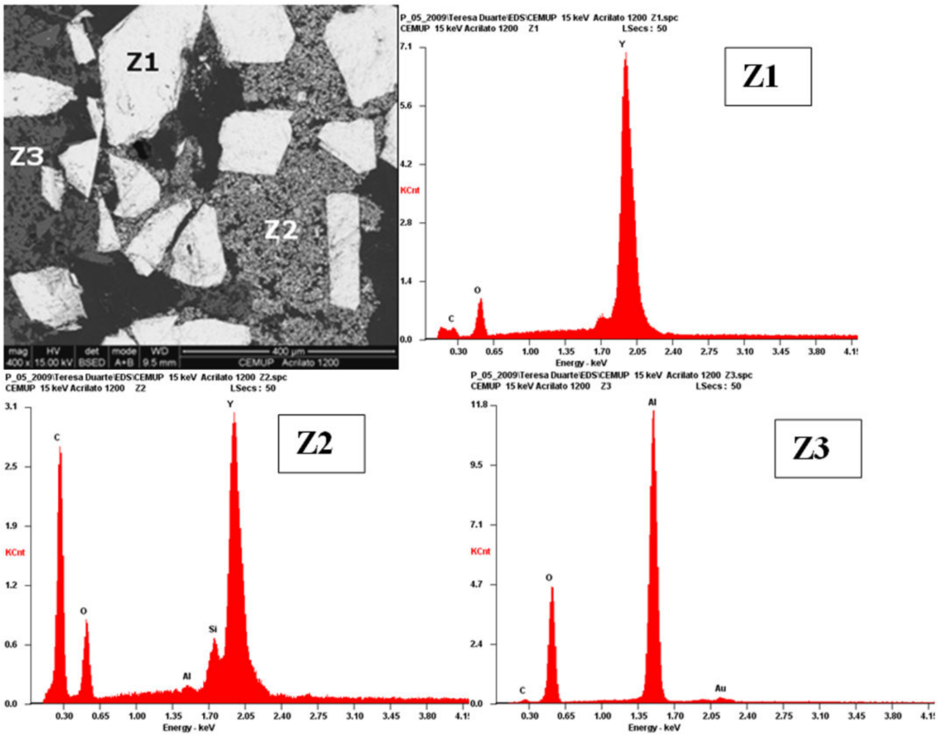


Fig. 13 From left to right: Back-up (Z3) and face coat - system organic binder/yttria (Z2) with yttria particles (Z1): Z1 - EDS profile - Y_2O_3 particles; Z2 - EDS profile - Slurry with organic binder (carbon) and Y_2O_3 and traces of silica contamination; Z3 - EDS profile - Alumina back-up

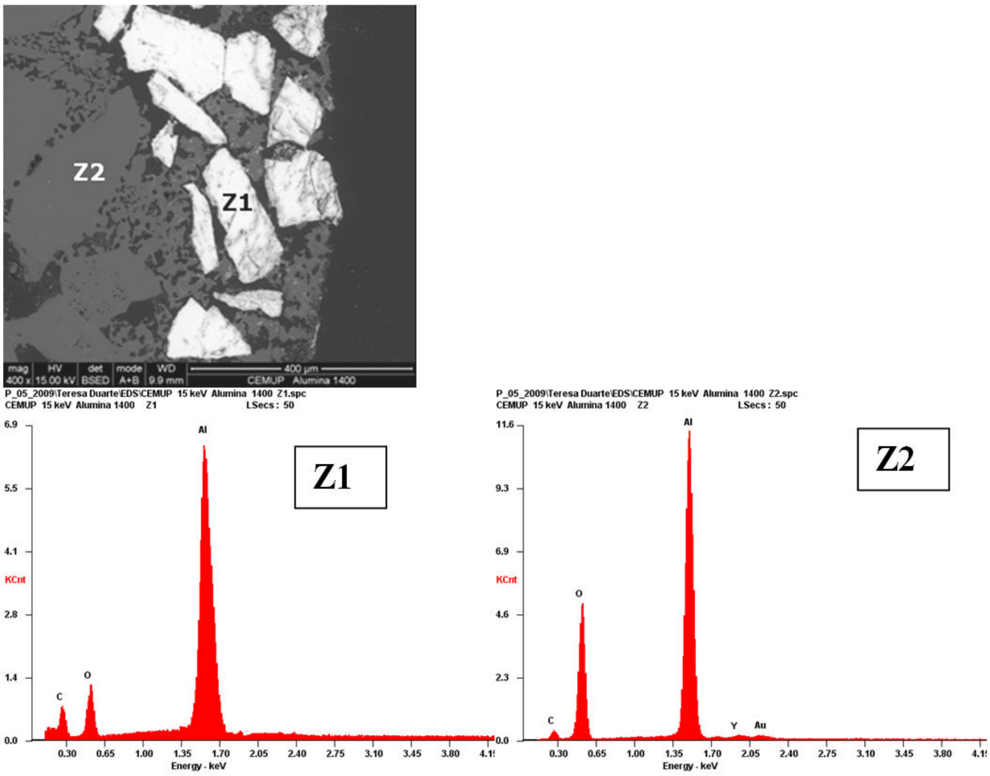


Fig. 14 From left to right: Back-up (Z2) and face coat - system silica binder/alumina (Z1): Z1 - EDS profile – face coat with Al_2O_3 particles; Z2 - EDS profile - Alumina back-up

CONCLUSION

To produce high quality metallic parts in titanium alloys by investment casting it is fundamental to select the right raw materials and sintering temperature for manufacturing adequate ceramic shells. Increasing the sintering temperature improves the ceramic shell strength to withstand the casting stage of Ti alloys. A sintering temperature lower than 900 ºC (silica slurries) and lower than 1200 ºC (organic binder slurries) produces high friable shells not compatible with quality castings.

The influence of sintering temperature in permeability was not clearly demonstrated due to results oscillation.

The correct selection of the raw materials, taking into account the standard free energy variation of oxides formation (ΔG^o), softening temperature, thermal expansion coefficient and thermal conductivity allows the manufacture of ceramic shells with a compromise resistance for the knockout and casting operation.

Dimensional variations are face coat independent, but controlled by the alumina back-up. Microstructural analysis of the ceramics shells shows a homogenous particles distribution and no special particles bonding (adequate for shells knockout) or phase changes of the raw materials.

Further work for the control of the entire process will be the study of binder composition in different yttria based face coats in terms of reactivity (α case extension and the effect of oxygen content and yttria dissolution and mechanical behaviour (tensile strength) of casted titanium parts.

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