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Experimental characterization of ceramic shells for investment casting of reactive alloys

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Abstract

The investment casting of reactive Ti and TiAl alloys requires the use of selected ceramics in the face-coat layer to prevent the reaction between the cast metal and ceramic shell, avoiding the formation of a hard layer at the metallic components surface. This work aims to study the influence of ceramic shells composition in some of its characteristics such as flexural strength, friability and dimensional accuracy. The microstructure of the shells was evaluated by SEM. Changes in the face-coat and back-up ceramic shells composition determines the ceramic shell strength to withstand the casting stage with adequate mould permeability and thermal conductivity, and a compromise resistance for knock-out. All the non-conventional ceramic shell systems with interest for reactive alloys, based on fumed alumina binder and alumina sand for the back-ups, present higher dimensional stability (low shrinkage or expansion) compared with traditional systems based on colloidal silica binder and zircon and aluminosilicates back-ups. In this work, better mechanical strength and lower friability were obtained with non-conventional face-coats of alumina and polymer binders, both with yttria flour and stucco, followed by alumina back-ups. Selecting the right ceramic shell composition, it is possible to achieve adequate properties for casting titanium alloys.

1. Introduction

The key requirements of a ceramic mould for investment casting are: enough green unfired strength to withstand wax removal without failure, sufficient fired strength to resist the metalostatic pressure, high thermal shock resistance to prevent cracking during metal pouring, high chemical stability and low reactivity with the metals being cast to reach adequate surface finishing and no alpha case formation on surface of Ti and Ti alloys parts. The mould also needs to present a level of permeability to be easily filled by molten metal, and a thermal conductivity to allow thermal transfer through the mould wall, allowing the metal to cool, and low thermal expansion to limit the dimensional changes and produce proper components. These requirements are mandatory to obtain metallic components without defects and with dimensional accuracy. Fig. 1 shows a production scheme to obtain a ceramic shell for investment casting and Fig. 2 depicts the generic structure of a ceramic shell.

Coating the pattern with the usual ceramic slurries [1] (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 (400-600 HV), cracked and weak reaction layer, called alpha case [2]. This surface layer is a result of the Ti reaction with the metallic oxides of the ceramic shells and is composed by brittle intermetallic compounds that significantly reduce the mechanical properties of the cast parts and raise machining problems [3].

To overcome this problem, titanium alloys should be poured into special ceramic shells that avoid or significantly reduce this type of reaction.
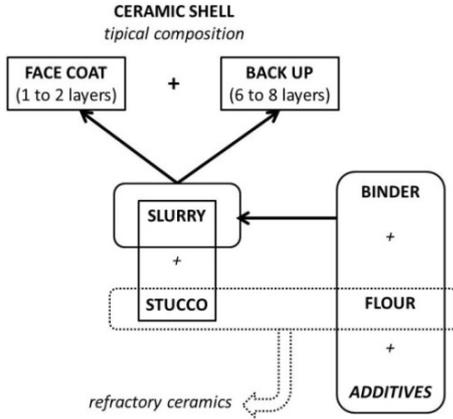
http://dx.doi.org/10.1016/j.ctmat.2016.07.014

Fig. 1. Generic scheme to produce a ceramic shell.
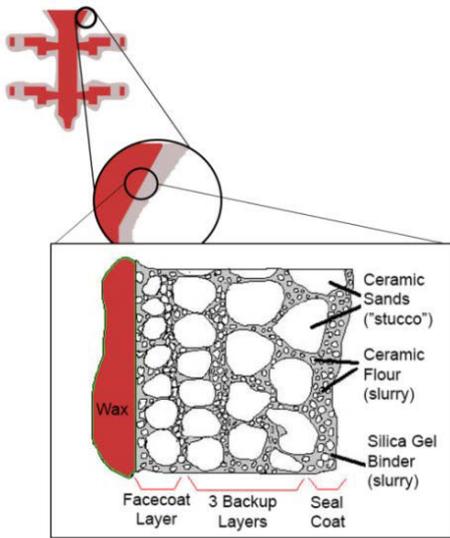
Fig. 2. Schematic of a ceramic shell for investment casting.

Fig. 3. Ellingham diagram for the more common oxides used in investment casting [4,5].

Table 1. Thermal properties and standard free energy of formation of different ceramic materials [7,8].

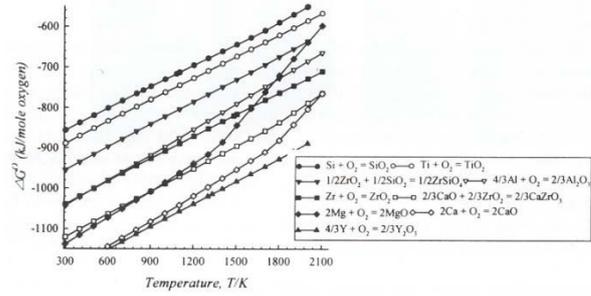| Ceramic	Thermal expansion coefficient $(\times 10^{-6} K^{-1})$	Thermal conductivity $(W/(m\ K))$ 20-26°C	Gibbs Free Energy ΔG^O $(kJ/mol\ O_2)$	Softening temp. (°C)
Zirconia (ZrO_2)	10.0	2.5	-743 (at 1900 K)	2010
Yttria (Y_2O_3)	8.1	8.0-12.0	-989 (at 1469 K)	1855
Alumina (Al_2O_3)	8.0	28.0-35.0	-711 (at 1900 K)	1540
Silica (SiO_2)	0.5-0.8	1.2-1.4	-610 (at 1685 K)	1280
Zircon ($ZrSiO_4$)	4.5	8.0	not available	1815

In this case, to select the most suitable ceramics one should take into account, as shown in Fig. 3, the standard free energy of formation of oxides (ΔG^o). Ceramics such as CaO, ZrO_2 and Y_2O_3 must be adopted as mould materials and binders for the face-coat because their standard free energy of formation is more negative than that of TiO_2, preventing interface reactions [6]. Table 1 presents the main thermal properties and free Gibbs energy of formation of some ceramics used in shells production.

The melting temperature of the Ti and its alloys, 1400-1600°C [9], determines the temperature range to be analysed in the Ellingham diagram. As shown in Fig. 3, the lines related to the free energy of oxide formation in the lower part of the diagram (Al_2O_3, MgO, ZrO_2, CaO and Y_2O_3) mean that the oxide is thermodynamically more stable.

With a softening temperature of 1855°C, above the melting temperature of the Ti alloys, and larger standard Gibbs free energy of formation than all oxides that could be used in the ceramic shells (-989 kJ/mol at 1469 K), yttria is undoubtedly the most promising refractory material for face-coat in terms of reactivity. Its use in ceramic shells only began to be more common in the last 15 years because, despite its potential, there were enormous difficulties in producing an yttria based slurry which did not gelify prematurely, preventing parts production in large series. In 1993, Horton [10] used successfully face-coat yttria slurries, applying colloidal silica as a binder and with the addition of hydroxide ions. This procedure avoided premature gelling of the slurry [11]. Different combinations of binders, flours (particle size and composition) and manufacturing techniques have conducted to the current state of the art of ceramic shells performance, where yttria, as described in reference [12], is the ideal ceramic with the lowest reactivity to cast reactive alloys.

2. Experimental Procedure

Table 2 presents the generic composition of tested samples in terms of face-coat and back-up ceramic shells, developed in this research to obtain accurate and sound metallic components in Ti or Ti alloys. The experimental details, as the number of layers, time between layers' deposition, drying and dewaxing conditions, sintering temperatures and others are presented in previous works [7,8,13]. For example, to obtain the samples of each composition, the sintering conditions (1100-1450°C) defined were the ones that could create a compromise between enough strength during pouring and solidification and easy knock-out [7,8,13].

Table 2. Generic composition and particles size of tested samples in terms of face-coat and back-up ceramic shells.

| Specimen | Face-coat | | |
	Binder	Flour	Stucco
AY	Polymer	Fused Yttria	Yttria 125-150 μm
AAFY	Polymer and fumed alumina	Fused Yttria	Yttria 125-150 μm
AFZrYc	Fumed Alumina	Zirconia and fine Yttria	Zirconia 50-100 μm
AFAL	Fumed Alumina	Alumina	Alumina 106-150 μm
AFZr	Fumed Alumina	Zirconia	Zirconia 150-300 μm
SZ	Colloidal Silica	Zircon	Zirconia 150-300 μm
SAIT	Colloidal Silica	Alumina and Ti powder	Alumina 106-150 μm

| Specimen | Back-up | | |
	Binder	Flour	Stucco
AY	Fumed Alumina	Fused Alumina	2x Alumina 212-300 μm and 4x 420-600 μm
AAFY	Fumed Alumina	Fused Alumina	2x Alumina 212-300 μm and 4x 420-600 μm
AFZrYc	Fumed Alumina	Fused Alumina	2x Alumina 212-300 μm and 4x 420-600 μm
AFAL	Fumed Alumina	Fused Alumina	2x Alumina 212-300 μm and 4x 420-600 μm
AFZr	Silica	Zircon	2x AlSi* 0.2-0.5 mm and 4x AlSi* 0.5-1 mm
SZ	Silica	Fused Silica	2x AlSi* 0.2-0.5 mm and 4x AlSi* 0.5-1 mm
SAIT	Silica	Zircon	2x AlSi* 0.2-0.5 mm and 4x AlSi* 0.5-1 mm

* Aluminosilicates

Fig. 4 shows some examples of the samples used to characterize the ceramic shells. All the tests were conducted on sintered samples.

The flexural strength tests were performed in an Instron 4802 universal testing machine (loading rate of 1 mm/min, supports span distance of 60 mm and 1 kN load), and five samples of each condition (Fig. 4 a)) were tested. The samples dimensions were about 32-33 mm width and about 100 mm length. The average thickness of each batch is presented in Table 3. The dilatometry tests (Fig. 4 b)) were obtained in a dilatometer Bach 810L model (heating rate of 100ºC/h up to 1200ºC, the maximum equipment capacity). The samples were about 40 mm length, 5 mm width and thickness varying between 4.51 and 8.33 mm (Table 3).
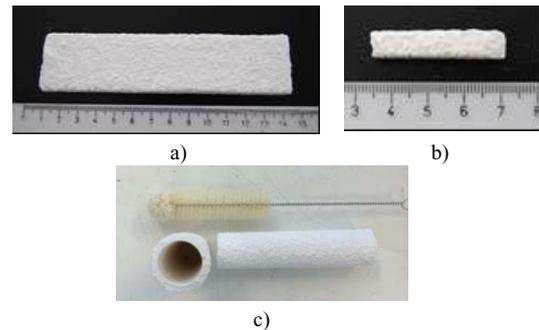

Fig. 4. Sintered samples for tests of: Flexural strength (a), Dilatometry (b) and Friability (c).

Table 3. Average thickness of the ceramic shells batches.

Specimen	Average thickness (mm)
AY	5.00
AAFY	7.23
AFZrYc	5.93
AFAL	4.51
AFZr	7.07
SZ	8.33
SAIT	7.21

The friability test was conducted based on the method proposed by C. Yuan *et al.* [14]. For this test, ceramic shell samples were produced (with about 150 mm length and 30 mm inner diameter) in order to replicate the behaviour of a ceramic mould. The test brush presented in Fig. 4 c) (Fisher Scientific 30 mm diameter) is the facilitator for the release of the small particles inside the ceramic mould. The samples were weighted in a precision balance (AND FR-200 MKII 0.0001 g) before and after the brush was pushed through the inside of the sample and pulled back (3 samples for each selected condition). The inner diameter and length of the sample were also measured. The materialographic preparation of samples for SEM microscopic analysis was done according to a procedure previously developed and briefly described in Table 4, using Struers consumables and equipments [15]. This procedure is very important to ensure that

the pull-out during sample preparation is minimized, allowing the correct interpretation of the ceramic microstructure. These observations were done to determine the homogeneity of different ceramic shells layers and measure the thickness.

Table 4. Grinding and polishing steps of ceramic samples vacuum infiltrated with epoxy resin.

Grinding (SiC)	180 mesh	320 mesh	500 mesh	800 mesh
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	15 µm	6 µm	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

3. Results and Discussion

The flexural strength, M_r (MPa), was calculated using the Eq. (1), where F is the force applied to the specimen (N), l the span (mm), b the width of the specimen (mm) and d the thickness (mm). Fig. 5 presents the flexural strength results (average of five samples in each condition) of specimens described in Table 2.

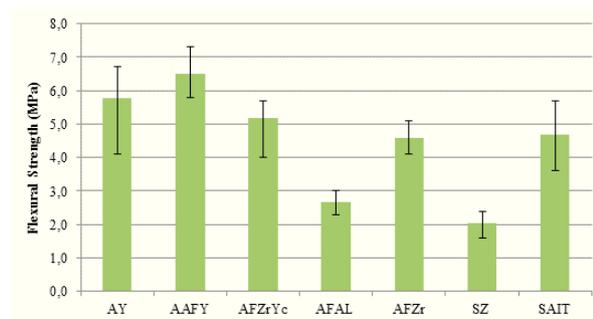$$M_r = \frac{3Fl}{2bd^2} \qquad (1)$$

Fig. 5. Flexural strength results of the ceramic shells of Table 2.

The flexural strength of the samples tested ranged from 2.0 MPa (SZ) to 6.5 MPa (AAFY), for slurries with face-coat of zircon and alumina (flour) and colloidal silica as a binder, and the ones composed by yttria (flour) and polymer and fumed alumina as a binder, respectively. Thus, it can be concluded that AAFY or AY compositions should be used since they have higher values of mechanical strength and they have a face-coat composition mainly based on yttria flour, which ensures lower reactivity in agreement to the theoretical principles described in the introduction and shown in Fig. 3.

Another reason for the fact that samples AAFY present the greatest mechanical strength and SZ the smallest may be due to the fact that AAFY are composed by only one type of ceramic material - yttria - as flour and stucco, while the SZ samples are composed by two ceramics - zircon and zirconia. The dissimilar values of the thermal expansion coefficients of the zirconia and zircon (see Table 1) can lead to different thermal expansion during sintering and appearance of residual stresses or micro-cracks and consequently mechanical strength reduction.

The particles size of AAFY samples stucco are thinner (yttria 125-150 µm) than SZ samples (zirconia 150-300 µm), which justifies higher densification during sintering and hence better mechanical resistance. However, it should be considered that excessive mechanical strength can promote hot tearing in castings.

The difference between the weights (initial and after brush crossing), G (g), the internal diameter, D (mm), and the length of the sample, L (mm), allows to calculate the friability (F) of the sample (g/m^2) through Eq. 2, and presented in Fig. 6.

$$F = \frac{G}{\pi DL} \qquad (2)$$

Friability tests were performed in only 3 batches of the samples described in Table 2 because these specimens are difficult to produce. They are very long and thin and this test requires a lot of rigor in its implementation due to the fact that it is manually done by the operator. The samples tested were chosen based on the results presented in Fig. 5: two batches of the most resistant ones (AY and AFZrYc) and a lesser resistant batch (SZ), to understand if there was any relationship between strength and friability. The results of friability presented in Fig. 6 are in agreement with the results obtained for flexural strength as the more resistant shells are the lesser friable (AY). Low friability is important in order to reduce inclusions in castings resulting from metal erosion, as also referred by Yuan *et al.* [14].

Fig. 7 and Table 5 present the dimensional changes of all ceramic shells tested. As one can see, the ceramic shells behaviour is quite different and dependent on shells' composition. Compared with traditional shells, based on colloidal silica binder, zircon and aluminosilicates (SZ), the unconventional shells

AFZrYc, AAFY, AFAL and AY practically do not undergo dimensional variations with temperature.
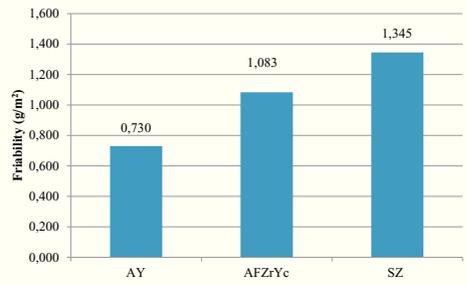

Fig. 6. Friability results for some ceramic shells of Table 2.

This is beneficial to their use in investment casting as dimensional changes do not occur in the final pieces as a result of shrinkage occurred during preheating. Shells AFZr, SZ and SALT suffer significant shrinkage, as shown in Table 5, during heating until 1200ºC, as a result of some densification.
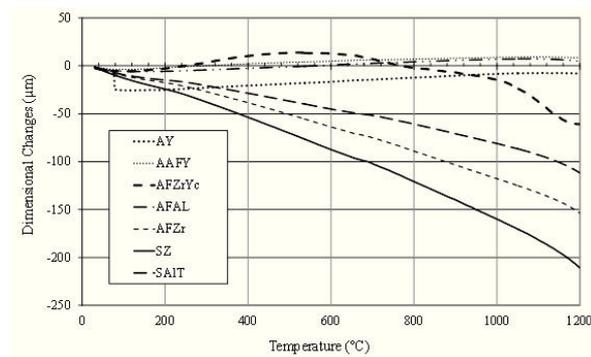

Fig. 7. Samples' dimensional changes with temperature (shrinkage).

Table 5. Dimensional changes with temperature: 1 - AY; 2 - AAFY; 3 - AFZrYc; 4 - AFAL; 5 - AFZr; 6 - SZ; 7 - SAIT.

ºC	Change in length (µm)						
	1	2	3	4	5	6	7
100	-25.4	-3.7	-5.6	-5.6	-10.1	-12.7	-9.2
200	-25.0	-2.1	-2.7	-5.7	-17.6	-24.3	-14.8
300	-22.8	0.2	3.6	-4.3	-27.0	-37.8	-20.7
400	-20.6	2.2	10.3	-2.6	-38.4	-53.7	-28.6
500	-18.5	3.7	13.6	-1.1	-50.8	-70.3	-36.8
600	-16.7	4.9	12.8	0.7	-63.7	-87.4	-45.1
700	-14.4	6.2	7.0	2.7	-75.0	-102.1	-51.8
800	-12.2	7.0	-2.1	4.3	-89.1	-120.8	-60.8
900	-10.4	8.0	-6.9	5.6	-103.3	-139.7	-70.8
1000	-8.4	8.8	-14.7	6.9	-117.6	-159.8	-81.0
1100	-7.6	9.3	-37.5	7.2	-132.6	-181.8	-92.9
1200	-8.0	8.4	-60.8	4.6	-153.7	-210.9	-111.8

This means that the dimensions of the shells composed by silica binder, zircon flour and aluminosilicates back-up are not completely stabilized. This is a serious problem for casting reactive alloys because it causes extra dimensional variations. It can be solved by using the other ceramic shells developed in this work based on alumina binder, yttria or alumina flours for face-coat and alumina for back-up.

Fig. 8 presents SEM images of some ceramic shells. The difference among shape, size and particles colour is due to the different ceramics used as flour, stucco and binder, as described in Table 2. The identification of particles by their composition and by colour was discussed in a previous publication [16]. The medium thicknesses presented in Table 3 are in agreement to Fig. 8.
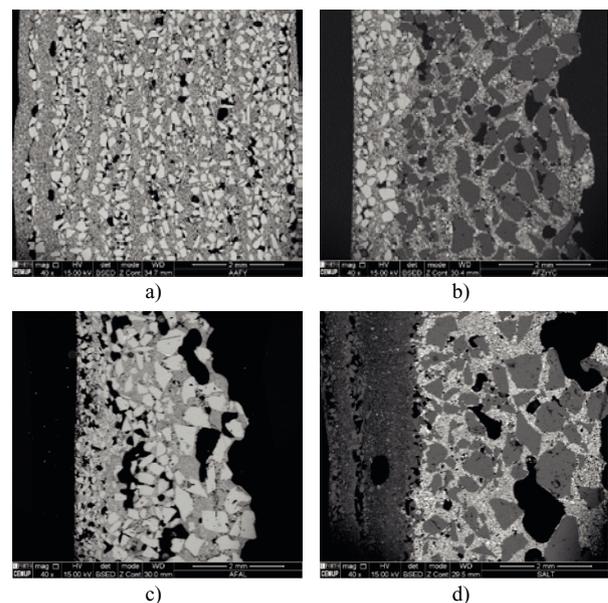

Fig. 8. SEM microstructures of some ceramic shells: AAFY (a), AFZrYC (b), AFAL (c) and SAIT (d). From the left to the right, images show the face-coat and back-up layers.

4. Conclusions

It is possible to produce ceramic shells for investment cast of titanium and its alloys with tailored properties with several ceramic flours and binders.

The shells AFZrYc, AAFY, AFAL and AY practically keep their dimensions during the preheating cycle. These negligible dimensional variations are beneficial to reach accurate tolerances during the manufacturing process.

Shells AAFY and AY are the most resistant ones due to highest flexural strength and lower friability, and so should be considered for this type of application.

Acknowledgements

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