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Effect of nanosized TiO2 on nucleation and growth of cristobalite in sintered fused silica cores for investment casting.

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Abstract

Sintered fused silica is often used for making sacrificial cores in investment castings of Ni superalloys. Their usage is fundamental in the manufacture of precise superalloy gas turbine components with complex internal cooling passages.
In this study $SiO_2/ZrSiO_4/TiO_2$ cores were prepared from fused silica powders with different grain size and zircon and TiO_2 content by slip casting method. Green samples were sintered at 1230°C at various soaking time: from 0,5 to 10 hours.
Thermomechanical and microstructural properties of optimized silica obtained by add of 1,5%wt of TiO_2 to $SiO_2/ZrSiO_4$ composition have been investigated by three point bending tests, XRD and Hg porosimetric analysis. The influence of cristobalite content on thermal stability at high temperature was studied by an optical dilatometer.
At temperature below 1200°C TiO_2 appears to act as a phase transformation inhibitor reducing the transformation rate of fused silica to cristobalite at high temperatures. At higher temperature it speeds up the formation of cristobalite.
A comparison with commercial silica cores made by injection moulding has been performed.
A prototype core was obtained and an investment casting was performed on that.

Introduction

Silica (SiO_2) based ceramic cores have been used for the casting of equiaxed, directly solidified, and single-crystal superalloys in the aerospace industry since the 1930s [1]. Their usage is prevalent in the manufacture of superalloy gas turbine components where internal structures, such as cooling passages, are desired. A practical method for forming these internal structures is to cast the metal around a leachable, via chemical means, fused silica ceramic core that has been previously fabricated by injection molding, transfer molding, or rapid prototype printing [2].
The manufacturer's challenge for more efficient turbine blades can be won by three ways:

- increasing the refractoriness of the metal alloy by higher temperature shell/core systems;
- reducing component weight by thinner blade walls, reachable objective by more rigidness and stability of shell core system during casting;
- increasing gas entry temperature through more complex cooling, reachable objective by introducing more complex and tightly controlled geometries on the blade;

A successfull ceramic core is one in which an optimum compromise between crushability and stability has been achieved; namely, the ceramic deformed rapidly enough to allow sufficient stress

relaxation in the metal (so that deleteriously high stresses do not initiate defects) and simultaneously being rigid or stable so to maintain intended dimensional tolerances of the metal component.
Cristobalite gives silica ceramics their high temperature creep resistance and strength. If the cristobalite content is too low the silica core will creep and sinter during investment casting but if the cristobalite is too much, the silica core will break while cooling after sintering or will shock during investment casting. Middle path is providing many cristobalite nuclei with small size ready to drive the crytallization of remaning amorphous silica.
Since TiO_2 is a well know nucleating agent in glass ceramic system[3], insoluble in SiO_2, the main goal of this study is to investigate the use of nanosized TiO_2 to obtain an accurate control on cristobalite content during sintering.

Experimental methods

Elaboration of materials. Silica/Zircon and Silica/Zircon/Titania mixtures have been prepared from corresponding powders by slip casting method. Characteristics of powders were shown in table I.

TABLE I. Characteristics and chemical composition of powders as provided by manufacturer

	Fused Silica (SiO_2)	Titania (TiO_2)
Trade Name	-	Degussa Millenium PC 105
Crystalline Structure	Amorphous Silica	100% Anatase
Particle size	325F - 200F (44 -74 µm)	15 – 25 nm
Specific surface area	-	85 - 95 m^2/g
Density	2,20 g/cm^3	-

Ceramic water based suspensions have been prepared using a polyelectrolyte dispersant. A nanosized titania (see tab.I) additive has been added on mixture to modify microstructure and increase thermo-structural performance of material.
The examined silica/zircon ceramic, designated as SZ, had a primary chemistry of 80%$_{wt}$ of silica (SiO_2) and 20%$_{wt}$ of zircon ($ZrSiO_4$) [4]. Second material, designated as SZT, had the same composition of SZ with add of 1,5 wt% of TiO2. Both ceramic compositions are referred as “Type-B” silicas in refractories lexicon according to ASTM C416 (i.e., the sum of the alumina and twice the alkali oxides contents exceed 1.5%) [5]. Green samples have been sintered at 1230°C at various soaking time.
Sintering Curve. Dilatometric test has been carried out by optical dilatometer of Expert System® to investigate transformations occurring during sintering. The test has been carried out on a SZT green bar of 52 x 5 x 5 mm at heating rate of 5°C/min to 1230°C with a soaking time of 6 hours and a cooling rate of 3°C/min.
Physical-Mechanical properties. Sintered at 1230°C for 6 hours SZT materials have been characterized. Room temperature three point bending strength has been evaluated according to ASTM C-1161 by dynamometer Lloyd LR5K model . Strength at 1500°C and residual strength at 1200°C have been also evaluated. All tests have been performed on bars of 45x4x3 mm. Measurements of porosity have been obtained by Hg porosimeter Pascal 140-240 from ThermoFinnigan. Thermal conductivity has been measured by Mathis TCi analyzer based on the

modified transient plane source technique. Bulk density has been measured by Archimede's method.

Casting simulation. The behaviour under casting of two SZ materials and one SZT material, subjected to different sintering treatments, have been examined. Previously materials have been subjected to XRD Analysis to investigate cristobalite content [6]. Then, dilatometric test has been carried out to simulate the casting of superalloy on ceramic core and to evaluate the thermal stability of elaborated materials. Test have been carried out on sintered bars of 52x5x5 mm at heating rate of 6°C/min up to 1500°C with a soaking time of 15 min and a cooling rate of 10°C/min.

Results and discussion

Sintering Curve. In fig.1 we can observe the sintering curve of SZT obtained by optical dylatometer. The upper curve of fig. 1 represents thermal treatment, whereas the lower curve represents the corresponding dilatometric curve. In fig. 1, five regions can be easily identify:

I) during heating from 30 to 1030°C, the material exhibits thermal expansion of 0,1%;

II) during heating from 1030 to 1230°C and for the first 1,5 hours of soaking time we observe initial solid sintering followed by liquid phase sintering with a shrinkage of 1,14%;

III) for the following 4,5 hours of soaking time at 1230°C we can observe nucleation and growth of β cristobalite with an expansion of 0,05%;

IV) during cooling from 1230°C to 200°C the material is experiences the thermal contraction of 0,22%;

V) finally during cooling from 200 to 150°C we observe a volumetric contraction due to Cristobalite β→α phase transition.

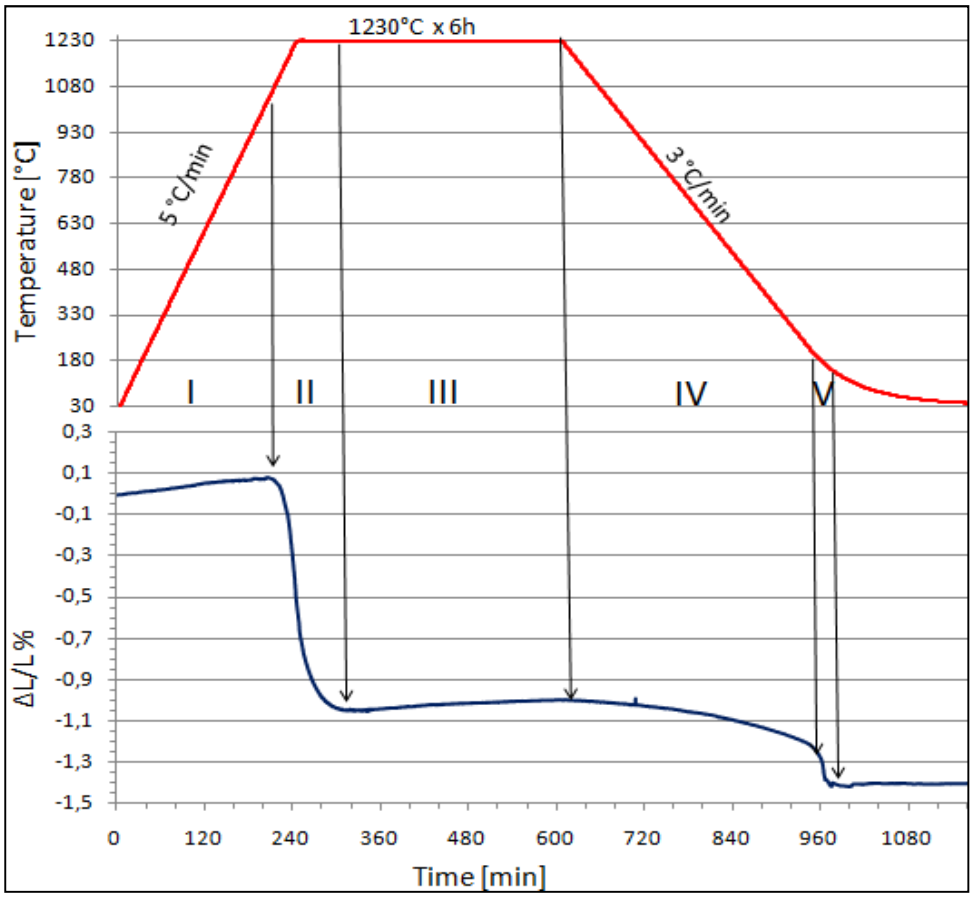

Fig. 1. Sintering curve of silica with TiO_2 nanopowders (SZT)

Physical-Mechanical properties. In table II, a comparison between properties of 1230°C - six hours sintered SZT and of a commercial ceramic core silica /zircon 80/20 made by Avignon® have been

summarized. Values of density and porosity appear very similar. Values of strength are instead higher for the SZT sintered at 1230°C for six hours.

TABLE II. Physical-mechanical properties of TiO_2 doped fused sintered silica VS Avignon S820

	SZT sintered at 1230°C for 6h	Avignon S820
Bulk density [g/cc]	1,68	1,71
Porosity	23%	29%
Average pore radius [µm]	0,6	-
Thermal conductivity [W/mK]	1,4	-
Room temperature strength [Mpa]	23 ± 5	12
1500°C - strength [Mpa]	66 ± 4	12
1200°C - residual strength [Mpa]	63 ± 4	19

Casting Simulation. As summarized in tab. III three different materials were subjected to casting simulation. All three materials are made of 80%$_{wt}$ of SiO_2 and 20%$_{wt}$ of $ZrSiO_4$. SZ_0,5h has been sintered at 1230°C for 0,5 hours, SZ_10h has been sintered at 1230°C for 10 hours and SZT_6h has been sintered at 1230°C for 6 hours.

TABLE III. Characteristics of materials subjected to casting simulation

Material	Composition	Sintering treatment
SZ_0,5h	$SiO_2/ZrSiO_4$ 80/20	1230°C x 0,5 hours
SZ_10h	$SiO_2/ZrSiO_4$ 80/20	1230°C x 10 hours
SZT_5,5h	$SiO_2/ZrSiO_4$ 80/20 + 1,5%$_{wt}$ TiO_2	1230°C x 6 hours

Before casting simulation materials have been subjected to XRD analysis (fig.2) to evaluate the influence of processing and composition on microstructure. As shown in fig.2 amount of cristobalite varies in investigated materials. In SZ_0,5h cristobalite phase is absent. SZ_10h shows a very high content of cristobalite and SZT_6h presents a small content of cristobalite.
In fig. 3 we can observe the behaviour of the three elaborated silica core during casting simulation. The *lower plot* of fig. 3 is referred to SZ_0,5h material sintered at 1230°C for 0,5 hours. In this case a shrinkage occurs between 1100° and 1150°C. If the cristobalite content is too low the silica core will creep and sinter during investment casting.
The *upper plot* shown in fig. 3 is referred to SZ_10h material sintered at 1230°C for 10h. In this case, long soaking time has allowed to formation of large amount of cristobalite highlighted by initial expansion at 200°C due to cristobalite α→β phase transformation. This material exhibits a good thermal stability at high temperature but cristobalite α→β phase transition during heating may compromise the geometrical tolerance of superalloy investment casting. Moreover, if the cristobalite content is too much, the silica core will break while cooling after sintering or will shock during investment casting.
Middle path (*middle plot* of fig. 3) is obtained providing many cristobalite nuclei with small size ready to drive the crystallization of remaining amorphous silica. This result have been obtained by adding titania nanocluster to composition. The *middle plot* represents casting simulation performed on SZT_6h material sintered at 1230°C for 6 hours.

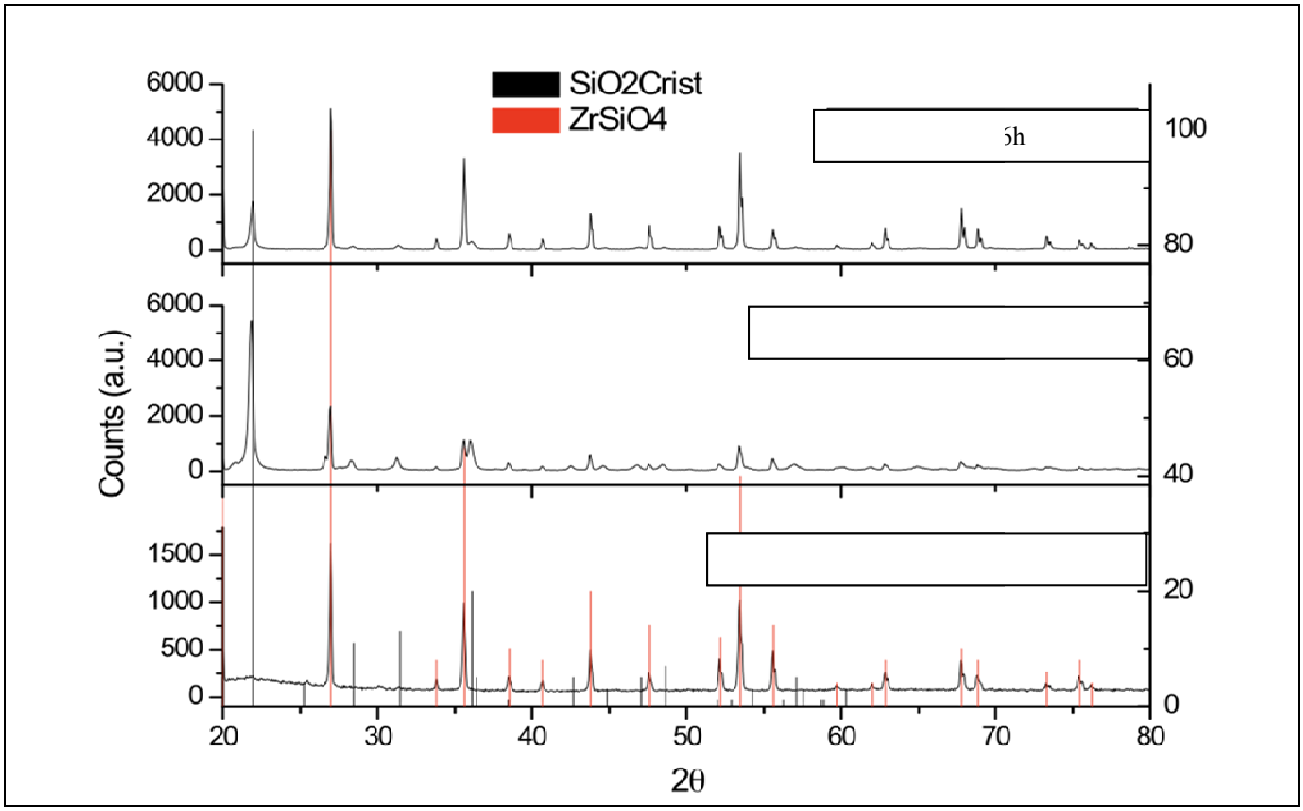

Fig. 2. XRD spectra on 80/20 Silica/Zircon sintered at 1230°C

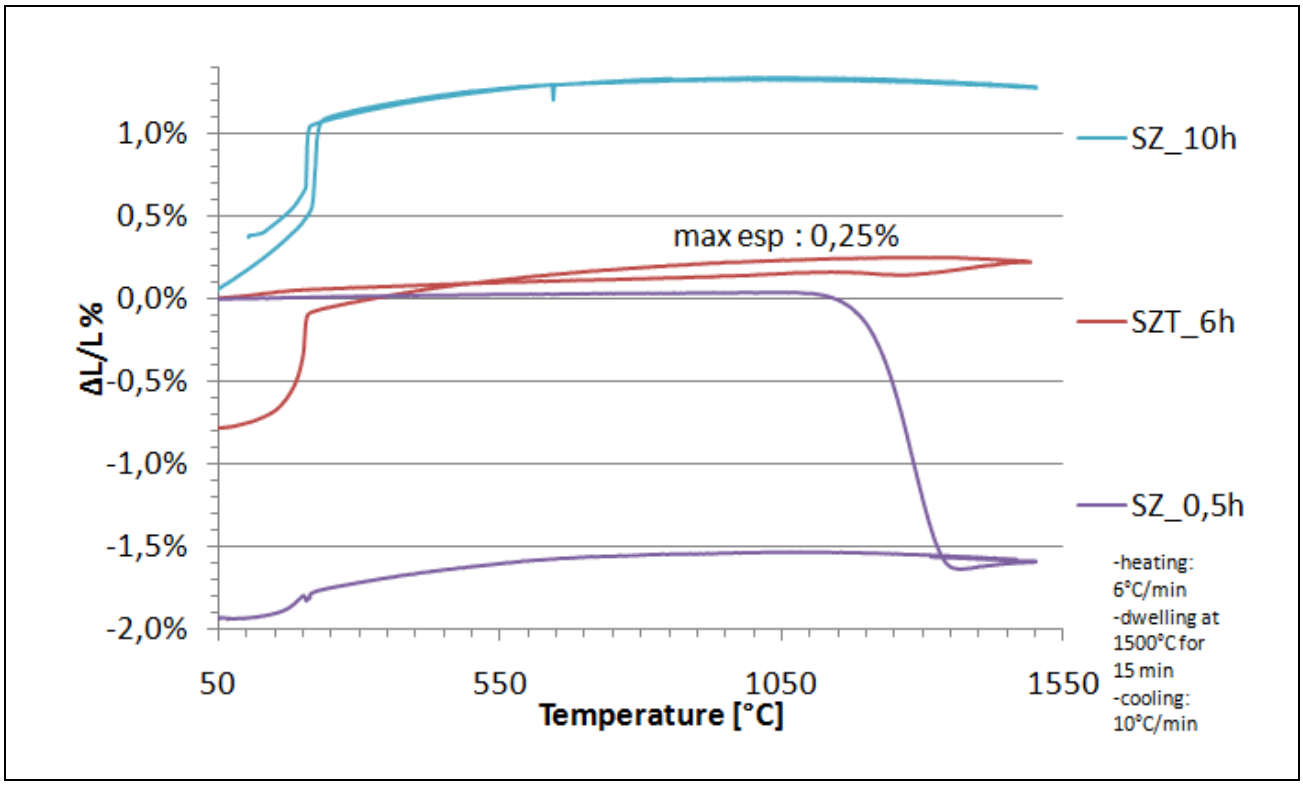

Fig. 3. Thermal expansion during casting simulation: a comparison between crystallised (SZ_10h), amourph (SZ_0,5h) and amourph + nanosized titania (SZT_6h) silica core.

Cristobalite content VS soaking time. In fig. 4 we can observe effect of different soaking time at 1230°C on microstruttural evolution of SZ and SZT. Results, obtained by XRD Analysis, show as increasing soaking time increase the cristobalite content. For SZ materials cristobalite content increases from 4% to 10% when soaking time goes from 5 to 7 hours. Presence of TiO_2 appears to

act a small inhibitor effect on cristobalite formation. Infact both 5 hours and 7 hours 1230°C sintered SZT show a lower content of cristobalite than corresponding SZ.

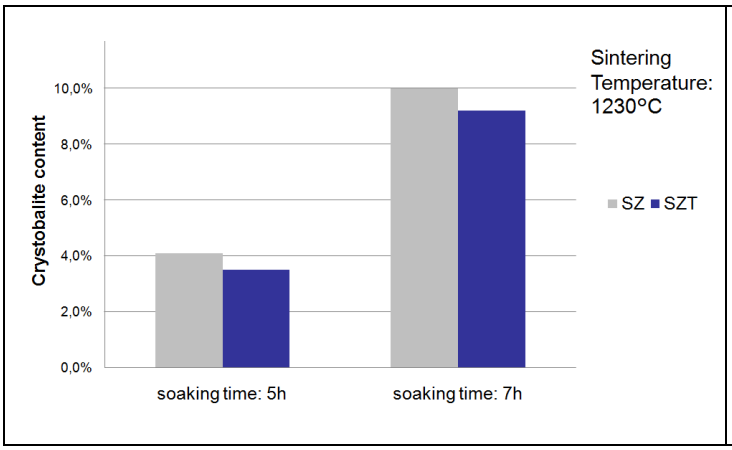

Fig. 4 Cristobalite content VS soaking time for SZ and SZT

Fig.5. Chemically etched, defect free SX blades cast from TiO_2 doped silica cores

Investment casting experiments on TiO_2 doped silica cores

Single crystal precision investment casting have been performed on superalloy CMSX-6 (0.70 Ni, 0.10 Cr, 0.05 CO, 0.03 MO, 0.02 Ta, 0.048 Al, 0.047 Ti, 0.001 Hf). After preheating and degassing, the mould receive the molten superalloy, which is poured under vacuum at a temperature of ~1550°C. After chemical etching no misalignment or defects have been found (fig.5).

Conclusions

Nanosized titania particles were succesfully incorporated in sintered fused silica cores and an accurate control on cristobalite content during sintering has been obtained.
Above Tg the cristobalite formation kinetics is fast enough to prevent creep and deformations of the core.
SX investment casting on superalloy has been simulated and performed. Preliminar characterization of leached and chemically etched blades show a defect free turbine blade (fig.5).

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