

Novel Zirconate Based Moulds for the Investment Casting of Titanium Alloy Melts

L. Freitag, St. Schafföner, N. Lippert, Chr. Faßbauer, C. Legner, U. E. Klotz, Chr. G. Aneziris

Dedicated to the 10th Anniversary of refractories WORLDFORUM

Investment casting allows the near net shape production of complex cast parts, but the investment casting of high melting and highly reactive titanium alloy melts is very difficult. Calcium zirconate (CaZrO_3) is a novel ceramic refractory material, which is particularly stable in a highly reducing atmosphere and in contact with extremely reducing titanium alloy melts such as Ti6Al4V. Besides the refractory, the choice of the binder is equally important because conventional silicate binders significantly impair the corrosion resistance. Although there have been successful attempts to develop CaZrO_3 investment casting moulds, silica-free CaZrO_3 investment casting moulds using a water-based binder have not yet been reported. For the first time, graded CaZrO_3 investment casting moulds using a silica-free water-based binder system were successfully produced [1]. Moreover, the chemical, physical, thermo-mechanical and microstructural properties of the moulds were described. A combination of fine-grained primary coats and coarse-grained secondary coats resulted in a high surface quality as well as sufficient mechanical stability of the moulds. Investment casting of Ti6Al4V led to an exceptionally low hardness increase of the cast part, suggesting that only a slight corrosion reaction took place. Thus, the silica-free CaZrO_3 investment casting moulds contributed to an improved investment casting of titanium alloys.

1 Introduction

Titanium alloys are key materials in aerospace as well as in biomedical and chemical industries due to their high strength combined with a low density and an excellent corrosion resistance. Investment casting allows the near net shaping of complex cast parts, using a ceramic refractory mould, which is produced by the lost-wax process, and filling it with the liquid metal melt. After

solidifying, the ceramic mould is removed by breaking the shell. Fig. 1 provides a general model of the ceramic coats produced by dip-coating and stuccoing on the wax pattern.

Due to the high reactivity and the high melting point of titanium alloy melts, much research was done to identify a suitable refractory material [1–7]. Yet, conventional refractories such as Al_2O_3 , SiO_2 , ZrO_2 , CaO

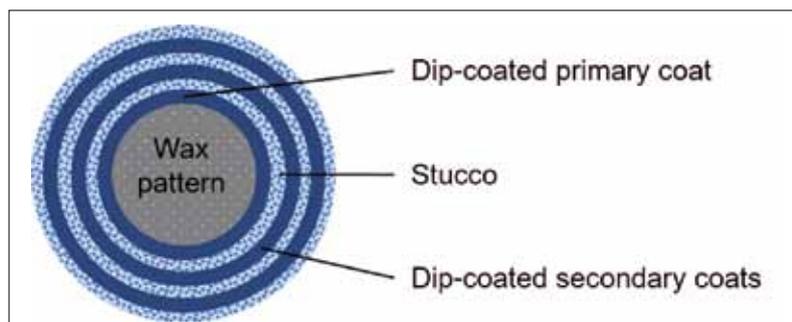


Fig. 1 Model of the coats on the wax pattern [1] (the coats are produced by dip-coating and stuccoing)

Lisa Freitag, Nicole Lippert,
Christina Faßbauer, Christos G. Aneziris
Institute of Ceramic, Glass and Construction
Materials, TU Bergakademie Freiberg
Freiberg, Germany
Stefan Schafföner
Department of Materials Science and
Engineering, Norwegian University of
Science and Technology NTNU,
Trondheim, Norway
Claudia Legner, Ulrich E. Klotz
fem Research Institute for Precious Metals
and Metals Chemistry
Schwäbisch Gmünd, Germany
Corresponding author: Lisa Freitag
E-mail: Lisa.Freitag@ikgb.tu-freiberg.de

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and Y_2O_3 were not sufficiently corrosion resistant and had further drawbacks. Recently, calcium zirconate ($CaZrO_3$), a novel refractory material with a high melting point of 2368 °C, was successfully evaluated in contact with titanium alloy melts [1, 3, 4]. The production of $CaZrO_3$ investment casting moulds was reported by Kim et al. [2], but was not yet presented in detail. Thus, investment casting moulds based on $CaZrO_3$ and a silica-free binder were developed and extensively described. Instead of silica binders, which remain in the mould and impair the corrosion resistance, a temporary binder based on a polymer dispersion was used. Required mould properties include corrosion resistance, thermal shock resistance, creep resistance, sufficient strength in green and sintered state, sufficient permeability and high surface quality. A graded composition of coatings combines the surface quality of a fine-grained facecoat with the high creep resistance and stability of coarse-grained secondary coats and might even lead to an improved thermal shock resistance by different thermal expansion coefficients of the coats.

2 Experimental

2.1 Slip production

First, stable coarse-grained and fine-grained $CaZrO_3$ slips with a maximum particle size of 1 mm (S_1) and 0,5 mm ($S_{0,5}$), respectively, were developed [1]. The used raw materials were fused $CaZrO_3$ (Imerys Fused Minerals Murg GmbH/DE) and $CaZrO_3$ produced by solid state reaction synthesis similar to Schafföner et al. [7] for the finest particle fraction. To ensure a good flowability and

to minimise the water demand, the particle size distribution of the slips was optimised based on the model of Funk and Dinger with a distribution modulus of $q = 0,22$. The batches are summarized in Tab. 1.

To improve the stability of the slips, xanthan gum (Axilat RH 50 MD, C.H. Erbslöh GmbH & Co. KG/DE) and food grade guar gum (Dragonspice Naturwaren/DE) were added to the solids. The amount of stabilizers was slightly higher for S_1 due to the coarser grains. Moreover, the content of solids in the slips was adjusted as high as possible (>90 %) to ensure a good wetting behaviour and to avoid cracks during the drying of the coats. Furthermore, an environmentally friendly and nonhazardous silica-free binder was used.

To begin with, distilled water was mixed with the dispersing and wetting additive (BYK LP-C 22134, BYK-Chemie GmbH/DE) and the defoamer (BYK LP-C 22787, BYK-Chemie GmbH/DE). This mixture was added to the solids followed by 5 min stirring with a high shearing laboratory mixer (RZR 2102 control, Heidolph Instruments GmbH & Co. KG/DE). Then, the polymer dispersion binder (BYK LP-C 22893, BYK-Chemie GmbH/DE) was added as a temporary binder and finally mixed for 5 min.

2.2 Mould production

Having prepared stable slips, which were shear-thinning and slightly thixotropic as described in a previous study [1], cylindrical wax patterns (height: 80 mm, diameter: 10 mm) consisting of Aqua Green Flake Wax (Freeman Manufacturing & Supply Company, Avon/US) were dipped into the

ceramic slurry for 10 s, and were then stuccoed after draining of the excessive slip for 30 s. The stucco material was fused $CaZrO_3$ with a particle size of 0,5–1 mm, and 0–0,5 mm after each dip-coating with S_1 and $S_{0,5}$, respectively.

For the stuccoing process a modified sieving machine was used. The wax patterns were attached to a screwing extension at a screw driller and a sufficient amount of the stucco material placed on a sieve. During the vibration of the sieving machine and the rotation of the wax pattern the stucco was then uniformly applied on the dip-coated pattern. The general procedure was to apply primary coats of $S_{0,5}$ and secondary coats of S_1 . Overall 3, 5 or 7 coats were applied, with a number of primary coats of $S_{0,5}$ varying from 0 to 3.

Later on, the coated samples were carefully dried at a temperature of 30 °C and a relative humidity of 60 % in a climate chamber (KPK 3533/15, Feutron Klimasimulation GmbH/DE). The drying times after the first coating and the next coatings were 2 h or 5 h, respectively. After the last coating step, the samples were dried for 7 d in the climate chamber and then for 7 d in an exsiccator in order to completely remove residual moisture because it was observed in preliminary experiments that such residual moisture can cause cracking of the moulds during dewaxing.

For dewaxing, the moulds were immediately placed into the hot drying furnace (UN450, Memmert/DE) at a temperature of 235 °C for 10 min because this was the best procedure for the used wax. Sintering of the dewaxed shell moulds was conducted in air with a heating rate of 1 K · min⁻¹ and dwell times of 2 h and 6 h at 900 °C and 1500 °C, respectively.

2.3 Mould properties

The shell thickness in the green state was evaluated prior to dewaxing. Thereby, 5 moulds of each composition were measured identically at the same cylindrical part at the middle of the sample using a conventional caliper.

After sintering, 5 samples of each composition were investigated regarding their apparent porosity using the Archimedes method based on the standard DIN EN 993–1 with water as the immersion medium. Moreover, the pore size distribution

Tab. 1 Composition of the coarse-grained slip S_1 and the fine-grained slip $S_{0,5}$

Product Name	Raw Material	Grain Size Fraction	d_{50} [µm]	S_1 [mass-%]	$S_{0,5}$ [mass-%]
Imerys fused $CaZrO_3$	$CaZrO_3$	1–0,5 mm	848,4	25	0
		0,5–0 mm	167,2	30	59
		–45 µm	12,61	25	12
		synthesized	2,14	20	29
Stoichiometric synthesis					
Axilat RH 50 MD	Xanthan gum	Mass relative to dry mass		0,05	0,02
Food grade guar gum	Guar gum			0,05	0,02
Water	H ₂ O			6,38	6,73
BYK LP-C 22134	Dispersing and wetting additive			2	2
BYK LP-C 22787	Defoamer			0,05	0,05
BYK LP-C 22893	Binder			4	4

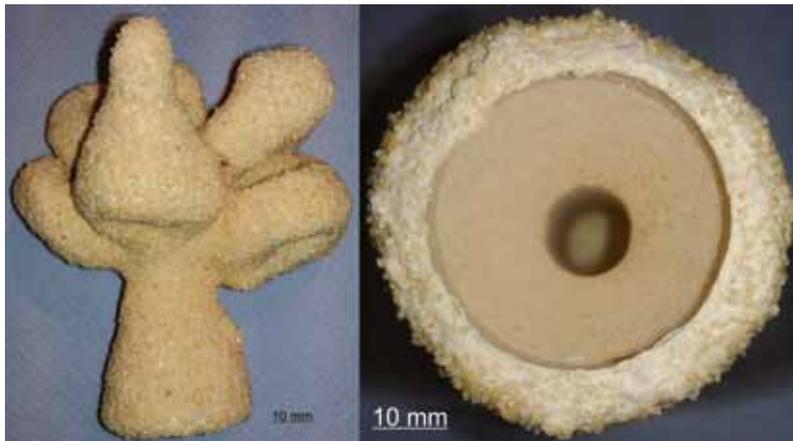


Fig. 2 CaZrO₃ investment casting mould for jewellery casting: mould (l.), inner surface (r.)

of one sample of each composition was determined using mercury porosimetry (AutoPore V 9600, Micromeritics GmbH/DE). These properties were investigated because they are related to the permeability of the mould, an important property, which is hard to measure for the original samples.

The thermal shock experiments were conducted by heating the samples in a pre-heated oven for 30 min and subsequent quenching in water. Regarding the heating temperature, preliminary experiments were carried out. The standard DIN EN 993-11 suggests 950 °C as the testing temperature, however, this program led to a too heavy destruction of the samples. Finally, 650 °C was determined as a suitable temperature which allowed the comparative evaluation of the moulds.

Furthermore, the cold modulus of rupture of a minimum of 10 samples with and without thermal shock exposure, respectively, was determined. Thus, the cylindrical hollow samples were exposed to a three point flexural test (TIRAtest 28100, TIRA GmbH/DE). The length of the support span was 3 cm, the testing velocity was 2 mm/min. Dependent on the shell thickness of the samples, the maximum bending force was evaluated in order to estimate the influences of shell thickness and thermal shock exposure.

Finally, the surface, microstructure and bonding of the samples was examined by a field emission scanning electron microscope (SEM) (XL30FEG, FEI Company/NL).

2.4 Investment casting

For the investment casting experiments, Ti6Al4V was used, being the most common

titanium alloy for investment cast products. Ti6Al4V was melted in an electric arc furnace (LK6, ALD Vacuum Technologies GmbH/DE) in a cooled copper crucible and subsequently tilt cast into the CaZrO₃ investment casting mould. After the melt solidified, the final cast part was obtained by breaking the ceramic mould. The water-cooled crucible ensured that no reactions between crucible and melt occur. The furnace was evacuated to $<5 \cdot 10^{-3}$ mbar and back-filled with argon to 400 mbar for melting. Any alteration of the metal is therefore caused by reactions with the CaZrO₃ mould.

Subsequently, the Vickers micro hardness profile was analysed according to DIN EN ISO 6507-1 in order to evaluate the hardness increase. The alpha case, a hard and brittle oxygen-enriched surface of the cast parts, originates from corrosion causing an increased hardness at the surface of the cast parts. In addition, the Ti6Al4V cast part was chemically analysed by glow discharge optical emission spectroscopy (GDOES) in order to evaluate the corrosion reaction of the CaZrO₃ investment casting mould in contact with the cast part. Because measuring the arched edge of the cast part was not possible, only the core of the cast part was analysed.

3 Results and discussion

3.1 Mould properties

After successful dewaxing and sintering, the surface of the moulds was homogeneous and smooth (Fig. 2). The properties of the investigated moulds are summarized in Tab. 2. Regarding the thickness of the moulds before firing, the average standard deviation was 6,2 %. Considering the manual coating process and the high maximum grain size, these variations are tolerable, so the shell thickness can still be seen as relatively homogeneous. The green shell thickness of all coarse-grained and graded moulds after 5 coats was $6,3 \pm 0,5$ mm. Generally, the shell thickness varied only slightly, but in most cases an increasing number of S_{0,5} front coats tended to result in a thinner shell. Surprisingly, this was not the case for 3 coats of S_{0,5}, as the shell thickness slightly increased. A possible reason might be the much better wetting behaviour of the slip S_{0,5}, which was adjusted to minimize draining, especially for the primary coat on the wax pattern. This slip might be less ap-

Tab. 2 Properties of the coarse-grained and the graded CaZrO₃ moulds including standard deviations

Coats	Primary Coats of S _{0,5}	Thickness (Green) [mm]	Apparent Porosity [%]	Median Pore Diameter [µm]
3	0	4,5 ± 0,2	23,7 ± 0,4	16,0
3	1	3,8 ± 0,2	25,8 ± 0,4	21,6
3	2	2,9 ± 0,2	24,2 ± 2,6	10,6
3	3	3,8 ± 0,2	29,7 ± 0,0	19,7
5	0	7,2 ± 0,5	22,9 ± 0,5	12,0
5	1	6,5 ± 0,2	23,7 ± 0,3	19,7
5	2	5,6 ± 0,6	22,6 ± 0,2	19,1
5	3	6,9 ± 0,4	27,1 ± 0,2	19,8
7	0	10,4 ± 0,5	23,5 ± 1,3	15,5
7	1	9,2 ± 1,0	22,6 ± 0,5	17,1
7	2	8,1 ± 0,4	21,8 ± 0,1	18,0
7	3	10,1 ± 0,5	26,8 ± 0,3	21,6

appropriate for the secondary coats because draining is necessary to cover the increasing surface while the stability is mainly provided by the coarser grains of S_1 .

The average apparent porosity of the coarse-grained and graded CaZrO_3 investment casting moulds of $23,4 \pm 0,9\%$ and $23,2 \pm 1,5\%$, respectively, did not significantly differ. Presumably, there were two interactive effects on the apparent porosity. The higher maximum grain size of S_1 might increase the apparent porosity but it appears that the broader grain size distribution also led to a denser packing and therefore to a decrease of the apparent porosity. Nevertheless, the values are regarded as beneficial for the corrosion resistance as well as the thermal shock resistance and are in the typical range for refractories [9]. In addition, the relatively high apparent porosity combined with the large median pore diameter of the coarse-grained and the graded samples of $14,5 \pm 2,2\ \mu\text{m}$ and $16,6 \pm 3,6\ \mu\text{m}$, respectively, might contribute to an improved permeability of the mould. However, the pore size should not be too high in order to avoid a critical drop in strength [9].

After thermal shock with $650\ ^\circ\text{C}$ as the testing temperature, no samples with 3, 5 or 7 coats respectively were completely destroyed. The degree of impairment decreased with increasing shell thickness. All tested samples with 7 coats remained undamaged, whereas most samples with 3 coats were damaged to varying degrees. Some of these samples, however, exhibited small previous cracks from dewaxing. Regarding the samples with 5 coats, 80% of the samples were undamaged and only 20% were slightly damaged.

During investment casting, thermal shock occurs as rapid heating, not as cooling. Yet, rapid cooling is more critical in case of ceramic materials, so if the material withstands rapid cooling, it usually also withstands rapid heating [9].

Fig. 3 displays the bending force [N] of the different samples as a function of the shell thickness [mm]. Despite a certain variation, there is a linear increase of the bending force with increasing shell thickness both for the samples without and with thermal shock exposure. In case of the thermally shocked samples, the slope is smaller, which can be explained when the effect of the

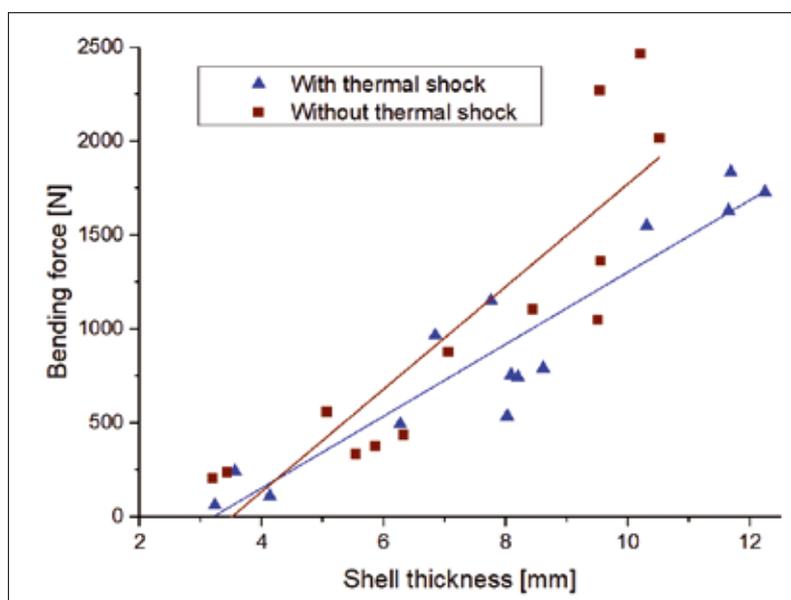


Fig. 3 Bending force as a function of shell thickness of CaZrO_3 investment casting moulds with and without thermal shock exposure

shell thickness is taken into account. In all cases, a minimum shell thickness is required to provide stability. Applying only 3 coats might not be sufficient.

However, with increasing shell thickness the difference between the samples with and without thermal shock exposure becomes

bigger, which is generally due to the drop in strength after thermal shock. This drop becomes more apparent as the shell thickness increases because the temperature gradient increases.

Therefore, the shell thickness should not be unnecessary high. In this case, a shell thick-

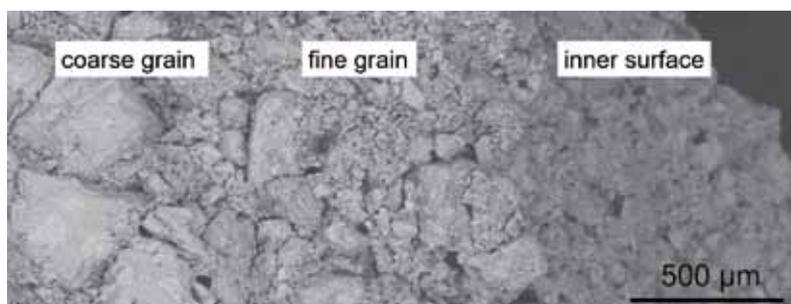


Fig. 4 Cross-section SEM image of an investment casting mould with 5 coats, thereof 2 front coats of $S_{0,5}$ (on the right there is the inner surface with a fine-grained structure, on the left the coarser grains of the secondary coats are clearly visible)

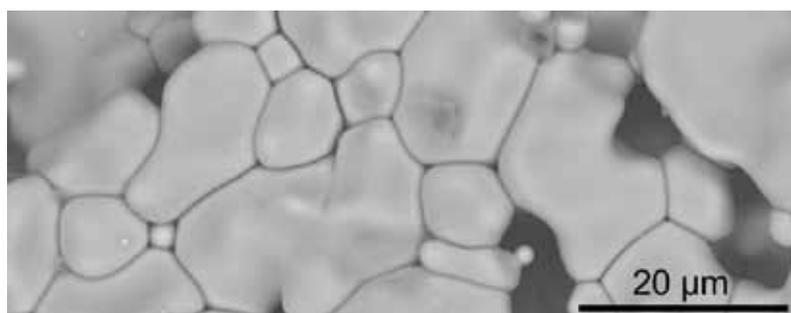


Fig. 5 SEM image of the inner surface of an investment casting mould with 5 coats, thereof 2 front coats of $S_{0,5}$ (the inner surface is even although there is a porous matrix)



Fig. 6 Cast part produced with investment mould with 3 coatings (the surface was smooth and shiny, suggesting that only a slight corrosion reaction occurred)

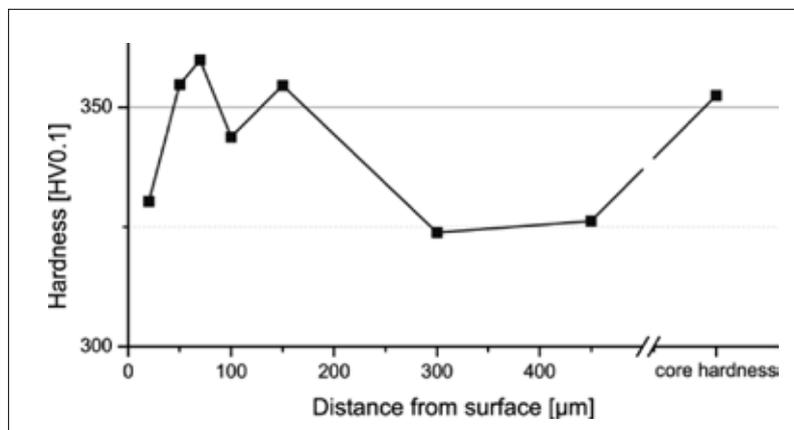


Fig. 7 Vickers microhardness profile of the Ti6Al4V cast part produced by melting in a cooled copper crucible and investment casting into a CaZrO₃ mould (there was only a negligible hardness increase compared to the starting material hardness of 312 HV0.1)

ness of 6–10 mm and about 5 coats of the slip system might be stable enough without generating a large temperature gradient. Moreover, the microstructure of a graded CaZrO₃ investment casting mould (2 fine-grained primary coats, 3 coarse-grained secondary coats) is presented in Fig. 4–5. Fig. 4 illustrates the build-up of the coats. Comparing the fine-grained structure of the inner surface and the fine-grained front coats and the coarse grains of the coarse-

grained coats, the contrast is remarkable. Nevertheless, an excellent bonding between the different coats was observed. The coarse grains are embedded in a fine-grained matrix. This composition contributed to a porous matrix and thus presumably to an improved permeability. Fig. 5 reveals the inner surface of the graded CaZrO₃ investment casting mould with 2 fine-grained primary coats. A uniform matrix of fine grains is apparent, which contains some

Tab. 3 Chemical analysis (GDOES) of the final Ti6Al4V cast part (data before/after casting)

Source	C [mass-%]	O [mass-%]	Zr [mass-%]
CaZrO ₃ moulds (this study)	0,02/0,03	0,14/0,15	<0,002/< 0,1
ASTM B348 specifications for Ti6Al4V	≤0,08	≤0,2	≤0,1
CaZrO ₃ crucibles by Schafföner et al. [4]	N/A	– /0,43	– /0,5

small pores. This combination of an even inner surface and open porosity is considered as beneficial for investment casting.

3.2 Investment casting

After investment casting using a coarse-grained CaZrO₃ investment casting mould with 3 coats, a cast part with a mainly smooth and shiny surface (Fig. 6) was obtained.

Due to the coarse grains of S₁, some rough parts are also visible. The mould withstood the thermal shock during casting and could be easily removed. As can be seen in Fig. 7, the surface hardness of the final cast part was 324–360 HV0.1.

Compared to the starting material hardness of 312 HV0.1, the hardness increased only slightly and no alpha case occurred. This is in line with the smooth and shiny appearance of the cast part. Kim et al. [1] reported similar low hardness values for silica-free CaZrO₃ moulds and much higher values for Al₂O₃ and ZrO₂ moulds in contact with Ti6Al4V. Consequently, it can be considered that only a slight corrosion reaction took place.

Tab. 3 presents the chemical analysis of the cast part by glow discharge optical emission spectroscopy (GDOES). The impurities measured by GDOES were lower than the ASTM B348 specifications and also lower than the data described by Schafföner et al. [4] for melting Ti6Al4V in CaZrO₃ crucibles, which was supported by the beneficial low hardness values. Yet, there are limitations regarding these comparisons.

Due to the shape, only the core of the cast part was chemically analysed, so the impurity contents on the surface might be slightly higher. Furthermore, it has to be considered that melting experiments in crucibles are characterized by longer contact times and melt movements during vacuum induction melting, which considerably increases corrosion [2].

4 Conclusions

- Generally, the slips were thixotropic and shear-thinning, which suggests sufficient stability and suitability for dip-coating. The coarse-grained slip also exhibited a stability-providing yield point.
- Silica-free coarse-grained and graded CaZrO₃ investment casting moulds with a

sufficient shell thickness were successfully produced.

- The high apparent porosity and the large median pore diameter might imply a good permeability.
- The microstructure investigated by SEM is characterized by a good bonding of coating layers and stucco as well as a porous matrix that results from coarse grains embedded in a fine-grained network. The use of the fine-grained slip for the first coating considerably improved the quality of the inner surface.
- The hardness increase on the surface of the final Ti6Al4V cast part was exceptionally low, suggesting that only a slight corrosion reaction occurred. These results indicate the high potential of silica-free CaZrO₃ investment casting moulds to replace conventional silica-containing investment casting moulds as a novel corrosion resistant material for

the investment casting of titanium alloy melts.

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