

CaZrO₃ REFRACTORIES FOR IMPROVED MELTING AND CASTING BEHAVIOUR OF TITANIUM ALLOYS

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ABSTRACT

For some applications in processing titanium and titanium alloys, ceramic materials were or are necessary if not indispensable. However, they are cursed with poor properties like bad thermal shock behaviour, high price, and insufficient chemical resistance. The latter leads to reduced lifetime of crucibles and decreased metal quality, elaborates postprocessing of casted goods or excludes applications. The present work investigated casted refractories based on a newly developed material: calcium zirconate (CaZrO₃). Cement-free, single phase crucibles and investment casting shells were successfully manufactured and tested. The material showed promising physical and thermomechanical properties. Melting tests as well as investment castings based on products made of the new material were examined. The results showed improved stability and good metal quality. Economically, the material might reduce post-processing cost due to a better surface of casted titanium alloy products. Additionally, it is less expensive compared to zirconia or yttria based materials and showed improved thermal and chemical stability advancing service time. It can enable more efficient technologies like vacuum induction melting in a hot crucible for processing titanium, its alloys and also other metallurgical applications.

INTRODUCTION

Melts of titanium and its alloys feature several challenges. It solves easily oxygen and therefore a refractory crucible material has to be stable, especially under vacuum conditions.¹ Recent studies showed the potential of fused calcium zirconate as refractory material for titanium alloy melts.²⁻⁴

Short time ago castables with cement binder were developed.³ However the fused material is not pure phase calcium zirconate due to the high temperature processing leading to calcia evaporation.⁵ Additionally, the used binder brought less stable phases into the material, too. A new approach for improved thermomechanical and corrosion behaviour is the usage of sintered monophasic calcium zirconate.⁶ Moreover the castable should be made without further phases for bonding.

Investment casting is a technology for the production of complex metal parts with a near net shape through casting. During the process, a ceramic refractory mould is filled with the hot, liquid metal melt. Beforehand, the mould has to be produced by the lost-wax process. After solidifying, the cast part and the ceramic mould are separated by breaking the shell or knocking it off, respectively.⁷ Figure 1 provides a schematic model of the ceramic coats produced by dip-coating and

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stuccoing on the wax pattern through which the mould is formed.

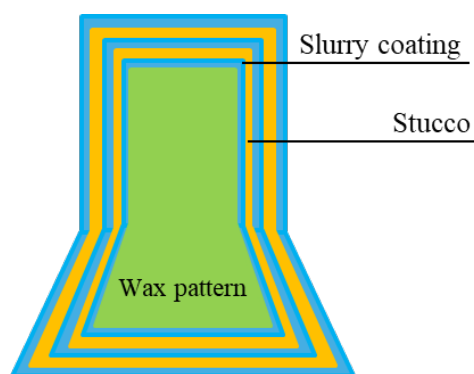


Fig. 1: Schematic illustration of the investment casting mould built up on the wax pattern with alternating slurry and stucco coatings.

In this paper the preparation of cement free calcium zirconate castables for titanium metallurgy is investigated. Essentially was the manufacturing of crucibles and investment casting moulds. The properties regarding refractoriness and mechanical behaviour were taken into account. Melting as well as casting tests were conducted with the titanium alloy Ti6Al4V. Afterwards, chemical and mechanical properties of the as casted parts were investigated.

EXPERIMENTAL

The starting material was solid state calcium zirconate recently described by Jahn et al. which was synthesised beforehand in an additional process step.⁶ Since larger amounts of material had to be produced, a scaled up adaption of the batch making procedure had to be used. For this purpose the raw materials were mixed within a laboratory mixer (Type EL5, Maschinenfabrik Gustav Eirich GmbH & Co KG, Hardheim, Germany). After mixing and shaping the material was fired at 1650 °C. Afterwards the synthesised CaZrO₃ was crushed into different grain size classes with jaw crushers (BB 50 and BB 200, RETSCH GmbH, Haan, Germany).

For the crucibles a vibration castable batch was composed using the model of Dinger and Funk.^{8,9} The maximum grain size was adapted to the dimensions of the respective crucibles. The

water content was about 8 wt.-% of the solids. As a dispersant Castament FS 20 (BASF Construction Solutions GmbH, Trostberg, Germany) and as a defoamer Contraspum K 1012 (Zschimmer & Schwarz GmbH & Co. KG, Lahnstein, Germany) were added. A conventional binder was used to prevent contamination with further substances after the firing process. For the preparation first the dry components were mixed for 2 min. Then the water and defoamer was added and all blended again for 5 min. Following the mixing of the castable, a plastic crucible mould was filled. At the same time the moulds were vibrated for about 5 min using a vibrating table (JMV 800/1000×800, JÖST GmbH & Co. KG, Dülmen, Germany) with 0.5 mm amplitude. After demoulding the samples and crucibles were dried at up to 110 °C for a total time of 24 h and then fired at 1650 °C.

For the thermomechanical and chemical investigations specimen bars of 25 x 25 x 150 mm³ were prepared and treated in the same way.

In a next step samples were prepared from the ceramic castable specimen for the phase analysis by X-ray diffraction (XRD) (X'Pert Pro MPD, PANalytical B.V., Almelo, Netherlands) and the true density measurement according to DIN 66137-2:2004 (AccuPyc II 1340, Micromeritics GmbH, Aachen, Germany). Therefore, sample material was milled in a vibratory disc mill. The pore size distribution was determined according to DIN 66133:1993 (Pascal 140-240/440, Thermo Fisher Scientific Inc., Waltham, USA), the apparent density according to DIN EN 993-17:1999. The cold modulus of rupture (CMOR) at ambient temperature was examined in accordance to the standard DIN EN 993-6:1995. For testing a servo hydraulic universal testing machine type TIRA (TIRAtest 28100, Tira GmbH, Schalkau, Germany) was used with a support distance of 125 mm and loading velocity of 0.15 N mm⁻² s⁻¹. The thermal shock resistance was investigated for one and five thermal shocks respectively. Therefore the specimens were heated for 30 min at 950 °C and then rapidly cooled down with pressured air with an overpressure of 0,1 MPa for five minutes. The residual strength after one and five cycles of

thermal shock was investigated according to the standard DIN EN 993 11:2008. Parallel to the thermal shock investigation the Young's Modulus at room temperature was determined in accordance with the ASTM E 1876 – 01 through impulse excitation method (RFDA-HTVP 1600, IMCE N. V., Genk, Belgium), using the analysing software RFDA MF v. 7.0.2. (IMCE N.V., Genk, Belgium).

A second usage of Calcium Zirconate was investigated regarding its potential usage as shell material for investment casting. Therefore, comparable slurries were prepared according to the study of Freitag et al.⁴ In contrast to that, no fused CaZrO_3 was used, yet the stoichiometric synthesised material. For the shell building wax patterns were dipped into the ceramic slurry and then stuccoed after draining of the excessive slip. Because of manual dip-coating, some slight variations of the coating thickness cannot be avoided. However, care was taken to ensure complete wetting during the dip coating, as the quality of the coats and their bonding in between are crucial for a good quality of the final product. For the stuccoing process CaZrO_3 material with a maximum diameter of 0.5 mm was used and sprinkled over the manually rotated, coated wax pattern using a sieve. Afterwards the sample was dried at 30 °C and a relative humidity of 60 % in a climate chamber. These steps of dipping, stuccoing, and drying were performed seven times. Afterwards the wax is removed in a dewaxing process through placing the mould in a hot furnace at 235 °C. Dewaxing was not performed in an autoclave because previous studies renounced that, too. It was pointed out that the moisture uptake in the humid atmosphere significantly impairs the green strength of the ceramic mould due to the softening of the binder in contact with steam.¹⁰ Sintering of the dewaxed shell moulds was conducted in air at 1200 °C and 1500 °C, respectively.

The investment casting experiments and metal analyses were performed at the Forschungsinstitut Edelmetalle + Metallchemie in Schwäbisch Gmünd. The most commonly used titanium alloy, Ti6Al4V, was used for the

experiments. Another reason was the comparability of the results of melting experiments with other crucibles. The alloy was melted in a casting machine (VTC 200 V/Ti, Indutherm Erwärmungsanlagen GmbH, Walzbachtal, Germany). The furnace chamber was evacuated and subsequently refilled with argon for the melting procedure. This furnace owns a tilting mechanism to pour the liquid metal into a copper mould to obtain metal samples melting reaction investigations and the CaZrO_3 investment casting moulds for casting interaction investigations. After the cooling, the solidified cast part was obtained by knocking off the ceramic shell. Afterwards, samples were prepared from the CaZrO_3 crucible as well as from the casted metal.

Subsequently, the quality of the casted metal specimen were investigated. Vickers microhardness profile was analysed according to DIN EN ISO 6507-1:2018 in order to evaluate the hardness increase. This is a result of alpha case formation. Thereby, a hard and brittle oxygen-enriched surface of the cast parts is built, originating from interaction of the ceramic shell in contact with the liquid metal during casting. This causes 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) and hot gas extraction in order to evaluate the impurities in the metal through corrosion reactions of the crucible as well as the shell mould. Additionally, metallographic sections were prepared and analysed.

RESULTS AND DISCUSSION

Physical and thermomechanical properties

In Figure 2 the XRD measurement of the slip casted specimen is given. Only one phase, the calcium zirconate was found. Neither free calcium oxide, zirconium dioxide nor calcia stabilised zirconia was identified. Also no other element oxides were found. Thus, the used binder system and the composition lead to no further phase transformation other than calcium zirconate.

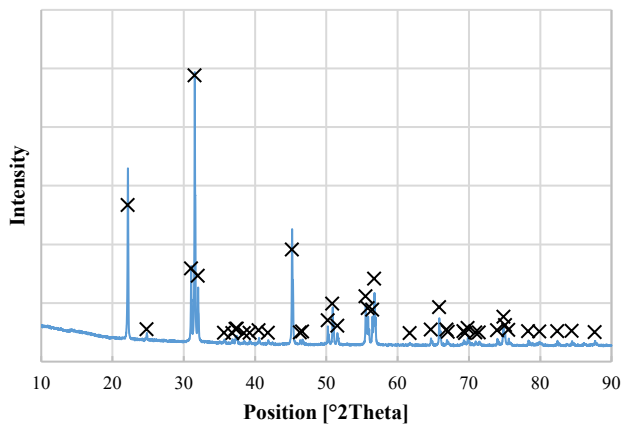


Fig. 2: XRD measurement slip casted material showing only CaZrO_3 , marked as crosses from the profile: PDF 01-076-2401.

In Table I all measured properties are displayed. The high porosity of about 21 % should be improved in future work, for example through adjusting the particle size distribution or changes in the firing regime. The reason for the porosity may also be the debinding processes while firing. Remarkable is the small median pore size, which could be beneficial for the corrosion resistance of the castable since infiltration by corrosive media is more unlikely for small pores. The thermomechanical investigation showed a surprisingly low CMOR. But the samples withstood the up to five thermal shocks without failure and also the application in the VIM showed no signs of thermal shock failure. The development of the Young's modulus as well as the CMOR therefore show that most structural changes occur after the first thermal shock. After that the properties might stabilise. Due to the coarser grains the structure was able to stop crack propagation. Of course a lower initial strength leads to fewer loss of strength after quenching.

Melting experiments

It was possible to use the CaZrO_3 crucibles up to 4 times. Although, this seemed only limited through the positioning of the crucible in the induction coil of the melting apparatus, since there is always a small residue of metal at the top of the crucible from pouring the metal into the copper mould.

Table I: Physical and thermomechanical properties of the castables.

Property	Note	Values including standard deviation
True density		4.75 g cm^{-3}
Apparent density		3.55 g cm^{-3}
Apparent porosity		$20.63 \pm 0.39 \%$
Mercury porosimetry	total porosity	21.53 %
	median pore size distribution by volume	$17.39 \mu\text{m}$
Young's modulus	Before TS	$20.86 \pm 1.06 \text{ GPa}$
	After 1 TS	$8.32 \pm 1.17 \text{ GPa}$
	After 3 TS	$4.55 \pm 0.69 \text{ GPa}$
	After 5 TS	$4.28 \pm 0.15 \text{ GPa}$
Relative loss of Young's modulus	After 1 TS	60.12 %
	After 3 TS	78.19 %
	After 5 TS	79.48 %
CMOR	Before TS	$5.32 \pm 0.44 \text{ MPa}$
	After 1 TS	$1.45 \pm 0.79 \text{ MPa}$
	After 5 TS	$1.15 \pm 0.81 \text{ MPa}$
Relative loss of CMOR	After 1 TS	72.74 %
	After 5 TS	78.38 %

Unfortunately, some melting experiments failed due to process control and led to incomplete casting. Yet, there was never a problem with the crucibles observed. The chemical analysis of the metal obtained from each showed, that it is possible to comply the ASTM standard for Ti6Al4V regarding impurities. Yet, there was no correlation of melting cycle and cleanliness of the melt. There was always some reaction of the liquid metal with the refractory crucible leading to measurable impurities in form of oxygen and zirconium but sometimes it was beyond the tolerated values and other times slightly above (see Table II). It is presumed that the melting parameter like time, maximum melt temperature, and stability of the atmosphere have a huge influence on the interactions. So far, it was hard to keep this parameter constant and as beneficial as possible.

Table II: Chemical analysis of the respective melt compared to the different melting cycles

Series	Oxygen content [wt.-%]	Zirconium content [wt.-%]
A I	0.2	0.0
A II	0.3	0.3
A III	0.2	0.1
B I	0.5	0.6
C I	0.3	0.2
C II	0.2	0.1

Investment casting experiments

The manufacturing of the investment casting shell with the CaZrO_3 slurry and stucco material worked very well. Dewaxing and sintering at the respective temperatures made no issues. In Figure 3 there are pictures of the shell mould after casting and the cast part after shell knock off. Some shells showed small cracks on the surface. However, this did not affect the quality of the casting, as they were on the outside. The surface of the cast had a bright metallic appearance. At first glance, this suggested that there was low reaction with the mould shell. Yet, SEM examination revealed a light-coloured rim which suggests the diffusion of zirconium into the metal surface and indications of gas bubble formation in the reaction zone (Figure 4). Partially porous structures are visible, which indicate the decomposition of CaZrO_3 (Figure 5). The EDX analyses of the reaction zone between metal and refractory showed fine CaZrO_3 inclusions present in the outer region. Partially, small precipitates of a Zr-silicide phase could be detected near the surface formed by impurities of silicon and zirconium. In the core, there is a basket-weave structure of alpha and beta titanium (Figure 6).

The variation of the sintering temperature of the shell moulds during preparation showed no significant difference in the hardness curves (see Figure 7) of the cast parts. The fluctuations within the hardness curves are in both cases due to the inhomogeneous metal microstructure consisting of titanium α and β structure. As cause of the hardening effects in both cases can be assumed to be the diffusion of oxygen.



Fig. 3: Images of the shell mould after casting (left) and of the cast part (right).

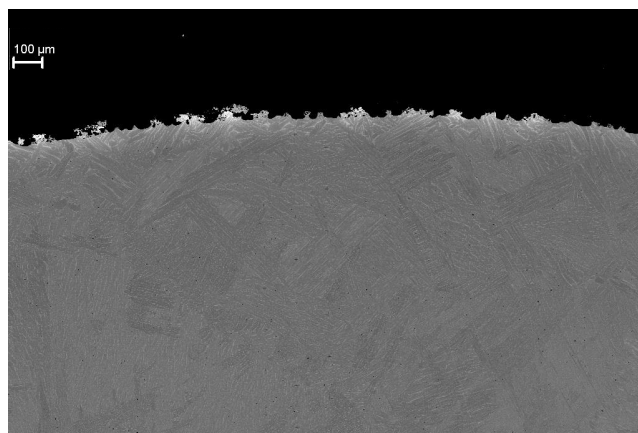


Fig. 4: SEM section image from the top of the cast part. Casting made with shell mould fired at 1500 °C.

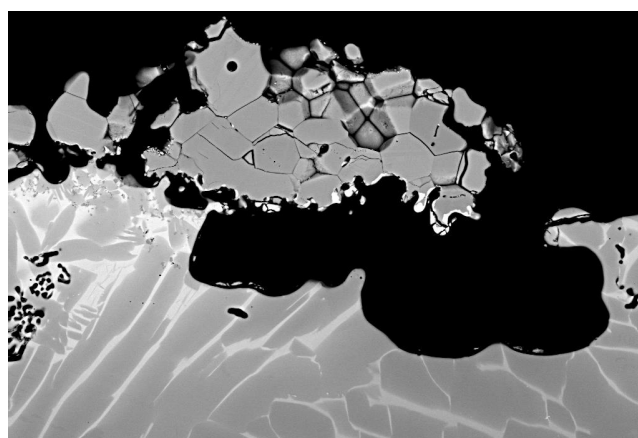


Fig. 5: SEM section image from the top of the cast part. Casting made with shell mould fired at 1500 °C.

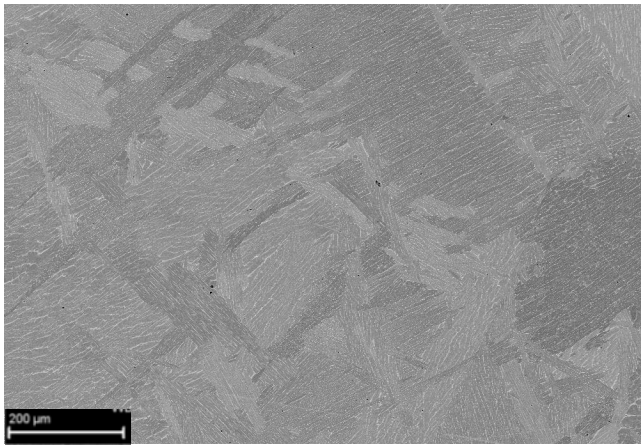


Fig. 6: SEM image of the metallic microstructure from the core of the cast part.

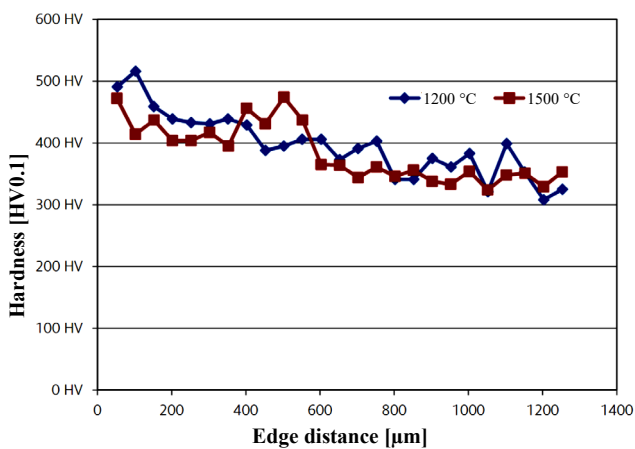


Fig. 7: Hardness measurements from edge to core of the cast parts for different sintering temperature of the investment casting mould.

CONCLUSION

In this study the preparation and properties of a calcium zirconate castable were investigated. Casted melting crucibles as well as slurries for investment casting were successfully prepared without yielding in other phases than CaZrO_3 .

It was observed that it is possible to melt the market dominant titanium alloy Ti6Al4V in a refractory crucible made of CaZrO_3 and still meet the typical specifications regarding its chemical purity. The repeated usability of the crucible for melting processes was remarkable. Yet, the process stability of the melting procedure has to be improved. The diffusion of zirconium and oxygen into the metal is the dominant corrosion result.

Investment casting mould made of CaZrO_3 were prepared through conventional dip coating

and stuccoing. The casted samples showed low alpha case formation. Yet, a reaction of the mould surface and the molten metal could not be prevented. The higher sintering temperature of 1500 °C of the mould during production showed slightly improved stability with lower oxygen concentration on the surface of the casting in contrast to those fired at 1200 °C but no difference in the surface hardening effect.

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REFERENCES

1. A. Kostov, B. Friedrich. "Predicting thermodynamic stability of crucible oxides in molten titanium and titanium alloys", *Comput. Mater. Sci.*, 38 [2] pp 374–85 (2006).
2. S. Schafföner, C. G. Aneziris, H. Berek, B. Rotmann, B. Friedrich. "Investigating the corrosion resistance of calcium zirconate in contact with titanium alloy melts", *J. Eur. Ceram. Soc.*, 35 [1] pp 259–66 (2015).
3. S. Schafföner, T. Qin, J. Fruhstorfer, C. Jahn, G. Schmidt, et al. "Refractory castables for titanium metallurgy based on calcium zirconate", *Mater. Des.*, 148] pp 78–86 (2018).
4. L. Freitag, S. Schafföner, N. Lippert, C. Faßauer, C. G. Aneziris, et al. "Silica-free investment casting molds based on calcium zirconate", *Ceram. Int.*, 43 [9] pp 6807–14 (2017).
5. S. Schafföner, C. G. Aneziris, H. Berek, J. Hubálková, and A. Priese. „Fused calcium

-
- zirconate for refractory applications“, J. Eur. Ceram. Soc., 33 [15-16] pp 3411–18 (2013).
6. C. Jahn, S. Schafföner, C. Ode, H. Jansen, C. G. Aneziris. "Investigation of calcium zirconate formation by sintering zirconium dioxide with calcium hydroxide", *Ceram. Int.*, 44 [10] pp 11274–81 (2018).
 7. P.R. Beeley, R.F. Smart (Eds.), "Investment Casting", The Institute of Materials, London (1995).
 8. D. R. Dinger, J. E. Funk, "Particle Packing III: Discrete versus continuous particle sizes", *Interceram*, 41 [5] pp 332–4 (1992).
 9. D. R. Dinger, J. E. Funk, "Particle Packing IV: Computer Modelling of Particle Packing Phenomena", *Interceram*, 42 [3] pp 150–2 (1993).
 10. C. Yuan, S. Jones, S. Blackburn, "The influence of autoclave steam on polymer and organic fibre modified ceramic shells", *J. Eur. Ceram. Soc.* 25 pp 1081–7(2005)