

Refractory castables for titanium metallurgy based on calcium zirconate

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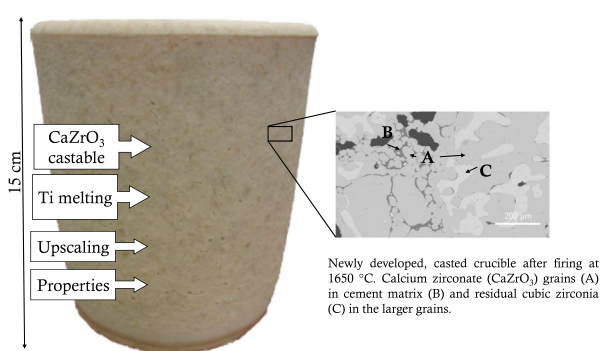
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HIGHLIGHTS

- Refractory castables based on calcium zirconate for the metallurgy of titanium alloys are presented for the first time.
- Calcium aluminate binders provide a fast processing and sufficient refractoriness for medium-sized melting crucibles.
- The whole range of the development of the castables including microstructural, mechanical and thermomechanical characterization is described.
- The developed castables using high melting perovskites are an important step for the industrial implementation of refractories for titanium metallurgy.

GRAPHICAL ABSTRACT



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ABSTRACT

Calcium zirconate (CaZrO₃) is a promising refractory material to melt titanium alloys. Therefore the present study investigated refractory castables based on CaZrO₃ to allow an upscaling to larger melting crucibles and refractory linings. The study first included the processing optimization of the refractory castable containing calcium aluminate cement using a full factorial experimental design. Then the physical, chemical, mechanical and thermomechanical properties that determine the practical application of the castable were analyzed. The properties were generally similar to the ones of uniaxially pressed refractories based on CaZrO₃. Nevertheless, the matrix containing calcium aluminates caused a pronounced sintering shrinkage leading to a smaller apparent porosity and a lower refractoriness compared to uniaxially pressed refractories. Finally, melting crucibles with an inner volume of 900 ml were successfully manufactured. Thus, this study provides an effective framework for the further development of large CaZrO₃ refractories.

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1. Introduction

Calcium zirconate (CaZrO₃) is a stoichiometric phase with a perovskite crystal structure in the pseudobinary CaO–ZrO₂ system. It has a high melting point of 2368 °C and a high chemical stability

was repeatedly reported [1–3]. Thus, calcium zirconate and calcium zirconate containing composites were often investigated for high temperature applications [4]. For example, doped calcium zirconate was studied as a sensor material for aluminum [5] and steel melts [6]. Calcium zirconate was also added to magnesia bricks for cement rotary kilns forming a composite refractory material [7–9].

Recently, electro fusion of coarse grained calcium zirconate qualities for refractory applications was reported. This refractory

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raw material was then used for melting crucibles for titanium metallurgy [4]. In further studies these crucibles were investigated regarding their corrosion resistance in contact with Ti6Al4V [10] and titanium aluminide (TiAl) melts [11] during vacuum induction melting. Moreover, using the electro fused raw material, silica-free investment casting molds were manufactured, which were then tested in contact with Ti6Al4V melts [12].

However, some calcium evaporated during the electro fusion production process, which caused the formation of cubic ZrO_2 ($c-ZrO_2$) impurities in the raw material [13]. It was later observed that these $c-ZrO_2$ impurities were predominantly dissolved by Ti6Al4V melts. Thus, the corrosion of the $CaZrO_3$ crucibles in contact with Ti6Al4V was significantly reduced by adding calcium hydroxide ($Ca(OH)_2$) to the crucible mixture. During firing the calcium hydroxide decomposed to calcium oxide and water. The calcium oxide reacted then further with the residual $c-ZrO_2$ impurities from the fused calcium zirconate raw material [10]. Although the apparent porosity increased due to the evaporation of the water, the melt corrosion was reduced to very promising values [10]. The low corrosion tendency of $CaZrO_3$ in contact with Ti6Al4V melts was confirmed during casting experiments using the newly developed $CaZrO_3$ investment casting molds [12].

All melting crucibles in these previous studies were produced by cold isostatic pressing (CIP). Yet, CIP is time consuming, needs a special press and is labor intensive. Moreover, large components are difficult to produce by CIP [14–16]. By contrast, larger melting crucibles and melting furnace linings are often prepared using refractory castables [17–19]. Thus, due to their cheaper price and generally easier installation, monolithic refractories including castables have an increasing share of total refractory consumption compared to pressed refractory products [18, 20].

Refractory castables are prepared by mixing an appropriate amount of coarse and fine grained particle fractions together with a binder such as calcium aluminate cements and water as the usual dispersing medium. Furthermore, several additives such as, for example, dispersing agents, defoamers and micro silica are often added to improve the processing of the castables and the properties after firing [20, 21].

However, although calcium zirconate is a promising refractory material for titanium metallurgy, calcium zirconate castables remain unstudied. Yet, castables of calcium zirconate would allow the much easier preparation and upscaling of melting crucibles. Thus, the aim of the present study is to prepare and evaluate the properties of refractory castables based on calcium zirconate using calcium aluminate cement as a typical refractory binder.

2. Method

The current study first involved the optimized processing of refractory castables based on calcium zirconate ($CaZrO_3$) using calcium aluminate cement as a binder. Secondly, the optimized castable was investigated regarding its physical, mechanical and thermomechanical properties together with its microstructure.

2.1. Materials and experimental design

In all experiments a recently presented electro fused $CaZrO_3$ refractory raw material (Imerys Fused Minerals Murg GmbH, Germany) was used [4, 13]. During the electro fusion production process of the $CaZrO_3$ raw material some calcium evaporated, which caused the formation cubic zirconia ($c-ZrO_2$) as a second phase. To adjust the stoichiometric composition, calcium carbonate ($CaCO_3$, 99%, Carl Roth GmbH & Co. KG, Germany) was added in different amounts during the batch preparation. Monoclinic zirconia ($m-ZrO_2$, CS02, Saint-Gobain ZirPro, France) was also added to ensure a similar particle size distribution with varying $CaCO_3$ contents. Furthermore, a calcium aluminate

cement (Secar 71, Kerneos S.A., France) was applied because calcium aluminate cements (CAC) are refractory binders for castables which generally provide a high refractoriness, easy processing and sufficient green strength. The calcium aluminate cement consisted mainly of $CaAl_2O_4$, while it also contained minor amounts of $CaAl_4O_7$ [22, 23]. The used calcium aluminate cement was selected because it has a low amount of impurities [24]. These impurities should be avoided since they could not only impair the refractoriness but also the corrosion resistance for later applications in titanium metallurgy [24, 25]. Finally, a polymeric dispersant (Castament FS 20, BASF SE, Germany) and a defoamer (Contraspum K 1012, Zschimmer & Schwarz GmbH & Co. KG, Germany) were added.

The chemical compositions of the mineral raw materials were determined by semi-quantitative wavelength-dispersive X-ray fluorescence spectroscopy (WDXRF, OPTIM'X, Thermo Fisher Scientific Inc., USA). The chemical compositions are given in Table 1.

All batches were designed according to a recently proposed modified Andreason particle size distribution model [18], which is given in Eq. (1).

$$CPFT = \left(\frac{d}{d_{max}} \right)^{\left(n_{min} + d \cdot \frac{n_{max} - n_{min}}{d_{max}} \right)} \quad (1)$$

In this particle size distribution model CPFT is the cumulative percentage of particles finer than a particle diameter d , d_{max} is the maximum particle diameter of the particle size distribution, n_{max} is the distribution modulus at d_{max} , whereas n_{min} is the distribution modulus at an infinitesimal particle size. For the calculation of the batches, the maximum particle diameter was always 3.15 mm, while the distribution moduli were set at $n_{max} = 0.8$ and $n_{min} = 0.28$, respectively. These distribution moduli were previously determined as highly beneficial for refractory castables to ensure a high flowability during vibration together with a low porosity [18]. The batch composition of the dry raw materials, which was used for the processing optimization, is given in Table 2.

To optimize the processing of the castables, a 2^3 full factorial experimental design was applied. In this full factorial experimental design, the effect of the added water amount (X_1), the added dispersant amount (X_2) and of the applied amplitude during the compaction by vibration (X_3) were investigated because these factors are generally considered as crucial for the processing of concretes including refractory castables [18, 26]. All three factors were varied on two levels, as is given in Table 3. The levels of the processing factors (X_1 , X_2 , X_3) were investigated in a range similar to other refractory castables [18, 19].

2.2. Castable preparation

To prepare the castable samples for further investigations, the same procedure was applied in all experiments. First 3 kg of the dry mass according to Table 2 and the dispersant according to Table 3 were mixed for 2 min using a concrete mixer (ToniMIX, Toni Technik Baustoffprüfsysteme GmbH, Germany). Then the water was added in three steps. Between these three water additions, the concrete mixer was carefully scrapped to ensure a homogeneous mixture. The water admixture was completed after 10 min.

Immediately after mixing, the prepared castable was filled into steel molds. Next, the molds were vibrated for 8.5 min using a vibrating table (JMV 800/1000×800, JÖST GmbH & Co. KG, Germany). Prior to filling the molds, the molds were lubricated with a small amount of standard machine oil. The size of the molds depended on the further investigations and is specified below.

The specimens were cured for 4 h before they were demolded. The curing time was sufficient because the samples already had a high green strength, which can be explained by a fast hydration

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