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CALCIUM ZIRCONATE REFRACTORIES FOR TITANIUM MELTS

S. Schafföner[1,*], B. Rotmann[2], H. Berek[1], B. Friedrich[2], C.G. Aneziris[1]
[1] Institute of Ceramic, Glass and Construction Materials, TU Bergakademie Freiberg, Germany
[2] IME Process Metallurgy and Metal Recycling, RWTH Aachen, Germany

ABSTRACT

This contribution examines the corrosion of coarse grain calcium zirconate as a crucible material for titanium melts. The corrosion was investigated by SEM in combination with EDX and electron back scatter diffractin (EBSD). Thereby the EBSD offered the possibility of detecting the phases formed of titanium in contact with calcium zirconate.

It was found that the dissolution of the refractory material was mainly controlled by the diffusion of zirconium and oxygen towards the titanium melt.

This indicates that there is a possibility of melting titanium in a calcium zirconate crucible if the infiltration and thereby the corrosion can be limited.

INTRODUCTION

Titanium and titanium alloys possess a remarkable combination of material properties. They have a high strength, low density, excellent corrosion resistance and show a superior biocompatibilty.[1] The energy intensive production by the Kroll process and inefficient recycling cause the high cost and therefore limit the wider application of titanium and titanium alloys.

Numerous investigations examined alternative production and recycling routes to generate cheaper titanium. Nowadays titanium alloys are still melted in a water-cooled copper crucible despite the considerable research effort to replace the vacuum arc remelting (VAR) process in the cold copper crucible by vacuum induction melting in ceramic crucibles.[2] The main obstacle for the use of ceramic crucibles is the high reactivity of titanium based alloys with oxygen, carbon and nitrogen of the crucible materials. Most authors have focused on yttria or calcia as refractory materials.[2] However, yttria has the disadvantage of a high price and calcia tends to react with water from the atmosphere to form calcium hydroxide. This reaction leads to a large volume expansion and the desintegration of the refractory material.[2]

Calcium zirconate ($CaZrO_3$) as an alternative refractory for titanium melts attracted much attentation during the last years[2] It is the only stable substance of the equimolar ratio in the pseudobinary phase diagram of of CaO and ZrO_2. The melting point of 2368 °C is very high and the orthorhombic phase is stable up to 1959 °C.[3] Besides, calcia stabilized zirconia was tested in contact with titanium in solid state and the interfacial reaction was investigated with scanning electron microscopy (SEM) and transmission electron microscopy (TEM).[4] There was a considerable diffusion of O and Zr towards the titanium melt with very limited solubility of Ca in Ti. What is more $CaZrO_3$ was formed at the interface to the titanium and in the titanium melt. Therefore it was concluded that $CaZrO_3$ is a stable phase in contact with titanium alloys and a potential refractory material.[4] Kim et al. used $CaZr0_3$ molds in contact with Ti and compared the performance to other ceramic molds. They concluded that $CaZrO_3$ had a similar performance like CaO. In contrast to CaO calcium zirconate refractories have the advantage of being inert to hydration.

Although calcium zirconate seems to be a promising crucible material for titanium melts there remains a need of clarification of the corrosion mechanism in contact with titanium melts.

One of the key techniques to study the corrosion of refractories is the investigation with SEM in combination with energy dispersive X-ray spectroscopy (EDX). From the results of the EDX element distribution conclusions on the stochiometry and phase distribution are drawn. However, the interpretation of the EDX analysis is still difficult because different phasees or phases with similar stoichiometry can not be distinguished. A further combination of EDX with electron backscatter diffraction (EBSD) offers the possibility of detecting the phase geometry and much better understanding of the corrosion of refractories can be achieved. Although the usefulness of EBSD analysis for ceramics is widely recognized, there remains the main obstacle of the difficult sample preparation.[5]

This paper focuses on the corrosion of calcium zirconate in contact with molten titanium and the subsequent investigation of the crucible corrosion with EBSD. The aim of this study is the understanding of the corrosion mechanism in order to improve the crucible performance to finally produce cheaper titanium and titanium alloys.

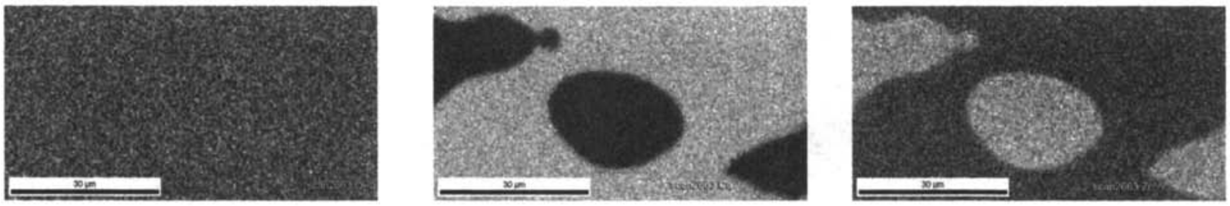
EXPERIMENTAL

This study investigates laboratory crucibles of calcium zirconate in contact with titanium melts and subsequently examines the corrosion of the crucibles with SEM in combination with EDX and EBSD. The materials used in this study were fused $CaZrO_3$ provided by Treibacher Schleifmittel which was grinded into four grain sizes with a maximum grain size of 3 mm. The crucibles were prepared by mixing a compositon according to the Alfred's model with $q = 0.37$.[6] The samples were first dry and then mixed with a PVA binder (PAF 60, Zschimmer & Schwarz) and subsequently pressed by uniaxial pressing to cylinders of 50 mm x 50 mm with 150 MPa. The samples were dried at 80 °C and at 110 °C for 8 h each. Then the samples were fired with a heating rate of 2 h at 1650 °C for 6 hour in air. After cooling a hole with a diameter of 35 mm and 20 mm depth was carefully drilled into the zylinders. The small laboratory crucibles were then placed in a vacuum induction melting (VIM) furnace with a graphite susceptor in order to provide enough heating. The crucible and the titanium were heated carefully to a temperature of $\approx$ 1740 °C and held at this temperature for about 15 min.

After cooling down the crucibles were cut. Unaffacted material as well as the interface between the crucibles and the titanium melt was investigated in an conventional W-cathode SEM Philips XL30 equipped with an EBSD system TSL and an EDX system Genesis in connection with an Apollo10 detector from Edax/Ametek. The samples were prepared by 20 h vibration polishing in a BUEHLER VibroMet2 using the Buehler suspension MasterMet2 (0.02 µm SiO_2). All samples were coated with PtPd20-layers in the nm range using a Cressington 208 HR sputter coater.

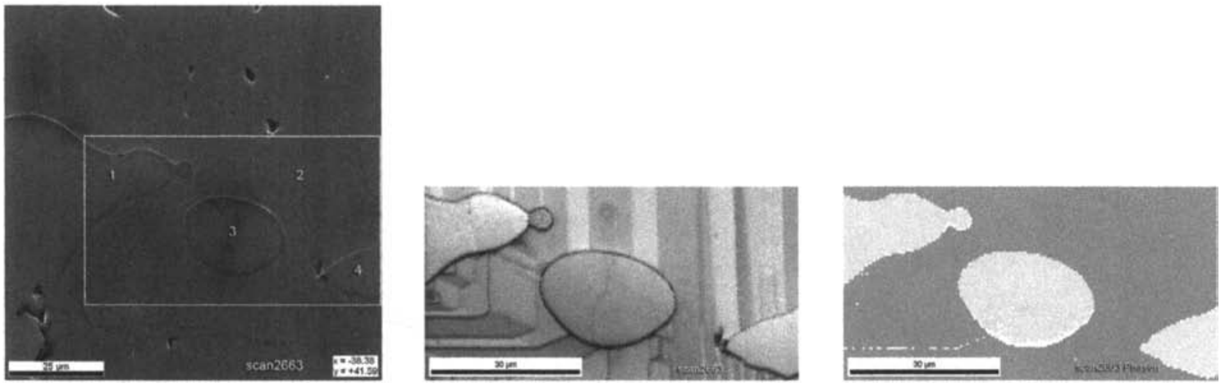
RESULTS

In this study fused $CaZrO_3$ zirconate was processed to small laboratory crucibles for titanium melts. The following section focuses on the investigation of the $CaZrO_3$ material



(a) Oxygen (b) Calcium (c) Zirconium

Fig. 1: Element distribution detected with SEM/EDX of a $CaZrO_3$ section



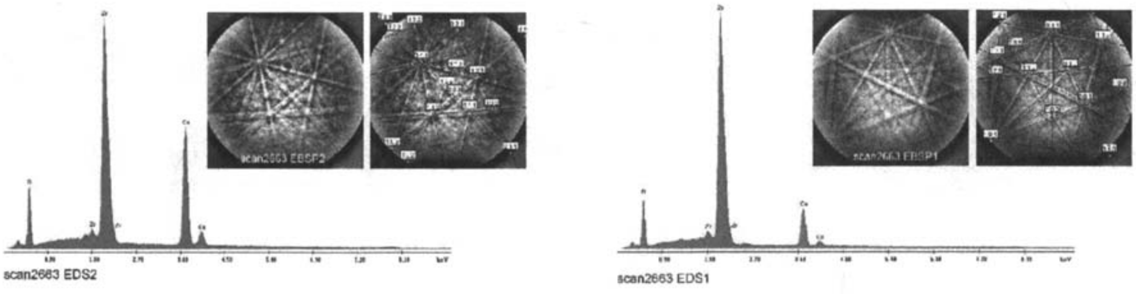
(a) SE image (b) Band contrast (c) Phase distribution

Fig. 2: SE image, band contrast and EBSD image of a $CaZrO_3$ section

before firing and after use in a vacuum induction melting furnace with and without the contact to the titanium melt by SEM in combination with EDX/EBSD to understand the corrosion mechanism to show a possibilty of using ceramic crucibles for titanium melts.

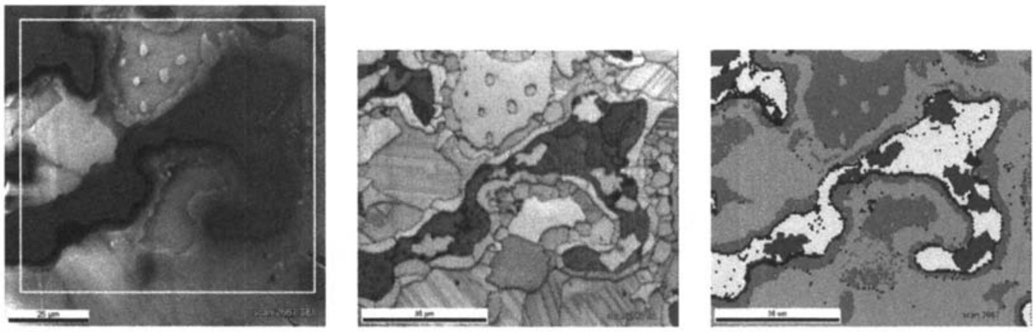
The XRD analysis of the $CaZrO_3$ raw material revealed a mixture of $CaZrO_3$ and oxygen deficient c$-ZrO_2$. In data not shown the stochiometry of the $CaZrO_3$ material was also examined by EDX as a raw material, as sintered and after use in the VIM furnace. Thereby a significant oxygen deficiency was detected in the raw material and after use in the VIM furnace. $CaZrO_3$ and c$-ZrO_2$ mixtures are widely recognized as oxygen ion conductors.[7] Therefore, the oxygen deficiency most probably results from the reducing atmosphere during the production of the $CaZrO_3$ raw material in the electric arc furnace and during use in the VIM furnace, respectively. In Fig. 1 the EDX element mapping of the $CaZrO_3$ material after use in the VIM furnace without titanium contact can be seen. The oxygen is homogenously distributed, whereas there is a distinct variation in the calcium and zirconium content.

Fig. 2(a) shows an SE image of a $CaZrO_3$ material section; Fig. 2(b) provides the corrosponding band contrast of the EBSD analysis. At black areas no detection of phases is possible. Main reasons for these black areas are preparation defects, grain boundaries, or amophous phases. The band contrast indicates a high image quality for the $CaZrO_3$



(a) $CaZrO_3$ (b) $c-ZrO_2$

Fig. 3: Kikuchi pattern and EDX spectra of raw material



(a) SE image (b) Band contrast (c) Phase distribution

Fig. 4: $CaZrO_3$ in contact with Ti (red: $c-ZrO_2$, green: $CaZrO_3$, yellow: α-Ti, blue: β-Ti)

material. Fig. 2(c) illustrates the homogenous phase distribution of the $c-ZrO_2$ in a $CaZrO_3$ matrix, being consistent with the results of the XRD analysis.

In Fig. 3 the Kikuchi pattern together with the EDX element analysis is shown. The high quality of the Kikuchi pattern proves the adequate sample preparation for the EBSD analysis. The crucible showed considerable infiltration of 12 mm at the bottom of the crucible after melting. The crucibles had an open porosity of 14.2 %. The control of the temperature in the small crucibles was difficult and possible overheating occured. Future work will use larger crucibles to improve the temperature control and will also further reduce the overall total porosity and lower the pore size to minimize infiltration.

Fig. 4(a) provides a secondary electron image of the $CaZrO_3$ -Ti interface. A clear distinction between the refractory, the interfacial reaction zone and the infiltrated melt can be observed. The band contrast shown in Fig. 4(b) provides a gray scale value ranging from black for the band contrast zero and white for the maximal band contrast and it indicates the quality of the diffraction patterns. Besides the defects mentioned above pores and cracks can

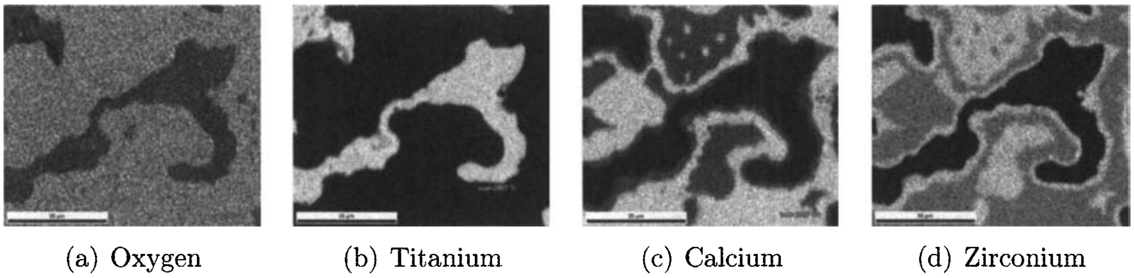

(a) Oxygen (b) Titanium (c) Calcium (d) Zirconium

Fig. 5: Element distribution of $CaZrO_3$ in contact with Ti

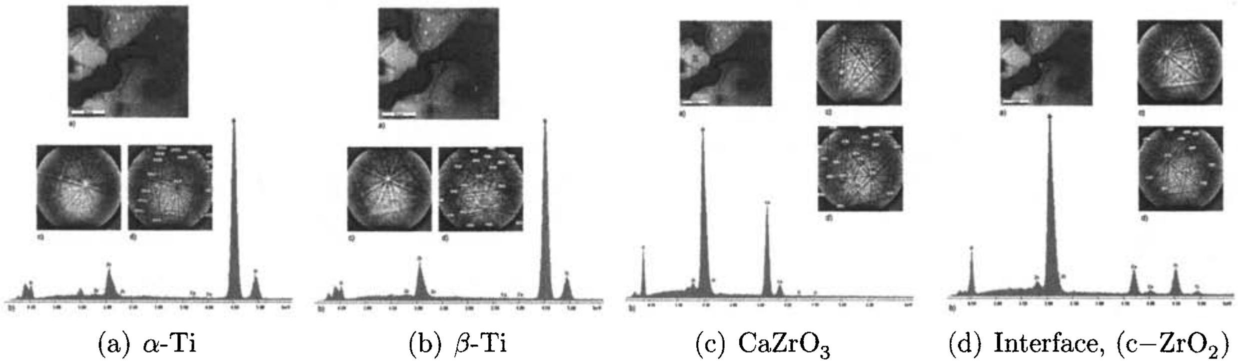

(a) α-Ti (b) β-Ti (c) $CaZrO_3$ (d) Interface, ($c-ZrO_2$)

Fig. 6: Kikuchi pattern of phases in contact with Ti

also be detected.

Fig. 4(c) summarises the phases indicated with EBSD. The red phase of $c-ZrO_2$ seems to be the reacting phase with the titanium melt. After the $c-ZrO_2$ apparently follows a $CaZrO_3$ layer. Whether the diffusion of the zirconium and oxygen stabilizes a $CaZrO_3$ phase as was stated previously[4] will be discussed in future work. Nevertheless the reported phase Ti_2ZrO_2[4] which was formed in contact of calcia stabilized zirconia and titanium in solid state was not detected in the present study.

The following EDX mappings in Fig. 5 illustrate the distribution of oxygen, titanium, calcium and zirconium. The EDX mapping of the oxygen in Fig. 5(a) indicates an oxygen distribution all over the picture, especially also in the titanium area. From the titanium EDX mapping in Fig. 5(b) a distinct difference of the titanium concentration between the refractory material and the titanium melt can be observed and there is evidence that no titanium diffused towards the $CaZrO_3$ material. Comparing Fig. 5(c) and Fig. 5(d) shows the difference in the calcium and zirconium distribution. At the interface of the titanium and the crucible material the zirconium concentration is higher than the calcium concentration. Two possible reasons could be assumed for this observation. First it could be possible that calcium was reduced and subsequently evaporated due to the low boiling point of calcium of 1484 °C.[8] Notwithstanding, no calcium or calcium oxide dust was observed after the experiment. However, the second possibility of a diffusion of zirconium and oxygen towards titanium seems to be more likely. Zirconium and oxygen are highly soluble in the titanium whereas calcium is not as soluble.[4]

Fig. 6 shows the typical compositions of the observed phases. At the marked points an EDX spectrum and an EBSD diffraction pattern are recorded and evaluated. The Fig. 6(a) and Fig. 6(b) show an α-Ti and β-Ti with an evident Zr peak. This result further confirms a diffusion of zirconium and probably of oxygen towards the titanium melt. The L-level X-ray line of titanium overlaps the indicated oxygen peak in the spectrum and therefore a quantitative statement would not be accurate. The areas marked in Fig. 6(c) and Fig. 6(d) were indicated as $CaZrO_3$ and $c-ZrO_2$, respectively.

CONCLUSIONS

This study investigated the corrosion of calcium zirconate refractories in contact with molten titanium in an SEM in combination with EDX/EBSD. The sample preparation was of very good quality and therefore an indexing by EBSD was possible. It is believed that EBSD will significantly expand the examining possibilities of refractory corrosion by metal and slag melts.

The material used was a fused calcium zirconate with a maximum grain size of 3 mm. The raw material was indicated as a mixture of $CaZrO_3$ and $c-ZrO_2$. It was shown that corrosion was mainly controlled by the diffusion of zirconium and probably oxygen towards the titanium melt. Future work will address the reduction of porosity of the crucibles and the examination how the two different phases ($CaZrO_3$ and $c-ZrO_2$) corrode in contact with titanium melts.

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