Investigating the corrosion resistance of calcium zirconate in contact with titanium alloy melts

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Abstract

This study investigated the corrosion behavior of calcium zirconate crucibles during vacuum induction melting of Ti–6Al–4V. Due to its production method the fused calcium zirconate raw material contained a significant amount of cubic zirconia as a second phase. Thus, the raw material composition was adjusted by adding calcium hydroxide as a calcia precursor during the crucible production. Crucibles with four different compositions were tested in contact with Ti–6Al–4V melts. The corroded crucibles were investigated by SEM in combination with EDX and EBSD, whereas a dissolution of the zirconia phase by the alloy melt was observed. The calcium zirconate phase however remained unaffected. This result compared well with the determined zirconium and oxygen contamination of the melts, which decreased substantially with a higher calcium zirconate content of the crucibles. An overstoichiometric composition in terms of calcia, however, caused the evaporation of calcia and should therefore be avoided.
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Keywords: Refractories; Calcium zirconate; Vacuum induction melting; Titanium alloy; Electron backscatter diffraction

1. Introduction

Titanium and titanium alloys combine several attractive properties such as low density, high strength, high corrosion resistance as well as creep resistance up to temperatures of about 550 °C. Furthermore, titanium and many titanium alloys exhibit a remarkable biocompatibility.[1,2]

Despite these excellent properties and considerable research effort regarding their physical metallurgy, the wider application of titanium and titanium alloys is inhibited by their high cost mainly caused by the extraction along the Kroll process chain with subsequent refining.[1,3]

Vacuum induction melting (VIM) in a refractory crucible with subsequent refining by pressure electroslag remelting (PESR) was recently proposed as a possible alternative for efficient recycling as well as for a low cost production of titanium alloys.[4,5]

The advantage of VIM are fast homogenizing of the melt due to electromagnetic stirring and the potential to add deoxidizing agents,[6,7] thus the possibility to use inhomogeneous and contaminated feed material.[4,8] Another advantage is the much lower energy demand for VIM compared to the conventional induction skull melting (ISM) in a water cooled copper crucible.[9]

However, the melts of titanium and its alloys react heavily with oxygen, nitrogen, and carbon impairing properties such as ductility accompanied with increasing hardness and strength.[1,3,10] Most studies investigating the melting of titanium in refractory crucibles favored oxide ceramics, mainly due to their low Gibbs energy.[11–14]

Titanium solves more than 14.5 wt% of oxygen even in the solid state.[1] Therefore, a considered crucible material has to be thermodynamically stable without dissolving into the melt.[9,11,15,16] Moreover, the refractory material has to withstand the highly reducing conditions at the melting and superheating temperature, because a decomposition of the refractory may lead to boiling at the liquid metal/solid refractory interface.[9,17] A rapid oxygen pickup by the melt follows and causes a kinetically fast dissolution of the refractory material.[3,9]

During VIM in metal oxide crucibles the refractory material is only heated by conduction and radiation. Reaching the melting point, the contact area and thus the heat conduction between the melt and the refractory material increases rapidly, often causing cracking. A third requirement on crucibles in VIM is thus a high thermal shock resistance to allow fast heating rates and repeated use of the crucibles.[18,13,19,15]

During the last decades several refractory materials were tested in contact with various titanium alloy melts, including yttria, calcia, zirconia and alumina.[11,12,14,20,21] However, none of these materials proved to be totally inert against titanium and titanium alloy melts.

Calcium zirconate, despite its high melting point of 2368 °C,[22] has only rarely been considered as a refractory material. Calcium zirconate is the stoichiometric phase in the pseudobinary CaO–ZrO$_2$ phase diagram and has to be synthesized because it is very seldom in nature.[23] During the synthesis the stoichiometric composition has to be tightly controlled because even a small over-stoichiometry in terms of calcia or zirconia results in the formation of free lime or cubic zirconia as a second phase.[22,24,25]

The thermal expansion coefficient of calcium zirconate with 10.45×10^{-6} K^{-1} in the temperature range of 25–1000 °C[24] is much lower compared to calcia (14.24×10^{-6} K^{-1}).[26] Moreover, calcium zirconate is inert toward water and the vapor pressure of calcium over calcium zirconate at about 1700 °C was calculated as about two orders of magnitude lower than over calcia.[27,28]

In recent years calcium zirconate was evaluated as a mold material in contact with commercially pure titanium (cp-Ti), Ti–6Al–4V, and γ-TiAl alloys showing a similar low corrosion like calcia.[29] Li et al.[30] tested calcium zirconate refractories with titania as a sintering aid in contact with Ti–6Al–4V and NiTi alloys. The corrosion behavior was evaluated as very promising, whereas the interfacial corrosion layer in contact with Ti–6Al–4V was about 300 μm thick. However, interface reactions between the metal and calcium zirconate based refractories taking into account the refractory composition or possible melt contamination remain unstudied.

In the previous study Schafföner et al.[24] described crucibles made of fused calcium zirconate material. The raw material showed a considerable amount of cubic zirconia, which was attributed to the evaporation of calcia during the electric arc melting of the raw material. The present study aims at investigating the corrosion behavior of these crucibles against Ti–6Al–4V melts and also addresses the improvement of crucible performance by adjusting the crucible composition. For that purpose especially the analysis of the phase distribution of the corroded crucibles with electron backscatter diffraction (EBSD) proved to be highly valuable.

2. Experimental

The present study investigated the corrosion behavior of crucibles made of fused calcium zirconate against Ti–6Al–4V alloy melts. The fused raw material (UCM Advanced Ceramics GmbH, Laufenburg, Germany) had a considerable amount of cubic zirconia (Ca$_{0.15}$Zr$_{0.85}$O$_{1.85}$) as a second phase, which was attributed to the evaporation of calcia during the electric arc melting of the raw material.[24] To compensate for the sub-stoichiometric composition regarding calcia, additional calcium hydroxide (PreCal 54, SCHAEFER KALK GmbH & Co. KG, Diez, Germany) with a particle size of $d_{50} = 0.4$ μm was added as a calcia precursor in three different quantities, as summarized in Table 1. Calcium hydroxide was chosen because during firing calcium hydroxide decomposes into water and calcia accompanied with a remarkable increase in specific surface and hence reactivity.[31–33]

The crucible production was essentially identical to the procedure recently described by Schafföner et al.[24] The calcium hydroxide and the fused raw were first dry mixed for 5 min in a concrete mixer (ToniMIX, Toni Baustoffprüfsysteme GmbH, Berlin, Germany). In a second mixing step of again 5 min 3.5 wt% binder (Optapix PAF 60, Zschimmer & Schwarz GmbH & Co. KG, Lahnstein, Germany) was added. Soon afterwards, to avoid drying of the mix, the crucibles were cold isostatically pressed (EPSI N.V., Walgoedstraat, Belgium) on a steel mandrel of 5.9 cm width and 11.9 cm height using a pressure of 150 MPa. All crucibles were dried at 80 °C and 110 °C for 6 h at both temperatures. Subsequently the crucibles were fired in air with a heating rate of 2 K min^{-1} with dwell times of 2 h and 6 h at 900 °C and 1650 °C, respectively.

To determine the effect of the calcium hydroxide addition on the physical and chemical properties as well, test cylinders of 50 mm height and 50 mm diameter were uniaxial pressed (ES 270, RUCKS Maschinenbau GmbH, Glauchau, Germany) with 150 MPa and later fired with the same cycle as the crucibles. The apparent porosity and apparent density were determined according to DIN EN 993-1 using water and eventually toluol as the testing medium. The mineralogical phases of the fired cylinders were also investigated using XRD and electron backscatter diffraction (EBSD) in an identical procedure as reported previously by Schafföner et al.[24] The ICDD cards considered for phase identification with XRD and EBSD, respectively, were CaZrO$_3$ (76-2401), Ca$_{0.15}$Zr$_{0.85}$O$_{1.85}$ (84-1827), α-Ti (44-1294), β-Ti (44-1288), and Ti$_2$ZrO (71-0879). Furthermore a quantitative phase analysis of the crucible material was performed with the Rietveld method to determine the fractions of calcium zirconate and cubic zirconia after firing.

For the melting experiments Ti–6Al–4V was chosen, because it is the most common titanium alloy and also because it has a high melting point of 1670 °C.[34] All experiments were performed in a high-frequency VIM furnace with a melting capacity of about 10 kg steel and a melting power of about 40 kW similar to the procedure described by Friedrich et al.[35]

The crucibles were placed in the VIM furnace and were then backfilled with a zirconia ramming mass to prevent damage of the induction coil in case of crucible failure. In all melting experiments the VIM furnace was first evacuated below 10×10^{-3} mbar and then flushed with high purity argon gas (grade 4.8) for at least two times. All melting experiments took place in an argon atmosphere of 600 mbar to 800 mbar to reduce the evaporation of volatile elements such as calcium.