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Corrosion behavior of calcium zirconate refractories in contact with titanium aluminide melts

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Abstract

This contribution investigated the corrosion mechanisms of calcium zirconate crucibles during vacuum induction melting of titanium aluminides. The crucibles withstood several melts and exhibited no cracking due to thermal shock. However, a significant amount of zirconium dissolved in the melt, whereas the oxygen content of the melt increased on a much lower level. In contrast to melting Ti6Al4V in the same crucibles an increased calcium zirconate content of the crucibles did not reduce the melt contamination of the titanium aluminide melts. The investigation of the corrosion front of the crucibles revealed the formation of calcium aluminates, whereas titanium was almost absent. The melting of titanium aluminides with subsequent refining by electro slag remelting could be a viable production route to produce titanium zirconium aluminum alloys. Furthermore, the relation between the corrosion of calcium zirconate refractories in contact with titanium based alloys depending on their composition should be further evaluated.

Keywords: Refractories; Calcium zirconate; Titanium aluminides; Vacuum induction melting; Electron backscatter diffraction

1. Introduction

Titanium aluminides attracted much attention during the last decades due to their outstanding properties such as low density, high specific modulus, high creep resistance combined with a remarkable oxidation and corrosion resistance.[1,2] Therefore numerous investigations studied titanium aluminides especially as high temperature materials.[3–5] However, high costs due to difficult processing and intrinsic material properties still hinder their wider application.[4,5]

Casting of near net shapes has been often proposed as a possibility to reduce the final product costs because machining of titanium alloys is quite difficult and also results in a large amount of scrap.[5–8] Another alternative to reduce the final product costs is an improved recycling of the scrap instead of downgrading it to the steel industry.[9–12]

Vacuum induction melting (VIM) in refractory crucibles instead of melting by vacuum arc remelting (VAR) or induction skull melting (ISM) is much less energy intensive,[13,14] while at the same time it allows higher super heating temperatures, thus eventually improving the cast parts.[14,6,15,16] Furthermore, VIM followed by oxygen refining with pressure electro slag remelting (PESR) was demonstrated as an efficient scrap recycling technique.[10] Thereby VIM allows a fast homogenization of the melt by electromagnetic stirring and also a first deoxidation.[10,11]

Several refractories have been investigated as crucible materials for melting titanium alloys. Most studies concentrated on Y_2O_3 and CaO, while ZrO_2 and Al_2O_3 were also often tested.[9,14,17–19]

However, calcium zirconate ($CaZrO_3$) despite its high melting point of 2368 °C and its remarkable high temperature stability[20] has been only rarely investigated as a refractory material for titanium alloy melts.

Li et al.[21] produced small crucibles of $CaZrO_3$ using a little amount of TiO_2 as a sintering aid. The crucibles showed only a slight corrosion in contact with Ti6Al4V and NiTi melts.

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In another study Kim et al.[22] tested Al_2O_3, ZrO_2, CaO, and $CaZrO_3$ molds in contact with commercial pure titanium (cp-Ti), Ti6Al4V, and γ-TiAl melts. $CaZrO_3$ together with calcia showed the least corrosion in contact with cp-Ti and Ti6Al4V, which was much better than for alumina and zirconia.

On the other hand, the corrosion behavior of crucibles in comparison to molds is much severer[19] and to the best of our knowledge the corrosion behavior of $CaZrO_3$ crucibles in contact with titanium aluminides has not yet been reported.

This article examines therefore the corrosion of $CaZrO_3$ crucibles in contact with γ-TiAl melts, whereas analyzing the interface reaction of the crucibles with the metal on different scales including XRD, ICP-OES, and in an SEM in combination with EDS and EBSD proved to be especially helpful.

2. Experimental

The main aim of this article was to evaluate the corrosion behavior of $CaZrO_3$ refractories during the VIM of titanium aluminides. Induction melting generally provides a relatively severe corrosive attack by the melt or slag.[23]

To begin with, melting crucibles with a maximum grain size of 3 mm were prepared similar to the procedure recently described by Schafföner et al.[24] The applied fused raw material (UCM Advanced Ceramics GmbH, Laufenburg, Germany) consisted of $CaZrO_3$ and cubic zirconia (c-ZrO_2, $Ca_{0.15}Zr_{0.85}O_{1.85}$) as a second phase. The c-ZrO_2 resulted from the inevitable evaporation of calcia during the electric arc melting of the raw material.[24]

The raw material composition of the crucibles is summarized in Table 1. The raw material mix was adjusted according to the model of Funk and Dinger[25] with a distribution modulus of $q = 0.4$ in order to obtain a dense particle packing. In addition to crucibles made of the fused raw material only, a second type of crucibles was produced by adding 6.61 m% of $Ca(OH)_2$, which is equivalent to 5 m% of CaO. During firing, this CaO reacted later with the excessive c-ZrO_2 to form $CaZrO_3$.

At first, the raw material was dry mixed in a conventional mortar mixer (ToniMIX, Toni Baustoffprüfsysteme GmbH, Berlin, Germany) for 5 min. In a second mixing step for again 5 min 3.5 m% of a polyvinyl alcohol (PVA) binder containing a pressing aid (Optapix PAF 60, Zschimmer & Schwarz GmbH & Co. KG, Lahnstein, Germany) was carefully added to provide a homogenous mixture without lumps.

The crucibles were prepared by cold isostatic pressing (EPSI N.V., Walgoedstraat, Belgium) on a steel mandrel with a pressure of 150 MPa. The crucibles had an inner diameter of 5.9 cm and an inner height of 11.5 cm. After pressing the crucibles were dried and then fired at 1650 °C for 6 h.

For the melting experiments the crucibles were mounted in a high frequency VIM furnace with a total melting capacity of about 10 kg steel and a melting power of 40 kW. To prevent damage of the melting coil in case of crucible failure, the crucibles were backfilled with a ZrO_2 ramming mass. For a better temperature control during melting, a small hole of 1.5 cm depth was carefully drilled into the bottom of the crucibles without impairing the tightness of the crucible. Then a type B (Pt-6Rh/Pt-30Rh) thermocouple was inserted into this hole to allow a continuous temperature control close to the melt. This thermocouple was calibrated by immersing another thermocouple of the same type into the first visible melt. This second thermocouple was only submerged for some seconds and protected by a Mo/Al_2O_3 pipe.

In all experiments the crucibles were first filled with about 210 g of γ-TiAl. To prevent thermal shock of the crucibles at any case, the power was only slowly increased; usually it lasted 2.5 h before the first melting occurred. After the first melt became visible about 750 g of metal was further added. This further batching took about 20 min and the power was then held constant for another 20 min before the melt was poured into massive steel molds. Immediately after pouring the melt, the crucible was refilled with fresh feed material to minimize the cooling and hence thermal shock of the crucibles. During the further melting cycles the power was increased in 30–40 min to prevent a cooling and hence thermal shock of the crucibles. The crucibles were used for three to four times (see Table 2) before they were dismounted for further investigation.

To investigate the corrosion behavior the crucibles were first cut with a buzz saw. Then some representive sections were examined with a digital microscope (VHX-2000, Keyence Corp., Osaka, Japan). Afterwards sections from the bottom of the crucibles were investigated with a conventional W-cathode scanning electron microscope (SEM) (XL30, Philips, Netherlands) equipped with an electron backscatter diffraction (EBSD) system TSL and an EDS system Genesis in connection with an Apollo10 detector from Edax/Ametek. The samples were

Table 1
Raw material mix of the crucibles.

		Mix identifier	
		C0	C5
	Grain size fraction in mm	Composition in m%	
Fused $CaZrO_3$	1 to 3	30	30
	0.5 to 1	25	25
	0 to 0.5	20	20
	0 to 0.045	25	25
$Ca(OH)_2$ relative to fused $CaZrO_3$	–	0	6.61

Table 2
Zirconium and oxygen content of the casted metal depending on crucible composition.

Crucible	Melt	Zirconium in melt in m%	Oxygen in melt in m%
C0	1	9.96	0.73
	2	2.71	0.50
	3	2.71	0.48
	4	3.26	0.45
C5	1	6.84	0.81
	2	5.05	0.63
	3	3.21	0.49