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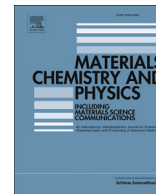
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# Investigation into the use of CaZrO<sub>3</sub> as a facecoat material in the investment casting of TiAl alloys



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## HIGHLIGHTS

- To determine the interactions between CaZrO<sub>3</sub> filler and stucco materials during shell firing.
- To study the reaction between the CaZrO<sub>3</sub> facecoat and TiAl alloy during casting.
- The Al<sub>2</sub>O<sub>3</sub> stucco can react with CaZrO<sub>3</sub> filler to form (Zr, Ca)O<sub>2</sub> and CaAl<sub>x</sub>O<sub>y</sub> at 1650 °C.
- O, Zr and Si ions from the ceramic moulds were observed to penetrate into the TiAl metal.
- The reaction products include (Ti, Zr)<sub>5</sub>(Al, Si)<sub>3</sub> and ZrAl<sub>2</sub> phase with high Ti ions solid solution.

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## ABSTRACT

Research was carried out to determine the interactions between the filler and stucco materials in CaZrO<sub>3</sub> based facecoats during shell firing as well as between the facecoat and a TiAl alloy during the casting process. A 'flash re-melting' technique, which gives a similar heating profile to the actual investment casting process, was used to study the phase transformations in the shell moulds. The chemical inertness of the facecoat was then investigated using a sessile drop test using a Ti–45Al–2Nb–2Mn–0.2TiB alloy. In this study, the facecoat compositions and the interaction products between metal and shells were characterized using x-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A severe interaction was found between CaZrO<sub>3</sub> filler and Al<sub>2</sub>O<sub>3</sub> stucco, which rapidly damaged the shell surface. As well as oxygen, zirconium and silicon ions from the shell moulds were also observed to penetrate into the TiAl metal to form (Ti, Zr)<sub>5</sub>(Al, Si)<sub>3</sub> phases in the metal/shell interfacial areas.

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## 1. Introduction

Gamma titanium aluminides are a family of low density, high performance alloys with the potential to replace current Ni-base superalloys used in the production of aero-engine components. Investment casting is one of the most economical methods to produce titanium and titanium aluminide alloy products, increasing the components' integrity and mechanical properties, whilst reducing material waste and machining cost [1]. Titanium aluminides are difficult to process mainly due to the low fluidity of the TiAl alloy around its melting temperature [2]. Due to the high

affinity of elements such as oxygen, nitrogen etc., titanium and its alloys can easily interact with mould materials during the investment casting process, resulting in an interaction hardened layer being generated at the metal surface [3,4]. This hardened layer contains a large amount of dissolved oxygen, and it is very brittle and susceptible to crack generation and propagation [5].

The research [6–8] shows that facecoat materials such as ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> have acceptable chemical inertness with interaction layer thicknesses around 200–300 μm. When using Y<sub>2</sub>O<sub>3</sub> as a facecoat material, the interaction layer thickness was greatly reduced to around 10 μm [8–10], therefore, it has been used in the investment casting of these reactive alloys since the 1990s [11]. Although yttria has excellent chemical inertness, it has a number of drawbacks in a production environment; combining high material cost, short slurry life and poor sintering properties. Some

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alternative, cheaper facecoat materials based on nitride compounds such as AlN and BN have been studied [12,13] but the poor chemical inertness of these materials made them unsuitable for use in TiAl alloy casting.

From 2001 to 2004, Kim et al. [14,15] demonstrated the use of CaZrO<sub>3</sub> based facecoat materials to cast Ti alloys. The results showed that the CaZrO<sub>3</sub> facecoat had comparable chemical inertness to ZrO<sub>2</sub>, with a hardened layer thickness around 200 μm, at a lower cost than yttria based systems. He also reported that the order of chemical inertness of various facecoats as Al<sub>2</sub>O<sub>3</sub> < ZrO<sub>2</sub> < CaO < CaZrO<sub>3</sub> when casting Ti64. Hence CaZrO<sub>3</sub> is a potential facecoat material for casting titanium and its alloys. Later, Li [16] developed a CaZrO<sub>3</sub> crucible by sintering a ZrO<sub>2</sub> and CaO powders (CaO: ZrO<sub>2</sub> = 1:1). In Li's study, an approximate 350 μm interaction layer thickness was detected at the Ti–6Al–4V (Ti64) alloy surface with some oxides apparent. In 2012, a study was proposed to use CaZrO<sub>3</sub> as filler material in the facecoat to cast titanium alloys [17].

However, most of the studies referenced above were based on the analysis of the chemical inertness of CaZrO<sub>3</sub> against Ti64 or pure titanium alloys. Due to increased interest in titanium aluminide alloys in the aerospace industry, this study initiated to enhance the understanding of the chemical inertness of CaZrO<sub>3</sub> as a facecoat material against molten TiAl alloys. Both Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> were used as stucco materials, and the interaction between stucco, filler and backup coats were characterized using SEM and EDS. The reactions between alloy and mould were investigated using a sessile drop method [18], and the interaction phases at the metal mould interface areas were identified using transmission electron microscope (TEM).

## 2. Experimental techniques

### 2.1. Sample preparation

The details of the individual primary and secondary shell mould layer constituents are listed in Table 1. The moulds were made by first investing the wax pattern with the primary slurry which consisted of a colloidal ZrO<sub>2</sub> binder (Remet, Ti-coat), CaZrO<sub>3</sub> filler (ABSCO, -325mesh), liquid polymer (EVO STIK, PVA), wetting agent (Remet, Victawet 12) and anti-foam (Remet, Burst RSD-10). Either Al<sub>2</sub>O<sub>3</sub> (Cermatco, Al20) or monoclinic ZrO<sub>2</sub> stucco (UCM 30/60 mesh) was then applied to form the primary facecoat. This coat was dried at a temperature of 21 °C, 50% relative humidity and 0.2 m/s air speed for 24 h. Six backup coats were then applied. An alumino-silicate stucco (IMERYS, Molochite 30/80 mesh) was applied as the secondary stucco in layer 2 and three. A coarser alumino-silicate stucco (IMERYS, Molochite 16/30 mesh) was applied as secondary stucco in layers 4 to 7. Each secondary coat was dried at a temperature of 21 °C, 50% relative humidity and 3 m/s air speed for 90 min. Finally a seal coat of secondary slurry was applied and dried

**Table 1**  
Details of composition of the mould system.

Mould code	Slurry type	Binder	Filler	Stucco
CA	Primary	Colloidal ZrO <sub>2</sub> sol	ZrCaO <sub>3</sub> -325 mesh	Al <sub>2</sub> O <sub>3</sub> -80 mesh
	Secondary	Colloidal SiO <sub>2</sub> sol	Fused silica -200 mesh; Molochite -200 mesh	Alumino-silicate -30/80 and -16/30 mesh
CZ	Primary	Colloidal ZrO <sub>2</sub> sol	ZrCaO <sub>3</sub> -325 mesh	Zirconia -50/100 mesh
	Secondary	Colloidal SiO <sub>2</sub> sol	Fused silica -200 mesh; Molochite -200 mesh	Alumino-silicate -30/80 and -16/30 mesh

at a temperature of 21 °C, 50% relative humidity and 3 m/s air speed for 24 h. The wax inside the ceramic mould was then removed by steam autoclaving at 8 bar pressure for 5 min, followed by a controlled de-pressurization cycle at 1 bar/minute using a Quick-lock Boilerclave™ (Leeds and Bradford Boiler Company Ltd., UK).

The shells were firstly isothermally sintered at 1000 °C for one hour and then they were placed into a 'flash re-melt' sessile drop test machine [18]. During this test, shells were first pushed into a furnace at 1650 °C for 60 s and pulled back to room temperature. Then, shells with metal placed on the top (facecoat) surface were tested under the same conditions, allowing the molten metal to interact with the ceramic shell. The titanium aluminide alloy used in this experiment was a Ti–45Al–2Mn–2Nb–0.2TiB (at%) alloy.

### 2.2. Sample characterizations

Ceramic shells were cut after the firing and reaction tests, allowing the cross section of the mould to be examined. Samples were then mounted and polished for microstructural analysis. The cooled metal drops were also cut in half vertically, mounted and polished for microstructural observation using scanning electron microscopy (SEM) (Jeol-7000 series), and the metal/shell interfacial compositions were characterized using energy dispersive x-ray analysis, EDS. A focused ion beam scanning electron microscope (FIB-SEM) was later used to prepare the sample, and the interaction phases were identified using transmission electron microscope (TEM) (Jeol-2100 series).

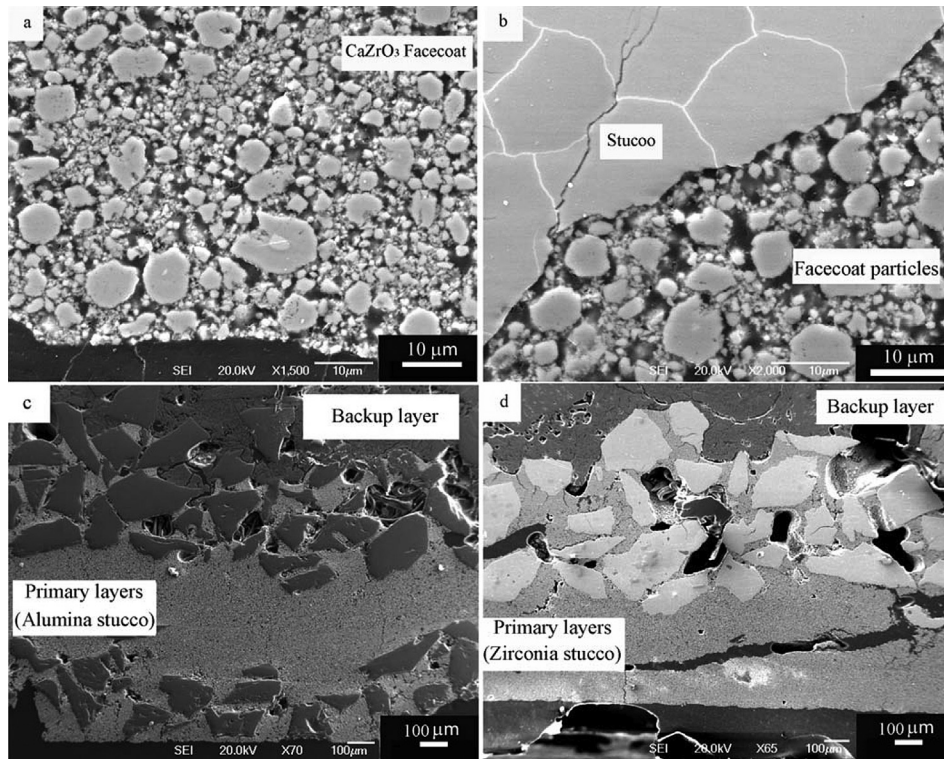
## 3. Results

### 3.1. Isothermal sintering of ceramic shells

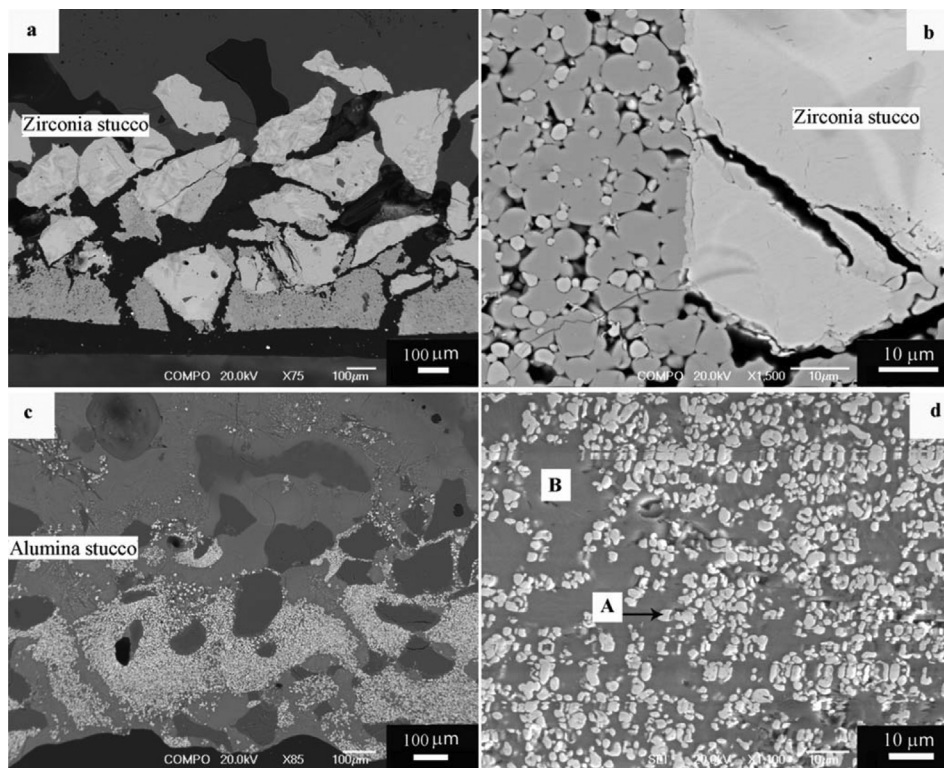
The microstructures of the test pieces, after sintering at 1000 °C, are shown in Fig. 1. An inhomogeneous structure was found in the moulds fired at 1000 °C with distinguishable original filler particles. The filler particles in the facecoat have varied shapes and the average filler particle sizes are around 10 μm. There are no 'necks' formed between filler particles after firing at 1000 °C. Fig. 1(b)–(d) illustrate the microstructures of mould cross section. The lower layer in the figures is the facecoat and the upper darker layers are the backup coats. The facecoat has an average thickness around 600–700 μm with the average stucco particle size around 200 μm, and no interaction was observed between the filler powders and stuccos. Some cracks appeared in the facecoat layer when using ZrO<sub>2</sub> as the stucco, which could be related to the change in the crystal structure of ZrO<sub>2</sub> material during shell firing [19].

### 3.2. Flash sintering of ceramic shells

After being pre-fired at 1000 °C for one hour, moulds were then put into a furnace at 1650 °C for 60 s, which represents the casting conditions in the investment casting process. The microstructure of the mould was examined, as shown as in Fig. 2. It can be seen from Fig. 2(a) that after flash sintering at 1650 °C for only 60 s, a significant sintering process took place in the facecoat, showing the fused spherical CaZrO<sub>3</sub> grains within a more homogeneous structure. EDS analysis of the bright inclusions identified the particles to be ZrO<sub>2</sub>, which is likely to originate from the binder materials. Also, as some ZrO<sub>2</sub> particles are similar in size to filler material, the formation of ZrO<sub>2</sub> particles may be due to the decomposition of CaZrO<sub>3</sub> filler in the facecoat. No significant interaction was found between the ZrO<sub>2</sub> stucco and facecoat materials after flash firing at 1650 °C for 60 s, as shown as in Fig. 2(a) and (b). However, a severe interaction was observed between the Al<sub>2</sub>O<sub>3</sub> stucco and the CaZrO<sub>3</sub> facecoat, leading to the dissolution of filler and stucco materials



**Fig. 1.** The microstructures of different mould systems after firing at 1000 °C for 1 h, (a) & (b) the stucco and facecoat particles interface, (c) the cross section image of CA mould, using alumina as stucco material and (d) the cross section images of the CZ mould, using zirconia as stucco material.



**Fig. 2.** The microstructures of different mould systems after firing at 1650 °C for 60 s (a) CZ mould using zirconia as the facecoat stucco, (b) Higher magnification BEI of CZ mould containing grey fused spherical  $\text{CaZrO}_3$  grains and bright  $\text{ZrO}_2$  particles, (c) mould CA using alumina as the facecoat stucco, (d) Higher magnification BEI of CA mould containing bright phase A and grey phase B.

between the facecoat and backup coats, as shown as in Fig. 2(c) and (d). The large dark  $\text{Al}_2\text{O}_3$  stucco particles are surrounded by grey and white phases, which are labelled as phase A and B in the higher magnification image 2(d). The EDS analyses of both phases A and B are listed in Table 2, revealing that phase A is a Zr and O rich phase, and phase B, with grey contrast, is a phase rich in Ca, Al and O. These results indicated that, during flash firing, the  $\text{Al}_2\text{O}_3$  stucco interacted with  $\text{CaZrO}_3$  in the facecoat, causing the outwards diffusion of  $\text{Ca}^{2+}$  ions and enrichment of  $\text{Zr}^{4+}$  ions in the fused  $\text{CaZrO}_3$  filler particles. According to the  $\text{CaO}-\text{Al}_2\text{O}_3-\text{ZrO}_2$  phase diagram [20], at 1873 K (1600 °C)  $\text{CaZrO}_3$  could interact with  $\text{Al}_2\text{O}_3$  to form a  $\text{ZrO}_2$  phase with CaO solid solution, and  $\text{CaAl}_x\text{O}_y$  phases, which is similar to the experimental observations.

### 3.3. The interaction between TiAl and the shell moulds

After the flash re-melt test, the metal/shell interfacial microstructures are shown in Fig. 3. Severe interactions were observed between TiAl alloy and CA and CZ moulds. With the CA mould, which has alumina as the facecoat stucco, an obvious hexagonal six-fold dendritic structure was observed across the complete sessile drop (3 mm height), and this structure is likely to have resulted from the high amount of oxygen as a solid solute in the metal [21]. New bright phases were also found randomly distributed at the grain boundaries as shown as in Fig. 3(a). Compared to mould CA, using the mould CZ, which has  $\text{ZrO}_2$  as facecoat stucco, more interaction products were formed at the grain boundaries, as shown as in Fig. 3(b), but no significant six-fold dendritic structure was observed. The higher magnification image of the bright phase in Fig. 3(d) shows that a second phase may also be present within its structure.

TEM techniques were used to identify the interaction products at the grain boundaries and the results are illustrated in Figs. 4 and 5. The TiAl metal matrix consisted of a typical lamellar ( $\alpha_2 + \gamma$ ) microstructure, and the EDS analysis results revealed that bright phases C, Fig. 4(a), contained The TiAl metal matrix consisted of a typical lamellar ( $\alpha_2 + \gamma$ ) microstructure, and the EDS analysis results revealed that bright phases C, Fig. 4(a), contained 45.26 at% of Ti, 17.46 at% of Zr, 22.65 at% of Al and 14.63 at% of Si concentrations. The diffraction pattern of this phase shows that it has a complex hexagonal D8 structure, similar to the phase  $\text{Ti}_5\text{Si}_3$ . The study carried out by Chen [22] indicated that Zr has high solubility in TiAl alloy and it is able to dissolve around 11 at% in  $\gamma$  phase, and more than 25 at% in  $\alpha_2$  phase [23, 24]. Meanwhile, the study carried out by Kotval [25] and Cheng [23] indicated that Al ions can dissolve in  $\text{Ti}_5\text{Si}_3$  as  $\text{Ti}_5(\text{Al}, \text{Si})_3$  phase. Hence the possible composition of phase C shown is a  $(\text{Ti}, \text{Zr})_5(\text{Si}, \text{Al})_3$  phase. The formation of  $(\text{Ti}, \text{Zr})_5(\text{Si}, \text{Al})_3$  phases at the TiAl alloy grain boundaries can be related to the reaction between the TiAl with the  $\text{ZrO}_2$  present in the facecoat of both types of shell moulds.

Besides phase C, another phase (phase D) was found to be present together with phase C, as shown as in Fig. 5. The EDS analysis shows that the phase D contains 53.53 at% Al, 42.35 at% Ti, and 4.12 at% Zr. The diffraction pattern of phase D has same crystal structures as phase  $\text{ZrAl}_2$  which was also revealed by Jia [7]. The composition of phase D is likely to be  $\text{ZrAl}_2$  phase with high Ti ions solid solution.

**Table 2**

The EDS analysis results of phase A and B in Fig. 2(d) (at%).

Phase	Ca	Zr	Al	Si	O
A	6.23	44.93	0.82	–	48.02
B	13.95	–	27.99	1.52	56.54

## 4. Discussion

### 4.1. The interaction between filler particles and stucco in the facecoat

The stability and the inertness of the  $\text{CaZrO}_3$  facecoats were investigated during the mould firing and casting process, using both  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  as facecoat stuccos. No interaction was observed between the  $\text{CaZrO}_3$  filler and stuccos when moulds were sintered at 1000 °C for both mould systems. When moulds were heated to 1650 °C for 60 s, a severe interaction was observed between the  $\text{CaZrO}_3$  filler and  $\text{Al}_2\text{O}_3$  stucco. The interaction causes the degradation and dissolution of the  $\text{Al}_2\text{O}_3$  stucco which penetrated from facecoat into the backup coats. In the surrounding areas of the  $\text{Al}_2\text{O}_3$  stucco, the composition of facecoat were changed from  $\text{CaZrO}_3$  and  $\text{Al}_2\text{O}_3$  to a mix of  $(\text{Zr}, \text{Ca})\text{O}_2$  and  $\text{CaAl}_x\text{O}_y$  materials. The reaction can be seen represented as:



No reaction was observed in the facecoat system using  $\text{ZrO}_2$  as the stucco material, although the cycling of mould temperatures caused crystal structure changes in the  $\text{ZrO}_2$  stucco, resulting in cracks generated in facecoat associated with the volume change in this stucco [19]. This work shows that, during the high temperature casting process, the inertness of facecoat materials is not only dependent on the composition of facecoat, but also related to interaction products between the fillers and stuccos.

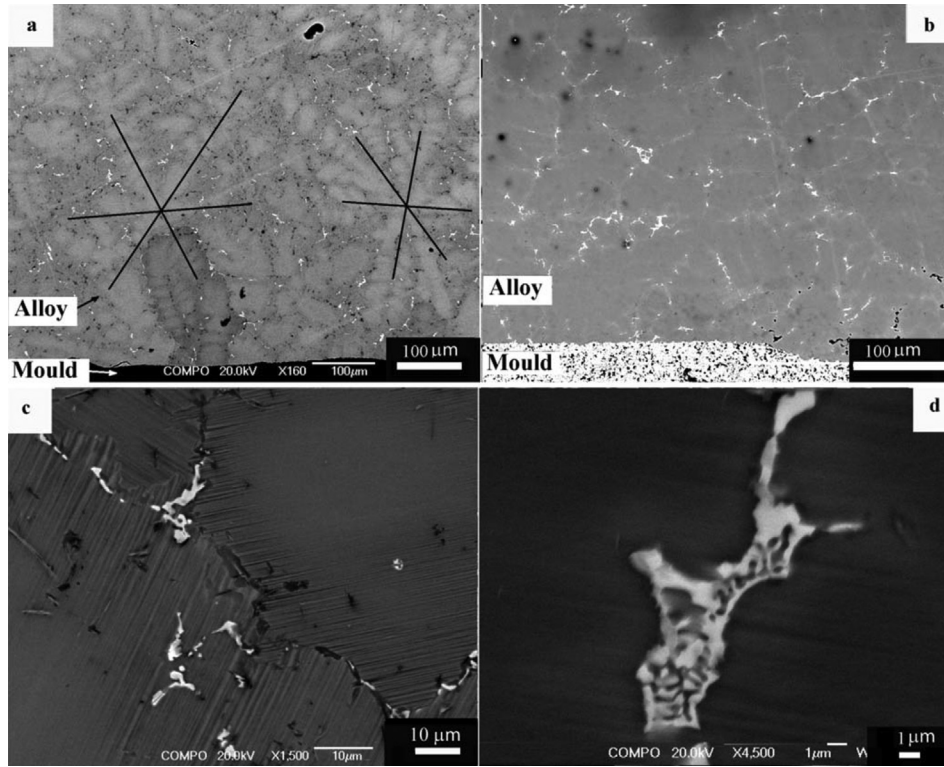
### 4.2. The interaction between the facecoat and TiAl alloy

As previously known, the reactivity of the facecoat and TiAl alloy was dependent on the Gibbs free energy changes during the interaction. According to the free energy calculations [17], the  $\text{CaZrO}_3$  facecoat thermodynamic inertness lies between CaO and  $\text{ZrO}_2$  materials. However, due to the reaction between the filler stucco materials, the actual interactions between the facecoat and molten TiAl were more complicated than previously understood.

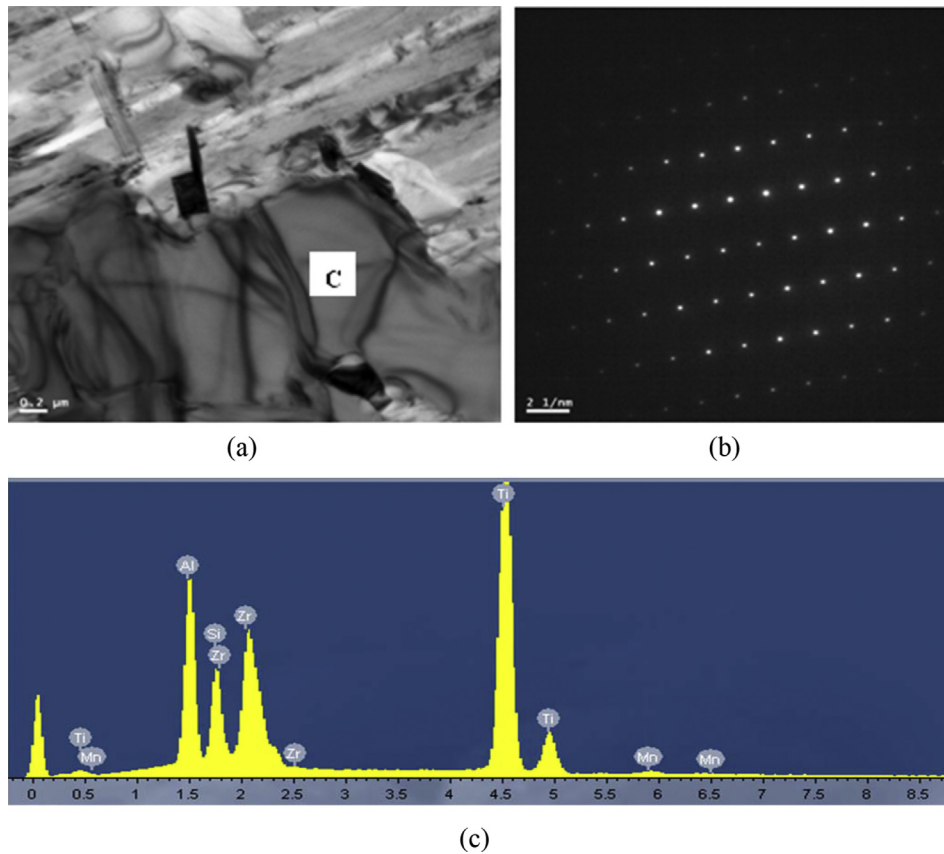
The use of  $\text{Al}_2\text{O}_3$  as the stucco material can cause an interaction to take place between the filler and stucco, resulting in the formation of phases  $(\text{Zr}, \text{Ca})\text{O}_2$  and  $\text{CaAl}_x\text{O}_y$  at the mould surface, directly in contact with the metal. During flash re-melting, molten TiAl interacted with  $(\text{Zr}, \text{Ca})\text{O}_2$  and  $\text{CaAl}_x\text{O}_y$  which formed a solid-solution with Si penetrating through from the backup coats [26]. Zr ions from the facecoat and Si from backup coats penetrated into the metal and reacted with TiAl to form a  $\text{Ti}_5\text{Si}_3$  with a Zr solid solute [24,25]. The reaction between Ti and Si is presented in equation (2):



Besides forming a silicide phase, Zr ions also form possible combined  $(\text{Ti}, \text{Zr})_5(\text{Si}, \text{Al})_3$  phase and  $\text{ZrAl}_2$  phase with a high Ti ions solid solution, which were also revealed in this work. Meanwhile, the obvious six-fold dendritic microstructure in the sessile drop microstructures illustrated that the oxygen from the facecoat also penetrated into metal during testing using mould applied with  $\text{Al}_2\text{O}_3$  as the stucco. The inertness of  $\text{CaZrO}_3$  was reduced by the reaction with  $\text{Al}_2\text{O}_3$ , forming phases  $(\text{Zr}, \text{Ca})\text{O}_2$  and  $\text{CaAl}_x\text{O}_y$ . Using  $\text{ZrO}_2$  as the stucco did not cause the filler/stucco interaction. But the cracks in facecoat due to the volume change of  $\text{ZrO}_2$  stucco did accelerate the penetration of Si from backup coat to the surface, producing more Si bearing interaction phases during metal/shell interaction. No Ca ions were detected at the metal interfacial areas,



**Fig. 3.** The microstructures of the sessile drop metals tested at 1650 °C for 60 s (a) with mould using Al<sub>2</sub>O<sub>3</sub> as stucco in the facecoat, (b) with mould using ZrO<sub>2</sub> as stucco in the facecoat (c) interaction products in metal (d) the higher magnification image of the interaction product.



**Fig. 4.** Showing (a) the TEM image of the interaction product, (b) the diffraction pattern of phase C and (c) the EDS analysis of phase C.

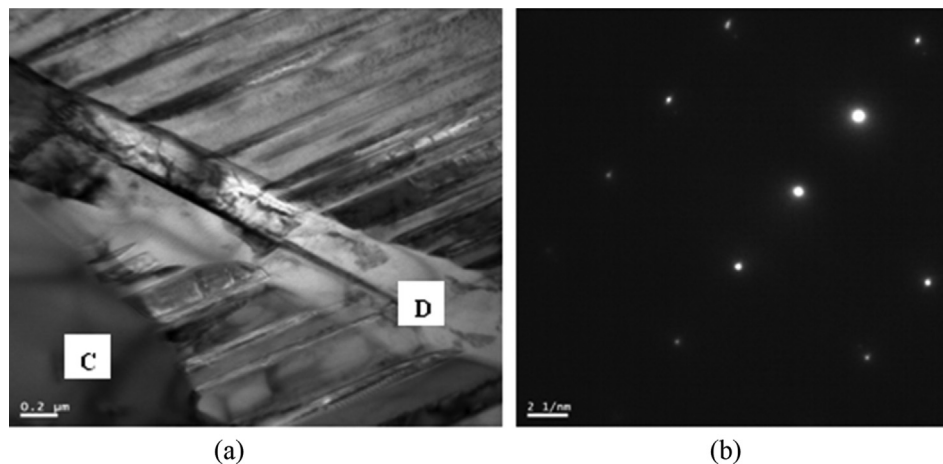


Fig. 5. Showing (a) the TEM image of the interaction products and (b) the diffraction pattern of phase D.

and the Ca ions could only be detected in the facecoat, similar to the results reported by Gomes [27].

## 5. Conclusions

In this experiment, a  $\text{CaZrO}_3$  based material was used as the facecoat material to investment cast a TiAl alloy. According to these results some conclusions can be summarized as follow:

The  $\text{Al}_2\text{O}_3$  stucco can react with  $\text{CaZrO}_3$  filler to form  $(\text{Zr}, \text{Ca})\text{O}_2$  and  $\text{CaAl}_x\text{O}_y$  at temperatures around  $1650^\circ\text{C}$ . No interaction was observed when using  $\text{ZrO}_2$  as the stucco material except for some cracks appearing in the facecoat due to the volume change of  $\text{ZrO}_2$  material during thermal processing. When evaluating the inertness of the facecoat material, the interaction products in the facecoat surface need to be taken into account at casting temperatures. The reaction between  $\text{CaZrO}_3$  filler and  $\text{Al}_2\text{O}_3$  stucco led to six-fold dendritic microstructures appearing in the TiAl alloy due to oxygen penetration from the facecoat. Besides oxygen, Si and Zr ions from the facecoat also penetrated into the TiAl alloy to form  $(\text{Ti}, \text{Zr})_5(\text{Si}, \text{Al})_3$  and  $\text{ZrAl}_2$  phase with high Ti ions solid solution. No Ca ions were detected in metal/shell interfacial area in this experiment.

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## References

- [1] W. Xinhua, Review of alloy and process development of TiAl alloys, *Intermetallics* 14 (2006) 1114–1122.
- [2] H. Nan, D. Huang, Z.X. Li, J.Q. Zhao, Research on investment casting of TiAl alloy agitator treated by HIP and HT, *China Foundry* 4 (2007) 112–115.
- [3] M. Lamirand, J. Bonnetien, S. Guérin, G. Ferrière, J. Chevalier, Effects of interstitial oxygen on microstructure and mechanical properties of Ti-48Al-2Cr-2Nb with fully lamellar and duplex microstructures, *Metall. Mater. Trans. A* 37 (2006) 2369–2378.
- [4] S.Y. Sung, Y.J. Kim, Alpha-case formation mechanism on titanium investment castings, *Mater. Sci. Eng. A* 405 (2005) 173–177.
- [5] B.J. Choi, Y.J. Kim, Effect of reacted compounds in  $\text{Al}_2\text{O}_3+\text{Ti}$  investment mold on alpha-case formation for Ti casting, *Met. Mater. Int.* 19 (2013) 439–444.
- [6] Q. Jia, Y.Y. Cui, R. Yang, A study of two refractories as mould materials for investment casting TiAl based alloys, *J. Mater. Sci.* 41 (2006) 3045–3049.
- [7] Q. Jia, Y.Y. Cui, R. Yang, Intensified interfacial reactions between gamma titanium aluminide and CaO stabilised  $\text{ZrO}_2$ , *Int. J. Cast Metals Res.* 17 (2004) 23–28.
- [8] J. Barbosa, H. Puga, C.S. Ribeiro, O.M.N.D. Teodoro, A.C. Monteiro, Characterisation of metal/mould interface on investment casting of  $\gamma$ -TiAl, *Int. J. Cast Metals Res.* 19 (2006) 331–338.
- [9] J. Barbosa, C.S. Ribeiro, A.C. Monteiro, Influence of superheating on casting of  $\gamma$ -TiAl, *Intermetallics* 15 (2007) 945–955.
- [10] R. Cui, M. Gao, H. Zhang, S. Gong, Interactions between TiAl alloys and yttria refractory material in casting process, *J. Mater. Proc. Technol.* 210 (2010) 1190–1196.
- [11] R. Horton, Method of casting a reactive metal against a surface formed from an improved slurry containing yttria, US Patent No. 5221336 A, 1993.
- [12] A.V. Kartavykh, V.V. Tcherdyntsev, J. Zollinger, TiAl–Nb melt interaction with pyrolytic boron nitride crucibles, *Mater. Chem. Phys.* 119 (2010) 347–350.
- [13] A.V. Kartavykh, V.V. Tcherdyntsev, J. Zollinger, TiAl–Nb melt interaction with AlN refractory crucibles, *Mater. Chem. Phys.* 116 (2009) 300–304.
- [14] S.K. Kim, T.K. Kim, M.G. Kim, T.W. Hong, Y.J. Kim, Investment casting of titanium alloys with CaO crucible and  $\text{CaZrO}_3$  mold, in: *Lightweight Alloys for Aerospace Application*, John Wiley & Sons, Inc., 2001, pp. 251–260.
- [15] M.G. Kim, S.K. Kim, Y.J. Kim, Effect of mold material and binder on metal–mold interfacial reaction for investment castings of titanium alloys, *Mater. Trans.* 43 (2004) 745–750.
- [16] C.H. Li, Y.H. Gao, W.Z.D. Xiong, G. Lu, Z.M. Ren, K. Deng, *Adv. Sci. Technol.* 70 (2010) 136–140.
- [17] C.H. Li, F.F. Zhou, X.G. Lu, K.L. Zhu, L.N. Chen, D. Zhang, W.Y. He, J.P. He,  $\text{CaZrO}_3$  mold shell used for titanium and titanium alloy precision casting and preparation method, CN Patent No. 103071764 A, [Filed in Nov 2012].
- [18] X. Cheng, C. Yuan, N.R. Green, P.A. Withey, Evaluation of the inertness of investment casting molds using both sessile drop and centrifugal casting methods, *Metall. Mater. Trans. A* 44A (2013) 888–898.
- [19] C. Yuan, P.A. Withey, S. Blackburn, Effect of the incorporation of a zirconia layer upon the physical and mechanical properties of an investment casting ceramic shell, *Mater. Sci. Technol.* 29 (2013) 30–35.
- [20] T. Murakami, H. Fukuyama, K. Nagata, M. Susa, T. Kishida, Phase diagram for the system  $\text{CaO-Al}_2\text{O}_3\text{-ZrO}_2$ , *Metall. Mater. Trans. B* 31 (2000) 25–33.
- [21] X. Cheng, X.D. Sun, C. Yuan, N.R. Green, P.A. Withey, An investigation of a TiAlO based refractory slurry face coat system for the investment casting of TiAl alloys, *Intermetallics* 29 (2012) 61–69.
- [22] X.F. Chen, R.D. Reviere, B.F. Oliver, C.R. Brooks, The site location of Zr atoms dissolved in TiAl, *Scripta Metallurgica Materialia* 27 (1992) 45–49.
- [23] R. Yang, Y.L. Hao, Y. Song, Z.X. Guo, Site occupancy of alloying additions in Ti aluminides and its application to phase equilibrium evaluation, *Z. für Met.* 91 (2000) 296–301.
- [24] G. Effenberg, S. Ilyenko (Eds.), *Light Metal Systems. Part 4, Al-Ti-Zr (Aluminium – Titanium – Zirconium)*, Springer Berlin Heidelberg, 2006, pp. 1–14.
- [25] P.S. Kotval, R.W. Calder, In situ identification of the silicide phase in super- $\alpha$  titanium alloys, *Metall. Trans.* 3 (1972) 1308–1311.
- [26] C. Yuan, D. Compton, X. Cheng, N. Green, P.A. Withey, Investigation into the use of  $\text{CaZrO}_3$  as a facecoat material in the investment casting of TiAl alloys, *J. Eur. Ceram. Soc.* 32 (2012) 4041–4049.
- [27] F. Gomes, B. Joaquim, C.S. Ribeiro, Induction melting of  $\gamma$ -TiAl in CaO crucibles, *Intermetallics* 16 (2008) 1292–1297.