$BaZrO_3$ refractory applied to the directional solidification of TiAl alloys

J He[1,a], C Wei[1,b], S Wang[1,c], D Meng [1,d], X Lu[1,2,e], H Wang[1,2,f], C Li[1,2,g]
[1] Shanghai Key Laboratory of Modern Metallurgy & Materials Processing, Shanghai University, Shanghai 200072, China
[2] Shanghai Special Casting Engineering Technology Research Center, Shanghai 201605, China

Email: [a] zhedudiao@163.com, [b] weichao1989@shu.edu.cn, [c] zmddahu@shu.edu.cn, [d] mengdz@sdju.edu.cn, [e] luxg@shu.edu.cn, [f] whb@shu.edu.cn, [g] chli@staff.shu.edu.cn

Abstract. Recently, much attention has been paid to the refractory used for the directional solidification process of TiAl intermetallics, the Y_2O_3 crucible/Y_2O_3 coated moulds seem to be the suitable candidate. However, the use of Y_2O_3 is limited by its low thermal shock resistance and high cost. In this work, a novel $BaZrO_3$ refractory was introduced to the directional solidification of TiAl intermetallics. The melt of this alloy contained in $BaZrO_3$ crucibles were heated for 30 minutes at 1600, 1650, 1700 °C, respectively, then cooled within the crucible for the investigation of the interface between the melt and the refractory. The scanning electron microscopy (SEM) was used to evaluate the surface topography and microstructure of the samples, and the energy dispersive spectroscopy (EDS) was used to analyse the chemical composition of the samples. The results indicated that no interfacial interaction layer and no obvious element diffusion were observed between the crucible and the metal, which may imply that the $BaZrO_3$ is a promising candidate of refractory for the directional solidification of TiAl alloys. This work can provide a basis for the further study of directional solidification of TiAl alloys by using $BaZrO_3$ shell mould.

1. Introduction

As a potential candidate of light-weight high-temperature structural materials, TiAl alloys have attracted much attention in recent years. However, the widespread use of TiAl alloys is limited by its intrinsic brittleness and poor ductility at room temperature [1-3]. It is demonstrated that TiAl alloys with a fully or nearly lamellar microstructure consisting of γ(TiAl) phase and α_2(Ti_3Al) phase have a good combination of strength and ductility, especially when the lamellar orientation is along the growth direction. However, it is difficult to control the lamellar orientation by simple casting process, thus, the directional solidification (DS) is proposed [4-6]. Recently, two typical processes were applied to discuss the DS of TiAl alloys, namely, the Bridgman process with a ceramic crucible, and the container less process like an optical floating zone method [7]. Compared with the latter, the Bridgman process enables higher superheating temperature, improved microstructure/composition homogeneity, as well as more complex geometry. However, this process was subjected to the high activity of titanium alloys and the inevitable reaction between the melts and the crucible at elevated temperatures, and until now, no refractory materials were found to be absolutely inert against the melt of titanium. In fact, much attention has been paid to the effect of refractory materials such as Al_2O_3, CaO, and Y_2O_3 on the contamination of TiAl intermetallics during the DS process, and it seems that the Y_2O_3 crucible/Y_2O_3 coated moulds may be the suitable one. However, the use of Y_2O_3 was limited by its low thermal shock resistance and high cost. Therefore, it is necessary to develop a new generation ceramic refractory for DS of TiAl alloys [8-13].

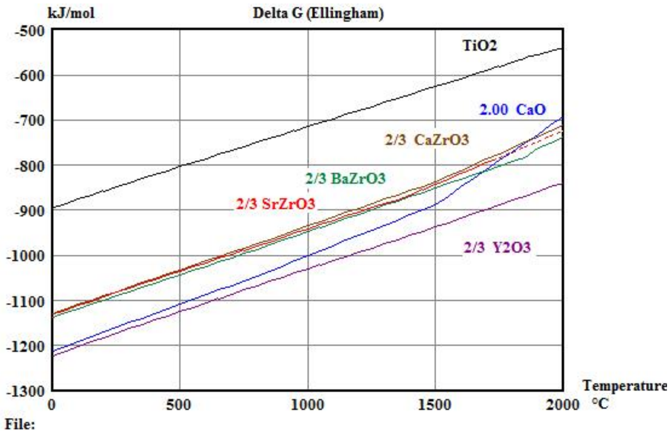

Figure 1. Variation of standard free energies of formation of some relative oxides with temperature.

Figure 1 shows the variation of the standard free energies of formation of some relative oxides with temperature. Generally, the Gibbs free energy of oxides below TiO_2 may be regarded as a candidate ceramic refractory for the DS of TiAl alloys, and other than the common oxides CaO and Y_2O_3, the zirconate family ($CaZrO_3$, $SrZrO_3$ and $BaZrO_3$) also show potential for the application. The zirconate family belongs to typical cubic perovskite, possess good mechanical strength, high thermal and chemical stability, and low coefficiency of thermal expansion. However, they are usually reported as high temperature protonic conductors rather than as the refractory used in melting titanium alloys. In our previous work, the zirconate family were made into ceramic crucibles and introduced to the vacuum induction melting of several titanium alloys, TiAl, TiNi, TiFe and Ti6Al4V [14-17], and it was found that $BaZrO_3$ exhibits a good chemical stability against the titanium melt. However, the long-term metal-crucible contact during the DS process required a higher chemical stability of the refractory than the refractory used in the induction melting. In this study, the melt of TiAl alloy contained in $BaZrO_3$ crucibles were heated for 30 minutes at 1600, 1650 and 1700 °C, respectively, then cooled within the crucible to investigate the long-term metal-crucible interaction. At the same time, the thermal shock resistance of home-made $BaZrO_3$ crucible was evaluated. The purpose is to provide a basic research for the further study of directional solidification of TiAl alloys by using $BaZrO_3$ shell mould.

2. Experiment procedure

The nominal composition of the raw alloy is Ti-48Al, with a sample size of Ø20mm×40 mm, and its chemical compositions are listed in table 1. Before melting, the alloy bars were polished, cleaned, and dried. The $BaZrO_3$ crucible was shaped by the isostatic pressing moulding technology with 2 wt% additional TiO_2 as a flux added into the $BaZrO_3$ powder, the green body was pre-sintered at 900 °C for 3 hours to remove organic compounds and achieve bisques with much higher mechanical strength. Subsequently, the final sintering was carried out at 1750 °C for 3 hours. Samples for thermal shock resistance test were shaped into disks of Ø20mm×1.8mm by isostatic pressing molding technology using 120MPa, and the test process followed the YB/T376.2-1995, which included four procedures: a) the disk samples were dried for 3 hours at 110°C to remove water; b) then quickly moved into a furnace which was preheated to 1100°C; c) after 20 minutes, the samples were moved out to cool in the air to room temperature; d) repeat processes b and c until cracks or distortions were observed on the disk surface. The final number of repetition was recorded to measure the thermal shock resistance.

Table 1. Composition of experiment used TiAl alloys.

Element	Al	Fe	O	N	Other	Ti
wt%	32.93	0.072	0.0473	0.0087	<0.01	Bal.

To well stimulate the long-term metal-crucible interaction during the DS process, the TiAl melt contained in the $BaZrO_3$ crucibles were heated for 30 minutes at 1600, 1650, and 1700 °C, respectively, in a carbon resistance furnace monitored by a Marathon type double colour infrared thermometer, and then cooled within the crucible. In order to reduce the oxygen content to a minimum level, the chamber was evacuated up to less than 10^{-2} Pa and backfilled with argon gas 5 times before heating, and the melting experiment was performed under a dry argon gas protective atmosphere at 0.06MPa.

The melted ingots were sectioned perpendicular to the cross section by electrical discharge machining (EDM) to samples with appropriate sizes and then mechanically polished following the standard metallographic procedures. The microstructure and interface morphology of the samples were examined using Scanning Electron Microscopy (JSM6700F), their elemental compositions were analysed by Energy Dispersive Spectrometer (JSM6700F), and the overall oxygen increase was measured by Nitrogen Oxygen Analyzer (TC-436) with a diameter of 2mm. Samples of length 10mm were cut from the alloys with the surface layer removed by grinding, and the samples were carefully drilled to achieve fine chips for oxygen measurements.

3. Results and discussion

3.1. Thermal shock resistance

The results of thermal shock resistance tests indicate that after 40 times heating-cooling cycle (heated to 1100°C in the furnace and then quickly moved out to the air and cooled to room temperature), no cracks or distortions are observed on the disk surface, which may imply that $BaZrO_3$ possesses a good thermal shock resistance. In fact, $BaZrO_3$ was successfully used as the crucible refractory in preparing the YBCO single crystal superconductor [18], and its thermal shock resistance can meet the requirement of DS process.

3.2. Interaction analyses

Due to the high activity of TiAl melt at elevated temperatures, a severe reaction layer might form between the melt and the crucible, and this layer may directly affect the solidification process. It was reported that when the Al_2O_3 crucible was used in the DS of TiAl alloys, the Al_2O_3 particles might dissolve and /or involve into the alloy matrix and form a reaction layer, while this reaction layer can be avoided when the Y_2O_3 crucible was applied [7]. However, due to its poor thermal shock resistance, Y_2O_3 was usually used as a coating or crucible with a properly designed porous structure, and this will bring the pollution of Y_2O_3 particles into the alloy [7,12,13,19].

Figure 2 shows the photographs of the crucible before and after melting (heated at 1650°C for 30 minutes). In order to analyse the metal-crucible interface, the whole crucibles containing the alloy were embedded with bakelite. It is observed that the alloy can be easily separated from the crucible when samples are sectioned perpendicular to the cross section by a water-cooled diamond wheel; the metal-crucible surface is still remained smooth, and no interaction layer is observed between the metal and the crucible, as seen in figure 2(b). This result is consistent with the prediction of thermodynamics, that the stability of $BaZrO_3$ tends to be higher than TiO_2 and no interaction exists between the TiAl metal and $BaZrO_3$.

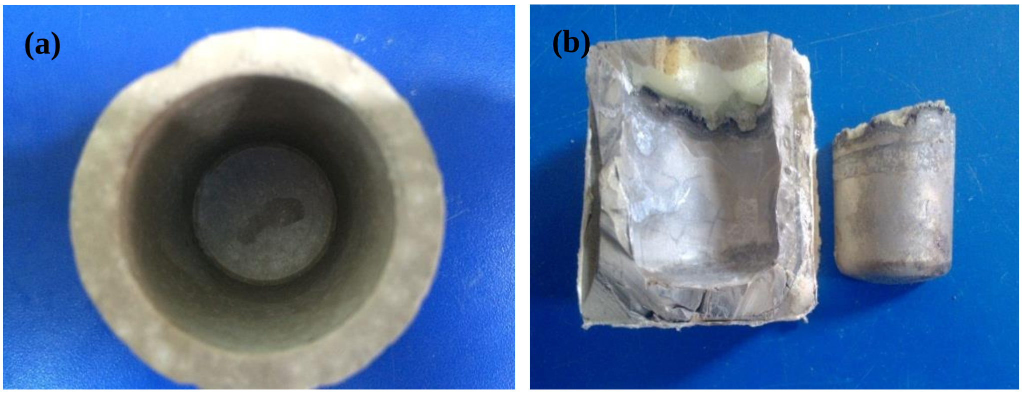

Figure 2. Photographs of crucible before and after melting (heated at 1650°C for 30 min).

Figure 3 shows the typical metal-crucible interfacial microstructures using the $BaZrO_3$ crucibles. It is reported that the Al_2O_3 particles may dissolve and /or became included into the alloy matrix and form a reaction layer between the metal-crucible surface, and the thickness of interaction layer will increase with the increasing of heating temperature and reaction time [7]. Compared with the Al_2O_3 crucible, the interface between the $BaZrO_3$ crucible and the TiAl melt remains quite clear at each temperature, as shown in figure 3 (a), (b), and (c). A layer with average thickness of about 15-60 um is attached to the alloy surface at 1600°C and 1700°C, and this layer is identified to be $BaZrO_3$ using the EDS analyses, as seen in table 2 (Point A, B and C). The formation of this layer may be affected by the density of crucible, but the maximum density of the crucible can only reach 97% in our lab. In addition, the exiting porous may become the channel of the penetration of metal into the refractory during the period of melting and solidification, and after solidification, the alloy finally stripped from the crucible surface to form a layer. By comparison, Y_2O_3 particles can be observed in the alloy matrix when it was used in the DS of TiAl alloys, as seen in figure 4(a). Meanwhile, the $BaZrO_3$ is just attached to the alloy surface, and no $BaZrO_3$ particles were found in the alloy matrix, as seen in figure 4(b). There exist some light-grey areas (point G and H), but their composition is still metal and not oxide, and the EDS results of alloy at different areas in table 2 also indicates that no obvious element diffusion is observed between the crucible and the metal.

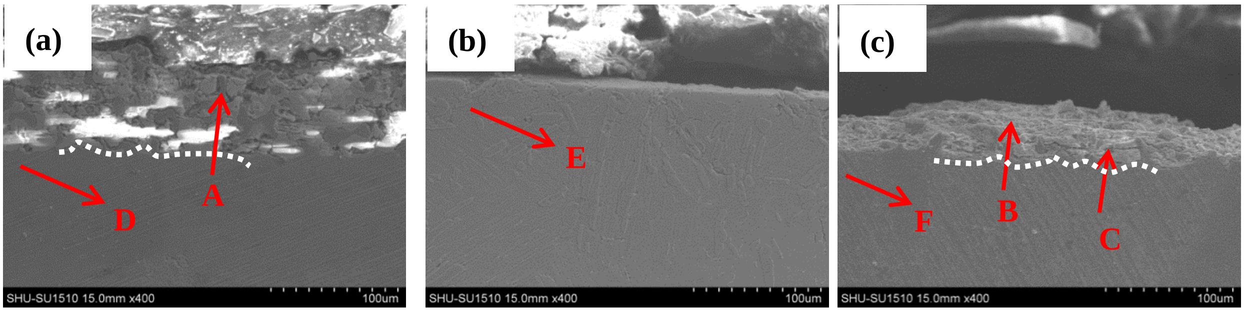

Figure 3. Metal–crucible interfacial microstructures of the ingots using $BaZrO_3$ crucibles, after 30 min at (a) 1600°C, (b) 1650 °C and (c) 1700 °C.

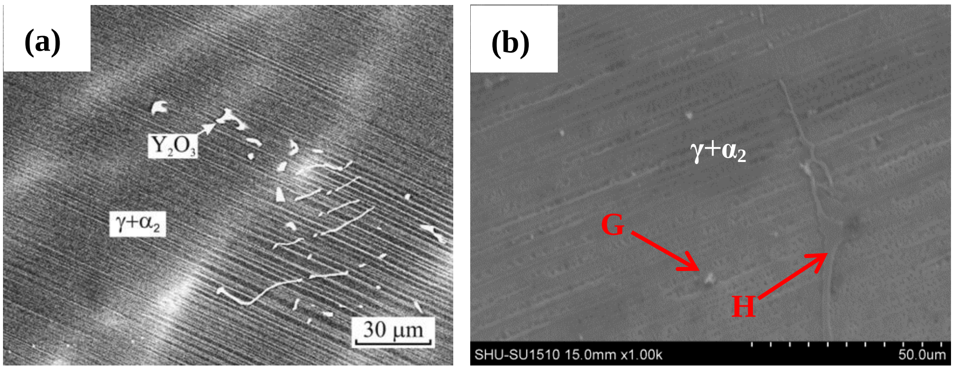

Figure 4. Microstructure of TiAl alloys melted by (a)Y_2O_3 crucible[19] and (b)$BaZrO_3$ crucible.

Table 2. The EDS results of alloy at different areas (at%).

	A	B	C	D	E	F	G	H
Ba	16.54	12.90	16.38	-	-	-	-	-
Zr	18.59	14.46	15.09	-	-	-	-	2.79
O	64.87	68.08	64.40	-	-	-	-	-
Ti	-	1.98	-	45.71	47.43	48.04	35.60	79.95
Al	-	2.59	4.13	54.29	52.57	51.96	64.40	17.26

3.3. Increase of oxygen in ingots

TiAl alloys are sensitive to interstitial atoms such as nitrogen, hydrogen, and oxygen. Among these, the oxygen concentration possesses a great effect on the properties and solidification process. During the DS of TiAl alloys in a ceramic crucible, there is unavoidable contact between the TiAl melt and the ceramic material and this might cause the increase of oxygen in ingots.

Figure 5 is the oxygen contents in ingots at heating temperatures of 1600, 1650, and 1700°C, and they are 2870, 3110, and 3730 ppm, respectively. Generally, it is accepted that the oxygen content in cast TiAl-based alloys should not exceed the limit of about 1200 ppm [19]. Although the recent results surpasses the limit by about 2000 ppm, the maximum oxygen content of 3730 ppm at 1700°C is still below a critical value of about 4800 ppm, which would lead to a change of primary solidification β phase to the α phase[20]. The reason for the oxygen increase may be from two main sources [12,19]; one is from the original master alloy, and the other is from the atmosphere since the vacuum of the present experiment is doubtful. This may contribute to the high oxygen content, but the truth is still unclear, and further study is necessary before the $BaZrO_3$ refractory can be commercially applied to the DS of TiAl alloys.

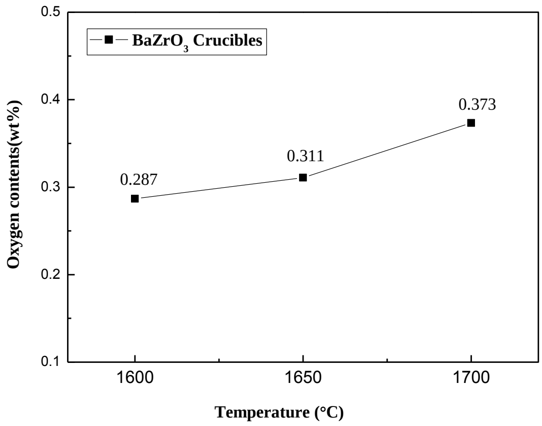

Figure 5. Oxygen contents in ingots at heating temperatures 1600, 1650 and 1700°C.

4. Conclusion

To well stimulate the long-term metal-crucible interaction during the DS process, the TiAl melt contained in $BaZrO_3$ crucibles were heated to 1600, 1650, and 1700 °C, respectively, in a vacuum furnace, and the thermal shock resistance of the crucible was measured, and the metal-crucible interaction and increase of oxygen in the alloy were also investigated. The main conclusions are as follows:

1. The thermal shock resistance test indicates that $BaZrO_3$ possesses a good thermal shock resistance and can meet the requirement of DS process.
2. At 1600, 1650 and 1700 °C, no interaction layer forms between melt of TiAl and $BaZrO_3$ crucible, no obvious element diffusion is observed between melt of TiAl and $BaZrO_3$.
3. No $BaZrO_3$ particles are found in the alloy matrix, the maximum oxygen content (3730 ppm for the samples of 1700°C) is below the critical value of about 4800 ppm.

Acknowledgments

The authors thank the National Basic Research Program of China (973 Program No. 2014CB643403), the National Nature Science Foundation of China (Grant No. 51225401 and No. 51374142) and the Science and Technology Fund of Scientific Committee of Shanghai (No.11520500100 and No. 14JC1491400).

References

[1] Clemens H, 2000 Heinrich Kestler. Processing and applications of intermetallic γ-TiAl-based alloys [J]. *Advanced engineering materials*, **2** 551-569.
[2] Saari H, Beddoes J, Seo D Y, etal. 2005 Development of directionally solidified γ-TiAl structures [J]. *Intermetallics*, **13** 937-943.
[3] Yamaguchi M, Inui H, Ito K. 2000 High temperature structure intermetallics [J]. *Acta mater,* **48** 307-322.
[4] Kishida K, Johnson D R, Masuda Y, etal. 1998 Deformation and fracture of PST crystals and directionally solidified ingots of TiAl-based alloys [J]. *Intermetallics*, **6** 679-683.
[5] Kim S E, Lee Y T, Oh M H, etal. 2000 Directional solidification of TiAl-Si alloys using a polycrystalline seed [J]. *Intermetallics*, **8** 399-405.
[6] Zhang H, Tang X, Zhou C, etal. 2013 Comparison of directional solidification of γ-TiAl alloys in conventional Al2O3 and novel Y2O3-coated Al2O3 crucibles [J]. *Journal of the European ceramic society*, **33** 925-934.

[7] Lapin J, OndrúŠ L, Nazmy M. 2002 Directional solidification of intermetallic Ti-46Al-2W-0.5Si alloy in alumina moulds [J]. *Intermetallics,* **10** 1019-1031.
[8] Lapin J, Gabalcová Z. 2011 Solidification behavior of TiAl-based alloys studied by directional solidification technique [J]. *Intermetallics,* **19** 797-804.
[9] Muto S, Yamanaka T, Johnson D R, etal. 2002 Effects of refractory metals on microstructure and mechanical properties of directionally solidified TiAl alloys [J]. *Materials science and engineering A,* **329-331** 424-429.
[10] Kuang J P, Harding R A, Campbell J. 2000 Investigation into refractories as crucible and mould materials for melting and casting γ-TiAl alloys [J]. *Materials science and technology,* **16** 1007-1016.
[11] Renjie C, Huarui Z, Xiaoxia T, etal. 2011 Interactions between γ-TiAl melt and Y2O3 ceramic material during directional solidification process [J]. *Trans. Nonferrous met. Soc.China,* **21** 2415-2420.
[12] Tetsui T, Kobayashi T, Kishimoto A, etal. 2012 Structural optimization of an yttria crucible for melting TiAl alloy [J]. *Intermetallics,* **20** 16-23.
[13] Zhao Z, Kailiang Z, Lanjie L, etal. 2013 Preparation of BaZrO3 Crucible and Its Interfacial Reaction with Molten Titanium Alloys [J]. *Journal of the Chinese ceramic society,* **41** 1278-1283.
[14] Zhao Z, Fangyuan X, Ming Z, etal. 2013 Vacuum induction melting of TiNi alloys using BaZrO3 crucibles[J]. *Materials science forum,* **765** 316-320.
[15] Lanjie L, Guangyao C, Zhao Z, etal. 2013 Interface Reaction Between Refractory BaZrO3 and TiM(M=Fe, Ni) Melt[J]. *Hot working technology,* **42** 49-54.
[16] Bo Y, Kailiang Zhu, Xionggang Lu, etal. 2012 Preparation of TiFe based alloy melted by CaZrO3 crucible and its hydrogen storage properties [J]. *The Chinese tournal of process engineering,* **12** 849-856.
[17] Erb A, Walker E, Fliikiger R. 1995 BaZr03: the solution for the crucible corrosion problem during the single crystal growth of high-TC superconductors REBa2Cu3O7-δ; RE = Y, Pr[J]. *Physica C,* **245** 245-251.
[18] Lapin J, Gabalcová Z, Pelachová T 2011. Effect of Y2O3 crucible on contamination of directionally solidified intermetallic Ti-46Al-8Nb alloy [J]. *Intermetallics,* **19** 396-403.
[19] Zollinger J, Lapin J, Daloz D, etal. 2007 Influence of oxygen on solidification behavior of cast TiAl-based alloys[J]. *Intermetallics,* **15** 1343-1350.