

Fabrication of coarse grain yttria composite and its corrosion resistance to molten titanium

Jingkun Yu^a, Chengwan Cui^{a,b}, Xinzhong Tian^c, Chun Wang^d, Xinli Wang^a and Wenbin Dai^{a,*}

^aNortheastern University, 313Box, Wenhua Road, Heping District, Shenyang, 110004, P. R. China

^bChina First Heavy Industries, Changqian Road, Fularji District, Qiqihar, 161042, P. R. China

^cXingtai Iron and Steel Corp., Ltd, South Gangtie Road, Xingtai, 054027, P. R. China

^dYingkou Qinghua Refractory Material Co., Ltd., Panlong Road, Dashiqiao, 115100, P. R. China

To fabricate coarse yttria grain with closed pores for improving the thermal shock resistance of yttria, a proper additive was firstly selected among calcium nitrate, cerium nitrate, and neodymium nitrate. Then, the appropriate amount of calcia added into yttria was investigated. Finally, the corrosion resistance of the fabricated yttria crucible was compared with pure calcia, and magnesia crucible. The results revealed that by adding 1 mol% calcia, lots of closed pores were distributed in coarse yttria grains and the composite has superior thermal shock resistance and excellent corrosion resistance with titanium alloy. The newly fabricated yttria might fit for the melting and casting of pure titanium and its alloys.

Key words: Additive, Yttria, Interface, Titanium alloy.

Introduction

Yttria possesses superior high temperature stability and excellent corrosion resistance to molten titanium, and it is considered as a promising crucible material for vacuum induction melting (VIM) process to melt and cast high purity titanium and its alloys at high temperature. [1-3] However, yttria has not been applied in industry for poor thermal shock resistance.

To improve the thermal shock resistance of yttria, By forming closed pores and tabular or elongated grains, tabular alumina with superior thermal shock resistance has been developed by Almatiss [4]. On the basis of the available knowledge of the relationship between microstructures and mechanical properties, it should be feasible to improve the thermal shock resistance of yttria by fabricating a microstructure with closed pores or tabular grains. [4-6] Generally, additives are utilized to modify sintering behavior by changing interfacial energy, grain boundary mobility, vacancy population, diffusion rate, and even phase stability. [7] Jorgensen has found that the segregation of ThO₂ solute at the grain boundaries can inhibit grain growth and the decrease of grain-boundary mobility allows pores diffuse to grain boundaries. [8] Katayama has reported the effect of divalent metal oxide on sintering and electrical properties of yttria, and proposed that small amount of divalent metal oxide can greatly improve the sinterability of yttria.

[9, 10] Recently, Kodo has investigated the effect of additives on the sintering behavior of polycrystalline yttria and concluded that the doping effect on the sinterability of yttria is probably related not only to the ionic valence of the dopant cations, but also to ionicity in the vicinity of the grain boundaries. [11, 12]

In present work, the proper additive was selected by dripping method, and the appropriate amount of additive was surveyed and the corrosion resistance was investigated by comparing with pure calcia and magnesia.

Experimental Procedures

Raw Materials

In present study, Fine yttria (Y₂O₃, Rongruida, Zibo, China, total rare earth oxide (TREO) 99.8mass%, RE impurities content (mass%/TREO): Y₂O₃ 99.99, CeO₂ 0.001, La₂O₃ 0.002, Pr₆O₁₁ < 0.002, Nd₂O₃ < 0.001, Sm₂O₃ < 0.001, Non-Re impurities content (mass%) Cl⁻¹ < 0.02, Fe₂O₃ < 0.002, PbO < 0.001, < 0.5 μm), calcium nitrate (Ca(NO₃)₂·4H₂O, Fortune Bio-tech, Shanghai, China, purity > 99.0%, Insoluble matter in water < 0.003mass%, Chloride < 0.003mass%, Sulfate < 0.01 mass%, Ammonium < 0.005mass%, Iron < 0.0002mass%, Barium < 0.005mass%, Alkali metals and magnesium < 0.2mass%, Heavy metals < 0.005 mass%), cerium nitrate (Ce(NO₃)₃·4H₂O, Fortune Bio-tech, Shanghai, China, purity > 99.0%, CeO₂ > 39.5mass%, CeO₂/REO > 99.95, Insoluble matter in water < 0.005mass%, Chloride < 0.002mass%, Sulfate < 0.01mass%, Ammonium < 0.005mass%, Iron < 0.0015 mass%, PbO < 0.001mass%), neodymium nitrate

*Corresponding author:
Tel : +86-24-8368-9981
Fax: +86-24-8368-9981
E-mail: wb_dai@hotmail.com

(Nd(NO₃)₃·4H₂O, Ziyi, Shanghai, China, purity > 99.0%, Nd₂O₃ > 36.0mass%, Nd₂O₃/REO > 99.95, Insoluble matter in water < 0.005mass%, Chloride < 0.002mass%, Sulfate < 0.002mass%, Iron < 0.005mass%, PbO < 0.001mass%), calcium carbonate (Dongdafulong, Shenyang, China, > 99.2mass%, impurities content (mass%) Si < 0.009, Al < 0.006, Fe < 0.005, Ba < 0.005, < 0.1 μm), calcium oxide (CaO, Sinopharm Chemical Reagent, Shanghai, China, purity > 98.0mass%, Insoluble matter in acetic acid < 0.05mass%, Ignition loss < 2mass%, Chloride < 0.01mass%, Iron < 0.015mass%, PbO < 0.005mass%, Alkali metals and magnesium < 0.5 mass%), and magnesia (MgO, Tianyuan, Shenyang, China, purity > 98.0mass%, Insoluble matter in hydrochloric acid < 0.01mass%, Soluble matter in water < 0.5mass%, Ignition loss < 2mass%, Chloride < 0.01mass%, Sulfate < 0.02mass%, Phosphate < 0.003 mass%, Total nitrogen < 0.001mass%, Sodium < 0.05 madd%, Calcium < 0.02mass%, Iron < 0.015mass%) were utilized as raw materials.

Preparation of samples

For dripping testing sample, pure yttria sample with the size at Φ20 × 6 mm was firstly polished from the compact heated at 1500 °C for 3 hrs. Then, as schematically shown in Fig. 1, the sample was settled on the 120 °C constant temperature oven and ten drops of solution made of calcium nitrate, cerium nitrate, and neodymium nitrate with the concentration at 5 mol/L were slowly dripped. After dried at 120 °C for 12 hrs, the sample was finally obtained by heating at 1600 °C for 5 hrs into a MoSi₂ resistance furnace under air atmosphere.

For calcia doped sample, pure yttria and calcium carbonate powders were elaborately weighted according to Table 1 and ball-milled. After the mixed powders were calcined at 1000 °C under air atmosphere to decompose calcium carbonate by CaCO₃CaO + CO₂, they were die-pressed into cylinders of Φ20 mm × ~ 7 mm under 100 MPa, and the green compacts were heated at 1300 °C for 1hr and 1600 °C for 5 hrs in a MoSi₂ resistance furnace and sintered under air atmosphere.

For corrosion test materials, the titanium alloy with the composition for Ti 45mass%, Ni 45mass%, Nb 10mass% was selected. The crucibles were made from 1 mol% calcia doped yttria, pure calcia and pure magnesia by heating at 1600 °C for 5 hrs in a MoSi₂

Table 1. Chemical compositions of samples (mol%).

Sample	CaCO ₃	Y ₂ O ₃
S1	0	100
S2	0.3	99.7
S3	0.6	99.4
S4	1.0	99.0
S5	3.0	97.0
S6	5.0	95.0
S7	7.0	93.0
S8	10.0	90.0

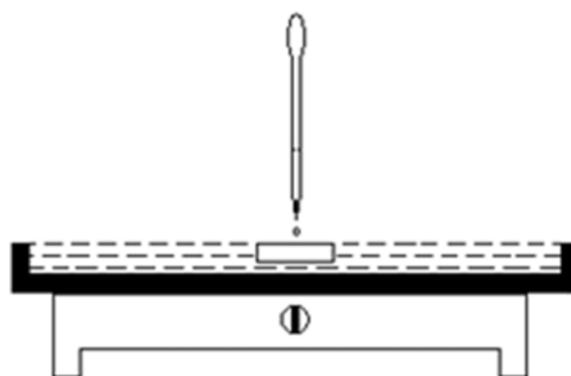


Fig. 1. Schematic of the dripping method.

resistance furnace and sintered under air atmosphere. In the course of the corrosion test, 20.0 g titanium alloy was firstly weighted and placed into the crucible. Then, the corrosion test was carried out at 1600 °C for 3 hrs in high purity argon (> 99.999%) flow (0.01 L/min) protected alumina tube furnace.

Characterization

The morphology was analyzed by scanning electron microscope (Model SSX-550, Shimadzu, Kyoto, Japan) equipped with energy-dispersive spectroscopy (EDS).

Results and Discussion

Figs. 2(a-c) show the microstructures of the samples dropped with calcium nitrate, cerium nitrate, and neodymium nitrate, respectively. A concentration gradient of the additive was found in these samples. The growth of the yttria grain has obvious difference with the change of the kind of additive and the penetrated depth

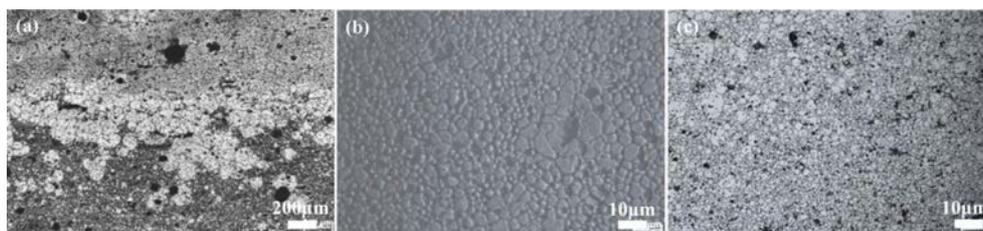


Fig. 2. Microstructures of the samples dropped with (a) calcium nitrate, (b) cerium nitrate, and (c) neodymium nitrate.

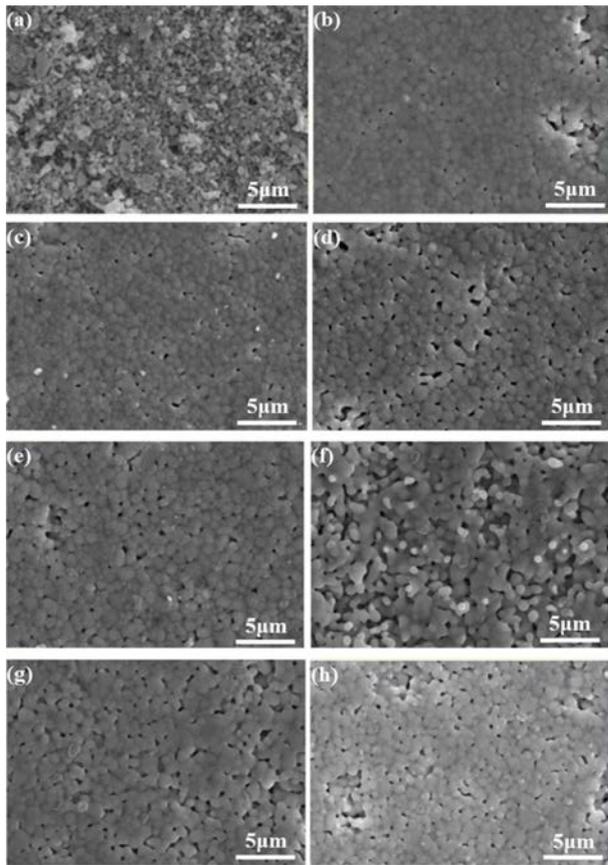


Fig. 3. Microstructure samples doped different amount of calcia sintered at 1300 °C for 1 hr; (a) None, (b) 0.3 mol%, (c) 0.6 mol%, (d) 1.0 mol%, (e) 3 mol%, (f) 5 mol%, (g) 7 mol%, (h) 10 mol%.

of the sample. As shown in Fig. 2(a), though the concentration of the calcia in the depth direction had a gradient, the grain size of calcia solved yttria on the interface ($\sim 100 \mu\text{m}$) was much bigger than that of pure yttria grain ($5 \mu\text{m}$), interestingly, it was also

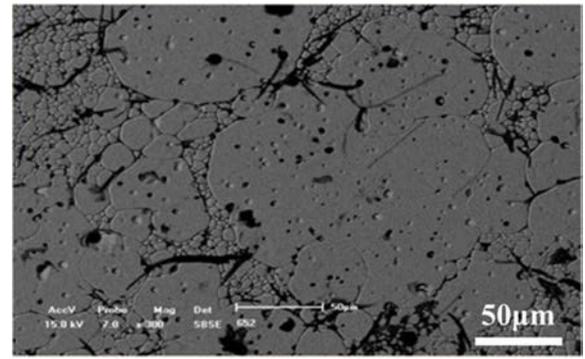


Fig. 4. Microstructure of yttria doped with 1 mol% calcia sintered at 1600 °C for 5 hrs.

bigger than that of high calcia concentration areas. It implied that the grain size of yttria could be coarsened by adding small amount of calcia and the high concentration of calcia did not lead to coarse yttria grains. In the ceria added sample shown in Fig. 2(b), the grain size of ceria contained yttria was about 2–10 μm and it was near to that of the pure yttria grain. Furthermore, seldom pores were distributed in the inner of grains. It implies that the ceria had not obvious effect on the grain growth of yttria. The grain size of neodymia contained yttria shown in Fig. 2(c) was about 10–15 μm and some closed pores were distributed in the inner of grains. In order to obtain the high grain growth speed, a proper amount of calcia might be the key.

Fig. 3 shows the microstructure samples doped different amount of calcia sintered at 1300 °C for 1 hr. Obviously, the sintering effect of the pure yttria sample was ambiguous and even in the samples added with low content of calcia, the grain size was coarsened and the compacts were sintered. Interestingly, it was found that in the samples with the concentration of calcia higher than 3%, there were lots of pores in the

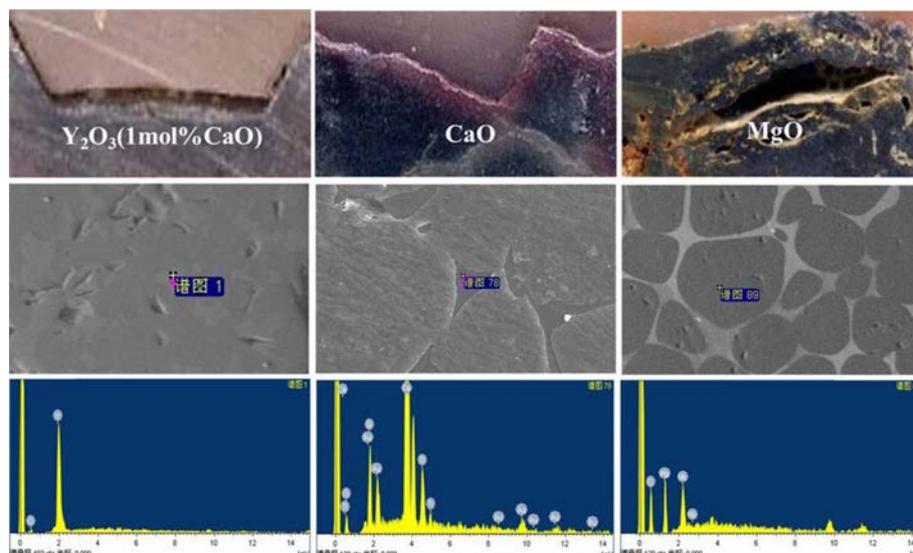


Fig. 5. Interface of the molten titanium alloy and the tested crucible.

compacts. Moreover, according to the phase diagram of CaO-Y₂O₃, it was known that the solid solution of calcia in the yttria was as low as 1.2 mol% at temperature as high as 1700 °C. On the consideration that the surplus calcia in the system could bring about the effect of hydration, 1mol% calcia was proposed to fit for our aim.

Fig. 4 shows the microstructure of yttria doped with 1mol% calcia sintered at 1600 °C for 5 hrs. The grain size was as large as 150 μm and lots of closed pores were distributed in the grains. Moreover, plenty of small grains less than 10 μm were surrounded the coarse grains. As a result, the thermal shock resistance was remarkably improved.

Fig. 5 reveals the interface of the molten titanium alloy and the tested crucible. The interface of the yttria crucible was clean and the matrix of the crucible had not change. However, the titanium element was detected in the grain boundary of calcia grain in the calcia crucible, and the niobium element was even determined in the coarse magnesia grain. Hence, the newly fabricated yttria composite possessed the superior corrosion resistance with titanium alloy.

Conclusions

1) The dripping test reveals that the grain growth of yttria can be greatly increased by adding calcia.

2) By adding 1 mol% calcia, an yttria composite with lots of closed pores distributed in coarse yttria grains can be obtained, and the thermal shock resistance of yttria could be remarkably improved.

3) The 1 mol% calcia added yttria excellent corrosion resistance with titanium alloy, and it might fit for the

melting and casting of pure titanium and its alloys.

Acknowledgments

This work is financial supported by the “National Natural Science Foundation of China” (Grant No. 51304039, No. 51674073), “The Fundamental Research Funds for the Central Universities” (Grant No. N110402008, N13040 2021, N150202003), and “Ph.D. Programs Foundation of Ministry of Education of China”(Grant No. 20090042120009).

References

1. C.C. Lin, Y.W. Chang and K.L. Lin, *J. Am. Ceram. Soc.* 91[7] (2008) 2321-2327.
2. R.J. Cui, M. Gao, H. Zhang and S.K. Gong, *J. Mater. Process Tech.* 210[9] (2010) 1190-1196.
3. R.R. Wang, G.E. Welsch and M. Castro-Cedeno, *Int. J. Prosthodont.* 11[1] (1998) 33-43.
4. W.E. Lee and R.E. Moore, *J. Am. Ceram. Soc.* 81[6] (1998) 1385-1410.
5. M. Fuhrer, A. Hey and W.E. Lee, *J. Eur. Ceram. Soc.* 18[7] (1998) 813-820.
6. R.M. German, in “Sintering Theory and Practice” (John Wiley & Sons, 1996) p. 180.
7. P.J. Jorgensen and R.C. Anderson, *J. Am. Ceram. Soc.* 50[11] (1967) 553-558.
8. K. Katayama, H. Osawa, T. Akiba, K. Urabe and H. Yanagida, *J. Mater. Sci.* 25 (1990) 1503-1508.
9. K. Katayama, H. Osawa, T. Akiba and H. Yanagida, *J. Eur. Ceram. Soc.* 6[1] (1990) 39-45.
10. M. Kodo, K. Soga, H. Yoshida and Yamamoto, *J. Euro. Ceram. Soc.* 30[13] (2010) 2741-2747.
11. M. Kodo, K. Soga, H. Yoshida and T. Yamamoto, *J. Ceram. Soc. Japan.* 117[6] (2009) 765-768.