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Densification behavior and properties of alumina–chrome ceramics: Effect of TiO_2

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Abstract

Highly dense alumina–chrome bodies with low porosity are usually used as corrosion and thermal resistant refractories. Alumina–chrome refractory with molar ratio 1:1 was developed using chemical grade hydrated alumina and chromium (III) oxide by conventional sintering route. Batch materials were attrition milled, isostatically pressed and sintered in the temperature range from 1000 °C to 1700 °C with 2 h soaking at peak temperature. Phase development of the sintered materials with temperature was studied by X-ray diffraction. Sintering temperature, sintering condition and addition of sintering aid (TiO_2) have immense effect on the densification of the alumina–chrome refractory. Highly dense alumina–chrome refractory with almost nil apparent porosity was developed at 1500 °C in reducing atmosphere. Flexural strength of the sintered materials at room temperature and at 1200 °C was also measured. 1 wt% TiO_2 gives the optimum result with respect to densification and flexural strength.

Keywords: A. Sintering; E. Refractories; Alumina; Microstructure

1. Introduction

Alumina (Al_2O_3) and chromia (Cr_2O_3) have the ability to form substitutional solid solution $(Al_{2-x}Cr_x)_2O_3$ $(0 \leq x \leq 2)$ over an entire range of composition at high temperature without formation of any eutectic as they have the same corundum crystal structure consisting of a hexagonal close packed array of oxygen anions with two-third of the octahedral interstitials occupied by the cations [1,2].

Alumina–chrome system is of significant importance owing to its high refractoriness and excellent chemical stability. Alumina–chrome refractories are used in various forms such as castables and shaped refractory in blast furnaces, electric arc furnace, fiber glass furnaces, gasifiers, carbon black reactors, various corrosion resistance refractory, incinerators and high level nuclear waste vitrification because of their superior mechanical properties, low solubility, chemical stability, slag/corrosion resistance and thermal shock resistances [3–6]. Solid solutions of Cr_2O_3 in alumina are widely used in the metal working industries, jewelry and have considerable potential for use in aviation engine [7].

Al_2O_3–Cr_2O_3 is expected to possess good corrosion resistance against molten salt due to its low solubility. Corrosion resistance of refractory does not depend only on their solubility, but also on the high relative density and low porosity of the sintered body [8]. The densification of the materials depends on various factors such as particle size of the raw materials, methods of preparation, sintering temperature, furnace atmosphere and addition of additives etc. [9–11]. There are a number of methods by which alumina–chrome solid solution can be obtained. Several researchers have investigated alumina–chrome system with various methods of preparation and unfolded the mechanism of solid solution formation, microstructure development and densification. However, information on microstructural properties is very limited [7,9,12–15]. It was observed by some authors that densification of Al_2O_3–Cr_2O_3 ceramics is controlled by cation diffusion [9,12].

In this present work, the prime endeavor is to develop highly dense alumina–chrome body with low porosity by solid

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oxide reaction route and study the phase development, microstructures and mechanical properties. To increase the reactivity of the mixture hydrated alumina with Cr_2O_3 powder was used as main raw materials. And we have optimized different parameters such as attrition milling time of the batch materials, furnace atmosphere and amount of additives sequentially for consequent experiments and characterization. The effect of TiO_2 on the densification behavior of Al_2O_3–Cr_2O_3 and properties of sintered bodies were studied systematically.

2. Experimental procedure

2.1. Preparation of samples

The major raw materials used in this investigation are LR grade hydrated alumina, chromium oxide (Cr_2O_3) and titanium oxide (TiO_2) as additive. All the materials are obtained from S.D. Fine Chemicals, India. The batch composition of alumina and chrome with molar ratio 1:1 were prepared with 0–3 wt% TiO_2 as additive. All the batches were uniformly mixed and attrition milled. Milling was done in isopropyl alcohol medium using zirconia pot with partially stabilized zirconia grinding media at a speed of 400 r.p.m. for 4 h. The milled slurry thus obtained were first air dried and subsequently dried in air oven at 100 ± 5 °C for 24 h. The dried mass was passed through 100 mesh sieve to break the agglomerate, mixed uniformly with 5% poly vinyl alcohol (PVA) solution as binder and uniaxially pressed into $0.6\ \text{cm} \times 0.6\ \text{cm} \times 7.5\ \text{cm}$ bars and briquettes of $2\ \text{cm}\ \Phi \times 1$ cm under a pressure of 100 MPa. Briquettes and bars thus produced were pressed isostatically under a pressure of 140 MPa. The green briquettes and bars were first air dried and then dried for overnight in air oven at 100 ± 5 °C and then sintered at different temperatures ranging from 1000 °C to 1700 °C. Sintering was done in a programmed controlled electric furnace in reducing as well as oxidizing atmosphere. The heating rate was maintained at 5 °C/min up to 1000 °C, then 3 °C/min up to the final sintering temperature with 2 h of soaking time and cooled down to room temperature.

2.2. Characterization

Fired briquettes and bars were characterized in terms of physical properties like bulk density, apparent porosity, phase development, flexural strength at room temperature (25 °C) as well as at 1200 °C; and microstructure. Bulk density and apparent porosity were determined by conventional liquid displacement method using Archimedes' principle in water medium. The room temperature MOR was determined in three-point bending mode (with a span of 40 mm and cross-head speed of 0.5 mm/min) using an Instron-5500R Universal Testing Machine. Measurement of hot modulus of rupture (H–MOR) was carried out at 1200 °C by three point bending method. Co-efficient of thermal expansion (CTE) and percentage linear change (PLC) were measured in high temperature dilatometer, Orton, USA. Phase identification was done by X-ray diffraction technique. The X-ray diffraction patterns of the finely powdered samples were obtained in a Philips X-ray diffractometer (Model PW 1730) using nickel filtered Cu-Kα radiation and diffraction patterns were recorded over a Braggs' angle (2θ) range of 10–70°. Micro-structural characterization was done by field emission scanning electron microscopy (FESEM), for which sintered samples were polished, thermally etched and coated with carbon to make the surface conducting. FESEM images were taken with the help of Gemini Zeiss Supra^{TM} 35VP Model.

3. Results and discussions

3.1. Raw materials and effect of milling time on specific surface area

The major raw materials hydrated alumina and chromia (Cr_2O_3) used in this study were of chemical grade with $>99\%$ purity. The XRD pattern of the hydrated alumina and chromia used in this study is shown in Fig. 1. It has

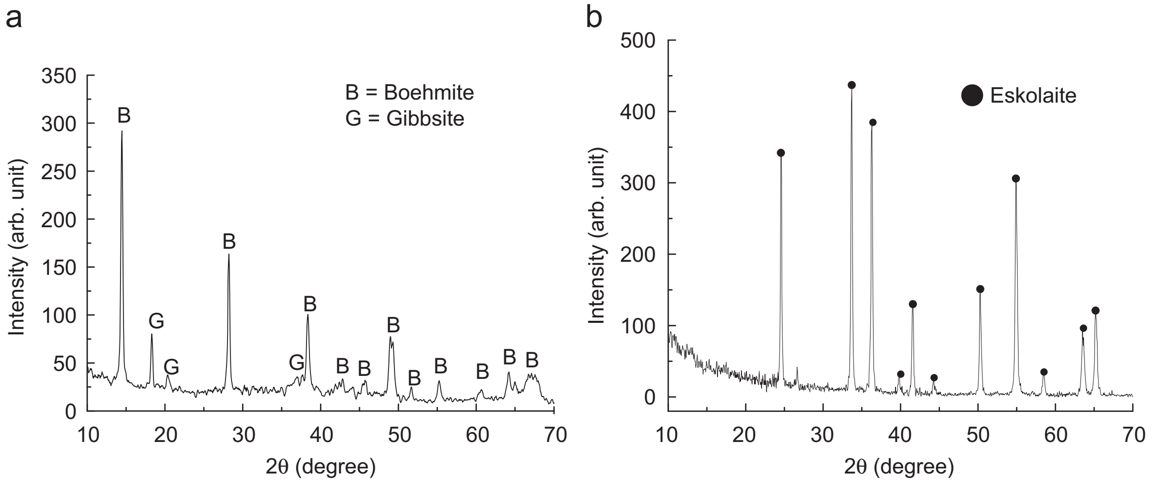

Fig. 1. X-ray diffraction pattern of raw materials used in the investigation: (a) alumina and (b) chromia.

been observed that alumina contains boehmite as the major crystalline phase with a small amount of gibbsite. Chromia (Cr_2O_3) contains eskolaite as its main crystalline phase.

The variation of specific surface area of the milled powder of batch materials with the milling time is shown in Fig. 2. It is observed that the specific surface area continuously increases with the time but the effect is more prominent up to 4 h. Therefore, an optimum milling time of 4 h is fixed throughout this study. However, it will change if we change any processing parameters such as, raw materials, amount of grinding media, speed of rotation etc. [16].

3.2. Phase development

XRD pattern of the materials, heat treated at various temperatures, is shown in Fig. 3. At 1000 °C, only corundum (JCPDS No. 046-1212, marked as C) and eskolaite (JCPDS No. 038-1479, marked as E) phases are observed; i.e., boehmite and gibbsite are converted to corundum. At 1400 °C and above, only one crystalline phase is detected. Al_2O_3 and Cr_2O_3 forms complete solid solution at 1400 °C and no free eskolaite phase is observed and position of diffraction peaks are in between corundum and chromia indicating solid solution formation [1].

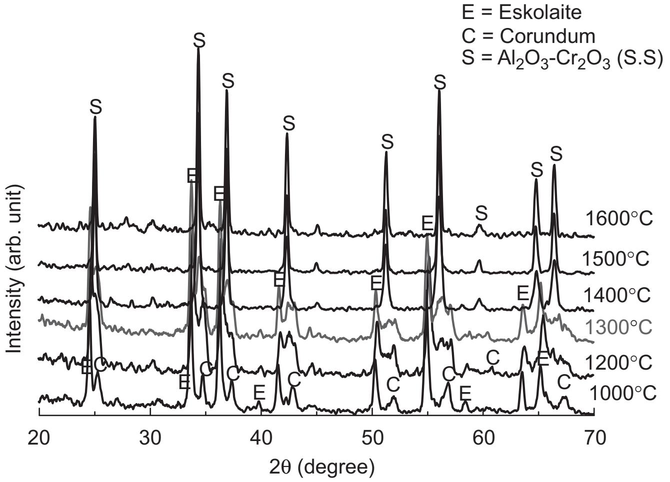

Fig. 3. Phase development of alumina–chrome samples without TiO_2 calcined at different temperatures.

3.3. Densification

In any ceramic forming process, densification is a very essential step. Densification behavior of the green compacts is studied by dilatometry. Fig. 4 shows the percent linear change of green compacts with the temperature, which clearly indicates that the densification of green compact starts at ~1100 °C and the firing shrinkage is very high from 1200 °C. Therefore, the sintering rate of these compacts should be slow from 1100 °C; otherwise very high shrinkage may generate crack in the sintered product particularly when the product size is bigger. Densification is measured by increase in bulk density and decrease in apparent porosity of the sintered compacts. The variation of bulk density and apparent porosity of the compacts (alumina–chrome without TiO_2) with the sintering temperature and furnace atmosphere are shown in Figs. 5 and 6. From Fig. 5 it is seen that up to 1200 °C there is no effect of sintering temperature and furnace atmosphere on the bulk density of the fired alumina–chrome samples without TiO_2. Previous dilatometric results also support this observation (Fig. 4). Bulk density gradually increases with temperature from 1200 °C. Under oxidizing atmosphere, the samples sintered at 1650 °C, are still porous and contain ~25% porosity. Samples sintered under reducing condition always show higher density than the samples sintered under oxidizing condition. In reducing atmosphere samples achieves its highest density at 1650 °C although apparent porosity drops down to zero at 1550 °C.

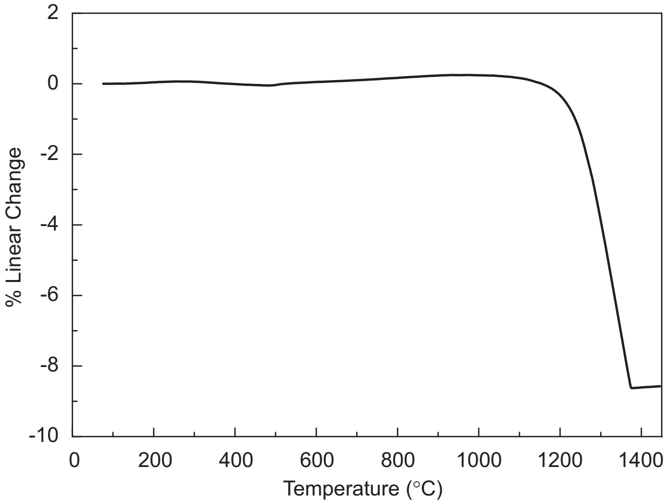

Fig. 4. Dilatometric behavior of green alumina–chrome compacts without TiO_2 under oxidizing atmosphere.

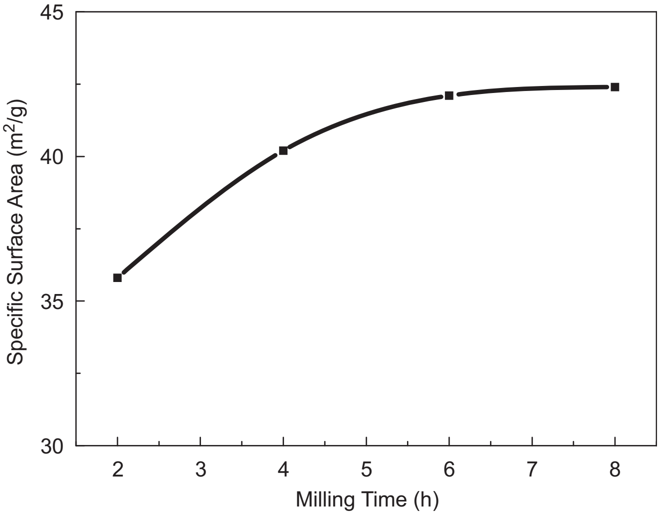

Fig. 2. Variation of specific surface area of alumina–chrome batch material with the milling time.

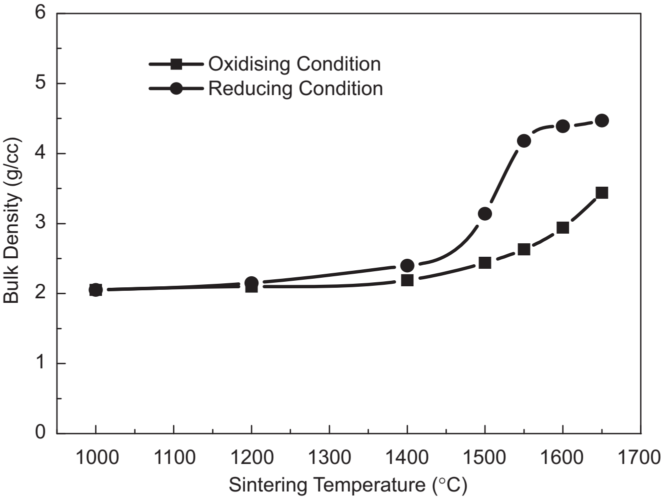

Fig. 5. Variation of bulk density of alumina–chrome samples (without TiO_2) with sintering temperature and atmosphere.

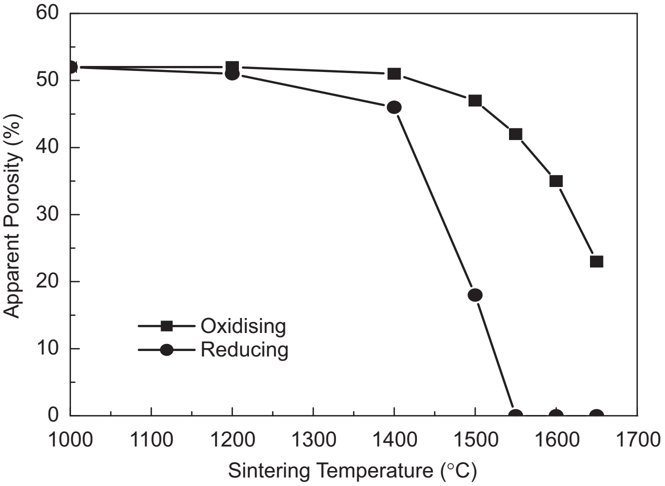

Fig. 6. Variation of apparent porosity of alumina–chrome samples (without TiO_2) with sintering temperature and atmosphere.

It is very difficult to get the dense sintered alumina chrome samples under oxidizing atmosphere because Cr_2O_3 oxidizes to CrO_2 and CrO_3 in atmosphere whose oxygen partial pressure is relatively high, e.g., air. The following reaction occurs:

$$Cr_2O_3(s)+1/2O_2(g)\longrightarrow 2CrO_2(g)$$

$$Cr_2O_3(s)+3/2O_2(g)\longrightarrow 2CrO_3(g)$$

The vapor pressure of CrO_3 and CrO_2 is high so that the sintered body of Cr_2O_3 containing samples becomes porous due to the evaporation of Cr-compounds when fired in air. So, sintering atmosphere should be controlled in such a way that it should have very low oxygen's partial pressure where Cr_2O_3 remains stable. Therefore, sintering atmosphere should be either reducing or inert [2,9].

Additive plays an important role in the sintering process. It favours the densification process by liquid phase formation or by the formation of vacancy. Variation of bulk density of Al_2O_3–Cr_2O_3 with TiO_2 content and sintering temperature is shown in Fig. 7. It is seen that samples without any additive exhibit a gradual increase in bulk density with sintering temperature up to 1700 °C. Addition of TiO_2 as sintering aid greatly enhances the densification process. At 1400 °C only 1 wt% TiO_2 addition enhances the bulk density from 2.4 g/cc to 3.5 g/cc. TiO_2 containing samples achieve their highest bulk density at ~1500 °C with almost nil apparent porosity. Beyond this temperature there is no appreciable change in bulk density with increase in temperature. Although the apparent porosity is nil, these samples contain some fine closed pores which is observed under microscope. Beyond 1500 °C, the increase in TiO_2 content (above 1 wt%) does not have appreciable effect on the bulk density. At 1700 °C all the samples exhibit almost similar bulk density. Higher TiO_2 containing samples have slightly lower bulk density due to the lower specific gravity of TiO_2 compared to Cr_2O_3. From Fig. 7 it was found that only 1 wt% TiO_2 addition is sufficient to favor the densification process. The above observation indicates that the densification takes place through solid state sintering process. When TiO_2 was added Al^{3+} and/or Cr^{3+} was replaced by higher valent Ti^{4+} ion and it generates the cation vacancy which enhance the cation diffusion thereby enhances the densification process. It is observed that diffusion of cation controls the sintering process of Al_2O_3–Cr_2O_3 system. Cation diffusion is enhanced by increase of cation vacancy. Many authors have observed that TiO_2 addition enhances the densification of Cr_2O_3 due to the formation of cation vacancy [17,18].

3.4. Mechanical property

The variation of flexural strength at room temperature and at 1200 °C of the samples with and without TiO_2 sintered at 1600 °C is shown in the Fig. 8. Addition of 1 wt% TiO_2 increases the room temperature flexural strength followed by decrease in strength with higher TiO_2 content. But with the increase in TiO_2 content, hot

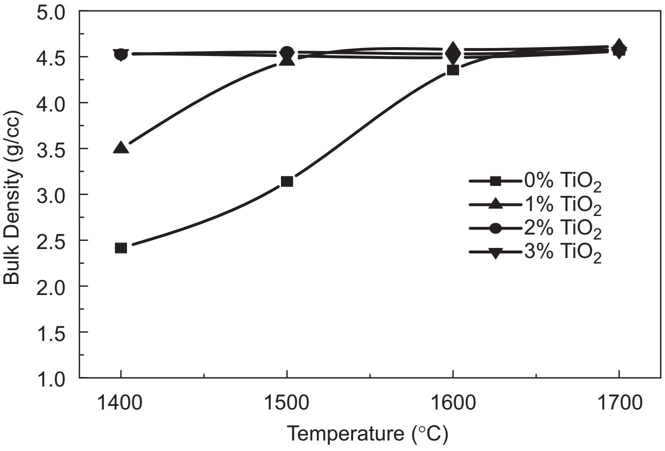

Fig. 7. Variation of bulk density with sintering temperature and TiO_2 content (0–3 wt%).

flexural strength at 1200 °C continuously decreases. The samples containing 1 wt% of TiO_2 have the flexural strength of 188 ± 24 MPa (at room temperature) and 193 ± 12 MPa (at 1200 °C).

Since, 1 wt% TiO_2 addition greatly improves the densification without much deterioration of flexural strength, so, 1 wt% TiO_2 addition is found to be the optimum and is selected for subsequent microstructural characterizations.

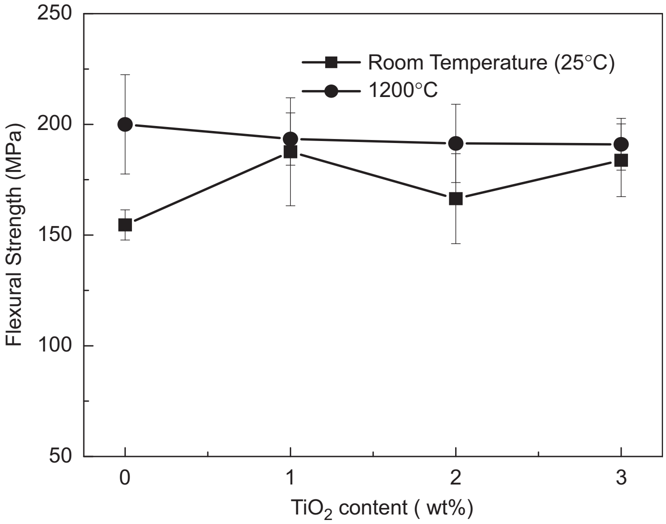

Fig. 8. Flexural strength at room temperature and at 1200 °C with variation of TiO_2 content (samples sintered at 1600 °C).

3.5. Microstructures

Since, the reducing atmosphere always gives better results in terms of densification; therefore, the samples, sintered under reducing condition, are selected for the microstructural study. Figs. 9 and 10 shows the scanning electron photomicrographs of the alumina–chrome samples without and with TiO_2 sintered at different temperatures. When the sample is sintered at 1500 °C (Fig. 9), it contains considerable amount of pores and average grain sizes are 1 μm and 1.3 μm for samples without and with TiO_2 additive respectively. But on increasing the temperature to 1600 °C (Fig. 10) grain to grain interlocking is better, the intergranular porosity has been decreased and there is an increase in average grain size (1.6 μm and 5.2 μm for Fig. 10(a) and (b) respectively). Again from Fig. 10 it can be observed that although the apparent porosity of sintered samples is zero, sintered materials contain some closed pores. Addition of TiO_2 reduces this porosity and the microstructure is more compact [Figs. 9(b) and 10(b)]. TiO_2 addition also increases the average grain size of the sintered samples.

4. Conclusions

Highly dense alumina–chrome refractories were developed by conventional sintering route. It is not possible to get dense sintered Al_2O_3–Cr_2O_3 body in air/oxidizing atmosphere due to the removal of Cr compound. Al_2O_3–Cr_2O_3 samples

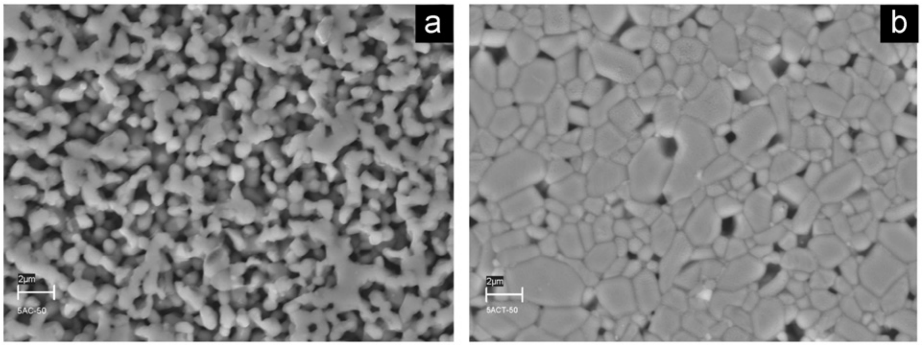

Fig. 9. Microstructures of alumina–chrome sintered at 1500 °C: (a) without TiO_2 and (b) with 1 wt% TiO_2 (scale = 2 μm).

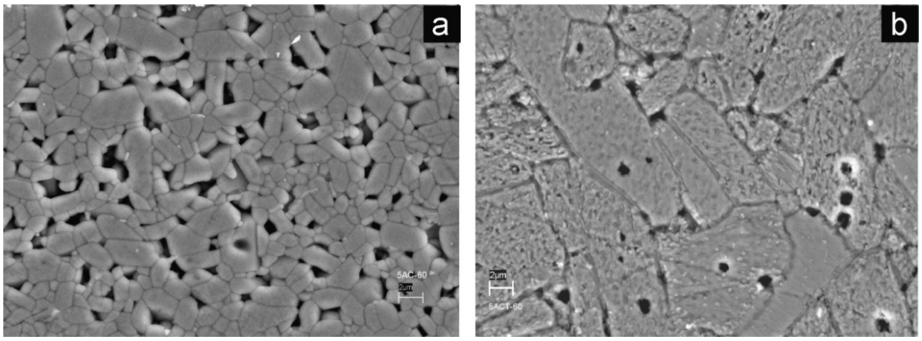

Fig. 10. Microstructures of alumina–chrome sintered at 1600 °C: (a) without TiO_2 and (b) with 1% TiO_2 (scale = 2 μm).

without TiO_2 sintered in reducing condition, always exhibit higher bulk density than the sample sintered in air atmosphere. At 1600 °C, sintered body of Al_2O_3–Cr_2O_3 without TiO_2 having almost nil apparent porosity is obtained in reducing atmosphere. Addition of TiO_2 as sintering aid favours the densification by the formation of cation vacancy. TiO_2 containing samples achieve highest density and almost nil apparent porosity at 1500 °C in reducing condition. Hot modulus of rupture at 1200 °C is almost same to the room temperature flexural strength. The TiO_2 containing sintered Al_2O_3–Cr_2O_3 body shows more compact grains with bigger grain size. 1 wt% TiO_2 gives the optimum results with respect to densification and flexural strength of Al_2O_3–Cr_2O_3 ceramics.

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References

[1] F. Bondioli, A.M. Ferrari, C. Leonelli, T. Manfredini, L. Linati, P. Mustarelli, Reaction mechanism in alumina/chrome (Al_2O_3–Cr_2O_3) solid solutions obtained by coprecipitation, Journal of the American Ceramic Society 83 (8) (2000) 2036–2040.
[2] H.G. Emblem, T.J. Davies, A. Harabi, A.A. Ogwu, C.S. Nwobodo, V. Tsantzalou, Solid-state chemistry of alumina–chrome refractories, Journal of Materials Science Letters 11 (1992) 820–821.
[3] J.P. Kiehl, Y. Le Mat, Use of chrome–alumina castables and shapes in blast furnace and carbon black reactors, Ceramic Bulletin 62 (7) (1983) 809–810.
[4] T. Hirata, T. Morimoto, S. Ohta, N. Uchida, Improvement of the corrosion resistance of alumina–chromia ceramic materials in molten slag, Journal of the European Ceramic Society 23 (2003) 2089–2096.
[5] T.J. Davies, H.G. Emblem, A. Harabi, C.S. Nwobodo, A.A. Ogwu, V. Tsantzalou, Characterisation and properties of alumina–chrome refractories, Journal of the British Ceramic Transactions 91 (1992) 71–76.
[6] A. Harabi, T.J. Davies, Mechanical properties of sintered alumina–chrome refractories, British Ceramic Transactions 94 (2) (1995) 79–84.
[7] A.G. Tarasov, V.A. Gorshkov, V.I. Yukhvid., Phase composition and microstructure of Al_2O_3–Cr_2O_3 solid solutions prepared by self-propagating high-temperature synthesis, Inorganic Materials 43 (7) (2007) 724–728.
[8] K. Nishida, K. Komeya, Corrosion resistivity of ceramics, Boshoku Gijutsu 35 (1986) 646–655.
[9] S.A. Cho, F.J. Arenas, J. Ochoa, Densification and hardness of Al_2O_3–Cr_2O_3 system with and without Ti addition, Ceramics International 16 (1990) 301–309.
[10] K. Shibata, M. Yoshinaka, K. Hirota, O. Yamaguchi, Fabrication and mechanical properties of Cr_2O_3 solid solution ceramics in the system Cr_2O_3–Al_2O_3, Materials Research Bulletin 32 (5) (1997) 627–632.
[11] A. Harabi, T.J. Davies., Densification and grain growth in sintered alumina–chrome powder mixtures, British Ceramic Transactions 94 (3) (1995) 97–102.
[12] T. Hirata, K. Akiyama, H. Yamamoto, Sintering behavior of Cr_2O_3–Al_2O_3 ceramics, Journal of the European Ceramic Society 20 (2000) 195–199.
[13] D.H. Riu, Y.M. Kong, H.E. Kim, Effect of Cr_2O_3 addition on microstructural evolution and mechanical properties of Al_2O_3, Journal of the European Ceramic Society 20 (2000) 1475–1481.
[14] H.T. Lin, B.Z. Liu, W.H. Chen, J.L. Huang, P.K. Nayak, Study of color change and microstructure development of Al_2O_3–Cr_2O_3/Cr_3C_2 nanocomposites prepared by spark plasma sintering, Ceramics International 37 (7) (2011) 2081–2087.
[15] Y.I. Yoshizawa, M. Toriyama, S. Kanzaki, Fabrication of textured alumina by high-temperature deformation, Journal of the American Ceramic Society 84 (6) (2001) 1392–1394.
[16] H.S. Tripathi, G. Banerjee, Effect of chemical composition on sintering and properties of Al_2O_3–SiO_2 system derived from sillimanite beach sand, Ceramics International 25 (1999) 19–25.
[17] P.D. Ownby, G.E. Jungquist., Final sintering of Cr_2O_3, Journal of the American Ceramic Society 55 (1972) 433.
[18] W.D. Collister, et al., Sintering chromium oxide with the aid of TiO_2, Journal of the American Ceramic Society 62 (1979) 208–211.