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Fabrication and thermal properties of Al_2TiO_5/Al_2O_3 composites

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Al_2TiO_5/Al_2O_3 composites with various Al_2O_3 contents were prepared. The phase compositions and microstructure evolution of the samples were observed via XRD and SEM, respectively. The thermal properties, including thermal expansion ratios and the erosion resistance of the Al_2TiO_5/Al_2O_3 composites to molten Al, were investigated. The experimental results show that the relative densities of the prepared Al_2TiO_5/Al_2O_3 composites are proportional to the Al_2O_3 content, and that the composite samples with high Al_2TiO_5 contents have good erosion resistance to molten Al.

Keywords: *Al_2TiO_5/Al_2O_3 composites; microstructure; thermal expansion ratio; erosion resistance to molten Al*

1. Introduction

Aluminum titanate (Al_2TiO_5) ceramics has some superior thermal properties such as low thermal expansion and thermal conduction coefficients, high melting point, high resistance to corrosion and thermal shock resistance [1–3], thus making it one of the best candidates for thermal and structural applications. However, there are two major disadvantages of $A1_2TiO_5$ ceramics, which limit the scope of its applications. Firstly, $A1_2TiO_5$ ceramics is susceptible to extensive microcracking which contributes to its low thermal expansion coefficient and results in its very low mechanical strength. Secondly, $A1_2TiO_5$ ceramics decomposes to Al_2O_3 and TiO_2 in the temperature range of 750–1300 °C [4, 5] which severely limits its structural applications. Thus, some research has focused on the improvement of $A1_2TiO_5$ ceramics [6–8]. It has been reported that thermal decomposition of Al_2TiO_5 can be prevented by some oxide additives such as Al_2O_3, SiO_2, MgO, Fe_2O_3, ZrO_2, $FeTiO_3$, etc. [9, 10] due to the formation of solid solutions.

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In order to explore an efficient way of solving the above two problems, in the present paper alumina (Al_2O_3) was introduced in order to suppress the decomposition of Al_2TiO_5 ceramics. Furthermore, Al_2TiO_5/Al_2O_3 composites were experimentally designed and fabricated in order to obtain a ceramic material which has greater mechanical strength than Al_2TiO_5 ceramics.

In particular, as-prepared Al_2TiO_5/Al_2O_3 composites have been used as containers or pipes to transport molten Al; in such applications, Al_2TiO_5/Al_2O_3 composites are in contact with molten Al for a long time. Thus, investigation of thermal properties, including thermal expansion and erosion resistance of Al_2TiO_5/Al_2O_3 composites to molten Al, was also carried out.

2. Experimental

Raw materials used in this paper were: α-Al_2O_3 (Taimei Chemical Co., Ltd., Japan), anatase-TiO_2 (Guangdong Orient Ind. Sci. & Tech. Co., Ltd., China), MgO (Tateho Chemical Ind. Co., Ltd., Japan) and Fe_2O_3 (Taimei Chemical Co., Ltd., Japan). The characteristic features of the raw materials are shown in Table 1.

Table 1. Characteristic features of the raw materials

Material	Mean particle size [μm]	Purity	Density [g/cm^3]
α-Al_2O_3	1.5	≥ 99%	3.99
Anatase–TiO_2	0.3		4.25
MgO	1.0		3.58
Fe_2O_3	1.0		5.37

In accordance with the design prescription shown in Table 2, raw powders of various volume ratios were fabricated by mixing them uniformly in a three dimensional mixing facility for 5–7 h. The mixtures were then loaded in a die, having an inner diameter of 50 mm, and pre-pressed under 10 MPa for 1 min. After cold isostatic pressing (CIP) at 200 MPa, the samples were sintered for 2 h at 1450 °C, using an electric furnace. Finally, the samples were cooled down, in the furnace, to room temperature.

Table 2. Design prescription for the specimens

Sample No.	Volume ratio [%]			
	Anatase-TiO_2	α-Al_2O_3	MgO	Fe_2O_3
1	88	10	1.5	0.5
2	78.4	20	1.2	0.4
3	58.8	40	0.9	0.3
4	39.2	60	0.6	0.2
5	19.6	80	0.3	0.1
6	9.8	90	0.15	0.05

After preparation, the bulk densities of the sintered products were determined according to Archimedes' principle, using distilled water. The phase compositions were analyzed by X-ray diffraction (XRD) using a Rigaku-D/Max-IIIA diffractometer with Cu radiation at 40 kV and 50 mA. The scanning rate of 10 °/min was used to record the diffraction patterns in the 2θ range between 10° and 80°. The microstructure of the fractured surface of the prepared samples was observed by scanning electron microscopy (SEM). The samples were machined into bars of the dimensions 3 mm×4 mm ×35 mm. After polishing, the bars were soaked in a crucible filled with molten Al. After having been maintained at a temperature of 750 °C for 100 h, the samples were cooled in air. The lining and elemental distribution mapping were studied by electron probe microanalysis (EPMA).

3. Results and discussion

3.1. Phase compositions of the Al_2TiO_5/Al_2O_3 composites

In accordance with the design specifications shown in Table 2, the obtained Al_2TiO_5/Al_2O_3 composites were composed of Al_2TiO_5 solute with 5 mol % of $MgTi_2O_5$ and 1 mol % of Fe_2TiO_5 composites and Al_2O_3. The reactions for the formation of $MgTi_2O_5$ and Fe_2TiO_5 can be described by the following two equations:

$$MgO + 2TiO_2 = MgTi_2O_5 \quad (1)$$

$$Fe_2O_3 + TiO_2 = Fe_2TiO_5 \quad (2)$$

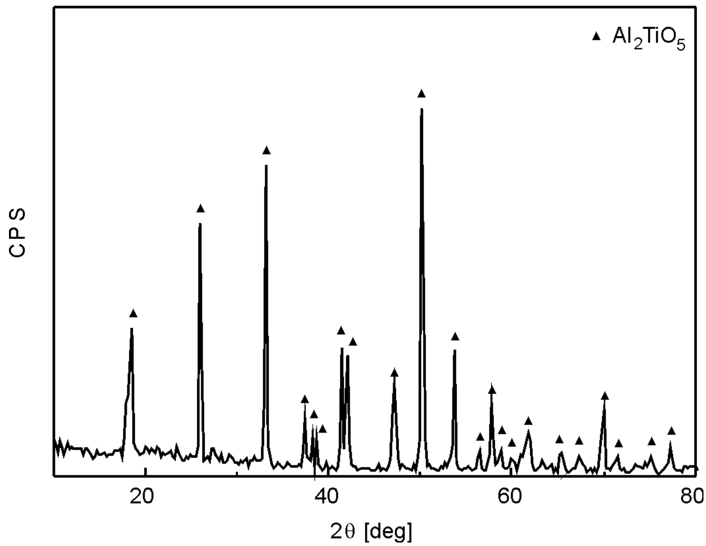

Fig. 1. XRD patterns of the Al_2TiO_5 sample with 5 mol % of $MgTi_2O_5$ and 1 mol % of Fe_2TiO_5 sintered at 1100 °C for 50 h

The XRD patterns of the Al_2TiO_5 sample with 5 mol % of $MgTi_2O_5$ and 1 mol % of Fe_2TiO_5 sintered at 1100 °C for 50 h are shown in Fig. 1. It is clearly visible that all the diffraction peaks are related to Al_2TiO_5. No other phase was detected by XRD, indicating that the composite solute consisted of 5 mol % of $MgTi_2O_5$ and 1 mol % of Fe_2TiO_5, and that the decomposition of Al_2TiO_5 can be effectively suppressed by using $MgTi_2O_5$ and Fe_2TiO_5 as the composite additives.

3.2. Densities and microstructures of the Al_2TiO_5/Al_2O_3 composites

Densities of the sintered Al_2TiO_5/Al_2O_3 composites are shown in Fig. 2. It is clearly seen that both the density and relative density are proportional to the Al_2O_3 content. The density reaches the maximum value of 3.86 g/cm^3 for the sample containing 90 wt. % of Al_2O_3, while the density reaches the minimum value of 3.51 g/cm^3 for the sample containing 10 wt. % of Al_2O_3. The reason is that Al_2TiO_5 is very difficult to fully dense sinter and its density is very low, while Al_2O_3 can easily be densified and has a higher density than Al_2TiO_5. As a result, both the densities and relative densities of the obtained Al_2TiO_5/Al_2O_3 composites are proportional to the Al_2O_3 content.

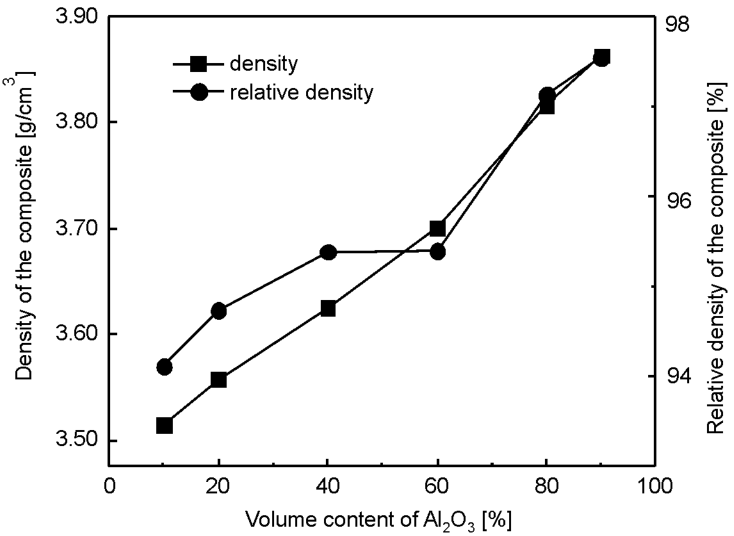

Fig. 2. Density and relative density of the obtained Al_2TiO_5/Al_2O_3 composites in function of the Al_2O_3 content

SEM images of the sintered Al_2TiO_5/Al_2O_3 composites are shown in Fig. 3. The sample with the Al_2O_3 content of 10 vol. % experiences significant grain growth (Fig. 3a); its grain size (after sintering) is ca. 20 μm. There are some pores in this sample, resulting in the incompact structure between the grains, which explains the low relative density shown in Fig. 2. It is also in Figs. 3a–f that the the grain size is inversely proportional to the Al_2O_3 content, and the number of pores decreases gradually as the Al_2O_3 content increases. When the Al_2O_3 content is higher than 40 vol. %, as shown in Figs. 3c, 3d, the average grain size of the sintered samples is lower than 5 μm,

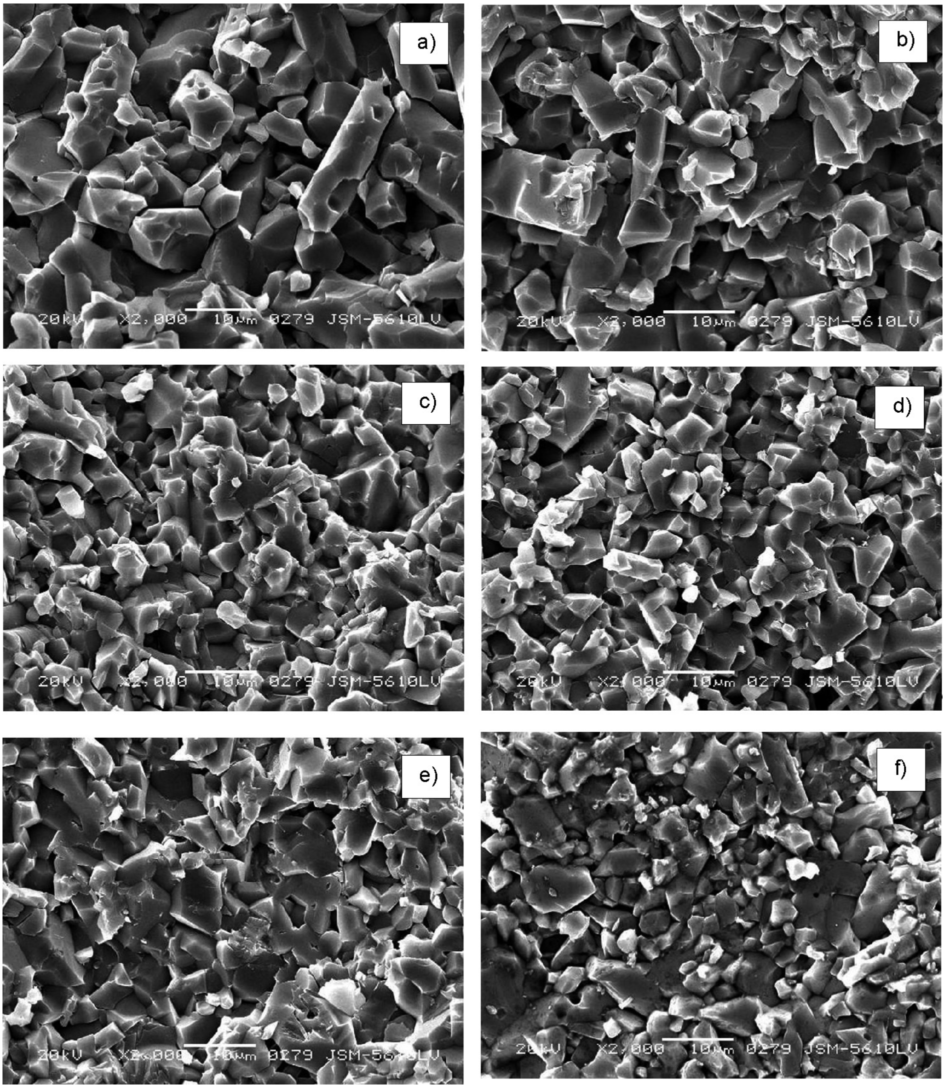

Fig. 3. SEM images of the Al_2TiO_5/Al_2O_3 composites with various Al_2O_3 contents: a) 10 vol. %, b) 20 vol. %, c) 40 vol. %, d) 60 vol. %, e) 80 vol. %, f) 90 vol. %

which is almost the same as the grain size of the raw Al_2O_3 powder. When the Al_2TiO_5 content is almost the same as the Al_2O_3 content, it is the Al_2TiO_5 that prevents further growth of grains of Al_2O_3. When the Al_2O_3 content is higher than 80 vol. %, as shown in Figs. 3e and 3f, the amount of Al_2TiO_5 is too small to prevent the growth of grains of the Al_2O_3, and as a result, many large Al_2O_3 grains can be observed in the SEM images. However, hardly any pores at all can be observed, indicating the samples are fully dense sintered. It can be concluded from these images that the density of a sintered sample is proportional to the Al_2O_3 content, whereas the porosity is inversely proportional to the Al_2O_3 content, which is quite in agreement with the intrinsic sintering behavior of Al_2TiO_5 and Al_2O_3: Al_2TiO_5 is very difficult to be fully dense sintered while Al_2O_3 can be sintered easily with high density.

3.3. Thermal expansion of the Al_2TiO_5/Al_2O_3 composites

Al_2TiO_5 has a very low thermal expansion coefficient, and thus very good thermal shock resistance. The thermal expansion ratios of the sintered Al_2TiO_5/Al_2O_3 composites having different Al_2O_3 contents are shown in Fig. 4.

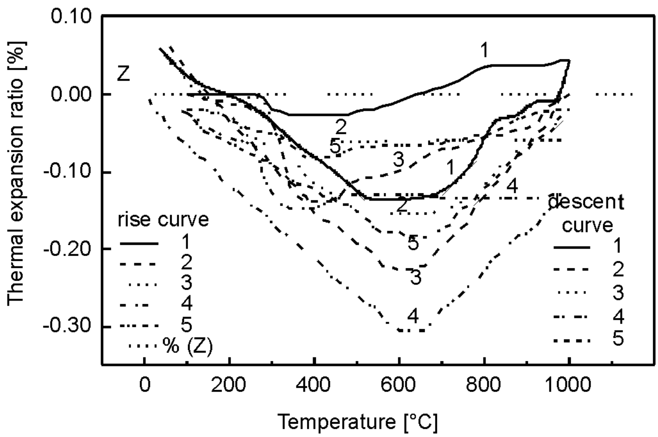

Fig. 4. Thermal expansion ratios of the Al_2TiO_5/Al_2O_3 composites with various Al_2O_3 contents

The thermal expansion ratios of all the samples firstly increase and then decrease as the temperature increases during the heating process, and they firstly decrease and then increase as the temperature decreases during the cooling process. Al_2TiO_5 crystals are composed of crystal domains, and the adjacent crystal domains have different orientations. As a result, the thermal expansion ratio of Al_2TiO_5 is anisotropic. Thus, during the cooling process, an individual crystal domain of the Al_2TiO_5 shrinks, which causes the anisotropy and the formation of the microcracks in the crystal domains. On the other hand, during the heating process, the individual crystal domain of Al_2TiO_5 expands, but the presence of the microcracks prevents the expansion of the crystal domains. As a result, no obvious expansion is seen between room temperature and 700 °C (see Fig. 4). Moreover, with the increase in the temperature, the microcracks among the crystal domains are totally repaired, no extra porous area exists for the expansion, and as a result, the thermal expansion ratio is increased, which is in close agreement with the results shown in Fig. 4.

3.4. Erosion resistance of Al_2TiO_5/Al_2O_3 composites to molten Al

The elemental distribution along the cross-section of a sample of Al_2TiO_5/Al_2O_3 composite containing 20 vol. % of Al_2O_3, after the sample had been soaked in molten Al and cooled in the furnace, was observed by EPMA, as shown in Fig. 5. It is completely obvious from Fig. 5a that a definite interface exists between Al and Al_2TiO_5/Al_2O_3 composites, and nearly no gradient distribution of Al and Ti elements is observed along the thickness direction according to the Al and Ti line distribution characterization, as shown in Fig. 5b. Moreover, the results of lining analysis of Al and Ti elements show that the thickness of Al atomic diffusion is only 10 μm, indicating that Al_2TiO_5/Al_2O_3 composites with high Al_2TiO_5 content have good errosion resistance to molten Al.

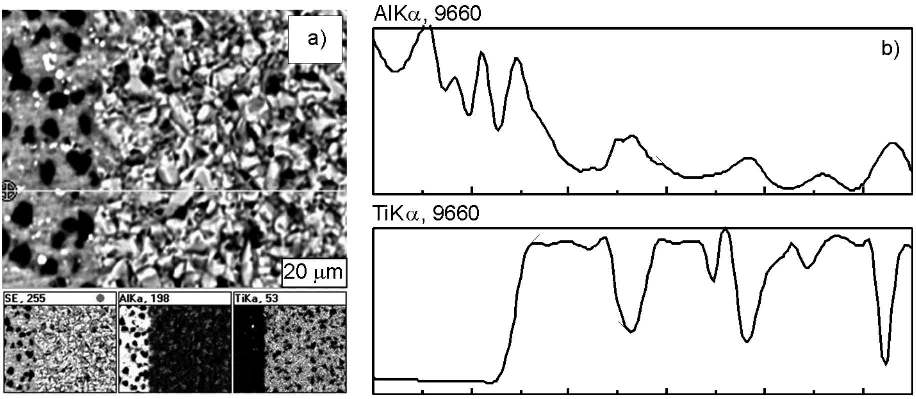

Fig. 5. Back-scattered electron image of a composite sample soaked in molten Al (a) and the lining distribution of Al and Ti along the thickness of the sample

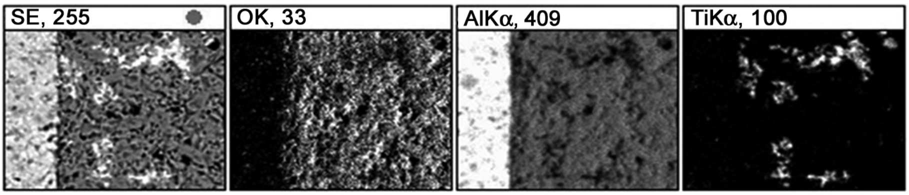

Fig. 6. Elemental distribution of O, Al and Ti along the thickness of the sample

The elemental distribution along the cross-section of a sample of Al_2TiO_5/Al_2O_3 composite having 80 vol. % of Al_2O_3, after the sample had been soaked in molten Al and cooled in the furnace, was observed by EPMA, as shown in Fig. 6. It is clearly evident that there is also a definite interface between the Al and Al_2TiO_5/Al_2O_3 composites having a low Al_2TiO_5 content. However, some molten Al can be seen to penetrate the main body of the material, as shown in Fig. 7. The reason is that when the sample is rapidly heated in molten Al, high thermal stress is induced on the surface of the sample.

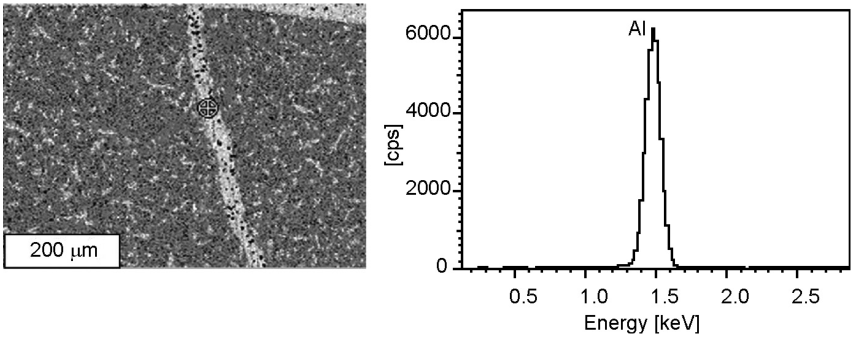

Fig. 7. Back-scattered electron image of a composite sample soaked in molten Al

On the other hand, if the sintered sample has a high Al_2O_3 content, it can have a high relative density, few cracks and low porosity; and these are properties which lead to rapid cracking. Existing cracks become expanded when they are infiltrated with molten Al, and some cracks run through the whole sample, resulting in severe structural damage to the material, indicating that Al_2TiO_5/Al_2O_3 composites with low Al_2TiO_5 content have poor erosion resistance to the molten Al.

4. Summary

Al_2TiO_5/Al_2O_3 composites with different Al_2O_3 contents were prepared, using Al_2O_3, TiO_2, MgO and Fe_2O_3 as the starting powders and by performing pressureless sintering. Some dramatic conclusions follow from the results of our experiments:

- Relative densities of the sintered materials are proportional to the Al_2O_3 content.
- The thermal expansion ratios of the Al_2TiO_5/Al_2O_3 composites are anisotropic.
- As Al_2TiO_5 has a very low thermal expansion coefficient, and very good thermal shock resistance, the thermal shock and the erosion resistances of the Al_2TiO_5/Al_2O_3 composites to molten Al can be improved by increasing the Al_2TiO_5 content.

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