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Effects of Nb_2O_5 addition on the sinterability, microstructure and mechanical behaviour of ZTM-$A1_2O_3$

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Abstract

ZTM–Al_2O_3 ceramics doped with Y_2O_3, MgO and Nb_2O_5 were studied. These ceramics could achieve high density at a sintering temperature as low as 1390°C. Results showed that there was a critical Nb_2O_5/ZrO_2 weight ratio. When Nb_2O_5/ZrO_2 was lower than the critical value, Nb_2O_5 addition had little influence on the sintering, otherwise the sinterability could be considerably improved. The microstructure of all the samples were homogenous; no obvious difference in microstructure had been brought about by Nb_2O_5. Despite this, X-ray diffraction measurement showed a continuous increase in m-ZrO_2 with Nb_2O_5, due to a deficiency of oxygen vacancy in ZrO_2. As a result, the mechanical properties of the ceramics, especially toughness, were greatly improved, because of the enhancement of microcrack toughening mechanism by m-ZrO_2.

Keywords: Mullite; Nb_2O_5; Toughening; Sinterability; ZrO_2; ZTM–Al_2O_3

1. Introduction

Mullite is recognized as one of the most promising engineering materials for applications at elevated temperature due to its excellent chemical stability, good creep resistance and low thermal expansion. However, its ambient temperature properties are poor, which gives a serious drawback to its utilization. In order to combat the inherent weakness of the material, many reinforcing agents, e.g. dispersed rigid particulate, fibers (whiskers) and ZrO_2, are incorporated, producing composites of much superior properties by utilizing the additive or even synergistic effects of many toughening mechanisms.[1–6] Composites making use of multi-toughening by the addition of ZrO_2 and SiC whisker were examined by Clausen and Petzow.[1] They measured the toughness of pure mullite, 10 vol.% ZrO_2-mullite, 20 vol.% SiC whisker-muillite and 20 vol.% SiC whisker-10 vol.% ZrO_2-mullite as 2.8, 3.5, 4.4, and 5.4 MPa $m^{0.5}$, respectively. The bending strengths were 244–452 and 580 MPa, respectively. A considerable multi-toughening is achieved by addition of ZrO_2 and SiC whisker. Yang Z.F.[2] Hong J.S.[3], Becher[4] and Ruh[5] also reported similar favorable results. Finally, Guo[6] used SiC particulate and ZrO_2 to reinforce mullite. He found that the two reinforcing agents had an additive effect on the toughness of mullite. However, SiC is prone to oxidation at high temperature. SiC whisker is expensive and harmful for human health. These limit the scope of application of the materials. In our experiment, $A1_2O_3$ was selected as the rigid dispersoid because of its high elastic modulus, good high temperature stability and good chemical compatibility with mullite. In order to lower the sintering temperature and, at the same time, to adjust the phase assemblage in the ceramics, MgO, Y_2O_3 and Nb_2O_5 were added. In this paper, we mainly study the effects of Nb_2O_5 on the sintering and mechanical properties of the ZrO_2-toughened-mullite–Al_2O_3 (ZTM–Al_2O_3) ceramics.

2. Experimental procedure

Industrial grade ZrO_2, Al_2O_3, fused mullite and other additives of analysis grade purity were used as starting materials. They were mixed together by a ball-milling process, using 3Y-TZP grinding medium in distilled water. After drying and calcining, the powder obtained was uniaxilly pressed into compacts of Ø50×10 mm

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dimension, then isostatically cold-pressed at 200 MPa. Sintering was conducted pressurelessly in open air. The sintered ceramic discs were ground with a diamond wheel and cut into $5\times2.5\times40\ mm^3$ rectangular bars for mechanical property measurement. Bulk density was tested by a water displacement method. X-ray diffraction (XRD) was carried out on a diffractometer using Ni-filtered Cu-K_α radiation for phase identification. The initial compositions of all the ceramics include 47 wt.% mullite, 32 wt.% ZrO_2, 2l wt.% $A1_2O_3$, 1.8 wt.% Y_2O_3, 0.2 wt.% MgO and 0.0 to 1.4 wt.% of Nb_2O_5. The content of Nb_2O_5 increases in an interval of 0.35wt.%, the corresponding samples are defined as Al to A5 in ascending order (Table 1).

3. Results and discussion

3.1. Sinterability of ZTM–$A1_2\ O_3$

For mullite ceramics, the addition of alkaline earth oxide and/or rare earth oxide usually introduces a liquid phase in the ceramics, which considerably enhances the densification process.[7–9] Regarding the effects of rare metal oxide, there are few reports. Fig. 1(A) shows the bulk density of ZTM–Al_2O_3 as a function of Nb_2O_5 (rare metal oxide) content. There is a critical Nb_2O_5 value. Nb_2O_5 less than 1.05 wt.% has little effect on the bulk density of the ceramics; however, the latter rises abruptly when Nb_2O_5 content exceeds this value. In fact, we have found a similar feature in a ZTM (ZrO_2-toughened-mullite) ceramics prepared by us in a parallel experiment. The composition of the ZTM consists of 24.2 wt.% ZrO_2, 75.8 wt.% mullite, 2.3 wt.% Y_2O_3 and various amounts of Nb_2O_5. In this case, the critical value of Nb_2O_5 content is 0.9 wt.% [see Fig. 1(B)]. However, what is interesting is that, in both cases, the critical weight ratios of Nb_2O_5 to ZrO_2 in these ceramics are all approximately equal to 0.035. This implies that the behaviour of Nb_2O_5 in promoting the sintering of mullite must be affected by the presence of ZrO_2.

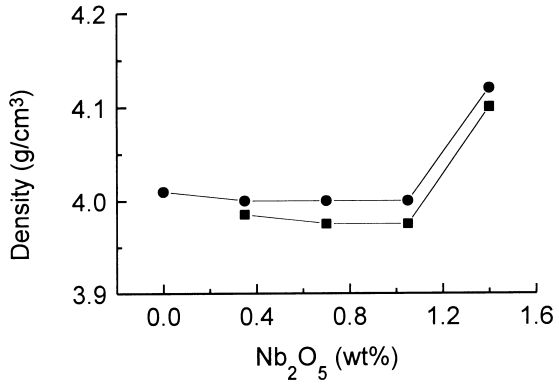
The solution of Nb_2O_5 in ZrO_2 has been unambiguously verified,[10] so it is reasonable to assume that when Nb_2O_5 content is low, Nb_2O_5 may preferably be incorporated into ZrO_2 to form solid solution rather than entering the liquid phase, hence its promoting effect on the sintering of the ceramics is offset. When Nb_2O_5 content exceeds a certain critical value (e.g. 1.05 wt.% in ZTM–Al_2O_3), a larger proportion of Nb_2O_5 enters the liquid phase, which considerably enhances sintering.

Table 1
Chemical compositions and serial numbers of ZTM–Al_2O_3 samples (wt.%)

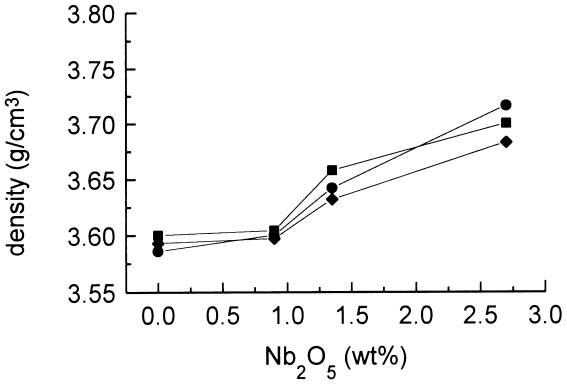
	Mullite	ZrO_2	$A1_2O_3$	Y_2O_3	MgO	Nb_2O_5
Al	47	32	21	1.8	0.2	0.0
A2	47	32	21	1.8	0.2	0.35
A3	47	32	21	1.8	0.2	0.4
A4	47	32	21	1.8	0.2	1.05
A5	47	32	21	1.8	0.2	1.4

3.2. Phase assemblage and microstructure

In order to clarify the changes that Nb_2O_5 has brought to the ZTM–Al_2O_3 ceramics, XRD was conducted on



(A) ZTM-Al_2O_3 (circle:1420°C; square:1390°C)



(B) ZTM (circle:1520°C; square:1540°C; diamond: 1560°C)

Fig. 1. Densities of ZTM(-$A1_20_3$) as a function of Nb_2O_5 content.

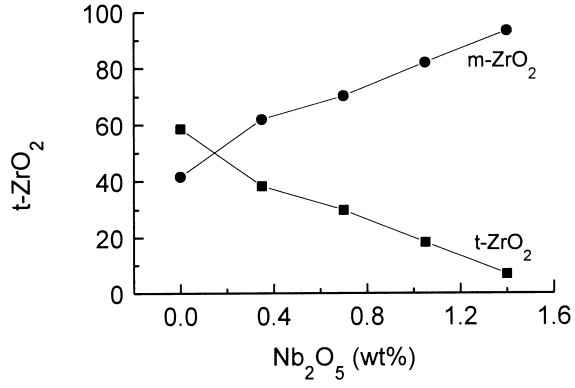


Fig. 2. (m,t)-$Zr0_2$ content as a function of Nb_20_5 addition.

the samples sintered at 1420°C for 2 h. No other new phases existing in them were detected, except the already expected (t,m)-ZrO_2, mullite and Al_2O_3. However, the relative contents of t-ZrO_2 and m-ZrO_2 have changed, with the former decreasing and the latter increasing with Nb_2O_5 addition (Fig. 2). The authors ascribe the phenomenon to the more severe deficiency in oxygen vacancy in ZrO_2 with increasing Nb_2O_5 addition, which lowers the stability of the high temperature polymorphs of ZrO_2.[10]

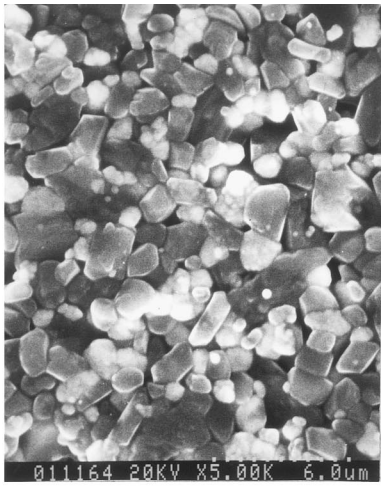
Fig. 3 presents the scanning electron microscope (SEM) micrographs of the thermally etched Al, A3 and A5 samples. The bright spherical particles are ZrO_2, other grey equiaxed ones are mullite and $A1_2O_3$. (Because the atomic numbers of Si and Al are very close, it is difficult to distinguish between Al_2O_3 and mullite in a secondary electron image.) Compared with mullite or Al_2O_3, ZrO_2 particles are smaller in size and most of them are located at grain boundaries, only a few very tiny ZrO_2 have entered mullite/Al_2O_3 grains. These intragranular ZrO_2 particles engulfed by growing mullite/Al_2O_3 grains are much smaller than intergranular ones and take a nearly perfect sphere geometry in order to minimize the energy of the composite microsystem.

In general, the microstructure of all these samples are relatively dense and homogeneous; there are essentially no obvious differences between them, no accelerated grain growth has occurred with increasing Nb_2O_5 doping. This suggests that Nb_2O_5 is a desirable additive, it does not accelerate the grain growth in the ceramics, although effective in promoting sintering.

3.3. Mechanical performances and toughening mechanisms

Plots of mechanical properties versus Nb_2O_5 content are illustrated in Fig. 4. The toughness of the samples

(A) A1



(B) A3

(C) A5

Fig. 3. SEM micrographs of ZTM–$A1_20_3$.

sintered at 1390 and 1420°C increase with Nb_2O_5, while the strengths rise to their maximum values at first then decline with Nb_2O_5.

According to the theories of fracture mechanics, for a brittle material such as ceramics the square of its fracture toughness (K_{IC}) can be expressed by the following equation.[11]

$$K_{IC}^2 = 2E\gamma \tag{1}$$

where E and γ are the elastic modulus and fracture energy of the material. Supposing that γ_0 and K_0 correspond to the γ and K_{IC} values of a crack-free ceramics;

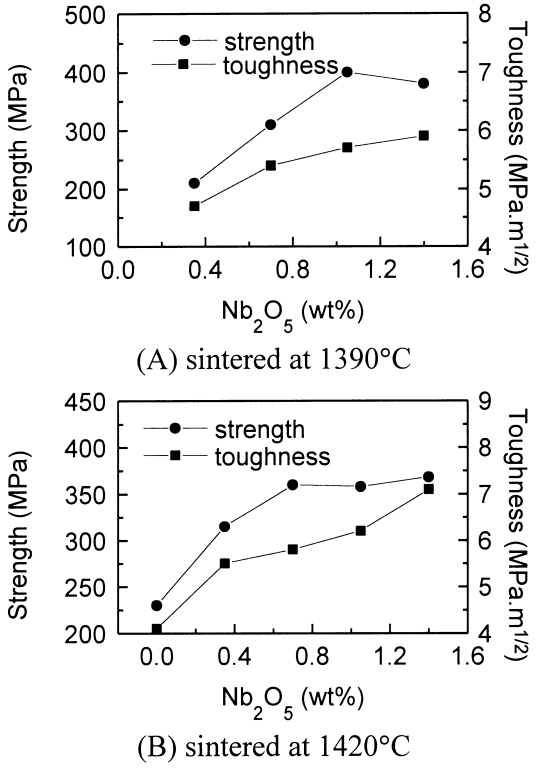


Fig. 4. Mechanical properties of ZTM–$A1_20_3$ as a function of Nb_20_5 content.

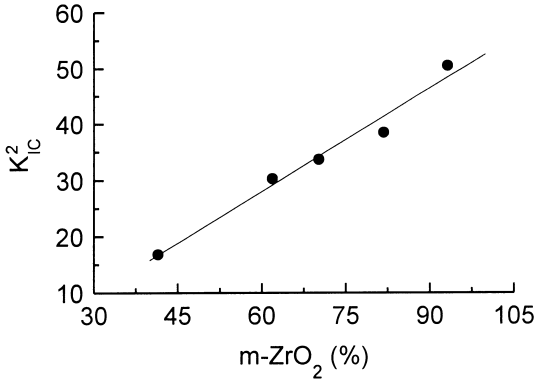


Fig. 5. Relationship between K_{IC}^2 and m-$Zr0_2$ content.

$\Delta\gamma$ and ΔK_{IC}^2 are the increases in γ and K_{IC}^2 of a microcracked ceramics relative to a crack-free one. Then the following formula exists:

$$\begin{cases} \gamma = \gamma_0 + \Delta\gamma \\ K_{IC}^2 = K_0^2 + \Delta K_{IC}^2 \end{cases} \tag{2}$$

Substitute (2) into (1):

$$\Delta K_{IC}^2 = 2E\Delta\gamma \tag{3}$$

Rice[12] argued that in a microcrack-toughened ceramics the upper limits of $\Delta\gamma$ could be expressed as:

$$\Delta\gamma = \frac{2\pi a\gamma_{mc}V_f L}{d} \tag{4}$$

where L and a are the long and short axes of the microcracked process zone; d and V_f are the diameter and volume fraction of the microcrack initiating second phase particulate; γ_{mc} is the microcrack interfacial fracture energy. Supposing that microcracks in ZTM–Al_2O_3 are mainly induced by m-ZrO_2, i.e. $V_f = V_m$, for microcrack toughened ZTM–$A1_2O_3$, K_{IC}^2 should be proportional to the volume fraction of m-ZrO_2 (V_m). Fig. 5 clarifies the relationship between and V_m in a ZTM–Al_2O_3 ceramics sintered at 1420°C. K_{IC}^2 increases linearly with m-ZrO_2

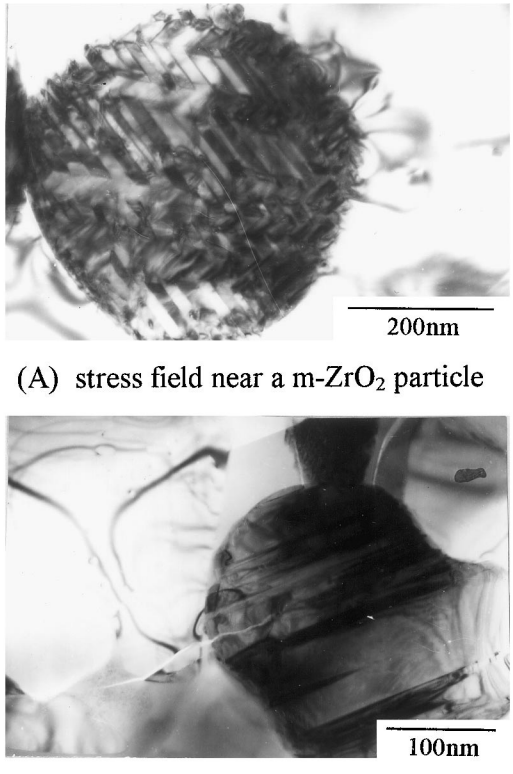


Fig. 6. TEM images showing the stress field and radial microcracks around m-$Zr0_2$ particles.

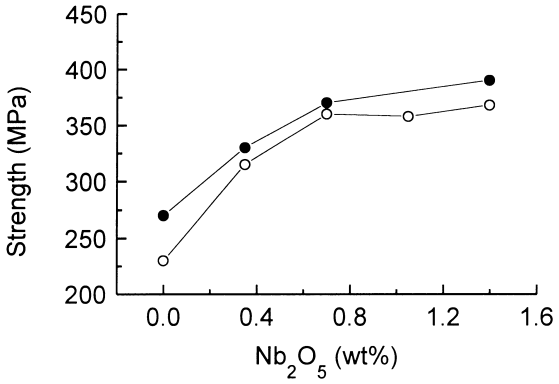


Fig. 7. Ambient temperature (open circle) and 800°C (solid circle) strength of ZTM–A1203 as a function of Nb_20_5 content.

content, which is consistent with the above prediction. Therefore, microcrack toughening should be one of the most important toughening mechanisms operating in the ceramics. And since the remarkable decrease in t-ZrO_2 content does not lead to deterioration to the toughness, stress induced phase transformation toughening should occupy a relatively less important position.

The existence of local stress field and microcracks around m-ZrO_2 is verified by the transmission electron microscope (TEM) micrographs in Fig. 6. In Fig. 6(A), the large spherical particle is m-ZrO_2, which can be determined from its twined structure. In the vicinity of the m-ZrO_2 particle, there are stress fringes resulting from the volume expansion associated with t-ZrO_2– m-ZrO_2 transformation. Fig. 6(B) shows the microcracks initiated by local stress around a m-ZrO_2. Because the tangential stress is a tensile one, all cracks radiate from the center of the m-ZrO_2. These microcracks and stress field around m-ZrO_2 will surely induce crack deflection and bifurcation, which can remarkably increase the energy consumption of a propagating crack. As a result, the toughness of the ceramics is improved. Fig. 7 presents the strengths of ZTM–Al_2O_3 ceramics at room temperature and 800°C versus Nb_2O_5 content. As can be seen, the strengths at 800°C are all relatively higher than their counterparts at room temperature. If stress induced phase transformation is the dominant toughening mechanism, the strength will decrease when the testing temperature is raised to 800°C because of the absence of the stress induced transformation of t-ZrO_2 particles. This also suggests that phase transformation toughening is not the major toughening mechanism in ZTM–$A1_2O_3$. The strength increase at 800°C probably results from softening of the glass phase at the grain boundary, because the plastic deformation of the softened glass phase can reduce stress concentration near the crack tip and increase the energy needed for crack propagation.

In Fig. 4, the m-ZrO_2 content in the ceramics will increase with Nb_2O_5; therefore, the improvement in mechanical properties is brought about by m-ZrO_2 enhanced microcrack toughening. The decrease in strength at a high Nb_2O_5 regime is the consequence of microcrack interlinking because of the high microcrack concentration in the ceramics, which seriously limits the strength of the material.

4. Conclusion

Now, we have discussed the influence of Nb_2O_5 addition on a variety of characteristics of ZTM–Al_2O_3. In summary, Nb_2O_5 is helpful for the sintering of the ceramics, if Nb_2O_5 content is greater than 1.05 wt.%. At the same time, Nb_2O_5 addition has led to the change in the relative content of m-ZrO_2 and t-ZrO_2, with the former increasing and the latter decreasing with Nb_2O_5. As a result, the mechanical properties of the ceramics are notably improved, due to an enhanced microcrack toughening.

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