TECHNICAL NOTE

PREPARATION OF ZIROCNIA-TOUGHENED ALUMINA BY DEFLOCCULATION-FLOCCULATION ROUTE

F. Moztarzadeh, G. R. Sarrafi-Nour and M. Solati-Hashjin

Department of Ceramics
Materials & Energy Research Centre
Tehran, Iran

Abstract Partially stabilizied zirconia (PSZ) agglomerate toughened alumina has been prepared by the "deflocculation-flocculation" technique, using 2 and 3 mol. % Y_2O_3-doped zirconia powders. Samples containing up to about 30 vol.% zirconia were obtained. The resulting microstructure seems to be mainly influenced by the physical properties of the starting powders, e.g. agglomerate size and the specific surface area. The mechanical properties, specially the strength of the samples are mainly limited by the flaws entering the microstructure through the differential sintering of the agglomerates relative to the surrounding matrix.

Key Words Composite, Alumina, Zirconia, Ceramic, Preparation

چکـیـده   آلومـینـای چقـرمـه شـده بـا اسـتـفـاده از ذرات زیـرکونـیـای تـثـبـیـت جزئـی شـده (PSZ) بـــــه روش دی فلوکولاسـیون-فلوکولاسیون و بـا استـفاده از ۲ و ۳ درصد مولی Y2O3 تـهیـه شد. نمـونه هایی حـاوی ۳۰ درصد حجمـی زیرکونیـا به دسـت آمد. به نظـر می رسـد که ریزسـاخـتار حاصل عمـدتأ تحت تاثیر خـواص فیزیکـی پودر اولـیه نظیـر انـدازه و سطح ویـژه آگلومره هـا قرار دارد. خواص مکـانیکی نمـونه ها – به ویژه اسـتحکام آنـها – عمدتأ توسط عیـوب ناشی از سیـنتر افتراقـی آگلومره های زیرکونیا نسبت به زمینه آلومینایی محدود می شود.

INTRODUCTION

Owing to its high toughness combined with its high strength, zirconia-toughened alumina (ZTA) has been of great interest to many researchers for more than a decade [1-7]. It is known that the mechanical properties of these materials are largely influenced by their microstructure.

The possibility of toughening alumina ceramics by dispersion of partially stabilized zirconia (PSZ) or tetragonal zirconia polycrystals (TZP) as a second phase is reported [8,9]. Because of a greater contribution of the crack deflection mechanism, the toughness of these composites should be less temperature sensitive in comparison to materials in which toughness is mainly achieved by the stress-induced transformation of tetragonal zirconia [10]. The aim of the present work has been to obtain such composites by deflocculation-flocculation [11] of zirconia-alumina mixes. The dispersion (deflocculation) and flocculation states were controlled by the pH of the suspension. The resulting microstructure is mainly influenced by the physical properties of the starting powders, which in turn affect the mechanical behaviour of the composite.

EXPERIMENT

ZTA composites were prepared using two co-precipitated Y_2O_3- stabilized zirconia powders

TABLE 1. Physical Properties of Raw Materials.

Material	BET (m²/g)	d$_{50}$ (μm)#	Primary Particle (μm)
Al$_2$O$_3$*	7.5	0.4	1
2Y-ZrO$_2$**	40	9.5	0.015-0.025
3Y-ZrO$_2$***	22.5	9.8	0.044

*CS- 400/M Martinswerk/Germany
**YC-2YB SICAS/Shanghai Institute of Ceramics /Chnia
***Y-TZP Lonza/Switzerland
#Laser Scattering Technique

containing 2 and 3 mol. % stabilizer, respectively, and a technical grade alumina powder. Table 1 shows the physical characteristics of these materials. The composites were prepared from these materials as follows: the selected composition was dispersed in a beaker containing distilled water-HCl solution at pH=2, resulting in a suspension containing 2.5 vol.% solids, as the best dispersion for such mixes occurs under these conditions [12,13]. The resulting suspension was stirred for 10 minutes and aged for 2 hours. The pH of the suspension was checked and maintained by the addition of HCl and stirred again for 10 minutes. Flocculation was achieved by the addition of NH$_4$OH to increase the pH to 8, which is known to be the isopotential point for such a mixture [11]. After settling, the supernatant liquid was poured off and the resulting material was washed by a generous quantity of distilled water to remove Cl ions. The material was then dried conventionally, crushed in an agate mortar and sieved on to a 150 μm screen, before being pressed uniaxially into discs (42 mm in diameter and 5mm in thickness) under 105 MPa. The discs were then sintered for 2 hours at 1560°C in air.

The density of the samples was determined by water-displacement. Sintered discs were x-rayed in their as-fired state and the amount of tetragonal zirconia in the samples was calculated with respect to the total zirconia [14]. The results of these tests along with the hardness values are summarized in Table.2. The sintered discs were cut into bars of 25×4×3 mm

by a diamond disc. Some of these bars were further polished to a diamond finish for the hardness and toughness tests. All the bars were then annealed for 30 minutes in 1250°C to remove surface stresses resulting from mechanical work done on the samples. The strength of the samples was measured by the four-point method using a bending fixture with a supporting spans' distance of 20 mm, a moving spans' distance of 10 mm and a cross-head speed of 0.5 mm/min. on an Instron Universal Testing Machine. Hardness determinations were performed with a Vickers indenter and a load of 98-N on a Zwick microhardness tester (at least 10 measurements on each samples). Fracture toughness was measured by the indentation technique [15] under the same conditions as stated for the hardness measurements. The polished and fractured surfaces of the samples were observed on scanning electron microscope (SEM) under the secondary electron mode.

RESULTS AND DISCUSSION

It can be seen in Figure 1 that in both cases of zirconia addition (2 and 3 mol.%) the strength of the resulting

TABLE 2. Density, Hardness and t-ZrO$_2$ Content of the Composites.

ZrO$_2$ (vol.%)	P$_{rel}$* (%)	H (GPa)	t-ZrO$_2$ (%)
2Y-ZTA			
5.2	98.5	16.6	45
10.4	97.4	15.1	45
15.7	98.3	14.2	42
21.4	97.5	13.1	37
26.1	97.2	12.6	31
31.4	97.3	11.1	25
3Y-ZTA			
5	97.3	16.3	100
10	96.9	15.3	100
15.2	95.7	13.5	80
20.9	95.3	12.5	71
25.3	94.5	11.9	81
30.3	94.3	10.1	89

* Theoretical density was calculated according to linear rule of mixtures

composites (hereafter referred to as 2Y-ZTA and 3Y-ZTA, respectively) decreases with the increasing volume fraction of zirconia. the toughness (Figure 2), however, shows first an increase and then a decrease. The SEM of the observations (Figure 3) on the samples revealed that the microstructure consists of zirconia agglomerates dispersed in an alumina matrix. These agglomerates range from 20-40 μm and 10-20 μm in the case of 3Y-ZTA and 2Y-ZTA, respectively. Circumferential crack-like internal surfaces are present around the agglomerates in 3Y-ZTA. Such cracks are due to the shrinkage of agglomerates caused by their higher sintering rate relative to their surrounding matrix i. e., differential sintering [9]. The density of such cracks increases with increasing volume fraction of zirconia, leading to decrease in the strength of the composite.

In case of 2Y-ZTA, however, only tangential cracks were observed arround the agglomerates (Figure 3c). Comparing the surface areas of 2Y-ZrO$_2$ and 3Y-ZrO$_2$ (Table 1), this phenomen seems to be caused by a relatively slower sintering rate inside these agglomerates in the latter. Under such conditions, as the defect size has been reduced, the

strength of the 2Y-ZTA shows a more gentle decreasing trend than 3Y-ZTA (Figure 1). It can also be seen in Table 2, that cracks in 3Y-ZTA have effectively reduced the density of the composites when the agglomerates are increased. While for 2Y-ZTA the density is not considerably affected by the presense of differential sintering cracks.

Further observations of SEM revealed that the agglomerates in 3Y-ZTA are more or less spherical, but in 2Y-ZTA they are of irregular shape. Since no initial observations were made on the morphology of the as-received zirconia powders, it is not adviseable to draw any definite conclusion in this regard. However, since both powders had been prepared by the co-precipitation route and particle size analysis, laser scattering technique showed that they had an almost indentical particle (agglomerate) size distribution. This difference in agglomerates shape could also be accounted for by differences in surface area of these powders, which might have led to a different flocculation behaviour. The agglomerates formed in the aforementioned microstructures are produced by seccondary flocci as shown by the presence of alumina grains engulfed within the
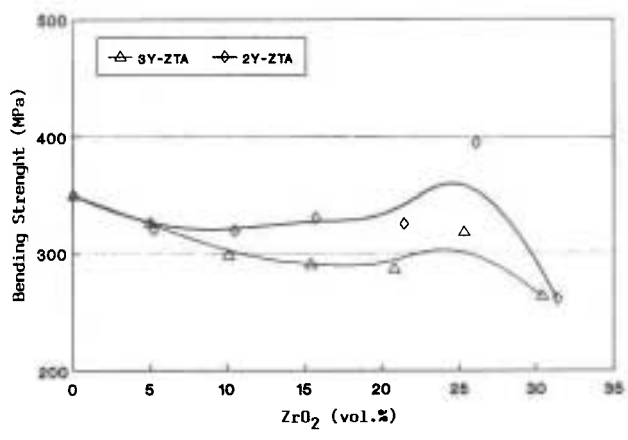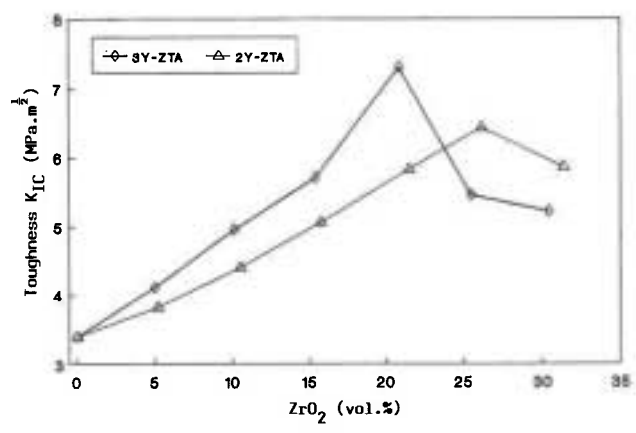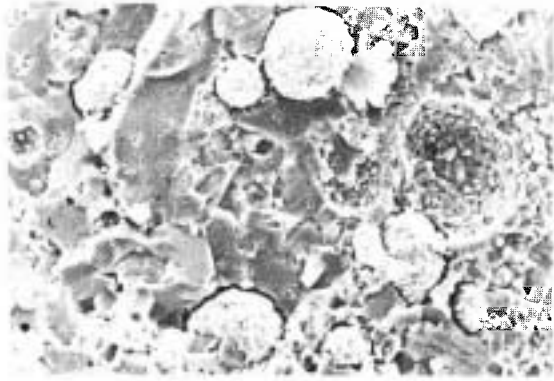

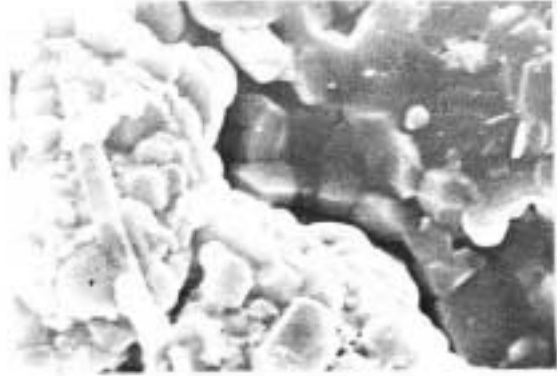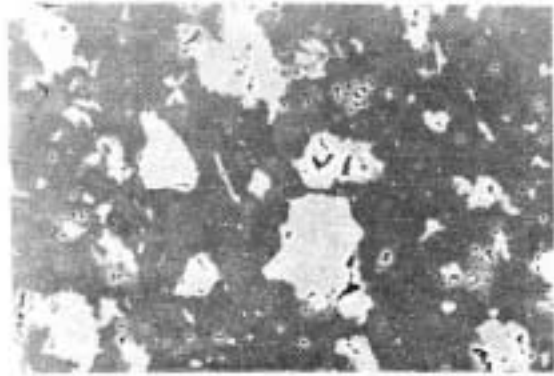**Figure 1.** Strength of the composites.

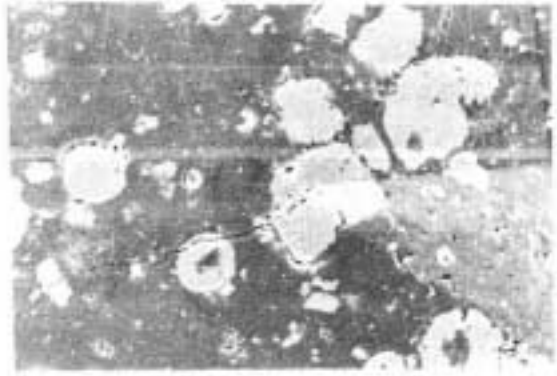**Figure 2.** Fracture toughness of the composites.

a) Fracture surface of 3Y-ZTA

c) Fracture surface of 2Y-ZTA

b) Polished surface of 2Y-ZTA

d) Indentation crack of 3Y-ZTA

Figure 3. SEM micrographs of the composites (dark phase alumina, light phase Zirconia), under secondary electrons mode.

zirconia agglomerates (Figure 3d).

The toughness increase (Figure 2) in all samples seems to be limited by the development of the same cracks, which also decreased the strength. X-ray diffractograms from the fracture surfaces of the composites could not detect any decrease in the tetragonal phase in 3Y-ZTA. This indicates the presence of non-transformable tetragonal zirconia phase [16]. Therefore, the toughness increase in such composite originates form non-transformation mechanisms, e. g., crack deflection and crack branching, which seems to have been more effective

in our case.

CONCLUSION

Flo-deflocculation route can be used for the preparation of PSZ agglomerate toughened alumina or other containing agglomerated second phases in their microstructure. Under such conditions a careful selection of the physical characteristics of the initial powders in necessary.

Differential sintering often strongly affects the mechanical properties of such composites.

Therefore this effect should be damped possibly by controlling initial agglomerate properties, like primary particle size, improving the sintering procedure or presintering the primary agglomerates.

In case of our composites, the toughness obtained by the addition of $3Y-ZrO_2$ addition was higher than $2Y-ZrO_2$ in a considerable range, which indicates that non-transformation mechanisms are more effective in such composites.

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