Preparation of Homogeneous Dense Composite of Zirconia and Alumina (ZTA) using Colloidal Filtration

H. Wakily, M. Mehrali, and H. S. C. Metselaar

Abstract—Homogeneous composites of alumina and zirconia with a small amount of MgO (<1 wt %) were prepared by colloidal filtration. The object of using ZrO_2 (15wt %) was to provide zirconia toughened alumina (ZTA). Suspensions of alumina and Zirconia with various solid loadings and various concentrations of Dolapix CE64 as surfactant were studied. The stability of these suspensions was investigated using rheological measurements. The optimum amount of using Dolapix was 0.8wt% for ZTA containing MgO suspension which gave low apparent viscosity in basic area (100 mPa s at shear rate of 50 s^{-1}). The satisfactory mixtures were made into sample pallets using colloidal filtration. The process was completed with pressureless sintering in suitable temperature. Phase, grain size and qualitative compositional analysis were done using X-ray diffraction (XRD) and scanning electron microscopy (SEM) images. ZTA containing 0.05 wt% MgO shows the lowest grain size for alumina around 0.5 μm. Densification studies show that near full densities (>99%) were obtained for ZTA ceramic containing 0.05 wt% MgO in 1500 °C.

Keywords—Colloidal filtration, Dolapix, MgO, Zirconia toughened alumina.

I. Introduction

ZIRCONIA toughened alumina (ZTA) composite is a composites consist of an alumina matrix in which there are embedded with 0-50 wt% zirconia particles, either unstabilised or stabilized [1]. It is well-known that this second phase addition results in an enhancement of basic mechanical properties like flexural strength and fracture toughness. Such improvements in mechanical properties makes it a candidate material for engineering applications that require high hardness, high wear resistance and moderate fracture toughness. It is also one of the most ferequently used bioinert ceramic for the replacement or reconstruction of affected or destroyed part of the skeletal system [2], [3]. Most investigators concluded that a optimum amount of zirconia should be in the turn of 8-15 vol%(in ZTA) considering a

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trade-off between improvements in fracture toughness, decrease grain size and lower hardness [4]-[6]. Beside all advantages of using ZTA, it is difficult to have ZTA with high density and always the reported bulk density of ZTA is lower than mono phase ceramic of alumina and zirconia which lead to lower definitive properties in applied engineering in the compare with research studies [1], [6], [7]. There exist many possible additives, mainly metal oxides which, with various efficiencies, act as sintering aids and grain growth inhibitors for alumina and in limit cases they are used for ATZ. One of the most used and also one of the most effective is magnesia (MgO). Because of its efficiency, very small amounts of MgO are needed for good densification and to limit abnormal grain growth during sintering [1],[5], [6], [8], [9], [10].

One of the main shaping technologies applied for ZTA composite is powder pressing even though having a homogenious body is a hard aim to reach by this method, then colloidal filtration can be one of the promising shapping methods to have a homogenious and very fine microstructure ceramic composite, where an indispensible condition is the preparation of an appropriate suspension without agglomerates or aggregates, exhibiting a rheological behaviour close to Newtonian in order to guarantee a homogenous microstructure of the formed body [4]. One disadvantage is the strongly basic nature of MgO displayed by a very high isoelectric point (pH 10.5). This gives rise to difficulties in accurately dispersing and stabilising MgO particles using conventional dispersants such as polyelectrolytes. Further, MgO has a high solubility in acidic and neutral conditions which make it impossible to use pure electrostatic stabilisation at low pH [8].

In this study Dolapix CE64 has been used for dispersing slurry of alumina and zirconia obtained MgO in small quantity.

II. Procedure

A. Sample preparation

High purity α-Al_2O_3 (99.95 Alfa Aesar), ZrO_2 (sigma Aldrich, 5.3wt% Y_2O_3) and MgO were used as starting

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powders. Their characteristics provided are presented in Table I. Dolapix CE64 which used as a dispersant is a commercial polyelectrolyte Dolapix CE 64 Zschimmer and Schwarz GmbH, Germany is a carbonic acid based polyelectrolyte, free from alkali and does not foam. According the manufacturer, the dispersant possesses bivalent groups. It has been reported earlier [11], [12], that Dolapix CE 64 is an enthanolaminic salt of citric acid and the average molecular weight is 320 g/mol. The Dolapix CE 64 possesses bivalent functional groups and is characterised by adsorption on the particle surfaces and complete dissociation at pH above 8.5[11].

Aqueous suspensions of the respective powders were prepared in PVC bottles in a horizontal ball mill (Pascall Engineering, 9VS) zirconium ball 10 mm diameter was used for mixing (mass ratio of ball to dry solids 1:2). Single phase suspension was prepared by mixing an adequate amount of dry powder (66.6 wt%,50wt% and 10wt% solid powders of A_2O_3, ZrO_2 and MgO respectively) with the necessary amount of distilled water which contained the corresponding amount of deflocculant (wt% based on dry solid mass). The deflocculant was mixed with distilled water for 20 min on stirred plate. The mixing procedure was continued with ball milling for over 16 hours. Single phase slurry of alumina and zirconia was mixed in the rate of 85wt% to 15 wt% respectively for 16 hours and then magnesium oxide slurry (0.05wt%) was added and mixed for 8 hours. The prepared homogeneous suspension was poured in the container and placed in an ultrasonic bath with frequency of about 20 kHz for 20 min, then right away was filtered using glass filter holder assembly using a cellulose nitrate membrane filter with pore size of 0.45μm(Whatman GmbH). The suspension surface remined in contact with the atmosphere while the driving force for the filtration was created by a vacuum at the other side of the membrane filter at a vacuum pressure of 590 mmHg. Castings were performed at 25 °C the disc-shaped green compact (diameter 25 mm) could easily be released from the membrane filter after 12 hours of drying in stagnant air at room temperature. The green compacts were dried for 12 h in oven at 120 °C then were placed into an alumina boat and heated to the 1000 °C using a 10 °C/min heating rate, then 1500 °C using 5°C/min and maintained at this temperature for 2 h under air atmosphere. After the heat treatment, the furnace was shut off and it was allowed to cool down. The samples were ground by means of SiC abrasive paper grade 500, 800, 1000, 1200 then polished with fine diamond disk

TABLE I
CHARACTERISTICS OF COMMERCIAL STARTING POWDERS

Powder	Average particle size	Y_2O_3 (wt%)	Melting Point (°C)	surface area (m^2/g)	Molecular Weight
α-Al_2O_3 99.95%	0.3-0.49 μm	-	2045	7-9	123.22
ZrO_2 99.5%	0.2-0.5 μm	5.3	2600	6.9	101.96
MgO	50nm	-	2852	11	40.30

and diamond suspensions which grain size 9 μm, 3 μm, 1 μm and finally using polishing cloths and suspension of 0.5 μm alumina particles. The samples were thermally etched in air for 20-40 min at temperatures 150 °C below the sintering temperature in order to form grooves at the grain boundaries and phase boundaries. With this heat treatment local relief between grains are formed allowing toseparate them on SEM images. Samples were characterized by Scanning Electron Microscopy (Phenom FEI CO). Identification of phases was carried out by X-ray diffraction technique (XRD), using Philips XPert MPD PW3040 XRD using CuKα radiation at 1.54056 Å X-ray wavelength. The samples were scanned from 10˚ to 80˚ 2θ angle at a step size of 0.20 º and a count time of 1.5 s at each step.

B. Sample Characterization

Density measurements were performed according to ASTM-C373-88[13] with using the Archimedes technique in water for sintered bodies from Equation 1:

$$\rho_1 = \rho_\circ W_a /(W_b - W_c) \qquad (1)$$

were ρ_1 is density of solid sintered body, Wa is the weight of the sample in air, W_b is the weight of sample when saturated in distilled water, W_c is the weight of sample when it is immersed in distilled water. For measuring saturated weight, Samples were kept in water bath in 90 °C and vacuum presser 640 mmHg was used for 30 min then with a cotton cloths water in the surface was absorbed. $\rho_\circ$ is the density of water, which is 0.9998 gr/cm^3 at 20 ºC.

The theoretical density was measured by the rule of density in composites from equation 2:

$$\rho_t = \rho_1 f_1 + \rho_2 f_2 + ... \rho_n f_n \qquad (2)$$

Which $f_1, f_2 \ldots f_n$ are the volume fractions of element in the composite which were calculated from the equation 3:

$$f_1 = m_1 \rho_1 /(m_1 \rho_1 + m_2 \rho_2 ... m_n \rho_n) \qquad (3)$$

$\rho_1, \rho_2 \ldots \rho_n$ are the density of different phases of composite. Relatively density simply was measured trough this formula:

$$\rho_r \% = (\rho / \rho_t) \times 100$$

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III. RESULTS AND DISCUSSION

A. Suspension Analysis

The zeta-potential behavior of Al_2O_3, ZrO_2 and MgO in the presence and absence of Dolapix CE 64 are presented in Fig 1.*a* and *b*. The isoelectric points (IEP) for Al_2O_3, ZrO_2 and MgO are 8.8, 5.4 and 10.1 respectively which is accorded with literature reported value [8], [11], [14]-[16]. It is obvious, that the suspension without dispersant obtain high positive charge which surface hydroxyl groups are responsible for that. It can be seen that the addition of dispersants causes significant changes in surface charge properties of oxides. The IEP of the bare particles was almost two pH units as well as all initial curves were shifted in the acidic direction with dispersant. Dolapix CE 64 is a carbonic acid dispersant which starts ionizing around pH 3.5 and increases with pH and is completely dissociated above pH 8.5[11]. Adsorption takes place due to electrostatic attraction between the positively charged surface of oxides and negatively charged functional groups of the dispersant. The charge reversal and increase in electronegativity in this pH range is based on concentration of the dispersant [8], [11], [17]

In the case of MgO because of the high solubility of this oxide in acidic area there is no record of zeta potential below pH 8.5. It is remarkable that reaction between MgO particles and liquid medium increase the ionic strength continuously with time. This increase might be responsible for the low and almost constant zeta potential values observed in the pH range 8.5-10.1. When decreasing the pH in this region the electric double layer will be compressed by the increased ionic strength compensating the higher surface-charge density. Although these results should be regarded with caution they indicate clearly that the use of a pure electrostatic stabilization mechanism could only be possible for pH values above 11.7. For lower pH values the opposite signs of surface charges on particles of individual oxides or an insufficient negative charge density on MgO particle surfaces will most likely lead to a hetero-coagulation phenomenon. Strong enough repulsive forces in this pH range can only be developed by using surface active agents or deflocculants[8].

From Fig 1.a In the area below IEP of zirconia 5.5 which is acidic and above IEP of alumina 8.2 which is basic, we can have stabilised suspension of alumina and zirconia, But the mix suspension of three oxides will be stabilised just in basic area in the presence of Dolapix CE 64 Natural pH for 65wt% suspension of Al_2O_3, 50 wt% ZrO_2 and 10wt% MgO in the presence of 0.6wt% Dolapix was measured 8.86, 8.74 and 10.23 respectively. The all single phase diluted suspension of different oxides have negative potential charge in natural pH,-37,-22 and -10 respectively. It is worth to note the mix

suspension of alumina,zirconia and magnesia with 60 solid load shows pH around 9.2, and this amount for dilute suspension of oxides are decreased to 9.
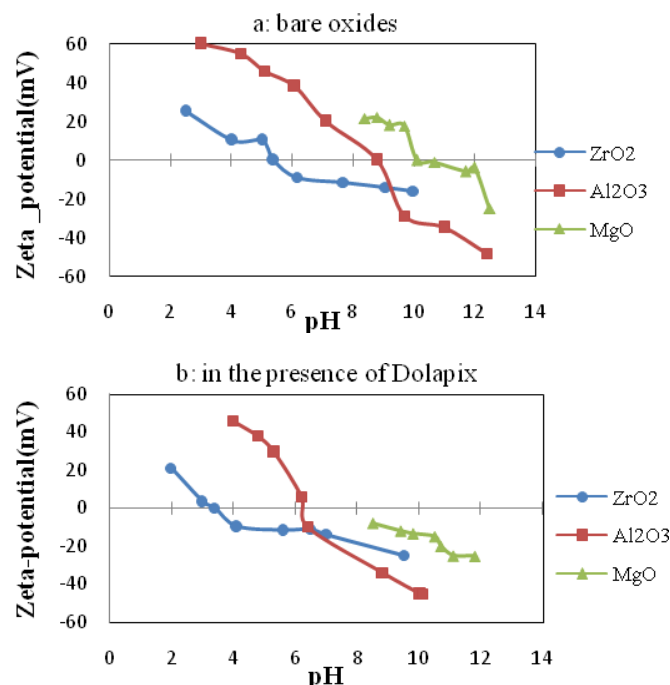

Fig. 1 Zeta-potential of zirconia, alumina and magnesia in *a*: presence and *b*: absence of Dolapix CE 64 as a function of pH.

From the literature Dolapix CE 64 was successfully used as deflocculant for Al_2O_3 [17], ZrO_2 [11], Al_2O_3- ZrO_2[11] and Al2O3-MgO[8] even though there is no record of using Dolapix for mix suspension of Al_2O_3, ZrO_2 and MgO. In these work experiments with Dolapix were done and results are give in Table II. ZTA suspension shows low viscosity in the presence of just 0.4wt% deflocculant while ZTA suspension with MgO need more amount of deflocculant. Viscosity is higher for the slips with MgO. These effects are consistent with electrophoretic results in that the strong repulsive interaction forces between alumina particles were disturbed by the presence of magnesia.

TABLE II
APPARENT VISCOSITY μ_A FOR DIFFERENT SUSPENSIONS

Apparent Viscosity(Pa. s) At 50 s⁻¹	Al_2O_3 65 wt%	Al_2O_3 30 wt%	ZrO_2 30 wt%	ZTA 65wt%	ZTA.MgO 60wt%
Dolapix CE64 0.4 wt%	0.04	0.004	0.006	0.06	0.4
Dolapix CE64 0.8 wt%	0.06	0.005	0.007	0.07	0.01

TABLE III
DENSITY OF THE GREEN AND SINTERED BODIES WHICH HAVE BEEN MADE FROM 65WT% SOLID LOAD SUSPENSION

	100wt%Al$_2$O$_3$	100wt% ZrO$_2$	ZTA 15wt% ZrO$_2$ (65wt% solid load)	ZTA 15wt% ZrO$_2$ (30wt% solid load)	ZTA 15wt% ZrO$_2$ 0.05wt%MgO
Relative ρ $_{sintered}$	99.2	99.7	99.4	98.5	99.6
Relative ρ $_{green}$	65-65	62-65	62-65	53	62

The detrimental effect of the additive on slip stability can arise from the relatively low charge density on the magnesia particle surfaces and from an increased ionic strength (compressed double layer) due to partial dissolution of this oxide, or adsorption of Mg(II) ions onto the alumina surface[15]

A. Sample Characterization

The balk density of Alumina, Zirconia and magnesia for material used in this work are 3.988, 6.1 and 3.58 gr/ cm^3 respectively, volume friction for alumina and zirconia for the composite of 85wt% Al$_2$O$_3$ and 15wt% ZrO$_2$ were measured 0.896 and 0.103 respectively. Therefore the theoretical density for ZTA 85wt% alumina and 15wt% zirconia was measured 4.19gr/cm3.From Table III can be observed that the maximum relative sintered density was achieved with pure zirconia, 99.7 and ZTA doped with magnesia 99.6 Magnesium oxide which was added to ZTA as sintering aid and inhibitor of grain growth has got good affect on the density of sintered body in ZTA. The density plot for alumina, zirconia and ZTA in this work is similar to the result which Maria et al reported [2], The density of composite increase with increasing of zirconia content, even though their solidification method was pressing.In some previous case the lower density for ZTA in the compare with pure alumina and zirconia was reported [1]. In the General it is easy to have near full density stabilized zirconia which is difficult about alumina. In the strong agreement with previous works, sintered density is depended to green density basically and Green density itself is affected by solid load and stabilising condition of the base suspension. Suspension with high solid load maximon, 65wt% shows the higher density in the compare with suspension with just 30wt% solid load.

Fig. 2 Illustrate the X-ray patterns of sintered Al2o3 ,ZrO2 and ZTA samples In these patterns is observed a reflection in 2h = 74.67º for ZrO2 corresponding to the 400 peak belonging to the cubic phase (c). In the same patterns it is important to note that no XRD peaks of the monoclinic phase were observed in the sintered sample under previously established conditions, suggesting a full stabilization of the tetragonal phase (t). Full stabilization of tetragonal (t) phase

[18] in stabilized ZrO$_2$ with 5.3 wt% Y2O3 which is in agreement with the grain size measured for the same ceramics in the present work. However, the present results
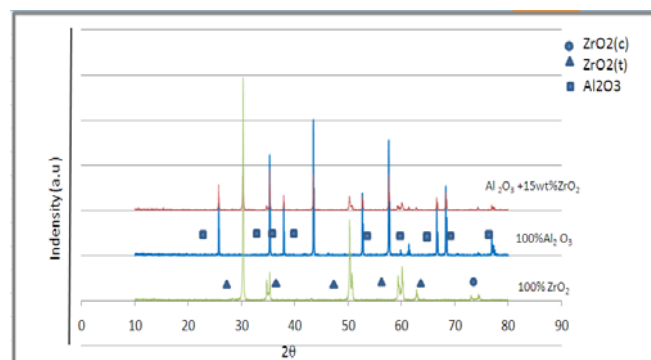

Fig. 2 X-Ray patterns corresponding to sintered and thermally etched samples of Al$_2$O$_3$,ZrO2 and ZTA(Al$_2$O$_3$+15 wt%ZrO$_2$)

Confirm that zirconia ceramics sintered above 1450 ºC can exhibit a dual microstructure, formed by cubic and tetragonal grains. Considering that the tetragonal-cubic phase transformation occurs during the final sintering stage, [1].

The Fig 3 shows representative SEM micrographs of polished and thermally etched Al$_2$O$_3$ (Fig. 3a) ; stabilized ZrO$_2$(Fig 3b) sintered at 1500 ºC during 2 h in air . From this figure it is clearly observed that all samples were crack –free with some isolated pores in the case of Al$_2$O$_3$ and ZTA. Grain boundaries in Al$_2$O$_3$ ceramic indicates rough and enlarged grain at temperature of 1500 ºC for Al$_2$O$_3$.In the compare ZrO2 shows very limit growth without any porosity in atomic scale which this characteristic also reported with Nevares et al [1] and others[1], [19]. However taking into account the Y2O3–ZrO2 phase diagram at the sintering temperature of 1500 ºC is highly probable to obtain cubic and tetragonal phases. According to this, the observed big grains in ZrO2 (Fig. 3b) seem to be cubic in nature, since a fraction of cubic (c) phase is also expected from the phase diagram and this appreciation can be supported with the X-ray pattern marked a in Fig. 2 corresponding to ZrO2 stabilised with 5.3 wt% yttria in the reflection 2h = 74.67º. Moreover, it is known that cubic zirconia has large grain sizes and high grain growth rates [21].Alumina grain size as a matrix has
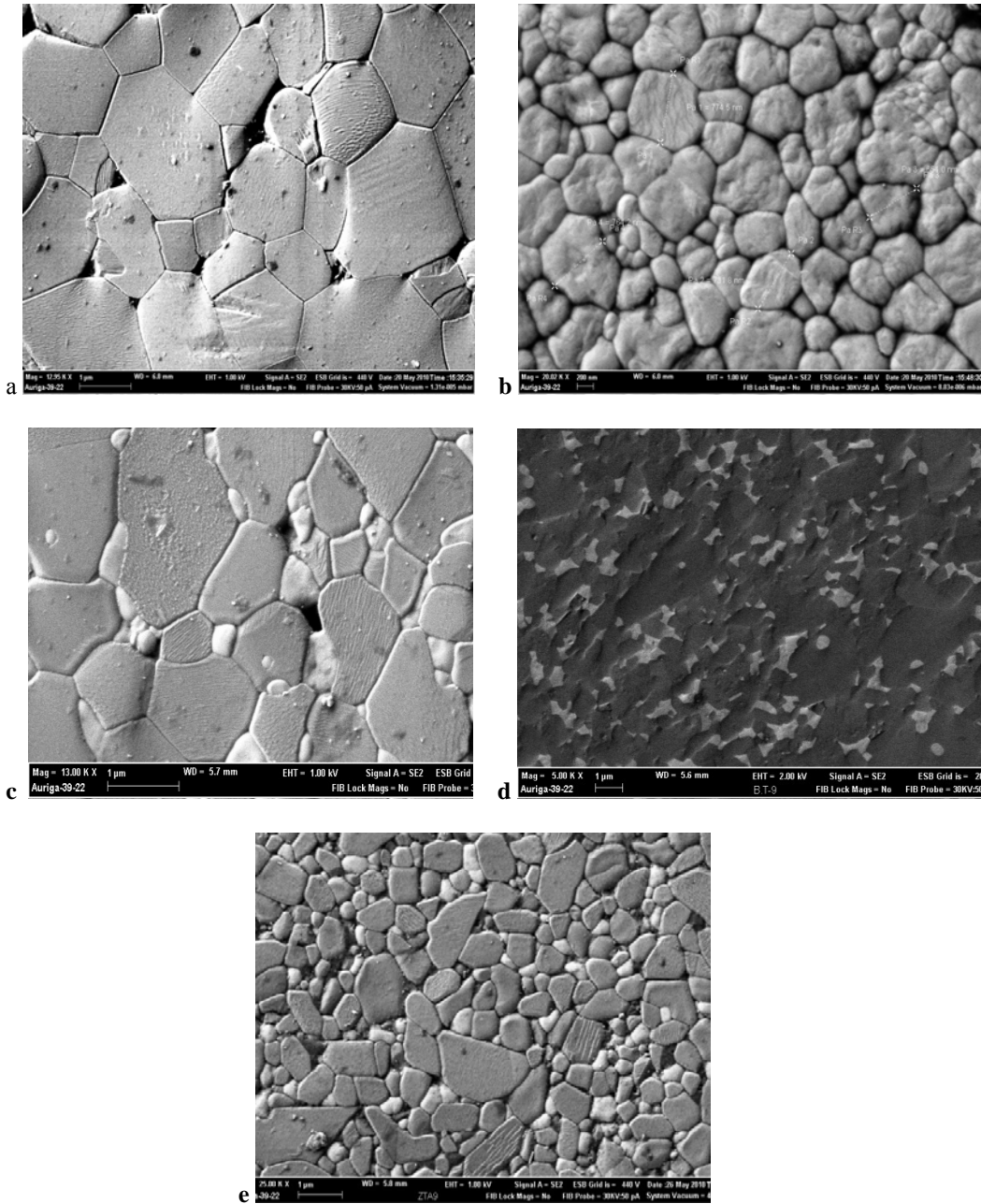
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Fig. 3 SEM images of thermally etched Al$_2$O$_3$ (a); ZrO$_2$ (b); Al2O3 +wt%15 ZrO$_2$ (c) and (d);
Al2O3 +wt%15 ZrO$_2$ with wt% 0.05 MgO (e) and

TABLE IV
DENSITY AND GRAIN SIZE OF DIFFERENT COMPOSITES

	Al$_2$O$_3$	ZrO$_2$	ZTA 30wt% solid load	ZTA 65wt% solid load	ZTA, MgO 0.05wt%
Density ρ(%)	99.2	99.7	97	99.4	99.6
Grain size Al$_2$O$_3$(μm)	1-2.5	-	-	0.6-2	0.4-0.7
ZrO$_2$ (μm)	-	0.3-0.6		0.2-0.5	0.2-0.5

important effect on the hardness and fracture toughness which is 1-2.5μm for alumina, adding zirconia particle prevent alumina grains from growing to big size(Fig 3c) but doping

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magnesia is more effective as it is observed from Fig 3e the alumina particles are around 0.4 -0.7μm .

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