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Active Alumina Sintering: Effect of Mixed Dopants (TiO_2 & Y_2O_3)

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ABSTRACT:

Alumina is a eminent material in the field of refractory as it is very much used as refractory in steel industries and it also takes place in the field of orthopedic implants. As the sintering temperature of alumina is very high, dopants are used to reduce the temperature as well as to ameliorate the strength. Primary aim of the paper is to select suitable dopants and investigate its various effects on alumina. It is also interesting to notice weather the dopants can cause grain growth which can enervate the mechanical properties.

KEYWORDS: Active Alumina, Dopants, Sintering

1. INTRODUCTION

In certain sintering system, the role of a minor additive is to segregate the grain boundaries & by stabilizing the fine grain structure permit full density to be achieved. Al_2O_3 is well known structural ceramics with acceptable mechanical & chemical properties. CaO, SiO_2 & TiO_2 addition is interesting because of anisotropic grains with interlocking could increase the bonding stress of ceramic matrix. When the mixture was sintered above the eutectic temperature of the system, a liquid phase was formed to help fast diffusion. The minor phase accumulated in the inter-granular regions in ceramics is usually associated with doping of additives. In TiO_2 doping the nanoparticles were created from a binary liquid in local equilibrium with segregation to grain boundary, which serves as transporting routes to form ternary liquid at the multigrain junction to initiate the main inter-granular phase of Al_2TiO_5. S Lartigue-Korinek et al[1] studied properties of Yttrium doping on polycrystalline alumina. They include yttrium distribution as a function as a function of grain size & atomic structural configurations around yttrium in grain boundaries. The role of yttrium on overall microstructure, grain growth along with sintering phenomena, creep behavior was discussed. Dusan Galusek et al[2] observed two stage sintering which can suppress the grain growth in the final stage of densification of polycrystalline ceramics. Addition of metal oxides(500ppm of MgO,Y_2O_3 or ZrO_2) retards the grain growth in the sintering. Addition of MgO enhances

densification, addition of yttria, zirconia impaired densification but addition of all three dopants resulted in the suppression of grain growth & microstructural refinement in comparison to undoped Al_2O_3. Karen Maca et al[3] investigated the influence of various dopants (500ppm of MgO &Y_2O_3, 250 ZrO_2) on sintering of fine grained alumina & activation energy of sintering was estimated. The lowest value of activation energy exhibited undoped alumina; the addition of MgO resulted in slight increase of activation energy. Y_2O_3 & ZrO_2 significantly inhibited the densification, which was reflected in the higher activation energies. The low activation energy in the final sintering step enables to choose proper sintering temperature in two step sintering process. Debra s Ham et al[4] studied grain growth in TiO_2 doped alumina, normal grain growth, anisotropic grain growth with 0.15-0.4 wt%. The present object of investigation is to study the effect of dopants TiO_2 & Y_2O_3 on active alumina sintering behavior. Katarína Bodišová et al[5] worked in grain growth suppression in Al_2O_3 via doping & two step sintering. Transition metal doped alpha-Al_20_3 with various dopant concentrations was prepared by straight forward template free sol-gel method. TiO_2 doped alumina can be prepared by new synthesis route ion exchange reaction & sulfidation. B. Lesage et al[6] investigated the influence of chromium and yttrium doping on transport phenomena in monocrystalline alpha-alumina. Electrical conductivity of single crystalline Al_2O_3 doped with Cr_2O_3 (800 and 8000 ppm) and Y_2O_3 (1000 ppm) was measured as a function of temperature (1200°C up to 1700°C) and oxygen partial pressure (1 atm down to 10−15 atm). Jagdish Prasad et al[7] studied the Sintering of Alumina (γ-Al_2O_3) in Presence of ($CaO + Fe_2O_3$). Diffusion coefficients of 51Cr, 59Fe and 63Ni are measured from 1200° up to 1700°C, in undoped alpha-alumina single crystals in air. Results indicate that “extrinsic” diffusion is preponderant and that cationic species diffusion occurs more rapidly than oxygen diffusion. By treating the intensity vs. penetration depth curves, it is possible to separate lattice diffusion from diffusion by dislocations. The influence of the amount of doping by a homovalent cation Cr^{+3} or Y^{+3} (molar concentration 800 and 8000 ppm Cr_2O_3, 1000 ppm Y_2O_3) on the electrical conductivity and diffusion in α-alumina single crystals is also studied in the same temperature range and for oxygen partial pressures higher than 10−15 atm. The electrical conductivity is found to increase at both high and low oxygen partial pressures, these variations being more pronounced in the case of the yttrium-doped sample. Furthermore, one observes that the electrical conductivity decreases when the concentration of chromium increases. P. G. Paul et al[8] observed alumina of submicron order was doped with MgO either as $Mg(NO_3)_2$ or magnesio-aluminate hydrate. The interaction of the additives with alumina powder was studied at 1450°C and 1500°C in the form of thin pellets. Grain size in partially sintered compacts of alumina was measured as a function of density. Where the porosity remained interconnected, grain growth was negligible; when the continuous pore network collapsed into isolated pores, grain grew rapidly[9].

1.1 Application

Active alumina used as catalyst in organic synthesis,used in spark plug insulation, aluminous porcelain, alumina membrane, used in grinding media, abresines, crucial for melting metals, hip prosthesis, drying org liquids such as LPG, propylene etc. Osteoblast adhesion on

alumina sample of 23nm grain size increased by 46% as well as increases mechanical property with nanomaterial improves orthopedic efficiency[10].

2. EXPERIMENTAL PROCEDURE

Present work deals with preparation of active alumina from microfine A R grade $Al(OH)_3$.

2.1 Preparation of Active Alumina

Microfine AR grade Aluminium Hydroxide gel is calcined at 550^0C for 1 hour. The calcined powder is agated to super fine powder.

2.2 Preparation of Batch Compositions

TiO_2 and Y_2O_3 are mixed intimately in proportion of 1:1 to be used as doping agent. Different batches are made with different weight % of mixed dopants in active alumina along with undoped batch.

2.3 Table 1 : Batch compositions

Sample code	% of Active Alumina	Wt % of mixed dopant
Batch 1	100	0
Batch 2	99.8	0.2
Batch 3	99.6	0.4
Batch 4	99.4	0.6
Batch 5	99.2	0.8

The batches are intimately mixed with respective wt% of dopants using minor Polyvinyl Alcohol (PVA) as binder.

2.4 Preparation of Binder

4-5 drops of 0.5% PVA solution are added in each batch.

2.5 Preparation of Disks and Bars

Disks and bars are made in every batch. Disks and Bars are pressed in hydraulic press with uniaxial pressing of 1000 Kg/cm^2 pressure

2.6 Drying and Firing

The prepared disks and bars are dried at 100^0C for 24 hours in air oven. They are fired at 1550^0 C with different soaking periods of 2 hour and 3 hour soaking period

3. CHARACTERISATION

3.1 Characterisation of active alumina powder

Characterization of active alumina powder is done by loose bulk density, surface density, surface area, XRD analysis, SEM studies.

3.1.1 Loose powder density

Loose powder density of active alumina powder is determined as 0.46 g/cc. The calcined precursor is soft, fluffy and white in appearance. The low powder density of calcined powder indicated the presence of fine particles.

3.1.2 XRD Analysis

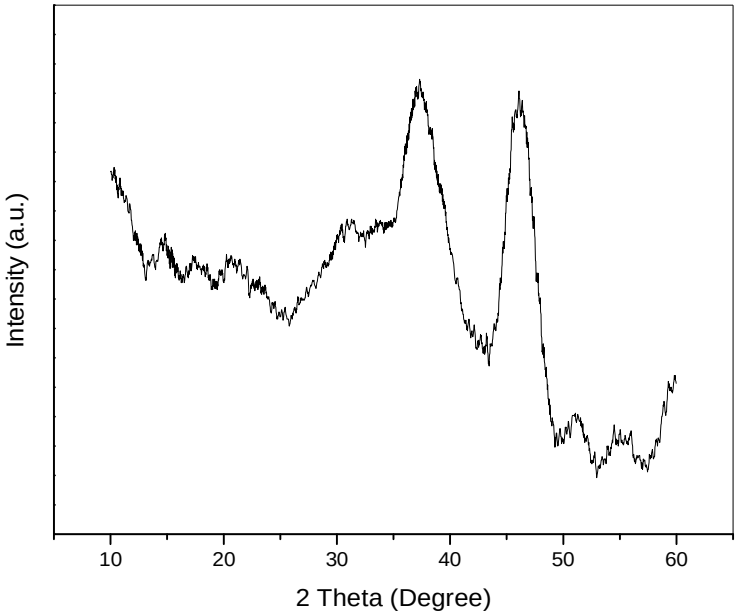


Fig: I Powder XRD pattern of Active Al_2O_3

The powder XRD pattern of preheated precursor at 550^0C clearly revealed a diffused characteristic peaks of crystalline ϒ – Al_2O_3.

3.1.3 SEM Studies

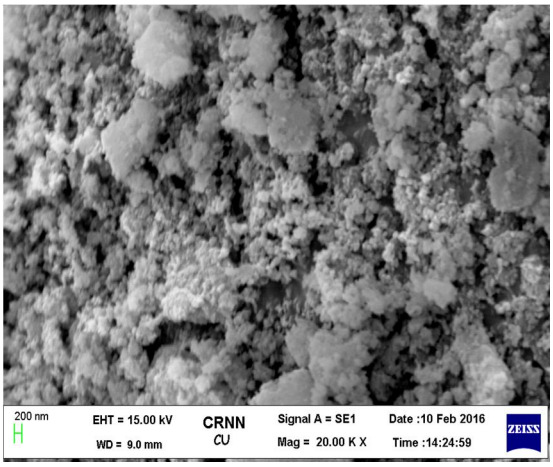


Fig II : Secondary electron image of active Alumina

When an electron beam is irradiated on a specimen surface, interaction between the electron beam and the atoms composing the specimen, produce various kinds of information. When scanning a surface by SEM of a specimen with a finely focused electron beam, information will be emited from each point of scanning. Usually the SEM is used to observe the image obtain by the morphology of its surface. However secondary electron image (SEI) and back scattering electron image (BEI) of active alumina powder reveals that it is composed of ultrafine nano particles of transition alumina phases[11].

3.2 Characterization of fired samples

The fired compacts of each batch are characterized by measurement of different principle properties such as spalling at 900^0C, shrinkage, AP, BD, MOR, XRD analysis and SEM studies.

3.2.1 Shrinkage

Linear and volume shrinkage of bars are measured by slide caliplus and for disks volume shrinkage are measured.

$$\% \text{ of volume shrinkage} = \frac{\text{Initial volume-Final volume}}{\text{Initial volume}}$$

3.2.2 Apparent Porosity and Bulk Density

Apparent porosity, Bulk Density, Water Absorbsion all are measured mainly by measuring the dry weight along with soaked weight, suspended weight. Principle which is mainly followed is Archimedis Principle.

$$\% \text{ of AP} = \frac{\text{Soaked weight-Dry weight}}{\text{Soaked weight-Suspended weight}} \times 100$$

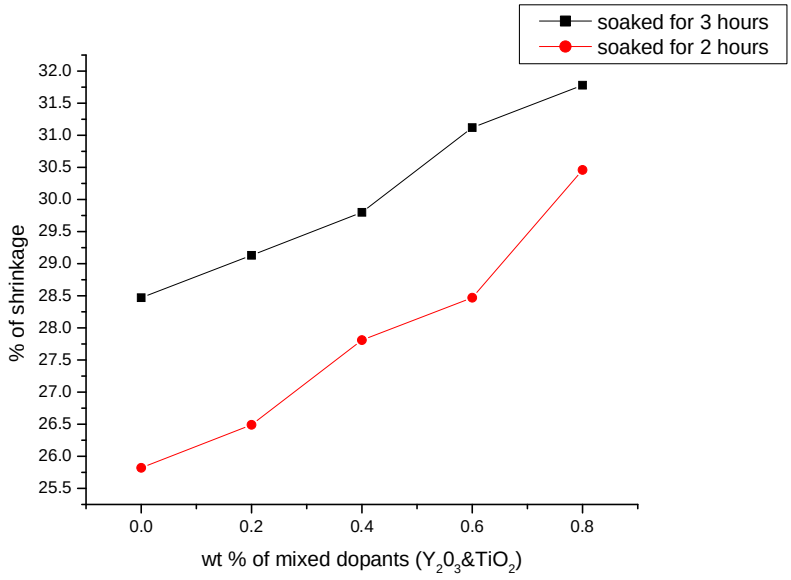
$$\text{BD (g/cc)} = \frac{\text{Dry weight}}{\text{Soaked weight-suspended weight}}$$

$$\text{Water Absorbtion (g/cc)} = \frac{\text{Soaked weight-Dry weight}}{\text{Dry weight}} \times 100$$

3.2.3 Table 2: Variation of Shrinkage of fired Al_2O_3 Compacts in presence of mixed dopants during firing at 1550^0C

Sample Code	Wt % of mixed dopant	Sample type	% of Shrinkage (Soaked for 2 hours)	% of Shrinkage (Soaked for 3 hours)
Batch 1	Undoped or 0%	Disk	25.82	28.47
Batch 2	0.2 %	Disk	26.47	29.13
Batch 3	0.4 %	Disk	27.81	29.80
Batch 4	0.6 %	Disk	28.47	31.12
Batch 5	0.8 %	Disk	30.46	31.78

3.2.4 Plots of firing shrinkage of fired compacts as a function of mixed dopant content fired at 1550^0C.



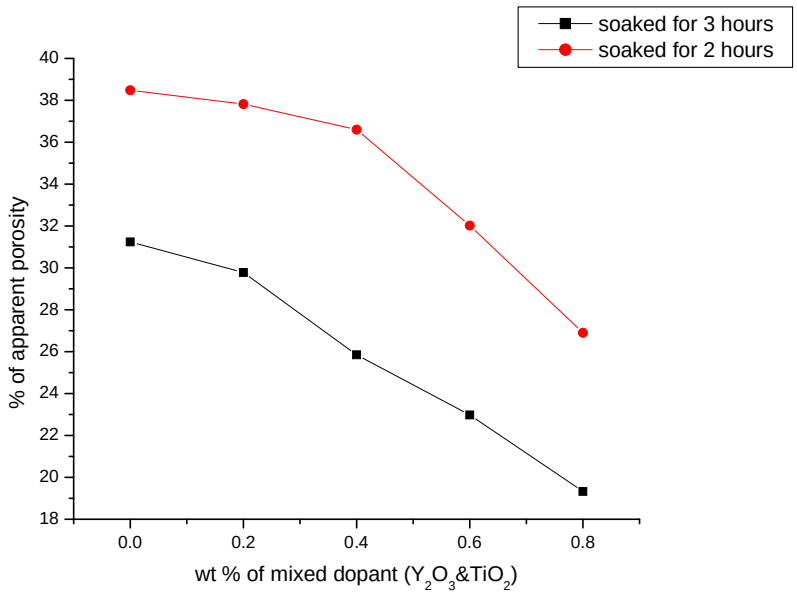
3.2.5 Table 3: The variation of AP, BD, Water Absorbtion of fired Al_2O_3 compacts in presence of mixed dopant during firing at 1550^0C soaked for 2 hours

Sample	Wt % of mixed dopant	% of AP	BD (g/cc)	% of H_2O Absorbtion
Batch 1	Undoped or 0%	38.48	2.40	15.99
Batch 2	0.2	37.82	2.42	15.64
Batch 3	0.4	36.60	2.48	14.72
Batch 4	0.6	32.02	2.65	12.04
Batch 5	0.8	26.09	2.83	9.50

3.2.6 Table 4: The variation of AP, BD, Water Absorbtion of fired Al_2O_3 compacts in presence of mixed dopant during firing at 1550^0C soaked for 3 hours

Sample	Wt % of mixed dopant	% of AP	BD (g/cc)	% of H_2O Absorbtion
Batch 1	0	31.24	2.66	11.72
Batch 2	0.2	29.78	2.70	11.00
Batch 3	0.4	25.85	2.84	9.26
Batch 4	0.6	22.98	2.94	7.79
Batch 5	0.8	19.33	3.70	6.30

3.2.7 Plot of AP of fired compacts as a function of mixed dopant content fired at 1550^0C



3.2.8 SEM STUDIES

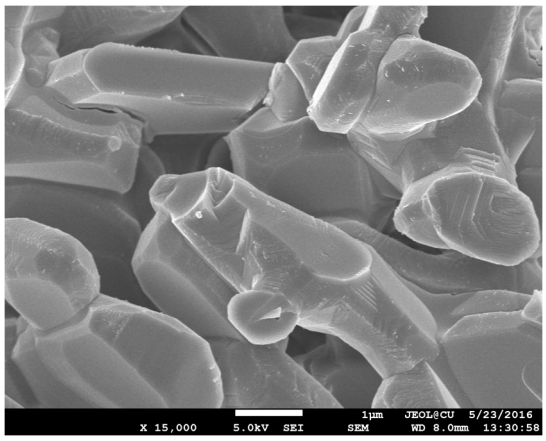


Fig: III

FESEM micrograph of undoped Al_2O_3 compact fired at 1550^0C

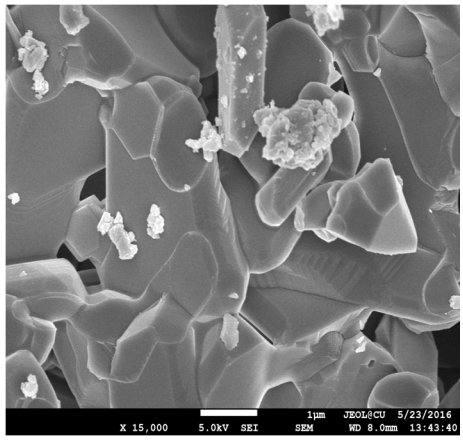


Fig: IV

FESEM micrograph of 0.2 % (Y_2O_3&TiO_2) doped Al_2O_3 Compact fired at 1550^0C

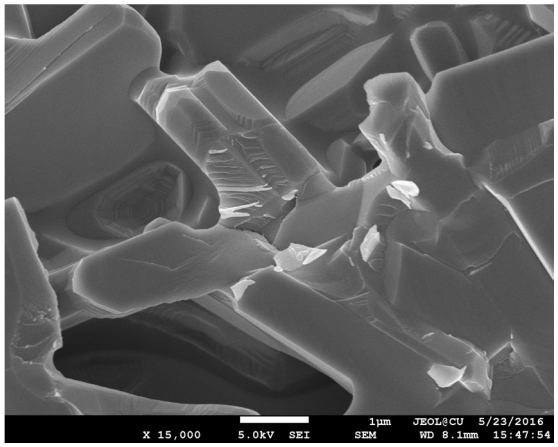


Fig: V

FESEM micrograph 0.8 % (Y_2O_3&TiO_2) doped Al_2O_3 compact fired at 1550^0C

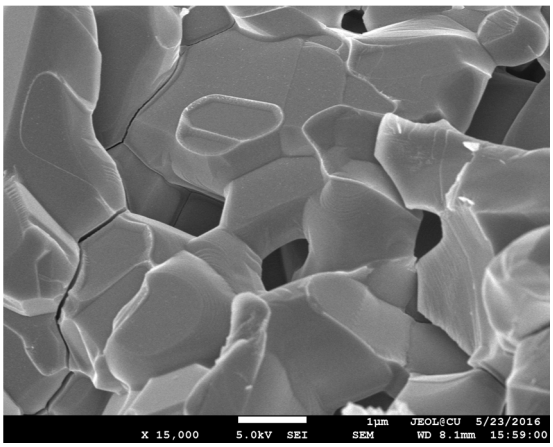


Fig: VI

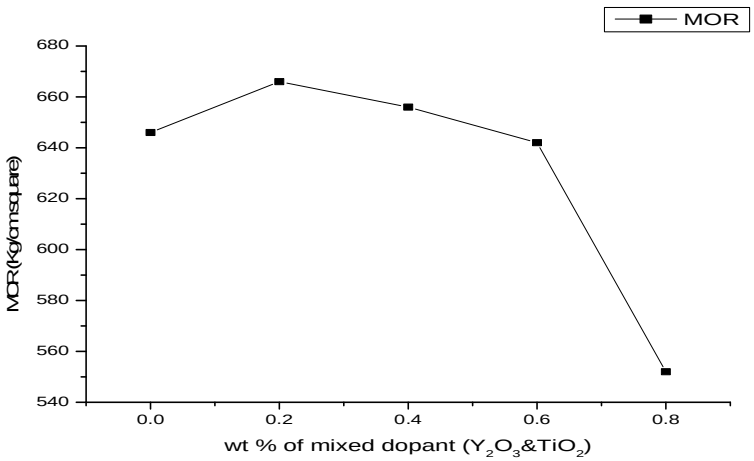
FESEM micrograph 0.6 % (Y_2O_3&TiO_2) doped Al_2O_3 compact fired at 1550^0C

FESEM micrographs of the sintered nano alumina compacts with and without mixed dopant during firing at 1550^0C for 3 hours are represented in the Fig IV to Fig VI. The dopant free alumina compacts exhibit a microstructure of elongated polygonal large corundum grains which are interlocked with one another through containing substaintial open pores.

3.2.9 Table 5: The variation of MOR of fired Al_2O_3 compacts in presence of mixed dopant during firing at 1550^0C with 3 hour soaking

Sample	Wt % of mixed dopant	Flexrual Strength (Kg/cm^2)
Batch 1	0	646
Batch 2	0.2 %	666
Batch 3	0.4 %	656
Batch 4	0.6 %	642
Batch 5	0.8 %	552

3.2.10 Plot of MOR of fired compacts as a function of mixed dopant content fired at 1550^0C



The variation of flexural strength with wt % of mixed dopant (Y_2O_3 & TiO_2) in active alumina fired at 1500^0C shows a dramatic changes as in the graph . The positive effect of dopant on the development of bending strength in fired alumina compact has not been evidenced. The steady reduction in MOR values of the fired compacts with increasing dopant content may be due to formation of low melting glassy phases at the grain boundary.

4. RESULT AND DISCUSSION

As the wt % of mixed dopant increases, the % of shrinkage increases of the fired compacts continuously whether the soaking period is 2 hours or 3 hours. The nature of shrinkage curve is similar in both cases. 0.8% of mixed dopant containing body showed highest shrinkage value of 30.46 and 31.78. Higher shrinkage results of all the samples respective of dopant content clearly signify the greater degree of densification of compacts in presence of mixed dopants. The relationship between apparent porosity and wt % of mixed dopant (Y_2O_3 & TiO_2) in active alumina fired at 1500^0C is shown in the graph. AP decreases as the wt % of dopant increases. The relationship between bulk density and wt % of mixed dopant (Y_2O_3 & TiO_2) in active alumina fired at 1500^0C shows the same relationship which can also correlate with shrinkage, as wt % of mixed dopant increases it increases shrinkage simultaneously increases BD. The graphical representation of apparent porosity Vs wt % of mixed dopant (Y_2O_3 & TiO_2) in active alumina bodies fired at 1500^0C is shown above. It is evident from plot 3.2.7 AP decreases sharply as the wt % of dopant increases. The relationship between bulk density and wt % of mixed dopant (Y_2O_3 & TiO_2) in active alumina fired at 1500^0C shows the similar relationship as that with shrinkage Vs wt % of mixed dopant curve. Batch 5 body exhibited maximum density as high as 2.83 gm/cc during firing of temperature at 1550^0C with 2 hour soaking while it is 3.7 gm/cc when fired at 1550^0C with 3 hour soaking period this reflected the positive effect of soaking time on densification behavior of Al_2O_3 compacts.

5. CONCLUSION

Correlating the crystallographic assemblage, microstructure of the sintered alumina compact with physical properties achieved, it may be concluded that the densification of active alumina is accelerated in presence of Y_2O_3 and TiO_2 as mixed dopant .The minor addition of mixed dopant brings about achievement of high BD and low porosity in the α –alumina compact as low temperature sintering of 1550^0C for 3 hours. The addition of 0.2% of mixed dopant only appears optimum for evolving dense fine grained microstructure for α –alumina compact based on active alumina.

6. ACKNOWLEDGEMENTS

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