

Influence of Ta₂O₅ Doping on the Microstructure, Physical and Mechanical Properties of α -Alumina Ceramics

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Abstract

The effects of Ta₂O₅ addition on the densification behavior, microstructure and mechanical properties of Ta₂O₅-doped alumina ceramics were investigated. The Ta₂O₅ addition to the alumina matrix was varied from 0.25 wt% to 0.75 wt%. In order to optimize the sintering temperature, the powders of each composition were uniaxially pressed at 220 MPa into discs and rectangular bars, which were then pressureless-sintered at a temperature ranging from 1500 to 1650 °C for 1 h. The phase constitution and microstructure of the sintered ceramic bodies were characterized with an X-ray diffractometer and a scanning electron microscope. The mechanical properties of the ceramic bodies were evaluated based on their Vickers hardness (HV1), bending strength and fracture toughness tests. It was found that Ta₂O₅ addition improved densification, reinforcing and toughening the bodies. The maximum bending strength, fracture toughness and Vickers hardness of the bodies with 0.75 wt% Ta₂O₅ were 53.4, 43.8 and 33.4 % higher than that of pure alumina.

Keywords: Doping, alumina, tantalum, microstructure, mechanical properties.

1. Introduction

Alumina (Al₂O₃) is one of the most widely used advanced ceramic materials because of its unique properties. It continues to attract the attention of researchers worldwide in efforts to modify its fabrication to improve its properties¹. However, undoped alumina is very difficult to sinter to theoretical density. The major factors that hinder densification are abnormal grain growth and pore detachment from the grain boundaries during boundary migration, which effectively leaves the pores permanently trapped inside the grains².

In recent years, numerous studies have been focused on the effects of small amount of additives, dopants or impurities on the sintering behavior of ultrapure alumina. Addition of rare earth dopants to alumina can reduce the melting point of ceramic composites, purifying the interface between the different phases of alumina composites and strengthening the grain boundary of alumina³. They are currently the most widely used oxides with maximum output⁴. Rare earth elements like Ce, Y, Pr, La, etc. can be used in the form of metal or oxide not only as a stabilizer for tetragonal ZrO₂, but also as sintering aids for Al₂O₃, TiB₂, TiC, etc.^{4,5}.

Mechanical properties of alumina-based ceramics have been improved with the incorporation of one or more reinforcing phases such as TiC, TiN, TiB₂, SiC par-

ticulates, SiC whiskers, B₄C, ZrO₂, WC, (W, Ti)C, Ti(C, N), Cr₂C₃, NbC, etc.⁶. The improvement in the fracture toughness of composites containing rare earth elements is due to the formation of complex rare earth compounds which increase the strength of the grains, weakening it at the interface to reduce the work done by a propagating crack for intergranular failure and to increase it for transgranular failure⁷. Rani *et al.*⁸ and Deng *et al.*⁹ reported that the addition of rare earth dopants to alumina resulted in a substantial increase in the proportion of intergranular fracture relative to the undoped material of the same grain size. They claimed that this is due to the significant reduction in the free surface energy that results from rare earth dopant segregation at grain boundaries, which reduces the required work of fracture for intergranular failure. Maiti and Sil¹⁰ showed that the hardness values of Y₂O₃-doped alumina ceramics with dopant concentration of 500, 1000 and 2000 ppm lie between 139 and 1444 MPa, while their fracture toughness values lie in the range 1.65–5.76 MPa m^{1/2}. On the other hand, alumina ceramics doped with 1000 ppm Yb³⁺, Er³⁺, and La³⁺ showed toughness values, *K_{IC}*, ranging between 4.5 and 5.4 MPa m^{1/2}⁸. Xihua *et al.*¹¹ studied the effect of mixed rare earth element (Nd, Ce, La and Pr) on the mechanical properties of alumina ceramics. They showed that the doped ceramics hot pressed in nitrogen atmosphere at 1550 °C exhibited bending strength values between 247.0 and 326.7 MPa, Vickers hardness ranging

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between 17.96 and 18.41 GPa and fracture toughness, K_{IC} , from 3.52 – 3.69 MPa m^{1/2}. The Vickers hardness and fracture toughness of pure alumina specimens depend on the starting material grain size as well as on the preparation method. Polycrystalline alumina studied by Anstis *et al.*¹² displayed Vickers hardness from 13 – 20 GPa and fracture toughness, K_{IC} , from 2.9 – 4.6 MPa m^{1/2} depending on the alumina grain size. Reverson *et al.*¹³ prepared alumina specimens from highly pure alumina starting materials with a grain size of 457 nm. Their samples exhibited Vickers hardness and fracture toughness of 15.1 GPa and 2.7 MPa m^{1/2} respectively. On the other hand, cold isostatically pressed Al₂O₃ specimens showed Vickers hardness of 1811 and fracture toughness of 2.69 MPa m^{1/2}.¹⁴

In the present study an attempt has been made to investigate the effect of Ta₂O₅ addition on the microstructural characteristics, physical and mechanical properties of Al₂O₃ ceramics. In particular, different amounts of Ta₂O₅ have been added ranging from 0.25 to 0.75 wt%, and the effect of the sintering temperature has been determined to optimize the physical properties (bulk density and apparent porosity) of the materials.

II. Experimental Procedure

(1) Materials and processing

Three compositions of 0.25, 0.5 and 0.75 wt% Ta₂O₅-doped alumina were prepared on the basis of powder mixing. The aluminum oxide used had 99.98 % purity (provided by Almatix GmbH Ludwigshafen/RH, Germany) and the tantalum oxide had 99.9 % purity (provided by SIGMA-ALDRICH, USA). The particle size of the as-received Al₂O₃ and Ta₂O₅ ranged from 135 – 150 nm and 100 – 120 nm respectively. All powders were mechanically mixed in a ball mill for 5 h using 5-mm zirconia balls and a polypropylene container with constant speed of 300 rpm. The powders obtained were formed by uniaxial pressing at 220 MPa into discs of 13 mm in diameter and 4 mm in height (for physical and microstructural characterization) and rectangular bars of dimensions of 6 x 6 x 60 mm³ (for mechanical evaluation). The bodies formed were pressureless-sintered in an electric oven at a temperature ranging from 1500 to 1650 °C with 50 K intervals and one hour soaking time. Heating and cooling rates were 5 K/min.

(2) Characterization

The densification parameters of the fired samples in terms of bulk density and apparent porosity were evaluated with the liquid displacement method (ASTM C-20). The different phases in the powdered samples developed during firing were identified by means of X-ray analysis (XRD) with a Philips X-ray diffractometer model PW 1730 with a Cu target and Ni filter. The XRD patterns were obtained at room temperature with a goniometric range of 5 – 80°, with a scanning rate of 0.005°s⁻¹ and a step size of 0.02°. The microstructure of the fractured surfaces was examined with a scanning electron microscope (SEM-Jeol JSM-T20). The samples were thermally etched at 1000 °C for 1 h in air atmosphere and coated with gold (thickness 15 nm) with an electro-deposition method to impart electrical conduction. The Vickers hardness of the sintered

samples was measured with a hardness tester (Omnimet automatic MHK system Model Micro Met 5114, Buehler USA). The composite samples were polished down to 0.25 µm surface finish with diamond paste and thermally etched at 1000 °C for 1 h in air atmosphere. Indentations were made on the polished surfaces with a load of 10 kg and 15 s dwell time. The average hardness of at least 30 indents was calculated according to the following equation¹²:

$$H = 1.8544(P/d^2)$$

where P is the load and d is the length of the impression diagonal.

Bending strength was measured in a three-point bending test on a universal testing machine (Model LLOYD LRX5K of capacity 5K N) at a crosshead speed of 1 mm/min, and support distance of 25 mm. At least ten specimens were measured for each data point. The fracture toughness, which is a critical mechanical property parameter and which characterizes the resistance of a material to crack propagation or to damage (including mechanical, thermal shock), was determined with the single-edge v-notched beam (SEVNB) technique¹⁵. For the SEVNB method, ground and polished rectangular specimens (3 mm x 4 mm x 45 mm) were notched on the surface (3 mm x 45 mm) using a diamond-charged cutting wheel, perpendicular to the length of the rectangular bars. The depth of the notches was approximately 0.7 mm, i.e. ≤ 20 % of the height of the specimen in accordance with DIN 51109¹⁶. The fracture toughness was determined by applying the following equation¹⁷:

$$K_{IC} = [L_{max}/(t(h^{1/2}))] \times [(L_0 - L_i)/h] \times [3 R_M (d/h)^{1/2}/2(1 - d/h)^{3/2}]$$

L_{max} is the maximum load, L_0 and L_i are the outer and inner roller spans; respectively, t and h are thickness and height of the specimen, d is the depth of the sharpened notch.

$$R_M = [1.9887 - 1.326 (d/h) - [3.49 - 0.68 (d/h) + 1.35(d/h)^2] (d/h) (1 - (d/h))/(1 + (d/h))^2]$$

III. Results and Discussion

(1) Physical properties and phase composition

The effect of sintering temperature on the bulk density and apparent porosity of the composites is shown in Fig. 1 (X0 = pure alumina, X1 = Al₂O₃ + 0.25 wt% of Ta₂O₅, X2 = Al₂O₃ + 0.5 wt% of Ta₂O₅, X3 = Al₂O₃ + 0.75 wt% of Ta₂O₅). The figure indicates that increasing the sintering temperature and the content of Ta₂O₅ increases the bulk density of the doped bodies and decreases their apparent porosity. The effect of the Ta₂O₅ content on the densification behavior of the alumina bodies is clearly seen in the behavior of the specimens' relative density. The relative density was measured on the basis of the theoretical density of pure alumina, 3.97 g/cm³, and pure tantalum, 8.2 g/cm³, respectively. Fig. 2. shows that the increase in the Ta₂O₅ increases the relative density of the obtained bodies fired at 1650 °C from 92.97 (X0) up to 98.75 % (X3), Table 1. The above-mentioned results are in full agreement with the results obtained by many researchers^{2, 8, 11}. They

showed that rare earth doping of alumina significantly improves the densification behavior. It was assumed that such improvement is due to the small ionic radius of the dopant (Ta₂O₅ ionic radius = 0.07 nm), which accelerates the densification rate. It was found that the smaller the dopant ionic radii, the better the densification rate⁸.

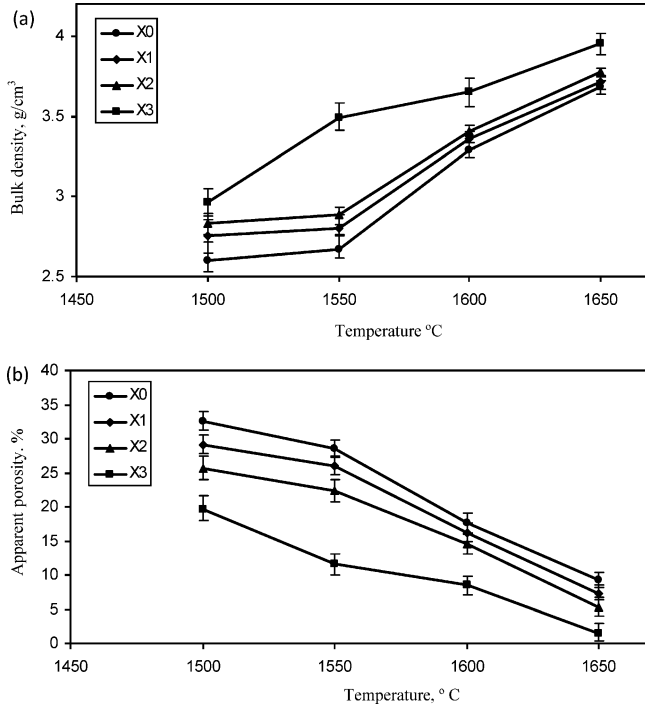


Fig. 1: Physical properties of the fired bodies, fired at different firing temperatures, (a) Bulk density, ± 0.1 and (b) Apparent porosity, ± 0.5 .

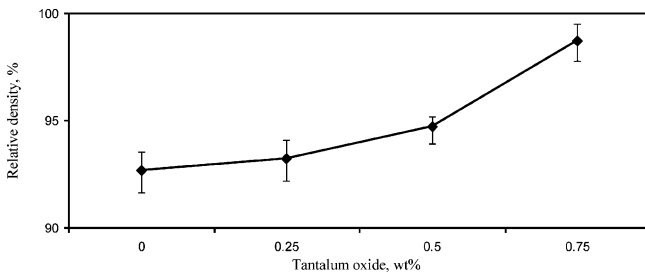


Fig. 2: Relative density of the sintered specimens.

Table 1: Theoretical and relative density of the studied batches.

Batch composition	Theoretical density, g/cm ³	Relative density, %
Pure alumina (Al ₂ O ₃) (X0)	3.97 g/cm ³	92.97 %
Pure Ta ₂ O ₅	8.2 g/cm ³	—
Al ₂ O ₃ + 0.25 wt% Ta ₂ O ₅ (X1)	3.98 g/cm ³	93.22 %
Al ₂ O ₃ + 0.5 wt% Ta ₂ O ₅ (X2)	3.99 g/cm ³	94.74 %
Al ₂ O ₃ + 0.75 wt% Ta ₂ O ₅ (X3)	4 g/cm ³	98.75 %

The XRD pattern of the as-received alumina is shown in Fig. 3. All detectable diffraction peaks correspond to those of α -Al₂O₃. The figure shows that alumina phase is the dominant phase present in the fired alumina-Ta₂O₅ bodies. The tantalum oxide phase is also present in a very minute proportion compared to the bulk Al₂O₃.

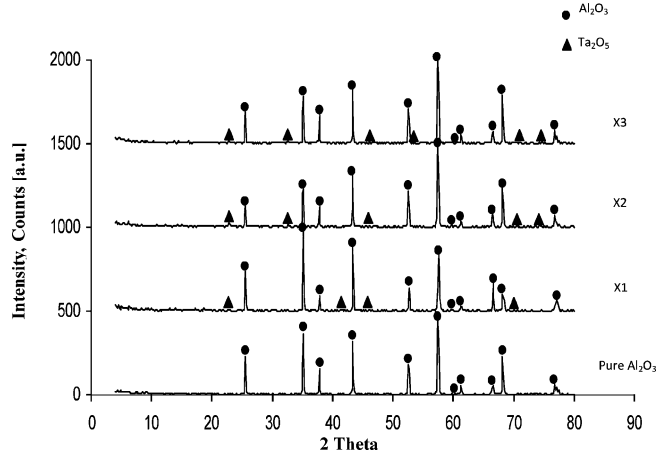


Fig. 3 : X-ray pattern of the pure alumina, X0 and X1, X2 and X3 bodies sintered at 1650 °C.

Considering these results, 1650 °C seems to be the optimum sintering temperature. Consequently, only the X0, X1, X2 and X3 samples sintered at 1650 °C have been subsequently characterized.

(2) Microstructure

The microstructure of the X0 sample shows abnormal grain growth of the alumina grains, Fig. 4a. Fig. 4 (b, c and d) shows that the microstructure of the X1, X2 and X3 samples sintered at 1650 °C consists of two types of grains. The small grains having a nearly square shape are Ta₂O₅ grains, and the large grains having irregular geometry including elongated shape are Al₂O₃ grains. Fig. 4 (b) shows the micrograph of the X1 sample doped with 0.25 % Ta₂O₅. It is clear that the alumina grains are completely enclosed by tiny Ta₂O₅ grains. The grain size of the Ta₂O₅ ranges between 647 and 29.14 nm. Figs. 4 (c) and (d) show that with the increase in the Ta₂O₅ content up to 0.5 and 0.75 wt%, some of the Ta₂O₅ dopants were consumed in the formation of Ta₂O₅ islands. Similar phenomena were observed in Nd³⁺-, Y³⁺- and La³⁺-doped Al₂O₃/SiC composites⁹. On the other hand, Fig. 5 indicates that Ta⁵⁺ cations segregate in the vicinity of the grain boundary in alumina composites. The boundary area is clear and no obvious traces of interfacial reaction are observed. Odaka *et al.*¹⁸ and Yoshida *et al.*¹⁹ demonstrated that Lu³⁺ ions segregate to Al₂O₃ grain boundaries without forming any secondary phase, which is in agreement with the present study results and confirmed by XRD analysis of the samples, Fig. 3. Accordingly, it could be concluded that the tantalum was accommodated only as a grain boundary and surface segregant.

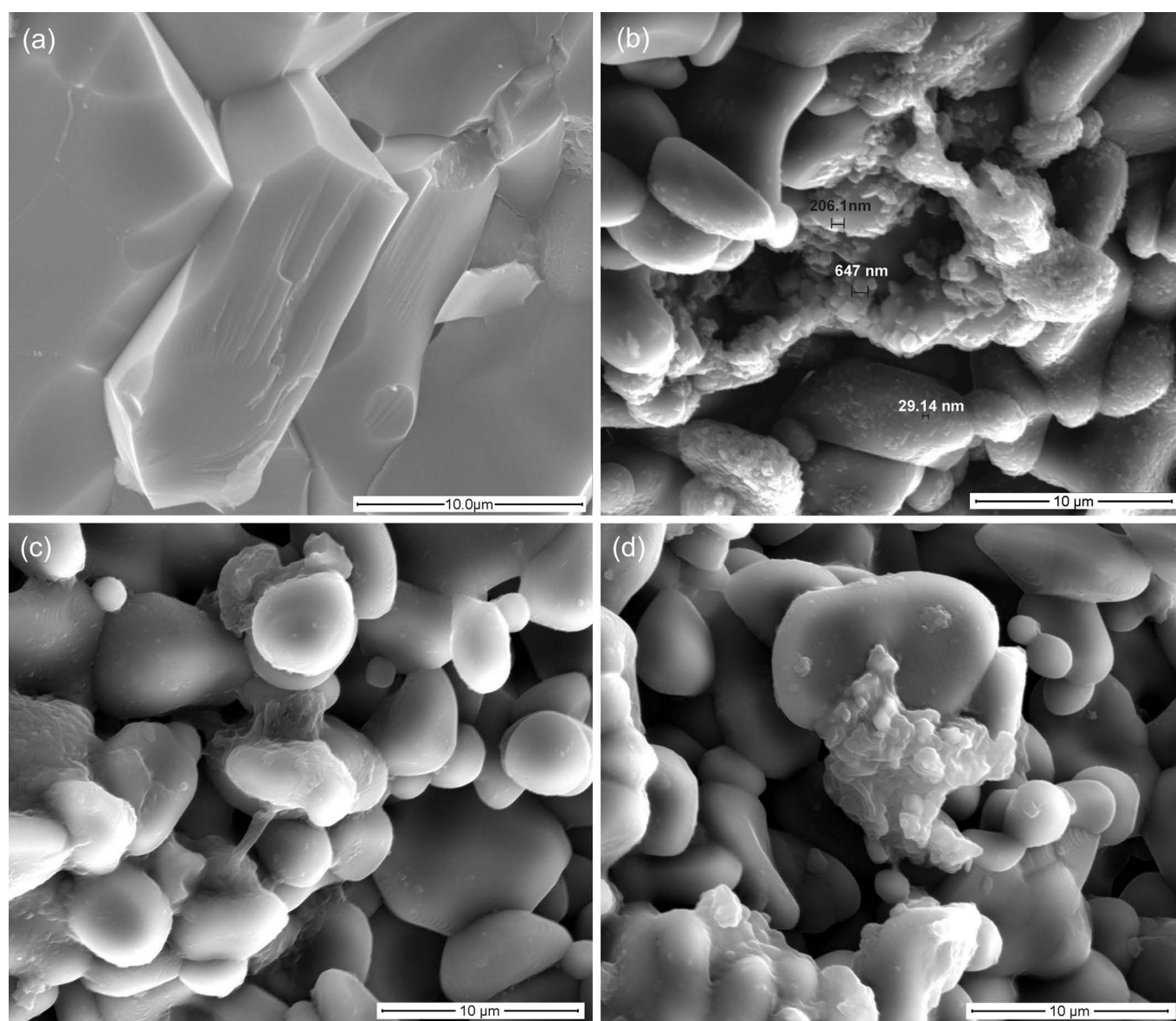


Fig. 4: SEM micrograph of the fracture surface of (a) X0, (b) X1, (c) X2 and (d) X3 samples fired at 1650 °C.

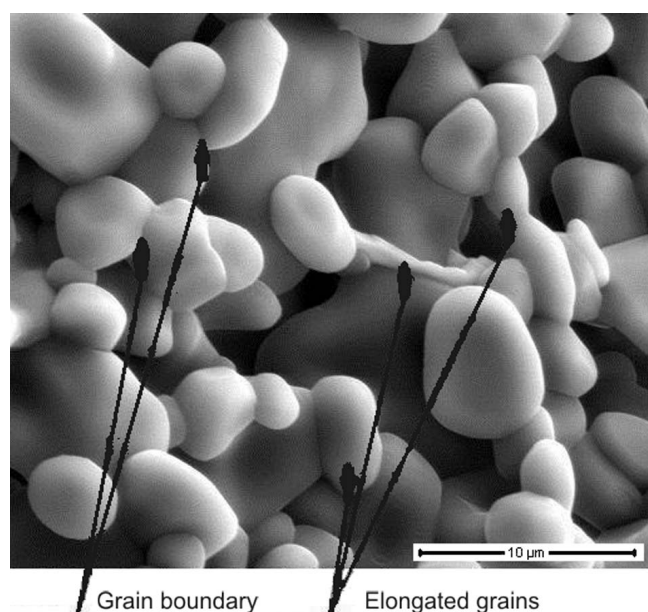


Fig. 5: SEM micrograph of X3 sample fracture surface indicating the presence of the elongated grains and the free grain boundary.

(3) Mechanical properties

Fig. 6 shows the bending strength of the studied samples. The figure indicates that the mechanical properties of the alumina/Ta₂O₅ bodies are affected by the amount of Ta₂O₅ addition. The strength of the bodies has been enhanced compared to that of the pure alumina samples. The increase in the bending strength with the increase in Ta₂O₅ content is mainly due to the decrease in the bodies' apparent porosity. Pores (size, shape and amount) reduce the strength of the ceramics because they reduce the cross-sectional areas over which a load can be applied²⁰. In addition, rare earth elements decrease the air holes in the composites, which is beneficial to improving the bending strength of the composites¹¹.

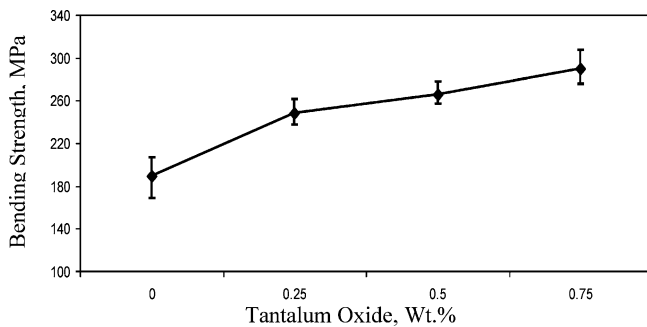


Fig. 6: Effect of Ta_2O_5 wt% on the bending strength of alumina bodies sintered at 1650 °C.

The fracture toughness and Vickers hardness of pure alumina and alumina/ Ta_2O_5 bodies are shown in Figs. 7 and 8. Both the fracture toughness and hardness of the samples have increased with the increase in the Ta_2O_5 content. Alumina/ Ta_2O_5 ceramics showed a notable improvement in the toughness and hardness at all Ta_2O_5 concentrations compared to the pure alumina samples. This is due to the formation of anisotropic elongated grains (Fig. 5), which can result in crack bridging and crack deflection. On the other hand, dislocation lines, dislocation rings, dislocation twisting and sliding can be observed inside the alumina grains (Fig. 9). According to Chonghai⁴ the forming mechanism for these kinds of dislocation patterns is complicated. However, the elastic strain energy can be deposited in the dislocation, which puts the dislocation in a sub-stable state. When the crack reaches the dislocation, this can absorb parts of the energy of fracture through its own deformation. The propagating crack will be pinned and the fracture toughness of the material will be increased.

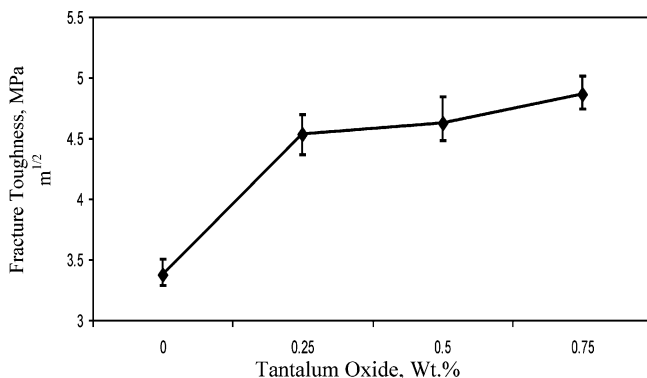


Fig. 7: Effect of Ta_2O_5 wt% on the fracture toughness of alumina bodies sintered at 1650 °C.

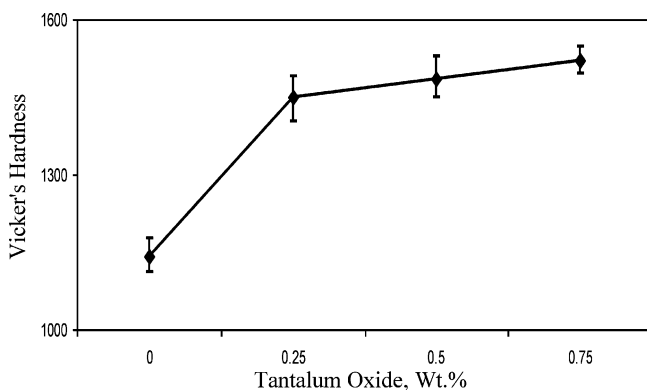


Fig. 8: Effect of Ta_2O_5 wt% on the hardness of alumina bodies sintered at 1650 °C.

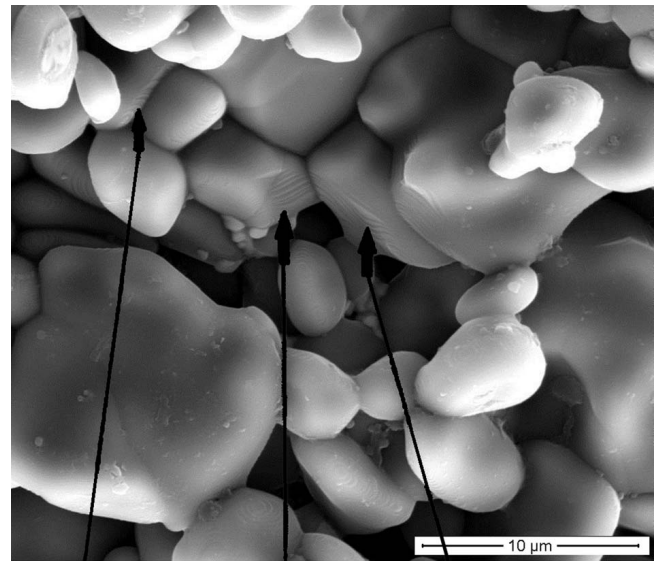


Fig. 9: SEM micrograph of the fracture surface of X2 sample indicating the presence of dislocation lines, dislocation twisting and dislocation rings.

IV. Conclusions

- 1 The density of the Al_2O_3/Ta_2O_5 ceramics increased with an increase in the sintering temperature from 1500 to 1650 °C. The optimal sintering temperature is 1650 °C. Addition of Ta_2O_5 improved the densification of bulk ceramic bodies and the best results (1 % of residual apparent porosity) were obtained after adding 0.75 wt% tantala.
- 2 The flexural strength of doped Al_2O_3 ceramics increased with increasing Ta_2O_5 percentage. The maximum bending strength of $Al_2O_3/0.75$ wt% Ta_2O_5 (290 MPa) was 53.4 % higher than that of pure Al_2O_3 (189 MPa).
- 3 The Vickers hardness of Al_2O_3/Ta_2O_5 ceramics increases with the increase in the Ta_2O_5 content. The maximum Vickers hardness of $Al_2O_3/0.75$ wt% Ta_2O_5 bodies (1522) was 33.4 % higher than that of pure Al_2O_3 (1141).
- 4 The fracture toughness of doped Al_2O_3 ceramics increased with increasing Ta_2O_5 percentage. The maximum fracture toughness of $Al_2O_3/0.75$ wt% Ta_2O_5 ceramics (4.86 MPa m^{1/2}) was 43.8 % higher than that of pure Al_2O_3 (3.38 MPa m^{1/2}).

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