THE EFFECT OF TANTALA AND NIOBIA ADDITION ON THE PHYSICAL AND MECHANICAL PROPERTIES OF $\alpha$ ALUMINA CERAMICS

S. M. Naga*, M. Awaad* and A. M. Hassan**

ABSTRACT

The effects of Ta$_2$O$_5$ and Nb$_2$O$_5$ addition on the densification behavior, microstructure and mechanical properties of Al$_2$O$_3$ ceramics were investigated. The Ta$_2$O$_5$ and Nb$_2$O$_5$ additions to the alumina matrix were varied from 0.25wt% to 0.75 wt%. The powders of each composition were uniaxially pressed at 220 MPa into discs and rectangular bars, then pressureless-sintered at 1650 °C for 1 h. The phase constitution and microstructure of the sintered ceramic bodies were characterized with a X-ray diffractometer and a SEM. The mechanical properties of the ceramic bodies were evaluated on the basis of their Vickers hardness (HV1), bending strength and fracture toughness. It was found that Ta$_2$O$_5$ addition enhanced the mechanical properties of alumina bodies in comparison to Nb$_2$O$_5$ addition. The maximum bending strength, fracture toughness and Vickers hardness of the bodies with 0.75wt% Ta$_2$O$_5$ were 14.2, 6.1 and 3% higher than that of 0.75 wt% Nb$_2$O$_5$ doped Al$_2$O$_3$ samples.

KEY WORDS

Doping, Alumina, Tantala, Niobia, Microstructure.

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INTRODUCTION

Alumina oxide attracted the attention of researchers due to its unique mechanical, electrical and optical properties. It is well known that properties of alumina influenced by trace impurities and additives [1,2]. The influence of rare earth oxides additions on the alumina properties was widely studied [3-9]. Odaka et al [9] reported that doping of $\text{Al}_2\text{O}_3$ with nanopowder rare earth oxides enhanced the densification at low temperature. They claimed that the synergistic effect between the nano-sized alumina particles and suppression effect of the homogenously segregated rare earth dopant on the alumina grain growth are the reasons of the excellent low temperature densification of rare earth/alumina doped bodies. On the other hand, Wang et al [8] showed that $\text{Nd}_2\text{O}_3$ doping inhibited $\text{Al}_2\text{O}_3$ densification. Fang et al [10] believed that the densification inhabitation is due to the suppression of grain-boundary diffusion resulted from the segregation of the rare earth ions misfitted to the $\text{Al}_2\text{O}_3$ grain boundaries.

Many authors studied the effect of rare earth dopants on the alumina body’s mechanical properties [6,11,12]. Rani et al [6] and Xu et al [12] reported that rare earth ions ($\text{Yb}^{3+}, \text{Er}^{3+}$ and $\text{La}^{3+}$) improve the mechanical properties of alumina. They showed that the formation of anisotropic elongated grains results in crack bridging and crack deflection that in turn improve the fracture toughness of the $\text{Al}_2\text{O}_3$ doped bodies. The present article mainly analyzes the effect of both $\text{Nb}_2\text{O}_5$ and $\text{Ta}_2\text{O}_5$ doping on the microstructure, mechanical and physical properties of alumina ceramics. $\text{Nb}_2\text{O}_5$ and $\text{Ta}_2\text{O}_5$ were added separately to alumina in a range of 0.25 up to 0.75 wt%.

MATERIALS AND METHODS

Materials and Processing

Compositions of $\text{Nb}_2\text{O}_5$- and $\text{Ta}_2\text{O}_5$- doped alumina were prepared on the basis of powder mixing according to Table. 1. The $\text{Al}_2\text{O}_3$ used had 99.98% purity (provided by Almatis Gmbh Ludwigshafien/RH, Germany), and both niobium and tantalum oxides had 99.9% purity (provided by SIGMA-ALDRICH chemistry, USA). The particle size of the as-received $\text{Al}_2\text{O}_3$, $\text{Nb}_2\text{O}_5$ and $\text{Ta}_2\text{O}_5$ is ranged between 135-150 nm and 100-120 nm respectively. All powders were mechanically mixed using a ball mill for 5 h using 5 mm zirconia balls and a polypropylene container with constant speed of 300 rpm. The obtained powders 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 mm$^3$ (for mechanical evaluation). The bodies formed were pressureless - sintered in an electric oven at 1650 °C for one-hour soaking time. Heating and cooling rates were 5 °C/min.

Characterization

Relative density was used to evaluate the densification behavior, while the developed phases were identified by X-ray diffraction analysis (XRD). The microstructure of the fractured surfaces of the sintered specimens was examined with scanning electron
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The Vickers hardness of the sintered samples was measured with hardness tester (Omnimet automatic MHK system Model Micro Met 5114, Buehler USA). 30 indents were made for each sample and average hardness was calculated according to the following equation [13]:

\[ H = 1.8544 \left( \frac{P}{d^2} \right) \]  

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, the fracture toughness was determined with the single-edge v-notch beam (SEVNB) technique [14]. The fracture toughness was determined by applying the following equation [15]:

\[ K_{1c} = \frac{P_{\text{max}}}{t (h^{1/2})} \times [L_0 - L_i / h] \times [3R_M (d/h)^{1/2} / 2(1 - d/h)^{3/2}] \]

where, \( P_{\text{max}} \) is the maximum load (N), \( L_0 \) and \( L_i \) are the outer and inner roller spans (mm); respectively, \( t \) and \( h \) are thickness and height of the specimen (mm), \( d \) is the depth of the sharpened notch (mm).

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

RESULTS AND DISCUSSION

Physical Properties and Phase Composition

The effect of pentavalent oxides (Nb\textsubscript{2}O\textsubscript{5} and Ta\textsubscript{2}O\textsubscript{5}) doping on the relative density of the studied bodies is shown in Fig. 1. The figure shows that the increase in the dopants content increases the relative density of the obtained bodies fired at 1650°C from 92.97 (X0) up to 98.66% (X3) and 98.75% (X6). The fine particle size of the dopants yields better powder flow ability and packing density, leading to higher green density values [16]. It was mentioned that the driving force for diffusion is increased by the increase in the specific surface area. It leads to the increase in the number of contact points between dopants and the alumina matrix, which in turn reduces the diffusion paths. Fine, dispersed pentavalent dopants occupying the voids between alumina particles have the effect of pinning the alumina and prevent grain growth [16]. Ta\textsubscript{2}O\textsubscript{5} doped ceramics possess better relative density values compared to the Nb\textsubscript{2}O\textsubscript{5} doped samples. This behavior is attributed to the solid solution formed at the grain-boundary triple junctions of alumina matrix of the Nb\textsubscript{2}O\textsubscript{5} doped alumina samples, Fig.2. Some authors [17, 18] claimed that the formation of amorphous glassy phase near the crystallized alumina grains hinders the diffusion of dopants into the alumina matrix. It forms an intergranular liquid phase that enhances the abnormal grain growth and leads to the trapping of pores within and between the abnormally grown alumina particles. Figure 3.a &b illustrates the effect of the grain size on the densification behavior of the alumina doped bodies.
The figure shows that the average grain size of Ta$^{5+}$ doped samples is smaller than that of Nb$^{5+}$ samples (6.11 µm respectively). It indicates that Ta$^{5+}$ ions suppression the alumina grain growth and enhances the samples densification [6].

Figs. 4a & b. show the XRD patterns of the fired alumina/ Nb$_2$O$_5$ and Ta$_2$O$_5$ bodies. The figure shows that the alumina phase is the dominant phase present in the Nb$_2$O$_5$ doped bodies. The shift in the alumina peaks indicates the formation of a solid solution between alumina and Nb$_2$O$_5$. The higher d values and lower 2θ shift are clearly shown in the XRD patterns of X2 and X3 samples, with 0.5 and 0.75% Nb$_2$O$_5$, Fig. 4a. In several studies of the binary Al$_2$O$_3$ system [19], Nb$_2$O$_5$ - Al$_2$O$_3$ compounds have been reported to occur at molar ratios of 1:1, 1:9, 1:11, 1:25 and 1:49. The most suggested binary compounds are at 1:1, 1:11, and 1:49 molar ratios. The structure of Al NbO$_4$ is built from distorted [NbO$_6$] and [AlO$_6$] octahedral sharing edges and corners, and linked together to give an infinite three-dimensional network [20]. XRD patterns of the fired alumina/ Ta$_2$O$_5$ bodies; Fig. 3b; illustrates that all detectable diffraction peaks are corresponding to those of α- Al$_2$O$_3$. The tantalum oxide phase is also present in a very minute proportion compared to the bulk Al$_2$O$_3$.

Microstructure

Figures 5 a, b, c and d show the microstructure features of the pure alumina and alumina bodies doped with 0.25, 0.5 and 0.75wt% Nb$_2$O$_5$ and sintered at 1650 °C. Abnormal grain growth is noticed in the pure alumina samples. While, alumina grains of the sample doped with 0.25wt% Nb$_2$O$_5$ mostly exhibit an equiaxed shape. With the increase of Nb$_2$O$_5$ content, the grains tend to show abnormal grain growth. The figure shows that in contrast to the approximately uniform microstructure of the X1 sample, the grain structure of X2 and X3 samples is bimodal, comprising coarse grains and fine grains. The microstructure of the samples with different Nb$_2$O$_5$ concentrations shows that some of the triple junctions are occupied by bright particles, which are Nb$_2$O$_5$, while some other Nb$_2$O$_5$ particles are present in the intragranular position within the alumina grains. The microstructure of Ta$_2$O$_5$ doped alumina samples; Fig. 6 (a, b and c); shows that it consists of two types of grains. The small grains having a nearly square shape are Ta$_2$O$_5$ grains, and the large grains having irregular geometry including elongated shape are Al$_2$O$_3$ grains. Fig. 6a shows that alumina grains are completely enclosed by tiny Ta$_2$O$_5$ grains. The grain size of the Ta$_2$O$_5$ ranges between 647 and 29.14 nm. Figures 6b and c show that with the increase in the Ta$_2$O$_5$ content some of the Ta$_2$O$_5$ dopants were consumed in the formation of Ta$_2$O$_5$ islands.

Mechanical Behavior

Bending strength

The bending strength of Al$_2$O$_3$ doped with Nb$_2$O$_5$ or Ta$_2$O$_5$ is higher than that of undoped specimens (Fig. 8). We believe that the increase in the bending strength of the doped samples is attributed to the addition of rare earth oxides. As shown in Fig. 1 the addition of Nb$_2$O$_5$ increases the fired samples’ relative density, which in turn enhances the bending strength of the bodies [21]. At the same time, the presence of the dopant particles reduces the crack length by forming sub-boundaries in the matrix grains could be afforded to the difference in the expansion coefficient of the phases conforming the body, Ta$_2$O$_5$ (6.72×10$^{-5}$/°C in 0–1000 °C), Nb$_2$O$_5$ (5.9x 10-6/°C in 0–
1000 °C) and Al₂O₃ (8.8×10⁻⁶/°C in 0–1000 °C) [22]. Such difference in the thermal expansion enhances the bending strength by inducing residual tension in Nb₂O₅ or Ta₂O₅ phases and residual compression in the Al₂O₃ matrix after cooling [21]. The increase in the bending strength of Ta₂O₅ doped samples in comparison to those doped with Nb₂O₅ is due to the improvement of the densification parameters of the Ta₂O₅ doped samples.

**Vickers hardness**

Figure.9 indicates that the increase in the dopants content increases the hardness of the samples. The doped bodies showed remarkable improvement in hardness at all Nb₂O₅ and Ta₂O₅ concentrations over that of the pure alumina samples. The maximum hardness of Al₂O₃ /0.75 wt% Ta₂O₅ (1522) was 33.4% higher than that of pure alumina (1141) and 3% higher than that of Al₂O₃ /0.75 wt% Nb₂O₅ samples (1478). Also, with lower percentages of doping Ta₂O₅ doped samples showed higher hardness' percentages than that of Nb₂O₅. This behavior could be attributed to the difference in the relative density of the two composites. It was reported that porosity reduces the hardness of ceramic materials by producing stress concentration points, which are a crack initiation points [23,24].

**Fracture toughness**

The fracture toughness of the samples increases with the increase in Nb⁵⁺ and Ta⁵⁺ ions contents. The increase in the fracture toughness values is a reflection of both the densification and microstructure. Formation of anisotropic elongated grains (Fig. 2), 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. 11). 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 substable state [25]. When the crack reaches the dislocation, some of the fracture energy can absorbed through the crack deformation. The propagating crack will have pinned and the fracture toughness of the material will increase. Also, it is clear that tantala doped samples show higher fracture toughness results than niobia ones. This could be attributed to the higher densification of tantala-doped samples.

**CONCLUSIONS**

1. Doping with Ta₂O₅ has much better effect on densifying α- Al₂O₃ than Nb₂O₅. The difference in the relative density is clear at lower weight percentages (0.25% and 0.5%) of dopant oxides while it is small at the high percentage of doping (0.75%), (ρ_d = 98.75 % and 98.66 % for Ta₂O₅ and Nb₂O₅ respectively).

2. Nb₂O₅ was observed at the triple junctions and the intergranular regions of the Al₂O₃ grains. Increasing the Nb₂O₅ content led to the formation of a rare-earth-containing liquid phase in the samples.

3. Even with small contents of Nb₂O₅ and Ta₂O₅, the bending strength, hardness and fracture toughness of alumina matrix ceramic bodies were all notably
Ta$_2$O$_5$ has much better effect in improving the mechanical properties rather than Nb$_2$O$_5$.

REFERENCES


Fig. 1. Relative density of the studied bodies fired at 1650 °C.

Fig. 2. Solid solution formed at the grain-boundary triple junctions of Nb$_2$O$_5$ doped alumina.

Fig. 3. Average grain size of Al$_2$O$_3$ (a)Ta$^{5+}$ doped (b) Nb$^{5+}$ doped samples.
Fig. 4. XRD pattern of (a) Al₂O₃/ Nb₂O₅ bodies, (b) Al₂O₃/ Ta₂O₅ bodies fired at 1650º C.

Fig. 5. SEM micrograph of X₀ (a), X₁(b), X₂ (c) and X₃ (d) samples fired at 1650ºC.
Fig. 6. SEM micrograph of X4 (a), X5(b) and X6 (c) samples fired at 1650ºC.

Fig. 7. SEM micrograph of X3 sample fracture surface indicating the presence of the elongated grains and the free grain boundary.

Fig. 8. Effect of dopants content on the bending strength of composites fired at 1650ºC.
Fig. 9. Effect of dopant content on the Vickers Hardness of composites sintered at 1650 °C.

Table 1. Compositions of Nb$_2$O$_5$ and Ta$_2$O$_5$ doped Al$_2$O$_3$ batches, wt.%.

<table>
<thead>
<tr>
<th>Batch Symbol</th>
<th>Al$_2$O$_3$, wt.%</th>
<th>Nb$_2$O$_5$, wt.%</th>
<th>Ta$_2$O$_5$, wt.%</th>
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<td>X0</td>
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<td>____</td>
<td>____</td>
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<tr>
<td>X1</td>
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<td>____</td>
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<tr>
<td>X2</td>
<td>100</td>
<td>0.5</td>
<td>____</td>
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<tr>
<td>X3</td>
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<td>____</td>
<td>0.25</td>
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<tr>
<td>X5</td>
<td>100</td>
<td>____</td>
<td>0.5</td>
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<tr>
<td>X6</td>
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