Characterization of nano ceramic composite of Mullite-Magnesia-Yttria stabilized Zirconia system

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Abstract. The oxide and nano ceramic system of Mullite-Magnesia-Yttria Stabilized Zirconia were studied. Some fracture toughness models were examined to evaluate the crack length parameter to comply with Palmqvist and median crack criteria at c/a ratio equal to 3.0. The mullite crystal structure was observed using SEM and looks likely needle, whereas 3YSZ crystal appears smoother. Through EDS analysis, it detected the oxides in Mullite system, i.e., Al2O3, and SiO2. With a similar method, some oxides observed in the Mullite-Magnesia-3YSZ system such as MgO, Al2O3, SiO2, Y2O3, and ZrO2. With XRD analysis, nano MMZ system shows containing Al6Si2O13, Corundum (Al2O3), Zirconia (ZrO2), and Quartz (SiO2). Fracture toughness KIC of the ceramic composite of nano mullite-magnesia-zirconia complies with Palmqvist and median crack criteria. Nano ceramic particle shows a higher value of hardness and fracture toughness while compared with oxide ceramic system.

1. Introduction

The ceramic materials have been developed to improve the physical, mechanical properties for various application. The TZP ceramic system advantage has higher bending strength while compared with alumina, Y16Al4V, and metal alloys such as SS316 and CoCr alloy. The ceramic system shows competitive hardness while compared with alumina and better among the others [1]. The zirconia granular is currently developed and produced commercially by several companies such as Astromet and Xylon (USA), Ceraver, SCT and Norton (France), Ceramtec (Germany), Kyocera and NGK (Japan), Metoxit (Swiss), and Morgan Matroc (UK).

The current progress in dental technology and application results better composition material for instance veneer Ceram (EMC) containing silica 60-65%, alumina 9-11%, zirconia 1-1.5%, titania 1-1.5%, etc. [2]. Some of dental ceramics are developed commercially, e.g., Vita Zahnfabrik, Ivoclar, Densply, Norton, Corning, Goodfellow, etc. [3].

The ceramic materials can be characterization through physical-mechanical properties, e.g., hardness. Through an indentation test, the ceramic hardness can be measured either through scratch hardness, indentation hardness, or dynamic hardness [4]. If scratch hardness indicates material resistance to tear strength, whereas indentation hardness depends on applied load related to permanent impression due to static indentation. While dynamic hardness depends on the indenter bench height, or impact energy.
It knew that Hertz (1881) firstly defined an absolute value of hardness with impress value under the ball indenter [5]. Next, Auerbach, Meyer and Hoyt measured the test specimen and led to defining of hardness theory, in which the hardness is equal to the maximum applied a load of indenter divided by contact area projection at maximum load [6-8]. Structural and mechanical characterization of mullite reinforced yttria stabilized zirconia ceramic composites [9]. Further Vickers indentation is used to evaluate the crack propagation scheme on brittle material through the fracture toughness test. The crack propagation is not always radial, but it can propagate everywhere or forms small branches. The crack area can be an assumption as a simple geometry around the indented zone. Generally, the surface area of microcrack has crack length, $c$, and crack width, $t$.

2. Method

In this experiment, specimens were prepared using both oxide and nanomaterials, i.e., silica, zirconia, mullite, and magnesia. First, these materials were weighed and mixed stoichiometrically. The mixed material was then dried press before sintered until 1400°C. The specimen cast into pellet and bar (rectangular) shape with refers to ASTM requirement.

The prepared specimens consist of 3% Yttria Stabilized Zirconia (3YSZ), Mullite, and Mullite-Magnesia 1%. Mullite was synthesized stochiometrically from alumina and silica. Yttria-stabilized zirconia was added into mullite-magnesia in different proportion to examine any influence of the properties of the new mixture of mullite-magnesia-yttria stabilized zirconia (YSZ) system.

In this study, Vickers hardness has calculated from the crack length after indentation with referring to the standard method of ASTM C1327-08. The elasticity modulus parameter was obtained using reference data per ASTM C769-98. The fracture toughness value of ceramic material is calculated mathematically if the crack length complies with Palmqvist crack criteria. The ceramic composite was characterized using SEM image, XRD, EDS to examine oxides content in the ceramic composite.

3. Result and discussion

To characterization of nano ceramic composite of mullite- magnesia-yttria stabilized zirconia system consists of crack model criteria, the indentation of Vickers hardness and granular size.

3.1. Crack model criteria

The correlation between fracture toughness, $K_{IC}$, against to modulus-to-hardness ratio ($E/Hv$) and Vickers hardness ($Hv$) has examined. These correlations comply with requirement of Palmqvist crack criteria (1957) at $c/a < 3.0$ or $l/a < 2.0$. The Niihara model (1983) is modified to be applied to define fracture toughness parameter, with a difference of limit value at $c/a \approx 3.0$ [10]. The fracture toughness of the modified model and also Niihara is higher than other fracture toughness values. This analysis assumes that crack propagation follows Palmqvist crack criteria.

Further analysis refers to crack propagation based on combined Palmqvist and median half a penny) crack criteria. In this case, the relationship between fracture toughness ($K_{IC}$) against $E/Hv$ and $Hv$ has shown at Figure 1. The crack propagation follows the requirement of Palmqvist crack criteria while $c/a < 3.0$ or $l/a < 2.0$ and median crack if $c/a \geq 3.0$ or $l/a \geq 2.0$. The modified Niihara model was proposed to define fracture toughness parameter, with the limit value at $c/a = 3.0$. In this case, the fracture toughness of the modified model and Niihara model also show a higher value than other fracture toughness proposed by previous researchers.
An analysis of c/a parameter can examine through the correlation between $K_{IC}$ and c/a. Figure 2 shows the correlation between Hv against to c/a. From the figure, each curve tends to cross at c/a = 3.0 or l/a = 2.0. It means under this value, it leads to comply with Palmqvist criteria. In the other hand, over this value, it leads to comply with the median crack criteria. The applied load of indentation varies from 1, 3, 5, until 13 kg, respectively. The modified Niihara model can define a parameter of fracture toughness by using transition value at c/a = 3.0.

3.2. Vickers hardness
The Vickers hardness of the oxide ceramic composite system shows a slightly lower value than the Vickers hardness of nano ceramic composite (Figure 3). The hardness of the pure 3YSZ oxide system of 13.65 GPa is lower than nano ceramic of 3YSZ of 15.45 GPa. The mullite and mullite magnesia in the form of oxide compounds also showed a lower value of Vickers hardness. The Mullite-Magnesia-3YSZ (MMZ) oxide system shows a lower value than the nano MMZ ceramic composite. Additional 3YSZ into mullite-Magnesia system tends to influence the Vickers hardness. However, both the oxide
system and nanoceramics show a similar tendency, in which any increase of 3YSZ content in the mullite magnesia system leads to increase Vickers hardness.

![Figure 3. Vickers hardness of oxide vs. nano ceramic MMZ system.](image)

3.3. Granular size

Through SEM image, it observed that the granular size of 3YSZ shows the typical size in the range of 25 to 50 nm, while nano mullite-magnesia has the size in the range of 50 nm to 75 nm. In the MMZ Nano system after the sintering process, the mullite particles appear to be surrounded by the Yttria-stabilized zirconia (3YSZ) particles (Figure 4).

![Figure 4. SEM analysis of nano Mullite-Magnesia-3YSZ (nano MMZ) system.](image)
The SEM image detected the crystal structure of mullite is likely needle, while the crystal structure of 3YSZ was observed smoother than mullite crystal. Through EDS analysis for the mullite system, it detected oxides, i.e., Al$_2$O$_3$ and SiO$_2$. Meanwhile, with a similar method, the ceramic system of nano Mullite-Magnesia-3YSZ (nano MMZ) was detected containing some oxides such as MgO, Al$_2$O$_3$, SiO$_2$, Y$_2$O$_3$, and ZrO$_2$. Through XRD analysis, it can observe the existence of Mullite in the form of Al$_6$Si$_2$O$_{13}$, Corundum (Al$_2$O$_3$), Zirconia (ZrO$_2$), and Quartz (SiO$_2$).

4. Conclusion

The mullite crystal structure was observed using SEM and appears likely needle, whereas 3YSZ crystal shows smoother. Through EDS analysis, in Mullite system can be detected the existence of oxides of Al$_2$O$_3$, and SiO$_2$. With a similar method for Mullite-Magnesia-3YSZ system, it contains some oxides such as MgO, Al$_2$O$_3$, SiO$_2$, Y$_2$O$_3$, and ZrO$_2$. With XRD analysis, nano MMZ system contains Mullite in the form of Al$_6$Si$_2$O$_{13}$, Corundum (Al$_2$O$_3$), Zirconia (ZrO$_2$), and Quartz (SiO$_2$).

The ceramic composite system of nano mullite-magnesia-zirconia follows the equation of fracture toughness $K_{IC}$ for Palmqvist and median crack criteria. The granular size of the ceramic system influences to increase hardness and fracture toughness. Nano ceramic particle shows a higher value of hardness and fracture toughness while compared with oxide ceramic system.

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