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Influences of Various Ceramic Oxides on Physical and Mechanical Properties of Zirconia Toughened Alumina (ZTA): a Review

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Abstract

Materials having light weight, high hardness and high fracture toughness are carrying need for advanced manufacturing. Zirconia Toughened Alumina (ZTA) based ceramic composites are widely accepted for that purposes due to such type of excellent properties. A limitation of ZTA based ceramic composite is its low fracture toughness and hence researches are going on ZTA based ceramic composites to improve the properties of ZTA. This paper organizes and summarizes the main themes along with recent progress and developments about the effects of various ceramic oxides as additives on the properties of ZTA. It is observed that CeO₂ largely influences the fracture toughness as well as hardness of ZTA ceramics, while TiO₂ and MgO influence the grain size of ZTA. Therefore the combination of two or more ceramic oxides added with ZTA may exhibit better properties than a single ceramic oxide added with ZTA.

Keywords: ZTA, Ceramic Oxides, Density, Hardness, Fracture Toughness.

1. Introduction

Ceramics, the wonder materials, exhibit improved wear resistance and outstanding biocompatibility compared to the ordinary metal and polyethylene materials. Alumina is the extensively used oxide ceramic material because it shows the brilliant combination of high compression strength, good abrasion resistance, high chemical inertness, high thermal shock resistance and a high degree of refractoriness and so the applications of alumina (Al₂O₃) based ceramic composites are increasing day by day [1,2,3]. Alumina (Al₂O₃) based ceramics are widely used in cutting tool inserts for these properties but there is a propensity to failure such as chipping of cutting tool during machining due to the lower fracture toughness of Al₂O₃ [4,5]. So the challenge of enhancing the toughness of alumina based ceramics has been a key motivation in the ceramic research field [6-8]. The lower fracture toughness of alumina can be improved by combining yttria stabilized zirconia with Al₂O₃ and eventually produce zirconia toughened alumina (ZTA). The transformation toughening phenomenon is mainly responsible for improving the fracture toughness of ZTA. When zirconia toughened alumina is subjected on stress, the zirconia particles are likely to change their crystal structure from tetragonal to monoclinic which causes a volume expansion that compresses the surrounding crack in the alumina matrix and finally the strength and fracture toughness is increased [2,9-12]. Many sintering additives such as Cr₂O₃, CeO₂, TiO₂, MgO, MnO₂, NiO, SrCO₃, CuO and CaCO₃ are used to enhance the microstructural and physical properties of ZTA at low sintering temperature [13]. Among all sintering additives, ceramic oxides have a noteworthy impact on physical, mechanical and microstructural properties of ZTA. Rejab et.al [14] found that ZTA prepared with CeO₂ additives showed an increase of 30% in fracture toughness compared to ZTA without additives due to the solid solubility between Ce⁴⁺ and Y³⁺ in the (Zr,Y,Ce)O₂ phase in stabilizing the transformability of t-m inside the ceramic composite. Smuk et.al. [7] reported that introduction of additives with tetragonal zirconia such as MgO, Y₂O₃, CaO and CeO₂ increase the fracture toughness of ZTA than pure Al₂O₃. R.D Bagley [15] & C-J Wang [16] reported that the addition of TiO₂ promotes the sintering and grain growth of alumina for the better diffusivity due to the increasing concentration of the Al³⁺ vacancies which is generated by the Ti⁴⁺ substituting for Al3+. Manshor et.al [17] showed that an addition of 0.6 wt% of Cr2O3 produces minimum wear area and an increase of 26 % in wear resistance capability. Al₂O₃ particle size plays a significant role on the properties of ZTA [18]. The fine particle size alumina powder is beneficial to the enhancement of mechanical properties due to the lowest porosity. Since the addition of various additives increases the properties of ZTA, so ZTA ceramics are used in automotive, aircraft structures, electronic and medical science also. Right now there are two

commercially available ZTA biomaterials for hip arthroplasty applications: BIOLOX Delta by ceram tec Medical products (Plochingen, Germany) and AZ209 by KYOCERA Medical (Osaka, Japan) [19].

This paper is a review study which will show the effects of various ceramic oxides as additives on the physical properties such as grain size, density and mechanical properties such as hardness and fracture toughness of ZTA composites. Although various additives are used in many researches but this paper will discuss only the effects of MgO, CeO_2 , TiO_2 and Cr_2O_3 on the properties of ZTA composites.

2. Various Testing Methods

2.1. Hardness Test

The hardness of ceramic composite materials can be determined using three indentation techniques including Vickers, Knoop, and nano indentation [20]. In the indentation test, a load is applied by pressing the indenter normal to the surface being tested [14]. Maximum researchers described in this paper used the Vickers indentation method to determine hardness.

2.2. Fracture Toughness Test

The fracture toughness of the samples are calculated using the formula of Palmqvist crack proposed by Niihara [21]

$$3K_{IC} = 0.035 (Ha^{1/2})(3E/H)^{0.4}(l/a)^{-0.5}$$
 (1)

Where K_{IC} denotes the fracture toughness, H is the Vickers hardness, a is the half-length of Vickers diagonal (μ m), E is the Young modulus of the samples and I is the length of the radial crack size (μ m). Rejab et.al [1], Manshor et.al [2], Rejab et.al [14], H.Manshor et.al [17] used this method to determine the fracture toughness.

2.3. Bulk Density Test

The bulk density and percentage of porosity of ceramic composites are obtained according to ASTM C 830-00 test procedure. The Archimedes principle and porosity tests can likewise be used to calculate the density by the following equation [22].

$$\rho = \rho_0 (1 - P) \tag{2}$$

Where ρ_0 is the pore-free density, ρ is the density to be determined, P is the porosity. Rejab et.al [1,14] used ASTM C 830-00 test procedure and H. Manshor et.al [2,17] used Archimedes principle to determine the density of the ceramic composite.

2.4 Phase Analysis

Phase analysis is carried out by X-ray diffraction (XRD). The phase fractions are obtained using the direct comparison method [23]. Scanning electron microscope (SEM), Field emission scanning electron microscope (FESEM), Transmission electron microscope (TEM) are used to observe the microstructure of ceramic composite polished samples and their grain growth. An image analyzer software is used to divide and measure the percentage of each phase of the SEM microstructure. Rejab et.al [1,14], H. Manshor et. al [2] used SEM and H. Manshor et. al [17] used FESEM to study the microstructure of the samples.

3. Effects of Oxide Additives

3.1. On Density:

Density is largely dependent on grain size. Lower grain size produces higher density. H. Manshor et.al [17] showed that the closely packed and smaller grains tended to have a higher density. The density of ceramics composite can also be improved by the addition of different additives. Having microstructure pinning effect, MgO and TiO₂ resist the unusual grain growth of Al₂O₃ [1,2]. Rejab et.al [1] showed that 0.3 wt% MgO added with ZTA-CeO₂ increased the density about 7.31% compared with 0 wt% MgO but MgO with more than 0.3 wt% decreased the density because a secondary phase is generated instead of pinning effect. It is noticed from

Manshor et.al [2] that at 3 wt% TiO_2 , the bulk density was maximum and began reducing from the addition of 5 wt% onward. The main reason is that after 5 wt%, TiO_2 has no longer ability to resist the grain growth of Al_2O_3 and forms a secondary phase. The coarser grain size has a reverse effect on densification and the secondary phase has a lower density than Al_2O_3 and TiO_2 [24,25]. According to H. Manshor et.al [17] with the increasing of Cr_2O_3 content from 0 wt% to 0.6 wt%, the density of the ceramics composite increased and further addition of Cr_2O_3 decreased the density due to the formation of pores and developments of various crystalline phases in the sintered compacts [26]. Figure 1 shows the effects of various ceramic oxides on the bulk density of ZTA. In this figure, the individual additives were used for optimum wt% added with ZTA at which the density was maximum. From this figure, it is observed that the addition of 5 wt% CeO_2 with ZTA have the maximum bulk density of $4.41 \, \text{gm/cm}^3$.

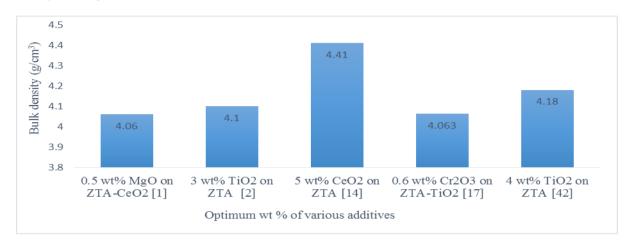


Fig. 1. Effect of additives on density of ZTA

3.2. On Hardness:

Hardness depends on the density [2], the higher the density the higher the hardness. As density depends on grain size, smaller grains result in a homogeneous and dense ceramics which in turn increases the Vickers hardness and reduces the porosity. In ceramics, the effect of grain size on strength has been studied over past 60 years [27-36]. The reduced grain size has two prominent effects. Firstly, the flaw sizes are reduced and secondly, the stresses produced from anisotropic thermal expansion are reduced in case of ceramic with anisotropic crystal structure [28-30]. The porosity also affects the hardness. The increase in porosity led to a reduction in hardness [1]. Porosity affects the strength in two ways. First, porosity creates stress concentration points and crack will form and propagate when stress reaches a critical level subsequently reduce strength. Second, pores reduce the cross sectional areas over which load can be applied and consequently lowers the strength of materials [14]. H. Manshor et.al [17] showed that the increase in hardness was consistent with the density of the composite and hence the addition of Cr_2O_3 from 0 to 0.6wt% increased the hardness of ZTA- ZTO_2 composite. However, the further addition dropped the hardness of the composite due to the decrease in weight of the composite as a result of volatization of ZTA- ZTO_3 Figure 2 shows that highest Vickers hardness is achieved with 5 wt% of ZTA- ZTO_3 due to the higher densification of ZTA- ZTO_3 samples but the hardness is dropped with the further addition of ZTA- ZTO_3 due to the lower density caused by the presence of ZTZ- ZTO_3 .

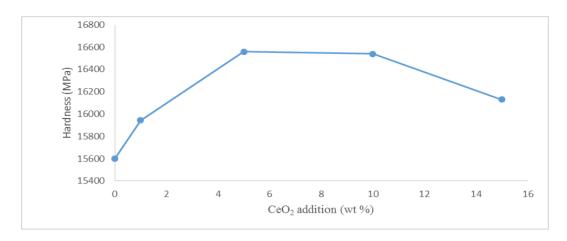


Fig. 2. Effect of CeO₂ addition on Vickers hardness of ZTA [14].

Figure 3 shows the effects of various ceramic oxides on the hardness of ZTA. In this figure, the individual additives were used for optimum wt% added with ZTA at which the hardness was maximum. From this figure, it is observed that the addition of 5 wt% CeO_2 with ZTA have the maximum hardness of 1688 HV.

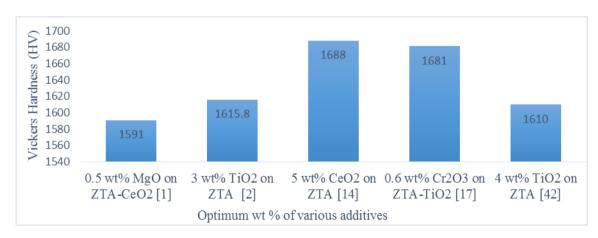


Fig. 3. Effect of additives on hardness of ZTA

3.3. On Fracture Toughness:

Fracture toughness is improved by the method known as transformation toughening. Fracture toughness is a function of elongated grains, i.e highest amount of elongated grains result in the highest fracture toughness value [2]. As indicated by Kruzic et. al [37] elongated grains in the microstructure force a crack to deflect in more than one plane to get around the grain. Subsequently, more energy is required to round through prolonged grains contrasted to flat platelets in the microstructure. A Larger number of crack deflections are also responsible to strengthen the ceramic composites [14,38,39]. Fracture toughness is also influenced by the porosity. The lower the porosity the greater the fracture toughness. Manshor [2] demonstrated that the fracture toughness of ZTA-TiO2 composites was increased up to 7.15 MPa \sqrt{m} by the addition of Cr_2O_3 up to 0.6 wt% but further increase in Cr_2O_3 reduced the toughness as a result of vaporization and condensation of Cr_2O_3 , which made the composites more porous [23,40,41] . According to Rejab et.al [14] with the addition of Cr_2O_3 the fracture toughness reached a maximum value of 8.38 MPa \sqrt{m} but with the further addition of CeO_2 the fracture toughness decreased.

Figure 4 shows the effects of various additives on fracture toughness of ZTA. In this figure, the individual additives were used for optimum wt% added with ZTA at which the fracture toughness was maximum. From this figure, it is observed that the addition of 0.5 wt% MgO with ZTA-CeO₂ has the maximum fracture toughness of 9.14 MPam $^{1/2}$.

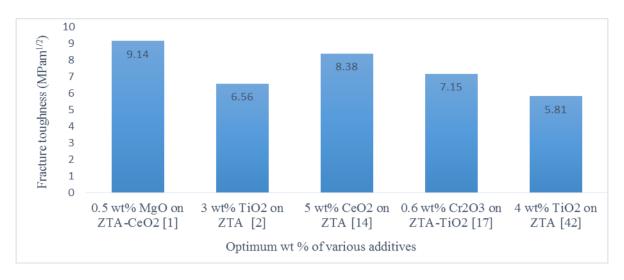


Fig. 4. Effect of additives on fracture toughness of ZTA

4. Conclusion

This paper reviews the effects of various ceramic oxides such as MgO, Cr₂O₃, TiO₂, and CeO₂ on grain size, density, hardness and fracture toughness of ZTA based ceramic composites. The study focuses the role of grain size on density and porosity. The optimum wt% of different ceramic oxides at which the ZTA composite shows better properties is also presented. From the review, it is noticed that ZTA added with 5 wt% CeO₂ has the maximum hardness of 1688 HV and ZTA-CeO₂ added with 0.5 wt% MgO has the maximum fracture toughness of 9.14 MPam^{1/2}. Although, ZTA added with a single ceramic oxide shows better properties than without any additive, the properties of ZTA can be more increased by the combination of two or more ceramic oxides with ZTA.

References

- [1] Nik Akmar, Rejab & Ahmad Azhar, Zahirani & Seng Kian, Khoo & Ratnam, Mani & Ahmad, Zainal. (2014). Effects of MgO addition on the phase, mechanical properties, and microstructure of zirconia-toughened alumina added with CeO₂ (ZTA-CeO₂) ceramic composite. Materials Science and Engineering: A. 595. 18–24. 10.1016/j.msea.2013.11.091.
- [2] Hanisah Manshor, Suriyana Md Aris, Ahmad Zahirani Ahmad Azhar, Ezzat Chan Abdullah, Zainal Arifin Ahmad, Effects of TiO₂ addition on the phase, mechanical properties, and microstructure of zirconia-toughened alumina ceramic composite, Ceramics International http://dx.doi.org/10.1016/j.ceramint.2014.11.080.
- [3] A.Z.A. Azhar, M.M. Ratnam, Z.A. Ahmad, Effect of Al₂O₃/YSZ microstructures on wear and mechanical properties of cutting inserts, J. Alloys Compd. 478 (2009) 608–614,http://dx.doi.org/10.1016/j.jallcom.2008.11.156.
- [4] Azhar, A. Z. A., Mohamad, H. Ratnam, M. M., & Ahmad, Z. A. (2010). The effects of MgO addition on microstructure, mechanical properties and wear performance of zirconia-toughened alumina cutting inserts. *Journal of alloys and compounds*, 497(1), 316-320.
- [5] Bućko, Mirosław M., and Waldemar Pyda. "Effect of inclusion size on mechanical properties of alumina toughened cubic zirconia." *Journal of materials science* 40.19 (2005): 5191-5198.
- [6] A.Z.A. Azhar, L.C. Choong, H. Mohamed, M.M. Ratnam, Z.A. Ahmad, Effects of Cr2O3 addition on the mechanical properties, microstructure and wear performance of zirconia-toughened-alumina (ZTA) cutting inserts, J. Alloys Compd. 513 (2012) 91–96. doi:10.1016/j.jallcom.2011.09.092.
- [7] Smuk B, Szutkowska M, Walter J. Alumina ceramics with partially stabilized zirconia for cutting tools. J Mater Process Technol 2003; 133:195-8.
- [8] B. Basu, J. Vleugels, O. Van der Biest, Toughness tailoring of yttria-doped zirconia ceramics, Mater. Sci. Eng. A. 380 (2004) 215–221. doi:10.1016/j.msea.2004.03.065.
- [9] T. Oungkulsolmongkol, P. Salee-Art, W. Buggakupta, Hardness and fracture toughness of alumina-based particulate composites with zirconia and strontia additives, J. Met. Mater. Miner. 20 (2010) 71–78.
- [10] D. Casellas, M. Nagl, L. Llanes, M. Anglada, Fracture toughness of alumina and ZTA ceramics: microstructural coarsening effects, J. Mater. Process. Technol. 143–144 (2003) 148–152, http://dx.doi.org/10.1016/S0924-0136 (03)00396-0.
- [11] K. Tahmasebi, M.H. Paydar, Microwave assisted solution combustion synthesis of alumina–zirconia, ZTA, nanocomposite powder, J. Alloys Compd. 509 (2011) 1192–1196,http://dx.doi.org/10.1016/j.jallcom.2010.09.176.

- [12] B. Basu, Toughening of yttria-stabilised tetragonal zirconia ceramics, Int. Mater. Rev. 50 (2005) 239–256,http://dx.doi.org/10.1179/174328005X41113.
- [13] Like Q, Xikun L, Guanming Q, Weimin M. Study on toughness mechanism of ceramic cutting tools. J Rare Earths 2007; 25:309-16.
- [14] Rejab, Nik Akmar, et al. "The effects of CeO₂ addition on the physical, microstructural and mechanical properties of yttria stabilized zirconia toughened alumina (ZTA)." *International Journal of Refractory Metals and Hard Materials* 36 (2013): 162-166.
- [15] R.D. Bagley, I.B. Cutler, D.L. Johnson, Effect of TiO₂ on Initial Sintering of Al₂O₃, J. Am. Ceram. Soc. 53 (1970) 136–141. doi:10.1111/j.1151-2916.1970.tb12055.x.
- [16] C.-J. Wang, C.-Y. Huang, Effect of TiO₂ addition on the sintering behavior, hardness and fracture toughness of an ultrafine alumina, Mater. Sci. Eng. A. 492 (2008) 306–310. doi:10.1016/j.msea.2008.04.048.
- [17] Manshor, Hanisah, et al. "Effects of Cr₂O₃ addition on the phase, mechanical properties, and microstructure of zirconia-toughened alumina added with TiO₂ (ZTA–TiO₂) ceramic composite." *International Journal of Refractory Metals and Hard Materials* 61 (2016): 40-45.
- [18] Zeng, Jinzhen, et al. "Effect of Al₂O₃ particle size on preparation and properties of ZTA ceramics formed by gelcasting." *Ceramics International*40.4 (2014): 5333-5338.
- [19] Steven M. Kurtz, Sevi Kocagöz, Christina Arnholt, Roland Huet, Masaru Ueno, William L. Walter, Advances in Zirconia Toughened Alumina Biomaterials for Total Joint Replacement, Journal of the Mechanical Behavior of Biomedical Materials, http://dx.doi.org/10.1016/j. jmbbm.2013.03.022.
- [20] Nastic, A., Merati, A., Bielawski, M., Bolduc, M., Fakolujo, O. and Nganbe, M. (2015) Instrumented and Vickers Indentation for the Characterization of Stiffness, Hardness and Toughness of Zirconia Toughened Al₂O₃and SiC Armor. Journal of Materials Science and Technology, 31, 773-783. http://dx.doi.org/10.1016/j.jmst.2015.06.005.
- [21] Niihara K. A fracture mechanics analysis of indentation-induced Palmqvist crack in ceramics. J Mater Sci Lett 1983; 2:221-3.
- [22] Asmani, M., Kermel, C., Leriche, A. and Qurak, M. (2001) Influence of Porosity on Young's Modulus and Poisson's Ratio in Alumina. Journal of European Ceramic Society, 21, 1081-1086.http://dx.doi.org/10.1016/S0955-2219 (00)00314-9.
- [23] Kero, Ida, Ragnar Tegman, and Marta-Lena Antti. "Effect of the amounts of silicon on the in situ synthesis of Ti 3 SiC 2 based composites made from TiC/Si powder mixtures." *Ceramics International* 36.1 (2010): 375-379.
- [24] Y. Ye, J. Li, H. Zhou, J. Chen, Microstructure and mechanical properties of yttriastabilized ZrO₂/Al₂O nanocomposite ceramics, Ceram. Int. 34 (2008) 1797–1803. doi:10.1016/j.ceramint.2007.06.005.
- [25] Y. Zu, G. Chen, X. Fu, K. Luo, C. Wang, S. Song, et al. Effects of liquid phases on densification of TiO₂-doped Al₂O₃–ZrO₂ composite ceramics, Ceram. Int. 40 (2014) 3989–3993. doi:10.1016/j.ceramint.2013.08.049.
- [26] T. Hirata, K. Akiyama, H. Yamamoto, Sintering Behavior of Cr₂O₃±Al₂O₃Ceramics, 20, 2000 195–199.
- [27] F.P. Knudsen, Dependence of mechanical strength of brittle polycrystalline specimens on porosity and grain size, J. Am. Ceram. Sot. 42 (8) (1959) 376-388.
- [28] A.G. Evans R. W Davidge, strength and fracture of fully dense polycrystalline MgO, Phil. Mag.20 (1969) 373.
- [29] H.P. Kirchner, R.M. Gruver, strength anisotropy grain size relations in ceramic oxides. J. Am. Ceram. Soc.53 (5) (1970) 232-236.
- [30] R.W. Rice, Grain-size and porosity dependence of ceramic fracture energy and toughness at 22°C J. Mater. Sci. 31 (1996) 1969- 1983.
- [31] R.W. Rice, S.W. Frieman, Grain-size dependence of fracture energy in ceramics: II. A model for noncubic materials, J. Am. Ceram. Sot. 64 (6) (1981) 350-354.
- [32] T. Iseki, T. Hase, Fabrication and properties of silicon carbide ceramics, in: S. Saito (Ed.), Fine Ceramics, Elsevier, New York, 1988, pp. 188-197.
- [33] H. Kodama, T. Miyoshi, Study of fracture behavior of very fme-grained silicon carbide ceramics, J. Am. Ceram. Sot. 73 (10) (1990) 3081-3086.
- [34] K. Niihara, Mechanical properties of chemically vapor deposited nonoxide ceramics, Ceram. Bull. 63 (9) (1984) 1160-1164
- [35] G.B. May, K.E. Perry, J.L. Shull, J.S. Epstein, H. Okada, C. Scott, S.N. Atluri, Nonsingular toughening and R-curve behavior in nominally pure alumina, Int. J. Fracture 59 (1993) 361-375.
- [36] G. Vekinis, M.F. Ashby, P.W.R. Beaumont, R-curve behavior or AlsO₃ ceramics, Acta Metall. Mater. 38 (6) (1990) 1151-1162.
- [37] Kruzic, J. J., R. M. Cannon, and R. O. Ritchie. "Crack-Size Effects on Cyclic and Monotonic Crack Growth in Polycrystalline Alumina: Quantification of the Role of Grain Bridging." *Journal of the American Ceramic Society* 87.1 (2004): 93-103.
- [38] Saha, A. and D. C. Agrawal. "Strengthening of alumina by cerium-zirconate (Ce2Zr2O7)." *Journal of materials science* 35.15 (2000): 3931-3937.
- [39] Akin, Ipek, et al. "Effect of CeO₂ addition on densification and microstructure of Al₂O₃–YSZ composites." *Ceramics International* 37.8 (2011): 3273-3280.

- [40] G. Magnani, A. Brillante, Effect of the composition and sintering process on mechanical properties and residual stresses in zirconia–alumina composites, J.E ur. Ceram. Soc. 25 (2005) 3383–3392,http://dx.doi.org/10.1016/j.jeurceramsoc.2004.09.025.
- [41] M. Hernandez, M. González, A. De Pablos, C-diffusion during hot press in the Al₂O₃-Cr₂O₃system, Acta. Mater. 51 (2003) 217–228, http://dx.doi.org/10.1016/S1359-6454 (02)00393-2.
- [42] Dhar, Sajib & Shuvo, Shoumya Nandy & Rashid, A.K.M.B. (2015). Mechanical and Microstructural Properties of TiO₂ doped Zirconia Toughened Alumina (ZTA) Ceramic Composites at different TiO₂ contents. American journal of Engineering Research (AJER). 4. 8-12.