The Effect of Copper Oxide on the Mechanical Properties of Y-TZP Ceramics

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Abstract. Small amount of Copper Oxide powder between 0.05 to 1 wt% were added into commercially available Y-TZP and its effect were investigated. The compacted samples underwent pressureless sintering in air at temperature between 1250°C to 1500°C. The mechanical properties of the samples’ such as bulk density, its Vickers hardness, and the samples’ fracture toughness were then evaluated. It was found that compared to Y-TZP without CuO content, doping ≥ 0.3 wt% of CuO was beneficial in enhancing Y-TZP’s mechanical properties by improving its densification rate, improving the matrix stiffness and also Vickers hardness when sintered at low temperatures such as below 1350°C. In addition, it also found that with the exception of undoped Y-TZP samples, there were enhancement of fracture toughness (KIC) of all samples when sintered below 1350°C.

1. Introduction
The oxide of zirconium is known as Zirconia (ZrO2) and was first identified by Martin Heinrich Klaproth [1]. In the late sixties, studies on zirconia is believed to have started as evident by the first research paper related to zirconia and its relevance in the biomedical field [2]. Zirconia is a very popular advanced material in the biomedical field as it is wide used for Total Hip Replacement (THR) as the ball heads and ever since the usage of zirconia ball heads discovered by Christel et al., (1988), ball heads for THR remains one of the most prominent uses zirconia [3]. Due to the successful debut of zirconia as a promising material for biomedical application such as THR’s, exploitation of zirconia involving solid solutions such as ZrO2-MgO, ZrO2-CaO, ZrO2-Y2O3 were tested as shown in Table 1. However recent years have witnessed research focusing on Yttria-Tetragonal Zirconia Polycrystals (Y-TZP) characterized by its fine nano-sized microstructure and also high tetragonal content enabling it to transform toughen when there is a stress induced propagating crack[4,5]. Y-TZP ceramics intended for use as implants for surgery need to comply with requirements as prescribed in ISO 13356 [6]. Zirconia ball heads market leaders tend to use Y-TZP for the manufacture of ball heads. Up to the
end of the 21st century, Y-TZP ball heads were mass manufactured and 300,000 Y-TZP ball heads or more have been implanted since the introduction six decades ago [7] with a 0.0067% failure rate reported [8].

Table 1 Properties of Three common ceramics used for biomedical applications [7].

| Property                     | Units       | Alumina                  | Mg-PSZ                  | Y-TZP                  |
|------------------------------|-------------|--------------------------|------------------------|------------------------|
| Chemical Composition         | gcm⁻³       | 99.9% Al₂O₃ + MgO        | ZrO₂+8-10mol% MgO      | ZrO₂+3mol% Y₂O₃       |
| Density                      | gcm⁻³       | ≥3.97                    | 5.74 - 6               | >66                    |
| Porosity                     | %           | <0.1                     | -                      | <0.1                   |
| Bending Strength             | MPa         | >500                     | 450 - 700              | 900 - 1200             |
| Compression Strength         | MPA         | 4100                     | 2000                   | 2000                   |
| Young Modulus                | GPa         | 380                      | 200                    | 210                    |
| Fracture Toughness           | MPam⁻¹/²    | 4                        | 7 - 15                 | 7 – 10                 |
| Thermal Expansion            | K⁻¹         | 8 X 10⁻⁶                 | 7 - 10 X 10⁻⁶          | 11 X 10⁻⁶             |
| Thermal Conductivity         | WmK⁻¹      | 30                       | 2                      | 2                      |
| Hardness                     | HV 0.1      | 2200                     | 1200                   | 1200                   |

In general, during Y-TZP ceramics’ sintering, the main variables that can be controlled are the starting particles’ characteristics, the powder composition which includes Y₂O₃ content, sintering parameters such as sintering temperature and also the addition of sintering additives. Although, all these variables can be exploited, the range of effects that can be achieved from the wide selection of additives have attracted a great deal of attention since doping with additives may be the simplest and economical solution to problems encountered during the sintering of undoped Y-TZP ceramics. In particular, small additions of transition metal oxides to zirconia ceramics have been reported by many researchers to be beneficial in enhancing densification at lower sintering temperatures without affecting the tetragonal phase retention at room temperature [9,10]. However, the mechanism involved has not been clearly documented but has been generally accepted to be associated with the presence of liquid phase during sintering. The effects of Fe₂O₃ on the sintering and conductivity of yttria-stabilised zirconia (YSZ) have been investigated by many workers [11-15]. Wilhelm and Howarth (1979) [14] also investigated the influence of iron oxide in 8 mol% Y₂O₃-ZrO₂ by using two different processing techniques (i.e. ball milling using iron oxide powder and by a freeze drying method using ferric nitrate). Further work on the efficacy of MnO, Fe₂O₃, and CuO additions on the densification behaviour and electrical properties of YSZ were undertaken by Hartmanova et al., (1994) [16,17], Luo et al., (1988) [18], Dravid et al., (1994) [19], Beck et al., (1990) [20], Matsui and Takigawa (1990) [21], Matsui (1995) [22] Davidson et al., (1988) [23], Appel et al., (2001) [24] and Matraszek et al., (2004) [25]. All these researchers generally concluded that the additives either form a solid solution in zirconia or migrates to grain boundaries. Nowadays, more complex ceramics like co-doped Zirconia (e.g., with Scandia) [26] are in use as solid electrolytes.

2. Methodology

The commercially available 3 mol% Y-TZP produced by Japanese manufacturer, Kyoritsu through co-precipitation method. The starting Y-TZP powder had a total impurity concentration of approximately 0.1 wt% with SiO₂, CuO, TiO₂ and Al₂O₃ as the major impurities. The specific surface area (SSA) of the Y-TZP powders was determined to be 12 m²/g while the mean particle diameter was 0.3 μm. High purity CuO (Sigma-Aldrich, USA) with varying weight concentration (wt%) of 0.05, 0.1, 0.3, 0.5, and 1 wt% was mixed with the Y-TZP powders. Using wet milling method with zirconia balls and ethanol as mixing medium, the CuO powders were mixed with Y-TZP to produce a slurry. The slurry produced was then dried in an oven and the dried slurry were crushed and subsequently sieved to obtain soft, ready-to press powders. Prior to Cold-Isostatic Pressing (CIP) to produce disc
and bar samples, the powders sieved were compacted at 300 kPa followed by CIP at 200 MPa. The dimensions of the disc samples is set to be 20 mm diameter and rectangular bar samples dimensions is 4 mm × 13 mm × 32 mm. After Cold Isostatic Pressing (CIP) using the sintering furnace manufactured by ModuTemp, Australia, the compacted samples were pressurelessly sintered in air between 1250°C to 1500°C with holding time of 2 hours. SiC papers ranging from grades 120 to 1200 were used to ground on one surface followed by polishing using diamond paste of 6 µm and subsequently polished with 1 µm diamond paste in order to obtain clearer images for SEM micrograph.

3. Results and Discussion

3.1. Bulk Density

The effect of doping Y-TZP with varying amounts of CuO (0 to 1 wt%) sintered at various temperate is as shown in Figure 1. The theoretical density (T.D.) of the samples is taken to be 6.1 Mgm⁻³, it is found that bulk densities for all samples increased significantly within the sintering range of 1200°C to 1400°C. The most significant increase was found to be for the undoped samples (0 wt% CuO). Undoped samples density increased from a relative density of ~73% at 1200°C to ~ 93% at 1400°C. All other doped samples exhibited an increase in the relative density from ~ 92% to ~ 97%. Kimura et al., (1986, 1988, 1999) have also made similar observation [27-29]. When sintering temperatures increased from 1400°C to 1500°C, densities of all doped samples were found to vary insignificantly between the range of 96% to 98%. At higher sintering temperatures i.e. 1400°C to 1500°C, undoped samples also exhibited an insignificant increase from 93% to 94%. The significant increase in densities as observed in all samples below 1400°C could be attribute to the sintering mechanism which promotes long range and short range diffusion as compared to grain size expansion. As a result of this, grains become denser as material diffuses across and along grain boundaries without any concomitant increase in the grain size as shown in Figure 2.

![Figure 1: The relative bulk density of undoped Y-TZP and Y-TZP doped with various amount of CuO sintered at various temperatures](image-url)
3.2. Vickers Hardness

The Y-TZP’s Vickers hardness doped with CuO is as shown in Figure 3. The general variation pattern for hardness of all samples do closely correlate with the relative densities. This observation is also in agreement with the work of other researchers as stated by Vasylkiv et al., (2003) [30]. Compared to doped samples, hardness of undoped samples sintered at same sintering temperature exhibited a significant decline. The lowest hardness among doped samples was observed in the 1wt% CuO samples with a value of ~ 8GPa. All other doped samples exhibited an initial hardness in the range of 8 – 11 GPa. The significant increase in harness of doped samples when compared to undoped samples at all sintering temperatures i.e. 1250°C to 1500°C is an indication of the beneficial effects of CuO as a dopant in enhancing the hardness of Y-TZP materials. At 1500°C, the hardness value for undoped samples was ~ 9.8GPa while all other doped samples exhibited values ranging between 11.8 to 12.2 GPa. The significant improvement of doped samples’ hardness when sintered at temperatures below 1400°C coincides well with the significant increase in densities within the same temperature range. It may be concluded that CuO has an instrumental role in the increase of hardness of Y-TZP materials and that between 1250°C to 1500°C, at this temperature range, the hardness trend variation is somewhat influenced by density.

Figure 3: The Vickers hardness of undoped Y-TZP and Y-TZP doped with various amount of CuO sintered at various temperatures
3.3. Fracture Toughness

The fracture toughness of undoped Y-TZP and Y-TZP doped with CuO sintered at various temperatures is as shown in Figure 4. Based on Figure 4, there were no significant increase in fracture toughness of undoped samples and its fracture toughness fluctuated from 2 to 2.2 MPam$^{1/2}$ when sintered at temperature range of 1250°C to 1500°C. The 0.05 wt% samples exhibited an initial fracture toughness of 2 MPam$^{1/2}$ (same as undoped) at 1250°C but begin to rise to 6 MPam$^{1/2}$ at 1350°C before decreasing to 2.8 MPam$^{1/2}$ at 1500°C. The 0.1 wt% samples exhibited the same trend but with the highest toughness value of 5.8 MPam$^{1/2}$ at 1300°C before decreasing to 2.8 MPam$^{1/2}$ at 1500°C. At low sintering temperatures i.e. (< 1300°C), the 0.5 wt% and 1.0 wt% exhibited the highest initial fracture toughness of 6.2 MPam$^{1/2}$ before reaching a maximum value of 9.7 MPam$^{1/2}$ at 1300°C. The significant increase in fracture toughness values of all samples with the exception of the undoped samples seem to reach a maximum value when sintered at 1300°C. Thus, it could be inferred that 1300°C is the optimum temperature that allowed the diffusion of CuO into the Y-TZP matrix enveloping tetragonal grains formed after sintering. The general decrease in the toughness values of all doped samples after 1300°C could be attributed to the high relative movement of CuO into the Y-TZP matrix leading to the formation of a densed protective layer of CuO along the tetragonal grain boundaries causing these tetragonal grains to become over stabilized and therefore inhibiting the transformation toughening effect by these over stabilized tetragonal grains.

![Figure 4: The fracture toughness of undoped Y-TZP and Y-TZP doped with various amount of CuO sintered at various temperatures](image)

4. Conclusion

In this work, small amount of CuO addition into Y-TZP matrix has shown to enhance the mechanical properties of Y-TZP. Addition 0.3 wt% CuO has shown to be the most optimum amount of CuO that is effective in enhancing mechanical properties. It has also been revealed that the hardness behavior across all samples is similar to the density behavior of all samples regardless of the doping amount. In addition it has also been revealed that the optimum temperature for the migration of CuO along tetragonal grain boundaries was observed to be 1300°C. Fracture toughness was optimum for the 0.5 wt% and 1.0 wt% at 1300°C which was attributed to the migration of CuO along grain boundaries to form higher amounts of over stabilized and under stabilized yielding the latter to be more susceptible to transformation toughening.
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