Two-Stage Sintering of Nb$_2$O$_5$ Doped Zirconia Toughened Alumina (ZTA) Composites

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Abstract. It is estimated that 130 million people will suffer from osteoarthritis by 2050 which require patient to undergo a surgical procedure known as total hip replacement which has lifespan of 20 years and failure rates of ~1%. This research would highlight the effects of doping Niobium Oxide (Nb$_2$O$_5$) between 0 vol % to 0.8 vol % into Zirconia-Toughened Alumina (ZTA) composites which is the main biomaterials used to manufacture total hip arthroplasty. The samples were sintered using two-stage sintering (TSS) between 1400°C and 1550°C for first-stage sintering temperature at heating rate of 20°C/min. At second stage, the samples were sintered at 1350°C and hold for 12 hours. It was found that TSS combined with addition of Nb$_2$O$_5$ as dopants were beneficial in producing fine-grained ZTA composites with improved mechanical properties compared to undoped ZTA composites produced via TSS. Compared to undoped ZTA composites, samples doped with Nb$_2$O$_5$ and sintered at $T_1$ ≥1400°C were fully densified (>98%), achieved Vickers hardness more than 20 GPa and Young’s modulus higher than 410 GPa and at the same time fracture toughness of more than 8 MPam$^{1/2}$. Based on the findings, production of ZTA composites with enhanced mechanical properties with longer lifespan is possible which is beneficial in ensuring the well-being of osteoarthritis patients.

Introduction

The United Nations Sustainable Development Goals (SDG) is a call to all countries to hearken to 1 call aimed at promoting prosperity while protecting the planet. The 3rd SDG focuses on Good Health and Well-Being with 13 key targets that needs to be achieved. Currently globally, ~400,000 hip replacements are performed on patients over 65 years of age. Malcau et al. [1] and Schulte et al. [2] have reported that 90-95% of patients undergoing THR procedures after 10 years while ~85% experience the same fate after 20 years. Good Health and Well-Being (SDG-3) aims to ensure healthy life and to promote well-being for all at all ages. Quality of life after surgery approximates a pivotal matrix in referencing a healthy lifestyle [3]. Total hip replacement (THR) has been regarded as one of the most innovative intervention in medicine [4,5]. Most of the improvements through THR can be realized within 3 months of surgery [6].

ZTA composites exhibits high hardness from alumina, high strength and fracture toughness from zirconia and most importantly it is not susceptible to ageing when exposed to hostile environments [7]. Besides widely used in industry as cutting tools, ZTA composite is a popular material in biomedical field as a dental implant or for hip replacements [8]. The main attribute of ZTA’s high fracture toughness is mainly due to zirconia’s toughening mechanism caused by tetragonal (t) to (m) phase transformation when there is propagating crack. The increase fracture toughness is caused by the accompanying volume change around 4% to 5% caused by the phase transformation in the region of compressive back-stress in the crack wake. Since this occurs around the crack, the propagating crack would requires more energy to propagate hence leading to increase in fracture toughness. This phenomena is also known as stress induced transformation toughening [9-10]. Chen and Wang [11] successfully employed a sintering method known as two-stage sintering or TSS to suppress grain
growth as a result of high sintering temperature. The authors successfully produced Y\textsubscript{2}O\textsubscript{3} powders with ultra-fine grain size at the final sintering stage. This sintering method works by heating up the samples at high first stage sintering temperature known as T\textsubscript{1} followed by lower second stage sintering temperature T\textsubscript{2} with long dwelling time. TSS has also been successfully applied to other ceramics materials to produces ceramic bodies with small grain size [12-17]. There also researchers attempt to enhance densification by introducing small amounts of transition metal oxides as sintering additives and the authors has successfully shown the beneficial effect of these sintering additives when optimum amount are added [18-20]. Many researchers have investigated ZTA’s mechanical properties such as bulk density, Vickers hardness, Young’s modulus and fracture toughness which usually influenced by its microstructural properties such as grain size and phase transformability. There are also researchers [9,21,22] that uses small amount of sintering additives to enhance the composite’s microstructure. However, the effect of TSS and sintering additives on ZTA composites has yet to be widely researched. This research aims to investigate the effect of Niobium Oxide (Nb\textsubscript{2}O\textsubscript{5}) on the microstructure and mechanical properties of ZTA sintered via two-stage sintering. This paper reports an innovative approach by doping small amounts of Nb\textsubscript{2}O\textsubscript{5} into ZTA composites to enable the enhanced mechanical properties and the lifespan of ZTA composites primarily used within the biomedical field for Total Hip Replacement procedure.

Methodology

Commercially available powder of alumina Al\textsubscript{2}O\textsubscript{3} by Sigma-Aldrich, USA and 3Y-TZP produced by Kyoritsu, Japan where mean particle size of approximately 200 nm, specific surface area (SSA) of 13 m\textsuperscript{2}/g. ZTA powders with 10 vol% Y-TZP content were doped with small amount of Nb\textsubscript{2}O\textsubscript{5} (0, 0.2, 0.4, 0.6, 0.8 vol%) prepared using alumina ball milling method. The samples were named in the form of ZTAX where X represents the vol % of Nb\textsubscript{2}O\textsubscript{5} content in the ZTA composite. Sample with the name of ZTA8 would mean this sample contains 0.8 vol% of Nb\textsubscript{2}O\textsubscript{5}. The prepared powders were pressed using uniaxial press to be pressed into 20 mm diameter disc and 5 mm width, 5 mm height and 15 mm length rectangular bar. The pressed samples would then undergo Cold Isostatic Pressing (CIP) followed by pressureless sintering in air using sintering furnace made by ModuTemp, Australia. The CIP-ed samples were sintered using sintering method known as two-stage sintering and the first stage sintering temperature T\textsubscript{1} were set ranging from 1400°C to 1550°C at a heating rate of 20°C/min with 1 minute dwelling time. The samples were then rapid cooled to second stage sintering temperature T\textsubscript{2} set at 1350°C at 50°C/min and 12 hours dwelling time. To obtain clear SEM micrographs, the samples were thermally etched and one face of the sintered samples were grinded using SiC papers with grades ranging from 120 to 1200. Subsequently, diamond paste of 6 µm and 1 µm were used for polishing the surface. Using water immersion technique (ASTM C373-00), the bulk density of the samples were determined. Based on the rule of mixture, the theoretical density (T.D.) of the samples were calculated and ZTA’s theoretical density (T.D.) is taken to be 4.183 g/cm\textsuperscript{3}. The Vickers hardness of the samples were determined using Vickers indentation method with indentation load set at 10 N for 15 seconds. The H\textsubscript{v} values were taken ten times and the average value calculated. The Young’s modulus of the samples were determined using standard ASTM C769 and using Eq. 1 proposed by Niihara et. al., [23] which has been employed by many researchers [24-29], the samples’ fracture toughness can be determined;

\[
\left(\frac{K_{IC\phi}}{H_{v}\sqrt{a}}\right)^{2} = 0.035 \left(\frac{L}{a}\right)^{-\frac{1}{2}}
\]  

(1)

Using the SEM micrographs obtained, scanning line intercept method were used to determine the samples’ grain size. The grain size were measured from five different locations on the SEM micrographs and the average value of the grain size were calculated.
Results and Discussions

The relative bulk densities of undoped and doped ZTA composites sintered via two-stage sintering at various $T_1$ is shown in Fig. 1. Based on Fig. 1, the undoped ZTA samples achieve maximum of only 95.9% when sintered at $T_1$ of 1550°C. The density of the sample also increases as Nb$_2$O$_5$ increases where samples with 0.6 vol% Nb$_2$O$_5$ sintered at $T_1$ of 1400°C were able to achieve 99% regardless of $T_1$.

![Figure 1: The relative bulk densities of ZTA composites with various amount of Nb$_2$O$_5$ sintered via two-stage sintering at various $T_1$](image1)

Fig. 2 shows the Vickers hardness of ZTA composite without Nb$_2$O$_5$ and with various amount of Nb$_2$O$_5$ sintered via two-stage sintering. Based on Fig. 2, positive correlation between Nb$_2$O$_5$ content and the Vickers hardness can be observed. The maximum Vickers hardness were recorded to be 20.4 GPa which belongs to ZTA8 and sintered at $T_1$ of 1550°C. Compared to undoped ZTA sintered at same $T_1$, the Vickers hardness is recorded to be 18.9 GPa which means with addition of Nb$_2$O$_5$, there is improvement of up to 8%. These findings are in agreement with the works of [18-19] where the Vickers hardness is influenced by the bulk density where high bulk density would yield high hardness. As ceramic materials has no plastic deformation, if there is a propagating crack, the crack would propagates until fracture occurs since ceramics have no mechanism to absorb any energy transformed to the material. Formation of new phase known as Nb$_2$Zr$_2$O$_{17}$ also plays a role as
formation of this new phase as phase interface and grain boundaries would be strengthened hence the cohesion between the grains increases [34-35].

The Young’s modulus of undoped ZTA composite and ZTA composite doped with Nb2O5 sintered via two-stage sintering are as shown in Fig. 3. Based on Fig. 3, as the amount of Nb2O5 increase, the Young’s modulus also increases. The maximum Young’s modulus were reported to be 421 GPa which belongs to ZTA8 sintered at T1 1550°C. Even at lower T1 of 1400°C, the values exceed 400 GPa when more than 0.6 vol% of Nb2O5 were added. Young’s modulus are known be influenced by the presence of pores and cracks as presence of these defects would reduce the Young’s modulus of the material [36]. Addition of nano-sized dopants such as Nb2O5 reduces the pores and inhibit grain growth in the matrix. Besides that, presence of nano-sized dopants segregation would also leads to formation of sub-boundaries in the matrix grains which also enhance the Young’s modulus.

Figure 3: The Young’s modulus of ZTA composites with various amount of Nb2O5 sintered via two-stage sintering at various T1

Figure 4: The fracture toughness of ZTA composites with various amount of Nb2O5 sintered via two-stage sintering at various T1
Based on Fig. 4, the fracture toughness of the samples increases as amount of Nb₄O₉ increases. With addition of up to 0.8 vol% Nb₂O₅, the value of fracture toughness can go up to 8.1 MPamⁱ/₂ when sintered at T₁ of 1550°C. These results are in agreement with the works of Kim et al. [37] where the authors attributed the enhancement of fracture toughness to the increased transformability of (t) to (m) phases due to addition of pentavalent oxides such as Nb₂O₅ and Ta₂O₅. Presence of new phase such as Nb₂Zr₂O₁₇ as shown in Fig. 5 also contributed to the fracture toughness enhancement as the nanoparticles of Nb₂Zr₂O₁₇ reinforced the alumina matrix.

Table 1 shows the grain size of undoped and doped ZTA via two-stage sintering of T₁ = 1550°C and T₂ = 1350°C and holding time of 12 hours. There is minimal effect on the grain size of Al₂O₃ due to addition of small amounts Nb₂O₅ up to 0.2 vol%. Most of the ZrO₂ particles were present as small grains mostly located around the triple junctions adjacent to alumina grains. Based on Fig. 5, the formation of new phase particle Nb₂Zr₂O₁₇ which resembles a square shaped particles which assisted as strengthening mechanism.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Nb₂O₅ Content [Vol %]</th>
<th>Grain size [µm]</th>
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<tbody>
<tr>
<td>ZTA0</td>
<td>0</td>
<td>0.86</td>
</tr>
<tr>
<td>ZTA2</td>
<td>0.2</td>
<td>0.84</td>
</tr>
<tr>
<td>ZTA4</td>
<td>0.4</td>
<td>0.57</td>
</tr>
<tr>
<td>ZTA6</td>
<td>0.6</td>
<td>0.46</td>
</tr>
<tr>
<td>ZTA8</td>
<td>0.8</td>
<td>0.38</td>
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Figure 5: SEM micrographs from thermally etched sample of ZTA8 sintered at 1550°C showing the formation of new phase Nb₂Zr₂O₁₇

**Conclusion**

Doping of more than 0.6 vol% Nb₂O₅ sintered at T₁ above 1400°C has shown to be capable of producing superior ZTA composites with finer grain size and enhanced mechanical properties. The samples were able to achieve Vickers hardness exceeding 20 GPa, Young’s modulus exceeding 410 GPa and fracture toughness of more than 8 MPamⁱ/₂. This shows that through two-stage sintering and addition of sintering additives such as Nb₂O₅, it is possible to produce ZTA composites that comply with international standards hence providing an avenue for wider usage of ZTA composites. The findings from this research would bring us closer in achieving SDG 3 by ensuring healthy life and well-being of all people at all ages which for this paper, would address the well-being of osteoarthritis patients.
References


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