Fabrication and Densification Behavior Analysis of Metalizing Targets Using ZrO\textsubscript{2} Nanopowders by Magnetic Pulsed Compaction

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In this study, sintered bodies of ZrO\textsubscript{2} nanopowders were fabricated by combined application of magnetic pulsed compaction (MPC) and subsequent sintering and finally, their density and shrinkage were investigated. The Optimum mixing conditions of PVA, water, and TiO\textsubscript{2} nanopowder for compaction was found to be 1.8 mass\% PVA, 10.7 mass\% water, and 87.5 mass\% of ZrO\textsubscript{2} powder at the sintered bulks. High pressure and rapid compaction using magnetic pulsed compaction (MPC), enhanced the density with increasing MPC pressure up to 3.5 GPa and significantly reduced the shrinkage rate (about 10–12\% in this case) of the sintered bulks compared to the general process (about 18\%).

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1. Introduction

ZrO\textsubscript{2} nanopowders can be considered as one of the distinctive materials due to their excellent mechanical properties that attracted attention of the researchers throughout the world.\textsuperscript{3} They have been extensively used as materials for metalizing targets and their demands have been gradually growing in recent times.

In order to apply ZrO\textsubscript{2} in various kinds of fields, it is necessary to consolidate the nanopowders through the powder metallurgy techniques that provide a precise dimension, uniform structure, fine grain density and a superior microstructural property of the compact. In addition, the cracks are easily formed in the bulks fabricated by the general process making it further inconvenient. Since the microstructures of sintered bodies are also largely affected by the initial microstructure and characteristics of the powder,\textsuperscript{2,3} many attempts have been made to prepare an agglomeration free, well-compact nanosized powder in order to fabricate fully-dense nanostructured ceramics.\textsuperscript{4,5}

It is necessary to obtain a higher density of ZrO\textsubscript{2} bulks for industrial applications through convenient methods of densification, which in turn represents the most economical, cost-effective way and finally, justifies the performance. Therefore, a lot of techniques, including classical sintering, hot pressing, sinter-forging and spark plasma sintering (SPS)\textsuperscript{6,7} were employed to obtain the bulk with improved quality in terms of density. During consolidation process, various accompanying factors, such as pressure, temperature etc. all must be optimized to retain the initial grain size, as well as to achieve higher density, simultaneously.

In order to eliminate all of the above mentioned undesirable consequences and to utilize the excellent properties of nano ceramic materials, a new forming technique is required along with a proper study on densification and sintering behavior. Hence, magnetic pulsed compaction (MPC) is considered as one of the latest consolidating equipment that works based on a dynamic plastic formation method.\textsuperscript{8-10} Since the compaction by MPC allows a densification of the powders in a very short duration (micron second) at a super high pressure (~4 GPa), therefore makes it possible to produce a high density compact reducing the required sintering temperature as well as the time significantly, and to retain the desired microstructure of the bulks.

In this present study, the dynamic compaction by magnetic pulsed compaction (MPC) is conducted to prepare the flat disk shape of ZrO\textsubscript{2} bulks for sintering. The effects of mixing conditions (i.e. ratio of water, PVA and ZrO\textsubscript{2} powder), MPC pressure, holding time and sintering temperature on density and shrinkage have been extensively studied in order to enhance the density of the final bulk.

2. Experimental

2.1 Consolidation of ZrO\textsubscript{2} powder

ZrO\textsubscript{2} nanopowders of nanocrystalline polygonal particles with an average size of 50–100 nm were used in this research. In case of specimens where the changes in densification behaviors were studied due to addition of Y\textsubscript{2}O\textsubscript{3} as sintering additives, ZrO\textsubscript{2} powders were mixed with Y\textsubscript{2}O\textsubscript{3} with a binder (water in this study) to form a solution through mechanical mixing while the rest of the specimens were prepared Y\textsubscript{2}O\textsubscript{3} free.

Densification experiments were performed on ZrO\textsubscript{2} powders using a die of superalloy 718 with 20 mm internal diameter and 100 mm external diameter, on a punch driven Magnetic Pulsed Compaction machine. Most of the experiments began by cold pressing a powder sample weighing ~10 g by loading up to 0.3–3.2 GPa range and holding the pressure for less than 6 microseconds. The cold compaction pressure was chosen so that a crack-free compact with a known low relative density could be produced. Cold
compaction pressures up to 3.2 GPa were used in the set of experiments carried out to study the effect of cold compaction on the hot pressing behavior. The mixture of PVA, water and ZrO$_2$ nanopowders having different compositions were consolidated to the shape of a disk by magnetic pulsed compaction (MPC).

The BN high temperature lubricant & mold release agent spray were applied on the die’s inner wall before placing the bottom punch. The layer with 0.2 mm thickness was placed between the powder and both the punches to prevent the powder entering the small clearance between the die wall and the punches. The densities after compaction were determined by measuring the mass and volume by the Archimedes method.

2.2 Sintering of as MPC-ed bulks

The as MPC-ed ZrO$_2$ powders compacted at room temperature and with varying pressure using direct uniaxial pressing to obtain cylindrical samples, having a diameter of ~20 mm, height of around 8 mm and less than 70% green density of the theoretical value of 6250 kg/m$^3$. These samples were sintered in a dilatometer furnace (Nestzch model 402 E), with a constant heating rate of 10°C/min and in an electrical furnace up to 1450°C and soaking time of 4 h at this temperature in atmospheric air. The densities after sintering were determined by measuring the mass and volume by the Archimedes method.

3. Results and Discussion

In this study, a number of specimens with various compositions of PVA, water and ZrO$_2$ powders were compacted by Magnetic Pulsed Compaction (MPC), and then sintered for 2 h, to investigate the optimum mixing conditions. Table 1 summarizes different mixing arrangement of PVA, water and ZrO$_2$ powders for the specimens, and also demonstrates the applied pressure, holding time, and surface condition in the finally sintered bulk. Although experiments were done to a much greater extent, but conditions that yielded cracks, weren’t considered for further experimentations. The edge cracks occur due to variations in PVA content, applied pressure in the sintered bulks and excessive amount of residual stress developing in the particles beyond certain limit. In this particular study, crack formation started to generate beyond 2.3 GPa with certain mixing conditions. As the pressure by MPC is applied within fractions of seconds, a possibility of crack formation arises since it does not ensure a prolonging homogeneous pressure

and this possibility increases with increasing pressure keeping while the time is kept constant. During compaction a crucial stress is exerted on the powders and due to presence of less amount of binder like PVA is present at the specimen, the edge crack arises at the time of sintering. In this case, since the bulk contains more degree of PVA, this evaporates in the midst of sintering causing such kinds of cracks. So, it seems that the percentage of PVA present in the mixture plays an important role, whether crack will generate or not and what kind of crack will develop. Therefore, it is expected that the contribution of PVA should be below 2–3%, not only to attain a sintered bulk without any generation of cracks, but also for the metal ions to get stabilized and form proper bonds with the oxide ions.$^{11}$

The variation of density and shrinkage of the bulks at different sintering temperature and mixing conditions can be visualized from the graphical presentation of Fig. 1(a) and (b) for the MPC-ed pressure of 1 GPa. In Fig. 1(a), in addition, it is possible to conceive from Fig. 1(a) and (b) that, both the maximum density and shrinkage were acquired corresponding to sample No. 05 with composition of PVA (1.79 mass%) & Water (10.71 mass%). Considering the composition of sample No. 05 as the standard mixing condition, a number of samples with various combinations were plotted for 0.7 GPa MPC-ed pressure and 1400~1450°C sintering temperature which showed similar density with a tiny fluctuation, since the contribution of PVA at the specimen ranged within 0~2%. The maximum density of 90% was achieved for the specimen with standard composition (i.e. sample 05). Such kind of densification behavior reassures the composition of sample No. 05 as the standard mixing condition. The characteristics of the standard composition (sample No. 05) were also examined further at different sintering temperature and MPC pressure. At 1300°C sintering temperature, the bulk shows a lower density of below 80%. However, the density becomes higher with an average of 83% and 87% for sintering temperature of 1350°C and 1400°C, respectively. The mixing condition of sample 6 (refer to Table 1) and the rest were not further tested as the densification started to drop from the mixing condition of sample 6. It appears that the sintering mechanism suggests that the density increases and varies with the increase of sintering temperature and the change of mixture respectively. Higher sintering temperature causes a greater diffusion of atoms and molecules between the contact points of particles, which substantially reduces the amount of pores. Such kind of thermodynamic phenomenon motivates the sintered bulks to gain a superior density.$^{12}$

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>PVA (%)</th>
<th>PVA (g)</th>
<th>H$_2$O (g)</th>
<th>ZrO$_2$ (g)</th>
<th>GPA</th>
<th>Temperature, $T/°C$</th>
<th>Holding Time, $t/h$</th>
<th>Surface Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>50</td>
<td>0.7</td>
<td>1300</td>
<td>2</td>
<td>O</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.25</td>
<td>6</td>
<td>49.75</td>
<td>0.7</td>
<td>1300</td>
<td>2</td>
<td>O</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.5</td>
<td>6</td>
<td>49.5</td>
<td>0.7</td>
<td>1300</td>
<td>2</td>
<td>O</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>0.75</td>
<td>6</td>
<td>49.25</td>
<td>0.7</td>
<td>1300</td>
<td>2</td>
<td>O</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>1</td>
<td>6</td>
<td>49</td>
<td>0.7</td>
<td>1300</td>
<td>2</td>
<td>O</td>
</tr>
<tr>
<td>6</td>
<td>2.5</td>
<td>1.25</td>
<td>6</td>
<td>48.75</td>
<td>0.7</td>
<td>1300</td>
<td>2</td>
<td>O</td>
</tr>
</tbody>
</table>
The resulting vertical and horizontal shrinkage of the bulks with varying sintering temperature is represented in Fig. 1(b) as a function of various experimental conditions. At 1300 °C sintering temperature about 8% shrinkage was observed in the bulks. However, the higher the sintering temperature, the higher the shrinkage, and the highest shrinkage of approximately 12% was obtained in the bulks sintered at 1400 °C. At each sintering temperature the specimens achieved almost constant amount of shrinkage independent of the mixing condition of the samples. Although sample no. 3 (Table 1) showed a maximum of 14% shrinkage, sample no. 05 (Table 1) was more desired in terms of both density and shrinkage performance. The difference in shrinkage was obtained between the sintering temperature of 1300 °C and 1400 °C, whereas the shrinkage between 1300 °C and 1400 °C were approximately close. It indicates that the incremental rate of shrinkage decreases after certain limit of the sintering temperature of the bulks.

Since the standard composition (sample No. 05) was obtained with temperature of 1400~1450 °C showing the optimum results in terms of both densification and shrinkage, it was hence needed to see the effects of pressure on densification and shrinkage keeping the temperature and sample composition constant. The change in the behavior of the density and shrinkage as a function of varying MPC-ed pressure and 1450 °C sintering temperature is delineated in Fig. 2(a) and (b) for the bulks having standard composition. Figure 2(a) indicates that both the density of the MPC-ed specimen and sintered specimen increases gradually with increasing the MPC pressure from 0.7 GPa to 1.7 GPa. For MPC-ed specimen, the increase of density was observed to gradual till 3.2 GPa without crack formation as opposed to sintered specimen where a gradual increase was found till 1.7 GPa and cracks started to form beyond the 2.5 GPa mark. High MPC-ed pressure can break-up the weak agglomerates in the powder during compaction, consecutively making the pores smaller and size distribution narrower.13) The increased green density is due to better packing associated with the smaller particles filling the voids between the bigger ones. The MPC pressure plays a role during the initial stage through particle re-arrangement and distribution of agglomerates as well as during the later stages of densification through plastic or super-plastic deformation.14) The removal of smaller pores require much lower sintering temperature and/or shorter sintering period compared to the larger ones. Therefore, a high initial green density is not only effective to enhance subsequent densification during sintering, but also reduces the duration and sintering temperature significantly. A number of studies have shown a correlation between the sintered density and the green density for the same sintering conditions. The sintered density is observed to decrease with decreasing green density for the values below 55–60% of the theoretical.15,16) Compact with green densities lower than 40–45% of the theoretical is often difficult to sinter to high density. Increasing green density is found to delay the onset of enhanced grain growth during the later stages of sintering.15) During sintering process, on a microstructural scale, the bonding between particles occurs as cohesive necks grow.
at the particle contacts. The bonds between contacting particles enlarge and merge as sintering progresses. At each contact, a grain boundary grows to replace the solid-vapor interface, resulting in two particles to coalesce into single particle. Now, while MPC process is being used prior to sintering, particles on a first level, form bonds between contacting particles and initiates particle coalescing to a certain extent, which is then further progressed during sintering, requiring less sintering temperature and time. This interparticle neck growth, with a slight loss of surface area, can occur in powder compacts while improving properties. The densification parameter of the sintering process depends also on the pore elimination process in powder compacts. Now, during this short period of time while MPC process is being executed, pores tend to diminish with increasing pressure until certain limit, which in turn also helps the consequent sintering process to act faster. Besides, disruption of atomic bonds and having defective grain boundaries during the initial phase of sintering are also reduces through MPC process. Apart from the contribution in particle coalescing and pore reduction, the pressure implied during MPC process also helps in shrinking the particles to a much greater extent compared to sintering process alone, given the same time. However, beyond certain extent, this gradually increasing pressure can produce residual stress so high, that it can cause formation of cracks within and along the particles and thus prevents the required neck growth. Therefore, it is evident and in agreement that the maximum pressure applicable by MPC for the sintered bulks without any crack generation is 1.7–1.9 GPa. In addition, according to Fig. 2(b), the bulk remains almost stable with a slight reduction in shrinkage beyond 1.6 GPa MPC-ed pressure at 1450°C sintering temperature with a holding time of 2 h.

Figure 3(a) displays the change in density with the increase of pressure within 1.7–1.9 GPa range and with varying temperature since Fig. 2(a) (sintered specimen) showed a stagnant behavior at this range with a fixed temperature of 1450°C before crack formation. Now it shows that although there are hardly any differences in terms of density as a function of pressure within this range, there is increase worth mentioning when density is a function of sintering temperature, reaching a maximum of 90% at 1450°C with other conditions kept constant. Sintered density in most cases is found to be increasing until certain extent and often observed to be proportional to incremental sintering temperature.17) The important role that MPC process plays is the reduction of pores and building initial neck growth even before sintering is commenced, helping it to be more efficient.

Figure 3(b) delineates the change in shrinkage with respect to sintering temperature variation within a certain range of MPC-ed pressure where it was found to be a maximum of 12% at 1450°C for both vertical and horizontal case. When looking at the individual mixes, the amount of shrinkage increased with increasing sintering temperature.17)

Now, as the optimum sintering temperature was found to be 1450°C along with an optimum MPC-ed pressure range of 1.7–1.9 GPa, it was required to figure out the changes in density as well as shrinkage as a function of holding time.
reduction in density was possibly due to the fact that while adding certain percentage of this additive, it reduced the amount of oxide contents and an immoderate primary Y-Zr phase was formed in the grain boundary.\textsuperscript{20} The reason for which an incremental densification behavior is not observed is due to the fact that during the first stage of temperature which is below 1500°C, the densification proceeds non-uniformly.\textsuperscript{19}

Hence it may be concluded that although this addition of Y_2O_3 was supposed to increase the amount of density by a certain percentage,\textsuperscript{20,21} it showed no effects in this study on MPC consolidated sintered ZrO_2 bulks.

Figure 6 shows a SEM image sequence obtained from consolidated ZrO_2 bulks sintered in the range of temperatures between 1300°C and 1450°C with 1.9 GPa pressure, as densification behaviors tends to be the maximum at this pressure range (1.8∼1.9 GPa). It was observed that the grain size tends to grow high as temperature increases, reaching a maximum of 3μm at 1450°C. One appreciates the progressive increase of grain size as the sintering temperature rises. According to what one observes in the images, this increase seems to be caused by the progressive grain growth of existing smaller grains. A gradual increase of the grain size can be appreciated as the sintering temperature is increased, although this change is especially significant above 1100°C. This increase is doubtless associated with diffusion phenomena favored by the high sintering temperatures.\textsuperscript{22,23}

Figure 7 also shows a SEM image sequence obtained from consolidated ZrO_2 bulks at a pressure range between 1.7 GPa and 1.9 GPa, subsequently sintered at 1450°C. It can also be delineated that the grain size is decreasing with increasing pressure and reached a minimum, ranging 2∼3 μm at 1.9 GPa pressure, with temperature kept constant at 1450°C; which is in good agreement with reported results by S. Li et al.\textsuperscript{24} and our previous work.\textsuperscript{25} Furthermore, in the sintered bulks, as shown in Fig. 7(a), pores can be observed although they are not widely dispersed and homogeneously distributed. As pressure tends to increase, pores are filled up and remarkably decreased as shown in Fig. 7(c).

Table 2 summarizes the change in powder morphology, grain size and shape with MPC-ed pressure and sintering temperature. Although a wide range of pressure was used during this study, but the powder and grain characteristics are shown for the optimum pressure range.

Ceramic target materials like ZrO_2 can be of immense potential, due to their characteristics including catalytic properties. For preparing such a target it is necessary to acquire the corresponding ceramic material having a moderately high density and uniformity in structure. In this study, by using MPC process, with a very short duration in use,\textsuperscript{12} successful consolidation of ZrO_2 powders was possible, which can help in reducing the initial sintering constraints, namely proper neck growth and temperature dependent gradual densification through pore elimination, proving it to be great for middle range densification of difficult-to-consolidate material powders like ceramics.

4. Conclusion

Nearly full dense ZrO_2 composites were successfully obtained by using magnetic pulsed compaction. The application of the magnetic pulsed compaction for consolidation of ZrO_2 nanopowder showed successful characteristics. Optimum mixing condition of ZrO_2 powder with PVA and water was 1.8 mass% PVA and 10.7 mass% water, receptively. The obtained density of the MPC-ed and sintered bulk increased with increasing MPC pressure till 3.5 GPa and 1.7 GPa respectively. Density for sintered specimen became stagnant beyond 1.7 GPa and followed till 2.5 GPa when crack started to form. It was possible to attain a commercially reasonable density of 90∼92% at 1450°C sintering temperature without crack formation. Moreover, the addition of...
Fig. 6 Microstructures of consolidated bulks with varying temperature (a) 1300°C, (b) 1350°C, (c) 1400°C, (d) 1450°C at 1.9 GPa MPC-ed pressure.

Fig. 7 Microstructures of consolidated bulks with varying pressure (a) 1.7 GPa, (b) 1.8 GPa, (c) 1.9 GPa at 1450°C.

Table 2 Change in powder morphology, grain size and shape with MPC-ed pressure and sintering temperature.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Pressure, ( P/GPa )</th>
<th>Temperature, ( T/°C )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>Grain Size, ( D/\mu m )</td>
<td>4~5</td>
<td>3~4</td>
</tr>
<tr>
<td>Grain Shape</td>
<td>Polygonal</td>
<td>Polygonal</td>
</tr>
<tr>
<td>Initial Powder Size</td>
<td>Agglomerated Powder (50~120µm)</td>
<td>Agglomerated Powder (50<del>120µm) Nanopowder (50</del>100 nm)</td>
</tr>
</tbody>
</table>
$\text{Y}_2\text{O}_3$ showed almost no effects during the entire course of study regarding densification of $\text{ZrO}_2$ composites. Finally, it was verified that the optimum compaction pressure by MPC, sintering temperature, and sintering duration was 1.7–1.9 GPa, 1450°C, and 2 hrs, respectively.

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