Densification of TiO₂ Nanopowders by Magnetic Pulsed Compaction

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In this study, sintered bodies of TiO₂ nanopowders were fabricated by the combined application of magnetic pulsed compaction (MPC) and subsequent sintering and then, their density and shrinkage were investigated. The optimum mixing conditions of polyvinyl alcohol, water, and TiO₂ nanopowder for compaction were found to be 2–3 mass% PVA, 15–20 mass% water, and 70–85 mass% of TiO₂ powder in the sintered bulks. High pressure and rapid compaction using magnetic pulsed compaction (MPC) enhanced the density with the increasing MPC pressure up to 0.7 GPa and significantly reduced the shrinkage rate (about 15% in this case) of the sintered bulks compared to the general process (about 18%). [doi:10.2320/matertrans.M2009324]

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1. Introduction

Ultra-fine TiO₂ nanocrystals are of considerable interest in a number of applications, and the properties of the sintered TiO₂ components are very dependent on its microstructure, which in turn, is influenced by the time-temperature sintering process. Especially, achieving a fully-dense nanostructured bulk is important in various fields of materials engineering due to their particular mechanical, electrical, optical, and magnetic properties. Numerous studies on the consolidation process of TiO₂ nanopowder have been performed by sintering techniques to obtain very-dense bulk substances.^{1,2)} However, preparing a fully-dense fine-grained TiO₂ specimen is difficult due to the rapid growth of grains during the later stage of sintering.^{3,4)} As the sintered microstructure is also significantly affected by the initial microstructure and characteristics of the powder, many attempts have been made to prepare an agglomeration free, well-compacted nanosized powders in order to fabricate fully-dense nanostructured ceramics.⁵⁾ Since, it is necessary to get the highest density of TiO₂ bulks for industrial applications through convenient methods of densification, which in turn represents the most economical and cost-effective techniques and finally, justifies the performance, many techniques including classical sintering, hot pressing, sinter-forging and spark plasma sintering (SPS)^{6,7)} were employed to obtain the bulk with an improved density. It is notable that the other aforementioned research activity was focused on the consolidation of either anatase or a mixture of anatase and rutile (30% <) nanopowders, while only the rutile type TiO₂ nanopowder was used to consolidate in this research. There is no report regarding to the consolidation of rutile nanopowders. During the consolidation process, various factors such as pressure, temperature, etc., must all be optimized to retain the initial grain size as well as to simultaneously achieve a higher density. In this study, the dynamic compaction by magnetic pulsed compaction (MPC)⁸⁾ was conducted to prepare a flat disk of TiO₂

bulks for sintering. The effect of the MPC pressure, sintering temperature and the mixing conditions; i.e., the ratio of water, polyvinyl alcohol (PVA: the same rules apply to the following) and rutile TiO₂ nanopowders on the density and shrinkage has been extensively studied in order to enhance the density of the final bulk.

2. Experimental

Rutile nanocrystalline polyagonal TiO₂ nanopowders with an average size of 100~300 nm were used in this research. A 7-gram sample of the raw TiO₂ nanopowder was loaded into a die and punch unit whose outer and inner diameters were 100 nm and 20 mm, respectively. For compaction of the TiO₂ nanopowders, a magnetic pulsed compaction (MPC) process was applied, which transforms the pulsed electric power to a mechanical pulse and concentrates the pulse in the compaction zone. In the present investigation, the action of the magnetic field was enhanced using special concentrators and pulsed pressures between 1 to 5 GPa were increased from 3 to 300 μ-sec in the compaction zone. In this experiment, TiO₂ bulks have been fabricated by the combined application of the magnetic pulsed compaction and subsequent sintering process. The mixture of PVA, water and TiO₂ nanopowders with different compositions were consolidated into the shape of a disk by the magnetic pulsed compaction (MPC). The pressure during the magnetic pulsed compaction varied from 0.3 to 1.5 GPa at room temperature. The MPCed bulks were then sintered in the range of 900~1450°C for 2 h in air atmosphere. The apparent density of the disk was measured by Archimedes method using water, and the values were averaged.

3. Results and Discussion

In this study, a number of specimens with various compositions of PVA, water and TiO₂ powders were compacted by Magnetic Pulsed Compaction (MPC) and then sintered for two hours in order to investigate the optimum

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Table 1 Mixing conditions and relative appearances of the sintered bulks compacted by MPC.

Sample NO.	PVA(mass%)	Water(mass%)	TiO ₂ (mass%)	Crack Formation
1	0.55	9.5	90	Edgy Crack
2	0.87	14.25	85	Edgy Crack
3	1.10	9	90	Edgy Crack
4	1.23	19	80	Edgy Crack
5	1.64	23.75	75	Edgy Crack
6	1.64	8.5	90	Edgy Crack
7	1.73	13.5	85	Edgy Crack
8	2.10	28.5	70	No Cracks
9	2.17	8	90	No Cracks
10	2.44	18	80	No Cracks
11	2.58	12.75	85	No Cracks
12	3.22	22.5	75	No Cracks
13	3.41	12	85	No Cracks
14	3.61	17	80	Wall & Face Cracks
15	4.11	27	70	Wall & Face Cracks
16	4.76	21.25	75	Wall & Face Cracks
17	4.76	16	80	Wall & Face Cracks
18	6.04	25.5	70	Wall & Face Cracks
19	6.25	20	75	Wall & Face Cracks
20	7.89	24	70	Wall & Face Cracks

mixing conditions. Table 1 summarizes the different mixing arrangement of PVA, water and TiO₂ powders (in terms of mass%) for the specimens and also demonstrates the appearance and different kinds of crack formations in the finally sintered bulk. A edge crack occurs when the PVA content is less than 2% in the sintered bulks. During compaction, a crucial stress is exerted on the powders and due to the presence of a lower amount of binder like PVA in the specimen, the edge crack occurs during sintering. Also, both a face crack and wall crack formed in the specimen that contains PVA greater than 3% as shown in Table 1. In this case, since the bulk contains a greater degree of PVA, this evaporates during of sintering thus causing such kinds of cracks. Therefore, it seems that the percentage of PVA present in the mixture plays an important role as to, whether or not a crack will be generated and what kind of crack will develop. Therefore, it is expected that the contribution of PVA should be within the range of 2–3% in order to attain a sintered bulk without any generation of cracks.

Besides, the variation in the density and shrinkage of the bulks for different sintering temperatures and mixing conditions can be visualized from the graphical presentation in Fig. 1(a) and (b) for the MPCed pressure of 0.7 GPa. In Fig. 1(a), it appears that the density increases with an increase in the sintering temperature. A higher sintering temperature causes a greater diffusion of the atoms and molecules between the contact points of the particles, which substantially reduces the number of pores. Such a thermodynamic phenomenon allows the sintered bulks to obtain a superior density. At a 900°C sintering temperature, the bulk shows a lower density of around 60%. However, the density becomes higher and reaches a maximum of 83% and 88% for the sintering temperatures of 1100°C and 1200°C, respectively. Additionally, it was also noticed that cracks were formed in the sintered bulks except for sample Nos. 8~13 and the maximum relative density of 88% was obtained in sample No. 10 corresponding to the 1200°C sintering temperature. This suggests that, although the density increases

Fig. 1 Variation in relative density (a) and shrinkage (b) based on different mixing conditions and sintering temperatures for 2 h at 0.7 GPa.

with the increasing sintering temperature, the maximum density without any cracks is dependent on certain conditions of the samples, i.e., the amount of PVA in the bulks.

The resulting vertical and horizontal shrinkage of the bulks with different sintering temperatures is represented in Fig. 1(b) as a function of the various experimental conditions. At the 900°C sintering temperature, no shrinkage was observed in the bulks. However, the higher the sintering temperature, the higher is the shrinkage and the highest shrinkage of approximately 12% was obtained in the bulks sintered at 1200°C, while apart from a certain regions in samples 8~13, cracks were attained. This maximum shrinkage of 12% is much lower than that of the general process⁹⁾ which is about 18%. At each sintering temperature, the specimens achieved an almost constant amount of shrinkage independent of the mixing conditions of the samples. The large difference in shrinkage was obtained between the sintering temperature of 900°C and 1100°C, whereas the shrinkage between 1100°C and 1200°C were approximately similar. This indicates that the incremental rate of shrinkage decreases after a certain limit of the sintering temperature of the bulks. In spite of the higher shrinkage at higher sintering temperature, there is also a greater possibility of crack generation. The likelihood of crack inducement reduces the efficacy of shrinkage in the compacted bulk. During sintering, it is more desirable to have the bulks that possess a higher shrinkage without any crack formation, as a higher shrinkage denotes a higher densification. Hence, it can also be suggested that the cracks developed during the high temperature sintering is due to the lacking of a standard mixing condition. Therefore, the aim of such experiments is to discover the ideal contribution of the binder (i.e. PVA) necessary to achieve the optimized density and shrinkage.

Fig. 2 Effect of composition change on density for the standard mixing condition (sample No. 10) at 0.7 GPa MPC pressure and 1200°C sintering temperature.

In addition, it is possible to determine from Fig. 1(a) and (b) that both the maximum density and shrinkage were achieved corresponding to sample No. 10 with a composition of PVA (2.2 mass%) and water (18%). Considering the composition of sample No. 10 as the standard mixing condition, a number of samples with various combinations were plotted for the 0.7 GPa MPCed pressure and 1200°C sintering temperature as indicated in Fig. 2. It seems that the variation in the density is approximately similar and remains almost constant with only tiny fluctuations, since the contribution of PVA in the specimen ranges within 2~3%. The maximum density of 88% was achieved for the specimen with the standard composition (i.e. sample 10). Such a densification behavior reassures the composition of sample No. 10 as the standard mixing condition. The characteristics of the standard composition (sample No. 10) were also further examined at different sintering temperatures and MPC pressures.

The change in the behavior of the density and shrinkage as a function of various MPCed pressures and 1350°C sintering temperature is shown in Fig. 3(a) and (b) for the bulks having the standard composition. Figure 3(a) indicates that both the density of the MPCed specimen and sintered specimen gradually increases with the increasing MPC pressure from 0.3 GPa to 0.9 GPa. The maximum density was obtained in the specimen compacted at 0.7 GPa, while a crack was formed in the bulks at an MPC pressure greater than 0.7 GPa. High pressure can break the weak agglomerates in the powder during compaction, thus making the pores smaller and the size distribution narrower.¹⁰⁾ The increased green density may be due to better packing associated with the smaller particles filling the voids between the bigger ones. The pressure may play a role during the initial stage through particle rearrangement and distribution of the agglomerates as well as at the later stages of the densification through plastic or super-plastic deformation. The removal of the smaller pores requires a much lower sintering temperature and/or shorter sintering period than the larger ones. Therefore, a high initial green density is not only effective to enhance the subsequent densification during sintering, but also significantly reduces the duration and sintering temperature.

Fig. 3 Effect of different MPC pressures on density (a) and shrinkage (b) of the bulks with standard composition sintered at 1350°C for 2 h.

Several 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 the decreasing green density for the values below 55–60% of the theoretical.^{11,12)} Compacts with green densities lower than 40–45% of the theoretical are often difficult to sinter to a high density. Increasing the green density is found to delay the onset of the enhanced grain growth during the later stages of sintering.¹¹⁾ Therefore, it is evident that the maximum pressure applicable by MPC for the sintered bulks without any crack generation is 0.7 GPa. In addition, according to Fig. 3(b) the bulk remains almost stable with a slight reduction in shrinkage when the MPC pressure increases from 0.3 to 0.7 GPa at the 1350°C sintering temperature.

Figures 4(a) and (b) reveals the density and shrinkage as a function of the different sintering temperatures for the bulks with the standard composition at the MPC pressure of 0.7 GPa. Figure 4(a) shows the proportional change in the density up to the sintering temperature of 1350°C beyond which the rate of change slows down. The density increased from 65% at 900°C to the highest of nearly 93% at a 1450°C sintering temperature. The density rapidly increased between the 900°C and 1200°C sintering temperatures, while after 1300°C, the acceleration rate of the densification decreased when reaching the maximum value. It might be possible to attain a higher density with a higher sintering temperature beyond 1450°C as long as no crack is formed. Moreover, to study the relation between the densification and grain size, the grain size of the sintered bulks was measured, and the maximum grain size of around 10 μm was obtained in the bulk sintered at 1350~1400°C for 2 h at the density of 93%. Furthermore, the interaction between the densification and

Fig. 4 Variation in density (a) and shrinkage (b) of the bulks with standard composition based on 0.7 GPa MPC pressure and different sintering temperatures for 2 h.

shrinkage significantly affects the final density of the sintered bulks. As can be seen from the trajectory of the shrinkage in Fig. 4(b), it grows from 4% at 900°C with a gradual change at almost a constant rate up to the sintering temperature of 1200°C and then slows down to the highest shrinkage of about 15% at the 1450°C sintering temperature. Thus, it is evident that the sintering temperature creates greater effects for the densification and shrinkage. As a higher shrinkage is related to a higher compaction, an enhancement in the shrinkage is very desirable. In this study, it is interesting that the result shows no anisotropic shrinkage, which is often observed as a deviation from the uniform shrinkage in different directions in the consolidated bulks during sintering.

Anisotropic shrinkage makes dimensional control of the final products difficult and particularly, it is a serious problem during the manufacturing of the industrial components such as multilayer ceramic capacitors, in which an exact dimensional tolerance must be achieved. The powder characteristics and the method used to form the powders into a green body are the major causes of anisotropic shrinkage. They may lead to density variations in the green body, anisotropy in the pore shape or alignment of non-equiaxial particles in the green compact. In this study, compaction by the MPC process at a very high speed and uniform pressure can prevent such kinds of anisotropic shrinkage at the sintered bulks and is capable of producing highly uniform final dimensions.

Ceramic materials like TiO₂ could be useful as the target materials for the deposition of a TiO₂ film. For preparing such a target, it is necessary to acquire the corresponding ceramic material having a high density and structure uniformity, which prevents nonuniform of sputtering and formation of a macrostructure on the surface of the ceramics

during sputtering. In this study, the successful consolidation of TiO₂ powders using a new process such as magnetic pulsed compaction (MPC) occurred. It was used for the densification of difficult-to-consolidate material powders like ceramics or inter-metallic compounds, since it has been considered that high pressure waves generated by explosions, i.e., shock waves may be effective for the densification of the difficult-to-consolidate powders. The combination of a very short duration and low temperatures, characteristic of this new densification technique, suggests that the mechanism involved is likely to be significantly different from that associated with the traditional densification techniques.

4. Conclusion

Nearly fully-dense TiO₂ dense composites were successfully obtained by magnetic pulsed compaction. The application of the magnetic pulsed compaction for consolidation of TiO₂ nanopowders was successful having an ultra-fine micro-structure. The optimum mixing condition of the TiO₂ powder with PVA and water was 2~3 mass% PVA and 15~20 mass% water. The obtained density of the MPCed and sintered bulk increased with the increasing MPC pressure from 0.3 to 0.7 GPa, but formed a crack on the surface beyond 0.7 GPa. It was possible to attain a higher density at higher sintering temperature beyond 1450°C as long as no crack was formed. Finally, it was verified that the optimum compaction pressure by MPC, sintering temperature, and sintering duration was 0.7 GPa, 1450°C, and 2 h, respectively.

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