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Sintering of Titania Nanoceramics: Densification and Grain Growth

M. Mazaheri, Z. Razavi Hesabi, A. M. Zahedi, S. K. Sadrnezhaad,
Materials and Energy Research Center (MERC), P.O. Box 14155-4777, Tehran, Iran,
mmazaheri@gmail.com, zrazavi2000@yahoo.com, sadrnezh@sharif.edu

Abstract: Two-step sintering (TSS) technique was applied to suppress the accelerated grain growth of TiO_2 nanopowder in the final stage of sintering. While the grain size of full dense structure produced by conventional sintering ranges between 1-2 µm, the application of two-step sintering method led to a remarkable decrease of grain size down to ~250 nm.

Keywords: "TiO_2", "Two-step Sintering", "Grain growth"

Introduction

To produce bulk nanoceramics different methods such as spark plasma sintering (SPS), hot pressing, and hot isostatic pressing have been used. For example, Angerer et al[1] used SPS method to produce a fully- dense TiO_2 structure with fine grains (~120 nm) while in conventinal sintering (CS) the final grain size was > 1 µm. Weibel et al[2] controlled the microstructure of nanocrysatalline TiO_2 by applying pressure>400 MPa during sintering. Additionally, one can control the grain growth with the addition of second phase. For instance, Tekeli et al [3] used Al_2O_3 nanoparticles to pin grain boundaries of zirconia during sintering. Another way to suppress the grain growth is two-step sintering (TSS) method developed by Chen and Wang [4]. This method modifies sintering regimes by high temperature (T1) firing followed by rapid cooling down to lower temperature (T2) and prolonged soaking of the samples at T2. This method has been successfully applied to different ceramic systems such as Y_2O_3 [5]. In the present work, TSS was employed to efficiently control the grain growth of TiO_2 nanopowder during sintering without deteriorating of densification. The changes of density and grain size of samples versus sintering temperature and time in CS and TSS were compared with the available results of SPS method found in the literature.

Experimental Procedure

TiO_2 nanopowder (P25, Degussa Co., Frankfurt, Germany) with the mean particle size of 19 nm was uniaxially pressed under 100 MPa and pellets with average green density of ~0.53 of theoretical one were obtained. Conventional sintering (CS) was conducted between 500-1000˚C for 1 h in air with a heating ramp of 5˚C min^{-1}. For two-step sintering (TSS) at first samples were heated up to 800˚C with heating ramp like as CS. After being held at 800˚C for 1 h, samples were cooled from T1 (800˚C) to T2 (700˚C) with a cooling rate of 50˚C min^{-1}. The samples were, then, soaked at T_2 up to 25h. To determine the grain size of sintered pellets, fracture surface of samples were studied using SEM(Philips XL30, Netherlands).

Results and Discussion

The changes of fractional density and grain size of conventionally sintered samples with temperature are shown in Fig. 1. As the sintering temperature increased from 800 to 1000˚C, an abrupt increase of ~650% in grain size was observed while the density just increased from ~91% to ~98%. It indicated the significant grain growth at the final stage of sintering.

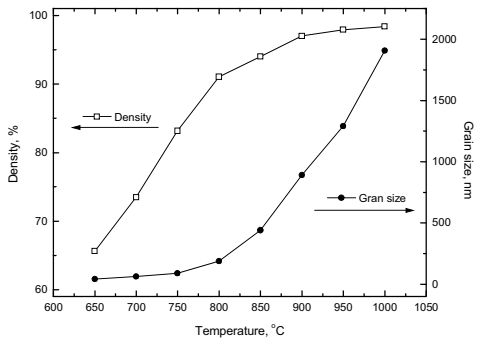


Fig. 1. Effect of temperature on density and grain size of conventionally sintered TiO_2 nanoceramics.

By taking the benefits of two-step sintering, the accelerated grain growth at the final stage of sintering was hampered (Fig. 2). Consequently, after prolong soaking at 700˚C nearly full-dense structure with grain size less than 250 nm was obtained. Negligible grain growth at the final stage of sintering could be related to the pinning of grain boundaries by triple junctions [4].

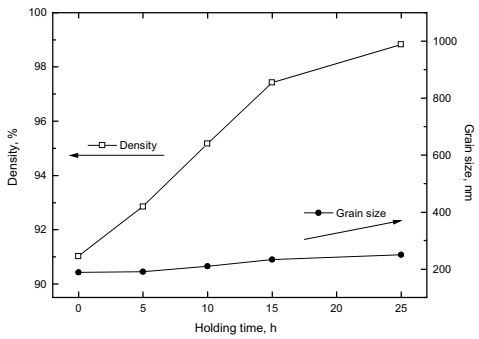
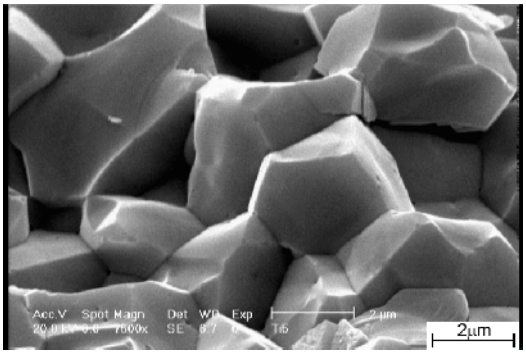


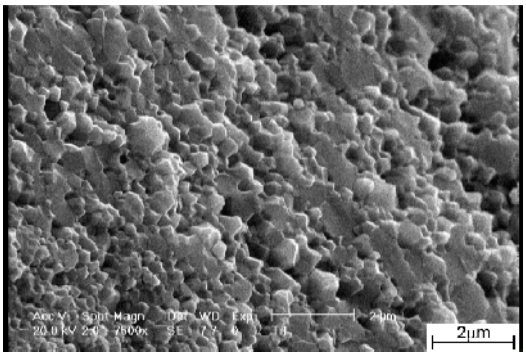
Fig. 2. Density and grain size of the specimens sintered under TSS condition versus holding time at 700˚C.

Fig. 3 shows the fracture surface of full dense specimens sintered by CS (at 1000˚C for 1h) and TSS (at T_1=800˚C

for 1h and T_2=700˚C for 25h). While the density of both sintered bodies is alike, the grain size of conventionally sintered pellet is 8 times more than that of one obtained by TSS method.



(a)



(b)

Fig. 3. Fracture surfaces of specimens obtained by a) CS at 1000˚C for 1h b) TSS (T1=800˚C, T2=700˚C for 25h)

Fig. 4 shows the sintering path of TiO_2 nanopowder produced by CS and TSS. In order to have a better comparison, results of samples sintered by SPS and CS, reported by Lee et al [6], are also represented in the aforementioned picture. In terms of CS graph, in densities below 90% TD, boundary dragging by the open pores in second sintering stage hindered the grain growth[4] while the collapse of open pores in the last stage led to an abrupt grain growth as reported by Lee et al [6]. In the present study, just on the base of grain boundary pinning by triple junctions formed at the first step of TSS, ultrafine-grained structure with density > 98% TD was formed. Interestingly, these results are comparable with those obtained via SPS. By using SPS method, Lee et al[6] produced nearly-full dense structure with the grain size of 200-300 nm. Therefore, in the present work without the addition of any second phase, applying any pressure or taking the benefits any sophisticated methods such as SPS one, a full-dense structure with grain size less than 250 nm was produced.

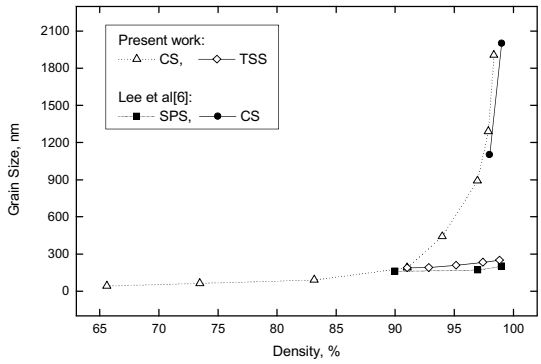


Fig. 4. Grain size-density diagrams of the specimens sintered by CS, SPS and TSS methods.

Conclusion

1. The application of two-step sintering (TSS) for densification of pressed TiO_2 nanopowder prohibited the grain growth in the final stage of sintering. While conventional sintering (CS) produced full dense structures with the grain size of 1-2 µm, TSS reduced the grain size down to ~250 nm.
2. The microstructure of two-step sintered samples is similar to those obtained via of SPS method.

References

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