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Effect of niobium doping on the densification and grain growth in alumina

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Abstract

The effect of niobium doping on the densification and grain growth of nano-sized α-Al_2O_3 powders during sintering has been investigated. The dopant concentration added ranged from 0.1 to 0.5 mol%. It was observed that addition of niobium oxide could improve the densification of the pure alumina with a lower sintering temperature, a shorter sintering time. The effect is strengthened by increasing the amount of dopant. It also demonstrated that niobium dopant significantly promotes the grain growth of alumina during sintering and the grain size of alumina increases with increasing the amount of dopant in the added range.

Keywords: A. Grain growth; A. Sintering; Densification; Dopant

1. Introduction

Dense and fine-grained alumina ceramics are widely used in practical applications, due to its outstanding mechanical, electrical and optical properties. The mechanical strength, dielectric properties and transparency are strongly affected by the microstructure of alumina ceramics, such as porosity, grain size and their distribution. For example, the transparency and mechanical strength of alumina were improved by decreasing the grain size, and the residual porosity less than 0.05% was required for obtaining a high transmission of light [1]. Therefore, the microstructure must be carefully controlled to get dense and fine-grained ceramics, which will improve their properties and reliability in many applications.

Alumina ceramics with submicrometer microstructure obtained by pressureless sintering have been extensively studied. In recent years nanocrystalline materials have been paid much attention because they possess a variety of interesting and novel physical properties. Research on the sintering of nanocrystalline ceramics has focused on the problem of achieving high densities without excessive grain growth. Particularly, as the relative densities increase over 90%, the phenomenon of grain coarsening becomes severe in nanocrystalline materials [2,3]. It seems very difficult to obtain fully dense ceramics with nanocrystalline grain size. However, attempts by applying high sintering pressure proved useful in achieving higher densities with nanocrystalline microstructure. Mishra et al. [4] reported that a fully dense specimen of α-Al_2O_3 with a grain size of 142 nm was obtained at a sintering temperature of 900 °C under a pressure of 1 GPa. Messing et al. [5] showed that 99.7% dense α-Al_2O_3 with grain size of 230 nm was obtained when it was sinter-forged at 1060 °C and 235 MPa. Liao et al. [6] demonstrated that, using a toroidal-type high pressure apparatus, bulk nanocrystalline α-Al_2O_3 samples with a relative density larger than 98% and a grain size smaller than 50 nm were produced by the high pressure/low temperature sintering. In addition, De Jonghe et al. [7,8] reported that a two-step sintering, involving an initial coarsening step prior to densification, was effective in refining the microstructure of Al_2O_3 powder compacts.

In the past, doping with minor additives was shown to be an important factor for controlling the microstructure of alumina ceramic. It was shown that additives, such as MgO, Y_2O_3, SiC, etc., were effective grain growth inhibitors for the micron-size Al_2O_3 particles [9–17]. The additions of TiO_2 and MnO were reported to increase the sintering rate and grain growth rate

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[12,18,19]. However, there are few papers on the effect of additives on the sintering of nanocrystalline alumina. In the present work, the effects of Nb_2O_5 additive on the sintering of nano-sized α-Al_2O_3 powders were investigated. They were mixed in a ball mill with a high-purity ethyl alcohol. The compacted samples were sintered at temperatures between 1200 and 1450 °C for various periods of time. The effect of niobium doping on the densification and grain growth during the sintering of nano-sized α-Al_2O_3 powders is then discussed.

2. Experimental procedure

The alumina powder used in this study was a nano-size α-Al_2O_3 powder (APD-100; Forever Chemical Co.), which has an average particle size of 100 nm, a surface area of 20 m^2/g, and a 99.5% purity level. In order to study the effect of Nb_2O_5 dopants on the sintering behavior of the nano-sized Al_2O_3 powder, various amounts (equivalent to 0–0.5 mol%) of high purity Nb_2O_5 powders (99.8%) were added and mixed in high-purity ethyl alcohol. The slurries were then ball milled with zirconia balls for 8 h to promote an uniform mixing of the dopant and of the α-Al_2O_3 powder. Subsequently, the mixed powders were dried and mixed with 3.5 wt% PVA and put through a sieve with 60 mesh, the sieved powders were pressed under the applied uniaxial pressure of 74 MPa to form disk compacts (diameter ≈ 13 mm, thickness ≈ 2.1 mm). The disk samples were preheated at 550 °C for 2 h to burn out the PVA, and then sintered at temperatures between 1200 and 1450 °C for various periods of time with a heating rate of 10 °C/min.

The bulk densities of sintered samples were measured using Archimeds method with deionized water as the immersion medium. The microstructure of sintered samples were observed by scanning electron microscopy (SEM, Hitachi S-4700), grain boundaries were revealed by thermally etching the polished surfaces at a temperature 100 °C below the sintering temperature for various times. The grain size was determined from SEM micrographs by the linear intercept method [20], in which the average intercept length was multiplied by 1.56. At least 200 grains were used for each sample. The phase analysis of sintered samples was performed by X-ray diffractometry (XRD, Rigaku D/max-B) using nickel-filtered Cu Kα radiation and energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Densification of sintered alumina

It was found in our previous study [21] that relative densities of Nb_2O_5 (0.5–2.0 mol%) doped samples larger than 95% theoretical density (3.986 g/cm^3 for α-Al_2O_3) could be obtained after sintering θ-Al_2O_3 compacts at 1350 °C, the value being independent upon the amount of Nb_2O_5 dopant. It was estimated that the sintering temperature was about 100–150 °C lower than that of the pure θ-Al_2O_3 powder sample for achieving the same density. There was a phase transformation (θ-Al_2O_3 transformed into α-Al_2O_3) during the sintering process. Therefore, a pure nano-sized α-Al_2O_3 powder was used in this study to eliminate the effect of the phase transformation, also the amount of Nb_2O_5 dopant was reduced to a range between 0.1 and 0.5 mol%. The relative densities of pure α-alumina samples doped with different amounts of Nb_2O_5 and sintered at various heating temperatures (1200–1450 °C) for 2 h are shown in Fig. 1. The sintered density generally increases with the sintering temperature for all samples. However, the degree of densification is affected by the amount of Nb_2O_5 dopant. There is a trend showing that the sintering temperature for densification of alumina shifts to a lower temperature as the amount of Nb_2O_5 dopant increases. In comparison with pure alumina, it also shown that a small amount of dopants does not improve the degree of densification of alumina at lower sintering temperature, but the relative density of doped samples significantly increases with increasing sintering temperature and amount of dopant. According to

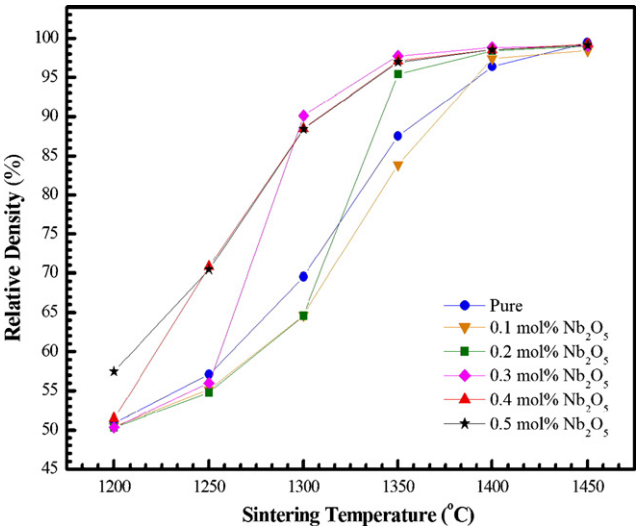

Fig. 1. Relative density of pure α-alumina powders and samples doped with different amounts of Nb_2O_5 sintered at various heating temperatures (1200–1450 °C) for 2 h.

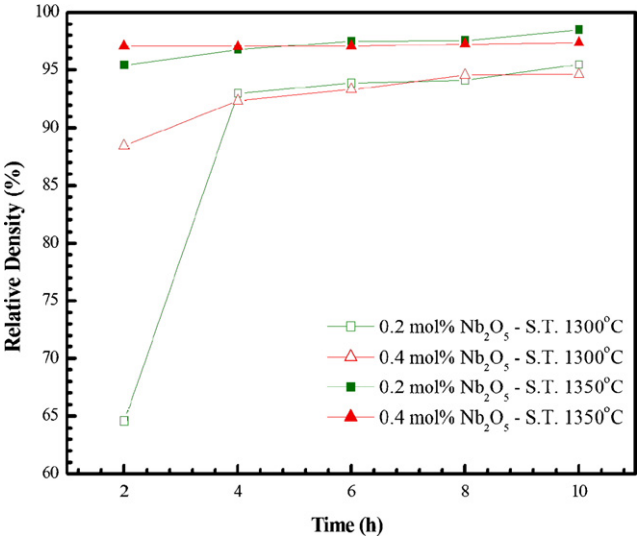

Fig. 2. Relative density of alumina doped with 0.2 and 0.4 mol% Nb_2O_5 sintered at 1300 and 1350 °C for various periods of time.

the results, the specimens doped with 0.2 and 0.4 mol% Nb_2O_5 were selected for further studies. Fig. 2 shows the relative density of alumina doped with 0.2 and 0.4 mol% Nb_2O_5 sintered at 1300 and 1350 °C for various periods of time. The relative density generally increases with the sintering times for all samples. It was found that the density of 0.2 mol% Nb_2O_5 doped samples sintered at 1300 °C increases abruptly with increasing soaking time from 2 to 4 h. Both doped samples sintered at 1350 °C exhibit a higher density than those of sintered at 1300 °C.

These results indicated that the specimens doped with Nb_2O_5 could densify at a lower sintering temperature, after a shorter sintering time and the effect is strengthened as the amount of Nb_2O_5 dopant increases.

3.2. Microstructural evolution

Fig. 3 shows the XRD patterns of undoped and 0.4 mol% Nb_2O_5 doped samples sintered at 1450 °C for 2 h as well as starting powder for comparison. The major constituent of the starting powder is α-Al_2O_3 and with a small amount of θ-Al_2O_3. The θ-Al_2O_3 phase was transformed completely into α-Al_2O_3 phase during the sintering process at 1200–1450 °C with various soaking times in this study. As shown in the XRD patterns of sintered samples, the major peaks belong to α-Al_2O_3 and there is a small peak at about 30°, which was attributed to zirconium oxide. The minor amount of zirconium oxide was checked to be introduced during the ball milling process. Although the solubility of Nb_2O_5 in Al_2O_3 is quite small [22], no other peak corresponding to second phase was found. Niobium atoms seem completely soluble in the α-Al_2O_3 matrix when the Nb_2O_5 addition is less than 0.4 mol%.

Fig. 4 shows the SEM micrographs of undoped alumina and samples doped with 0.2 and 0.4 mol% Nb_2O_5 sintered at 1350 °C for 2 h. It is obvious that the average grain size and relative density of doped samples are larger than that of

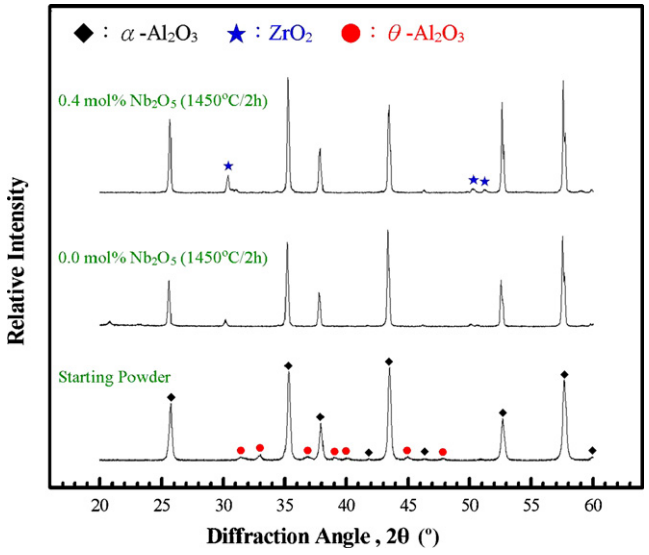

Fig. 3. XRD patterns of starting powder, 0.4 mol% Nb_2O_5 doped and undoped samples sintered at 1450 °C for 2 h.

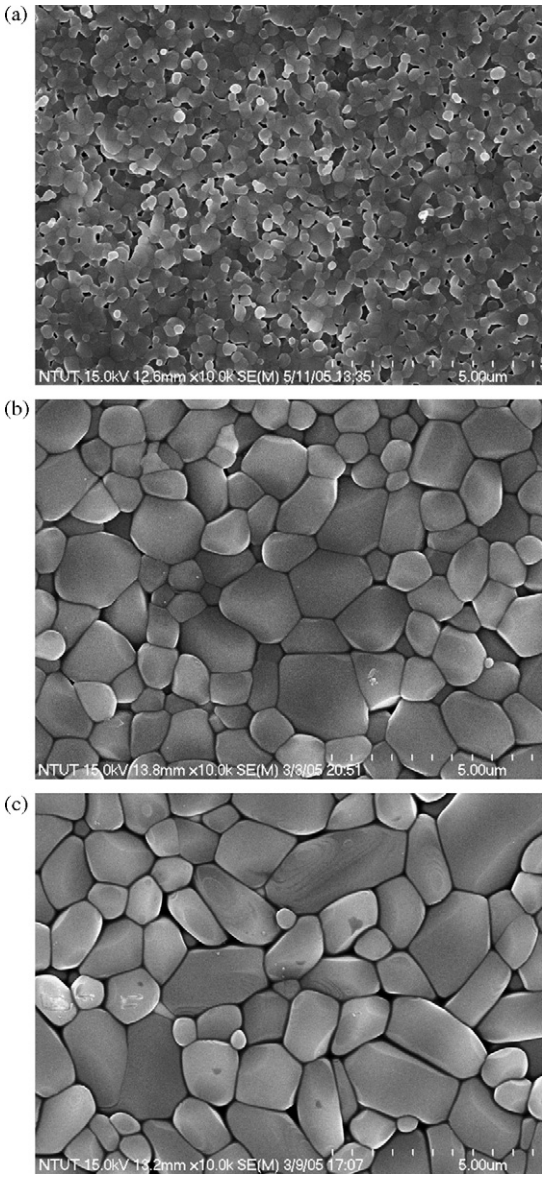

Fig. 4. SEM micrographs of undoped alumina and samples doped with 0.2 and 0.4 mol% Nb_2O_5 sintered at 1350 °C for 2 h, respectively. (a) Pure alumina (relative density is 87.5%), (b) 0.2 mol% doped sample (relative density is 95.4%), and (c) 0.4 mol% doped sample (relative density is 97.1%).

undoped alumina sintered at the same temperature and after same soaking time. As shown in the micrographs, the grain size of 0.4 mol% Nb_2O_5 doped sample is slightly larger than that of doped with 0.2 mol% Nb_2O_5, and both grain sizes are much larger than that of undoped alumina. These results indicate that the Nb_2O_5 dopant significantly promoted the grain growth of alumina during sintering, but the grain growth rates of doped samples seem to increase slightly with increasing the amount of dopant.

Fig. 5 is the plot of the average grain size versus the sintering temperatures of undoped alumina and samples doped with 0.2 and 0.4 mol% Nb_2O_5 sintered for 2 h. It indicates that the grain size of alumina increases with increasing sintering temperature and the amount of dopant. The grain sizes of doped samples are much larger than that of pure alumina as the sintered

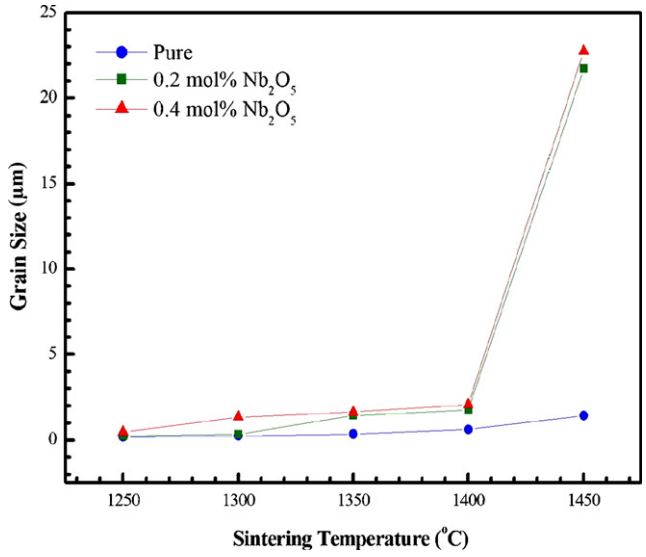

Fig. 5. Plots of the average grain size verse the sintering temperatures of undoped alumina and samples doped with 0.2 and 0.4 mol% Nb_2O_5 sintered for 2 h.

temperature increases to 1450 °C. That is the Nb_2O_5 dopant significantly promotes the grain growth of alumina during sintering.

Fig. 6 is the plot of the average grain size versus sintering time for samples doped with 0.2 and 0.4 mol% Nb_2O_5 sintered at 1300 and 1350 °C, respectively. The average grain size of all samples increases with sintering temperature and sintering time. The respective grain size of 0.2 and 0.4 mol% Nb_2O_5 doped samples sintered at 1300 °C is smaller than that of sintered at 1350 °C. However, the grain size of 0.4 mol% Nb_2O_5 doped samples is larger than that of doped with 0.2 mol% Nb_2O_5 at various soaking times and independent on the sintering temperature. It reveals that the average grain size of doped samples sintered at 1300 °C increases slightly with soaking time. But the grain growth with increasing soaking time becomes more significant as the sintering temperature increases to 1350 °C. The average grain size of doped samples increase abruptly and some exceptional large grains are observed in the microstructure of samples sintered at 1350 °C for 8 and 10 h, which is considered to be due to abnormal grain growth induced by a longer soaking time. As shown in Fig. 2, the relative density of alumina doped with 0.4 mol% Nb_2O_5 is about 97% when sintered at 1350 °C for various periods of time. Therefore, soaking time of 2 h is enough for obtaining a dense and homogeneous microstructure of alumina with small grain size (1.6 μm) by doping with 0.4 mol% Nb_2O_5 and sintering at 1350 °C. In comparison with the previous report [21], a higher amount of 0.5–2.0 mol% Nb_2O_5 was added into fine θ-Al_2O_3 powders and sintered, it demonstrated that the Nb_2O_5 dopant improved the densification and promoted the grain growth of alumina during sintering. However, the grain size of the doped samples decreased with the increase of Nb_2O_5 contents at the same sintering time, which is contrast to the results of this study. The behavior is due to the doping amount, since second-phase $AlNbO_4$ particles would appear in the doped samples when the amount of Nb_2O_5 dopant higher than 0.5 mol%. Since the higher the Nb_2O_5 contents, the larger the volume fraction of the second-phase particles, and the grain growth is retarded more significantly. It suggests that the Nb_2O_5 promoted the grain growth when the niobium solved in alumina as solid solution, but the grain growth would be retarded by the formation of second-phase particles as the niobium content was higher than the solubility in alumina.

The microstructure evolution of ceramics during sintering can be represented by a plot of grain size versus density [23,24]. Such a plot reflects the ratio of the densification rate to the grain growth rate. Fig. 7 shows grain size/density trajectories for undoped alumina and samples doped with 0.2 and 0.4 mol% Nb_2O_5 sintered at temperatures between 1200 and 1450 °C for 2 h. The grain size/density trajectories of doped samples

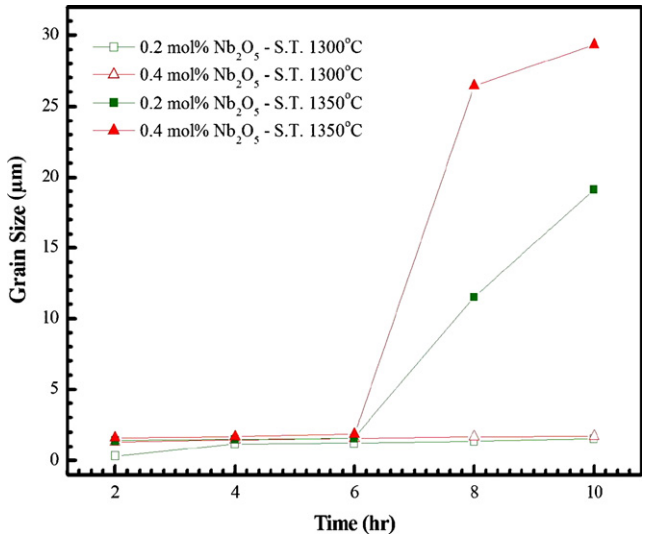

Fig. 6. Plots of the average grain size verse the sintering time of samples doped with 0.2 and 0.4 mol% Nb_2O_5 sintered at 1300 and 1350 °C, respectively.

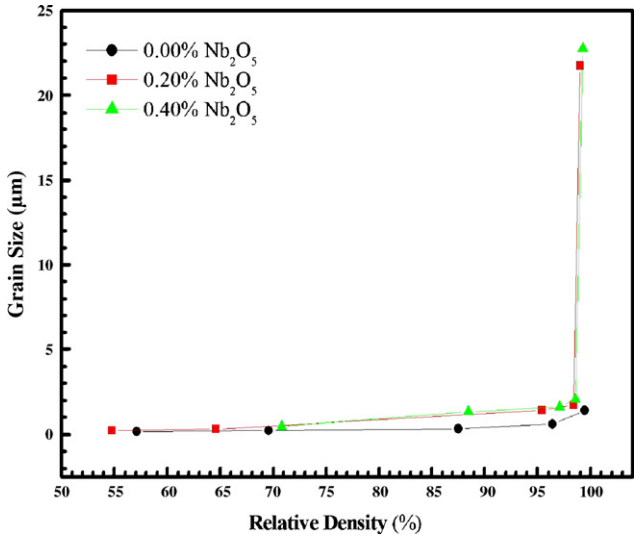

Fig. 7. Grain size vs. density trajectories for undoped alumina and samples doped with 0.2 and 0.4 mol% Nb_2O_5 sintered at temperatures between 1200 and 1450 °C for 2 h.

displace slightly from the undoped one, and the grain size/density trajectory of undoped sample is more flattening than that of doped sample. It indicates that Nb_2O_5 dopant only has a slight effect on the grain size/density trajectory of alumina during sintering. The slight oblique of the trajectories in the doped samples up to a relative density of 97% expresses that the doping of Nb_2O_5 increases the grain growth rate, compared to the densification rate. In addition, the grain size/density trajectories for samples doped with 0.2 and 0.4 mol% Nb_2O_5 overlap throughout, since the densification rate/grain growth rate ratio is similar for both samples, i.e., the sintering behavior is independent on the amount of dopant in these samples.

4. Summary

High purity nano-sized α-Al_2O_3 powder doped with various amounts of niobium (0.1–0.5 mol%) were mixed and compacted into disk samples, and then were sintered at temperatures between 1200 and 1450 °C for various soaking times. The results indicate that the niobium dopant improves the densification of alumina during sintering with a lower sintering temperature, a shorter sintering time and the effect is strengthened by increasing the amount of dopant. For example, a dense (relative density >97%) and homogeneous microstructure of alumina with small grain size (1.6 μm) is obtained by doping 0.4 mol% Nb_2O_5 and sintering at 1350 °C for the 2 h soaking time. However, the niobium dopant significantly promotes the grain growth of alumina during sintering and the grain size of alumina increases with increasing sintering temperature and the amount of dopant in the added range from 0.1 to 0.5 mol%. Therefore, a homogeneous microstructure of densified alumina with various grain size for different applications could be obtained by doping niobium and suitable sintering conditions.

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