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Phase transformation of alumina induced by high pressure spark plasma sintering (HP-SPS)

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ABSTRACT

Spark plasma sintering of nanocrystalline γ-Al_2O_3 at very high pressure was investigated up to 5 GPa. A SPS pressure/temperature diagram of α-Al_2O_3 and γ-Al_2O_3 phase was plotted. An in-house high pressure spark plasma sintering equipment (HP-SPS) was used. The capabilities and parameters control of this equipment greatly reduced the phase transition and sintering temperatures to obtain ceramics in contrast to conventional high pressure and high temperature sintering (HP-HT). The transition temperature could be lowered to ~500 °C from 1 GPa. The grain growth in ceramic was retained by the HP-SPS sintering. The density was also demonstrated to be optimized with HP-SPS.

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Alumina has numerous crystallographic phases, among which α and γ phases are the most widely used. The γ phase is known to irreversibly transform to α phase, under high pressure and high temperature conditions (HP-HT). α-Alumina (α-Al_2O_3) which is the most thermodynamically stable with high mechanical hardness has been used as abrasive, thermochemical insulator or biomaterial in dentistry [1–4]. Sintering of alumina has been then a topic of great interest for a long time since alumina-based ceramics are used in a wide range of applications. The phases and mechanical properties of the final sample depend on the starting powder as well as on the sintering process employed [5]. α-Al_2O_3 nanopowder precursors were found to favor an increase of density, transparency and hardness [1]. The sintering of α-Al_2O_3 can also be done from γ-Al_2O_3 powder ceramics.

Different sintering processes have been used in alumina processing. The pressure being one of the most studied parameters to obtain optimized sintering results. The advantage of high pressure in retaining grain growth and achieving full densification was demonstrated already in the literature [2–4]. In fine grain alumina, pressure was however demonstrated to favor grain coarsening during hot isostatic pressing (HIP) [5]. Beyond traditional sintering methods such as HIP and HP-HT, the spark plasma sintering (SPS) was found to help in controlling grain growth in the final α-Al_2O_3 [3,6]. The advantage of pulsed current in sintering process was clearly demonstrated for MgO-doped Al_2O_3 by Risbud et al. [7]. Among the evoked SPS advantages, the lowering of sintering conditions in material processing was underlined [8]. SPS was shown to be convenient to sinter transparent and hard α-Al_2O_3 at pressure up to 1 GPa though grain growth was observed [9,10].

Two distinct regimes were underlined during the SPS sintering on commercial α-Al_2O_3 depending on the sintering temperature [1,5]: a densification regime for temperature below 1100 °C and a grain growth regime for temperature above 1250 °C in which the pressure was shown to favor grain growth during SPS of commercial α-Al_2O_3 powder [1]. When the starting powder is γ-Al_2O_3, phase transformation can be initiated while sintering. The γ-α phase transition may go through intermediate δ, χ, ι, ε or θ phases [11].

The capability of coupling high pressure with SPS (HP-SPS) to sinter micro-sized grain γ-Al_2O_3 was reported recently [12]. This attempt demonstrated the advantage of HP-SPS to lower the phase transition conditions at 3 GPa in contrast with conventional high pressure and high temperature (HP-HT) process.

The present work aims to show the advantage of the SPS combined with high pressure allowing to deliver up to 5 GPa in material such as alumina leading to its phase transformation. The results were compared to previous studies [3,11] using conventional HP-HT process in order to emphasize the influence of high pressure in the SPS process. The detailed results are discussed in the following sections.

The starting powder was a commercial (CR125, Baïkowski) pure γ-Al_2O_3 (0.3 μm grain size).

Sintering experiments were first run at low pressure (ambient pressure and 100 MPa) using a conventional SPS equipment (Dr Sinter SPS 515S, Fuji) with 3.3 ms pulse duration. We used a sequence of twelve pulses of (40 ms) followed by two periods (6.6 ms) of zero current (12:2).

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SPS was also performed at high pressure using the HP-SPS equipment recently developed by coupling at high pressure belt apparatus to pulsed electric current source [12]. Experiments were run at 1.4, 3 and 5 GPa at different temperatures ranging from 400 to 1000 °C. The HP-SPS cell contained graphite furnace with 17 mm internal diameter corresponding to the maximum sample diameter. The sample was compressed with two graphite studs similar to conventional SPS die assembly [12]. The sintered sample had 17 mm diameter if it was in contact with the graphite furnace tube. However it is possible to have even 10 mm diameter, pre-compacted pellet in pyrophyllite or hexagonal boron nitride (h-BN) ring to obtain comparable sample size with conventional SPS 10 mm diameter die. The results presented in this work about phase transition took into account both diameters. The maximum temperature was maintained for 10 min during all experiments.

For all experiments, the pressure was first increased up to the desired value; the temperature cycle was then run with heating/cooling rate (50 °C/min). The decompression was done after cooling.

For experiments done with conventional SPS at low pressure (≤100 MPa), the starting powder was directly poured in to SPS 10 mm graphite die. For high pressure experiments, the powder was precompacted in pelletizer and pushed directly into graphite furnace.

Densities of sintered α-Al_2O_3 ceramics were measured by Archimedes' method with water as reference liquid.

The phase transition in the final samples was confirmed by powder X-ray diffraction (XRD). XRD was performed on milled samples using a PANalytical X'pert Pro MPD diffractometer with Cu K_α radiation and Bragg–Brentano geometry.

The microstructure of final α-Al_2O_3 samples were observed on the fractured surfaces with a JEOL JSM-840 SEM operating at 10 and 15 kV to estimate the grain size as well as the grain morphology.

XRD data were first collected for *in situ* heat-treated γ-Al_2O_3 at ambient pressure. Starting powders were heated by titanium filament mounted with the sample holder while data were collected. The experiment was performed between 1100 and 1250 °C with stepwise increase of 50 °C. The γ-α transition started around 1250 °C where diffractogram revealed a mixture of both phases. The transition was irreversible. A pressureless SPS experiment was performed by using abutment punches with the graphite die. The starting powder was SPS-heated at different temperature in a graphite chamber covered with papyex. As no pressure was applied, the sample remained as loose powder form instead of being in compact form. The transition started around 1200 °C. The SPS heat-treatment clearly enhanced the transition compared to the filament heating. The efficiency of heat generated in SPS [13] could be considered even in uncompressed sample.

Fig. 1 shows superimposed diffractograms of recovered samples after sintering at 3 GPa by using HP-SPS. Diffractograms of samples sintered between 450 and 500 °C showed signals from both γ and α phases. The temperature range of 450–550 °C was then a phase boundary region where the phase transition was initiated. The phase transition was complete at 600 °C (Fig. 1).

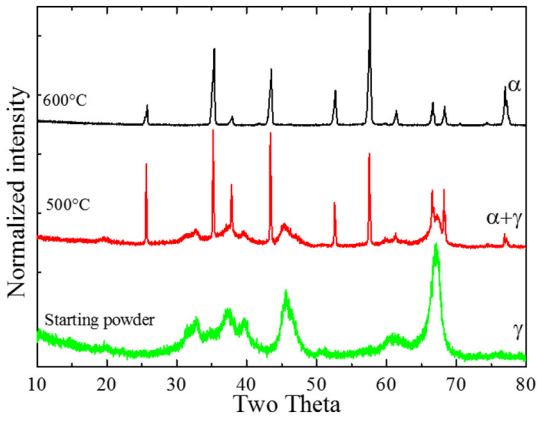

Fig. 1. Diffractograms of the starting powder and recovered samples sintered at 3 GPa, 500 °C and 600 °C by HP-SPS.

Between 1.4 and 5 GPa the diffractograms revealed the same phase boundary domain of 450–550 °C temperature range. This phase transition of γ-Al_2O_3 monoclinic phase (d = 3.56 g.cm^{-3}) to α-Al_2O_3 hexagonal phase (d = 3.98 g.cm^{-3}) is accompanied by a volume reduction of about 14% causing a large density increase. As in most of pressure-induced transformations [14], the unit cell volume per formula unit V/Z (where V is the unit cell volume and Z the number of formula units) decreased; the transition goes from V/Z = 49.7 A^3 for γ-Al_2O_3 to V/Z = 42.45 A^3 for α-Al_2O_3.

Once the transformation was completely done, a good densification of the final sample required temperature higher (>800 °C) than the transition temperature. The decrease of the unit cell volume due to the transition should have created local porosity.

The SPS phase diagram is plotted in Fig. 2. With reference to a similar study done earlier with conventional HP-HT process [3,11] plotted in red dashed line, the pulsed electric current seemed beneficial for phase transition at pressures lower than 5 GPa. The temperature of transition was lower by HP-SPS at a given pressure value. Assumptions on how materials behave under SPS [13,15] could be helpful to have accurate understanding of the observed results. In conductive media the interaction between electric current and the green compact was thought to be determinant [21]. It was believed that spark discharge appearing in the gap at the contact points between the grains is leading to a local high temperature. This causes melting and important diffusion which help in enhancing sintering even when measured temperatures are relatively low. The SPS effects for insulating materials sintering were also investigated [16,17]. In insulating media such as alumina the electrical field interaction was evoked [1]. This later was thought to enhance densification through grain boundary migration and matter transport [18]. However there was not a sound understanding of such assumption. Insulating materials were thought to get electrical conductivity at high temperature from the edges in contact with the graphite die [17]. Assumptions about SPS effects in conductive media could therefore be partially applied to insulating media at high temperature. Chaim [15] related the SPS effects in insulating media to a voltage breakdown during SPS sintering supports this linkage. The relative contribution of the surface current was found to increase when particles were smaller. This breakdown should start from the edges where the contact with conductive die causes higher temperatures [15]. Hensley et al. [19] demonstrated the crucial effect of pulsed electric discharge during the activation step. Current paths were then assumed to be partially passing

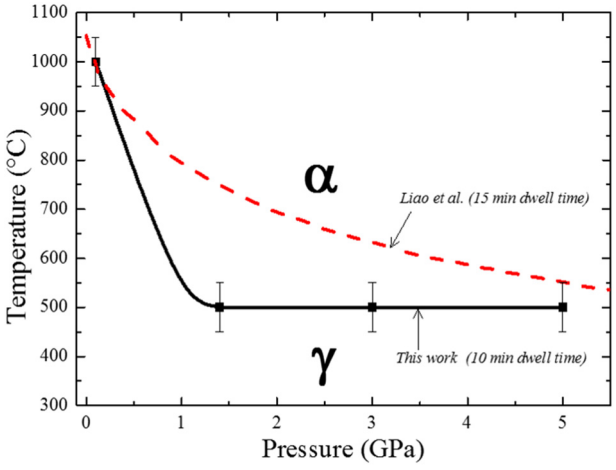

Fig. 2. Pressure-temperature diagram of α and γ phases of alumina obtained by SPS (conventional and HP-SPS) (solid line and square symbols). A literature data collected for 15 min dwell time and using HP-HT process [3] is given in dashed line. On the plotted lines the two phases coexist.

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