Spark plasma sintering of high-strength lightweight ceramics

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Abstract. This research paper provides an illustration of how to use the Spark Plasma Sintering technology (SPS) for powder materials in order to obtain lightweight ceramics Al₂O₃/ZrO₂ with enhanced strength properties. Optimization of SPS modes helps to produce ceramics with grain size of less than 400 nm, microhardness Hᵥ = 24 GPa, and crack resistance KᵥC = 4.2 MPa m¹/².

1. Introduction
Alumina is one of the most advanced ceramic materials for a wide range of structural applications, including aerospace engineering, owing to a combination of high hardness, thermal and chemical stability on the one hand, and availability on the other hand. One of the means of improving alumina performance properties is to develop composite structures by adding into original Al₂O₃ ceramic such fine powders as ZrO₂, SiC, TiC, TiN, etc. [1-5].

Due to high rupture resistance, Al₂O₃/ZrO₂ system has gained widespread use in industry [6]. Tetragonal-monoclinic phase transition of zirconium dioxide under high mechanical stress ensures high crack resistance of this composite material when subjected to loadings: a zirconium dioxide particle undergoes structural changes when appears on a crack path. During phase transition, ZrO₂ expands ensuring stress relaxation at the crack tip, thus further crack propagation slows down [7].

Traditional Al₂O₃/ZrO₂ composites contain from 5 volume % to 50 volume % of ZrO₂ [6, 8-9]. Since the specific weight of zirconia exceeds the specific weight of the alumina ~ 1.4 times, the weight of a finished product with 25 volume % of ZrO₂ is 10% bigger compared to the weight of a product made of pure Al₂O₃.

In this regard, ceramic materials based on alumina with low content of zirconia are becoming ever more relevant for aerospace applications, as they are lighter but ensure strength properties that are as good as those of traditional Al₂O₃/ZrO₂ composites.

In recent decades, the high-speed compaction technology known as Spark Plasma Sintering (SPS) has become a frequent practice in powder engineering [10]. One of the key features of SPS technology that distinguishes it from other consolidation technologies is its high control precision of sintering parameters. Review [11] shows that optimization of SPS modes allows to obtain almost any oxide ceramics with density close to 100% and grain growth factor below 2. At the same time, ultrafine-grained structure of sinter materials ensures high strength properties.

Nano powders, surfactants, and ultrasonic processing ensure very even distribution of strengthening dispersed particles in the base material and therefore significantly reduce the volume fraction of ZrO₂ particles required to boost crack propagation resistance.
From this perspective, it looks very promising to combine innovative approaches to obtaining powder composite systems and SPS technology to produce Al₂O₃-based lightweight high-strength ceramics, which is the goal of the present work.

2. Experimental

Al₂O₃ powders made by "Taimei Chemicals Co., Ltd." (Japan) and ZrO₂ made by "Pangea Int., Ltd" (China) constituted the target of this research. The microstructure of original powders is shown on figure 1.

Al₂O₃/ZrO₂ composite mixtures were obtained through mixing original powders for 4 hours in a planetary mill "FRITSCH - Pulverisette 6" with grinding media of zirconium dioxide in isopropyl alcohol.

Samples 12 mm in diameter and 3 mm high was carried out using spark plasma sintering method in a sintering unit "DR. SINTER model SPS-625 Spark Plasma Sintering System" (SPS SYNTEx INC. Ltd., Japan). The temperature was measured using a pyrometer centered on the outer surface of the graphite mold. The heating rate was 50 °C/min, while the applied load remained under 70 MPa. Sintering took place in 6 Pa vacuum. The sintering temperature did not exceed 1200 °C. Sintering modes are shown in table 1.

The density of sintered samples was measured using the hydrostatic weighing in distilled water using Sartorius CPA scales. Accuracy of density calculations was ± 0.005 g/cm³.

Vickers hardness (HV) was measured using an automated microhardness tester "Struers Duramin-5" with a 2 kg load. Crack resistance KIC was calculated using the Palmqvist method. Measuring accuracy of HV and KIC was ± 1.5 GPa and ± 0.5 MPa·m¹/² respectively.

The microstructure of samples was studied with the help of a scanning electron microscope Jeol JSM-6490. The average grain size in sintered ceramics was calculated after analyzing at least 400 grains. The microstructure of the obtained samples is shown on figure 2.

Figures 2a-2e show that new approaches to powder mixing help to improve evenness of distribution of ZrO₂ dispersed particles in sintered ceramics.

![Figure 1](image1.jpg)

(a) Al₂O₃ powder (d ~ 200 nm), (b) ZrO₂ powder (d ~ 30 nm). Scanning electron microscopy (SEM).
Table 1. Properties of composite ceramics obtained through SPS method.

| Material                        | T_sint (°C) | t (min) | d (µm) | ρ_{relat}(%) | H_v (GPa) | K_{IC} (MPa·m^{1/2}) |
|---------------------------------|-------------|---------|--------|--------------|-----------|-----------------------|
| Al₂O₃                           | 1200        | 0       | 0.5    | 99.5         | 22.3      | 2.2                   |
| Al₂O₃ + 1.5 vol.% ZrO₂          | 1200        | 0       | 0.3    | 96.1         | 20.9      | 3.2                   |
|                                 | 1200        | 3       | 0.4    | 99.6         | 24.0      | 4.2                   |
|                                 | 1200        | 10      | 0.6    | 99.6         | 22.0      | 2.7                   |
|                                 | 1200        | 30      | 0.9    | 99.6         | 21.0      | 2.8                   |
| Commercial ceramics (hot pressure sintering) | n.d.       | n.d.    | 1.5    | 99.1         | 19.1      | 3.0                   |
| Al₂O₃+5 volume % ZrO₂           |             |         |        |              |           |                       |

Figure 2. Microstructure of ceramics: (a) Al₂O₃, (b) Al₂O₃/ZrO₂ (at t = 0 min), (c) Al₂O₃/ZrO₂ (at t = 3 min), (d) Al₂O₃/ZrO₂ (at t = 10 min), (e) Al₂O₃/ZrO₂ (at t = 30 min), (f) commercial ceramics Al₂O₃+5 volume % ZrO₂. Bright particles – ZrO₂, dark particles – Al₂O₃. SEM

3. Results and discussion

It is well-known that the strength of sintered ceramic materials depends on their density and grain size. The larger is the grain, the lower is the strength. Besides, coarsening of grain causes increase in diffusion paths, which impedes higher density during sintering and consequently has a detrimental effect on strength.

The size of grain in sintered ceramics depends on the initial size of powder particles, size and volume fraction of dispersed second phase particles and pores. It is crucial to note that unless a continuous net of grain boundaries is formed, coarsening of grain is impeded. A net of grain boundaries is considered to be formed at relative density of ρ ~ 90%. During sintering of spherical particle with r radius, the sample microstructure at that moment consists of equiaxed grains, with grain size d_{grain} = r and pores size d_{pore} = 0.15·r. From this point an intense grain growth is observed [12].

In this context, in order to obtain materials with maximum density and minimum grain size it is required to optimize temperature and isothermal time after the material passes through ρ ~ 90%.
At high sintering temperature, boundary migration speed is generally high, boundaries may "come off the pores" leaving them in the grain volume. In this case, pores dissolution rate as well as contraction will be controlled by volume diffusion rather than grain boundary diffusion. Since [13] the volume diffusion coefficient at Al₂O₃ sintering temperatures (1200 °C) is two orders less than the grain boundary diffusion coefficient, sintering-out of voluminous pores is rather slow and occurs in modes when boundaries come off pores. Dense materials are therefore hard to obtain.

To eliminate the come-off effect, boundary migration speed shall be slowed down. It can be achieved through reducing the sintering temperature after reaching the 90%-density point. This approach is known as "Two Step Sintering", «Multi Step Sintering», «Rate Control Sintering» [14-16].

Lowering the temperature at the second sintering stage helps to reduce grain growth rate while maintaining pores dissolution rate at a reasonable level. This becomes possible through SPS technology that offers ample opportunities for temperature control.

4. Conclusion
Due to high accuracy achieved when controlling sintering parameters, SPS technology enables multi-step sintering modes and high-density nano- and ultrafine-grained materials with improved physical and mechanical properties, which opens up new opportunities to optimize the existing ceramics and develop new structural ceramics.

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