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Viewpoint article

View point on hydrothermal sintering: Main features, today's recent advances and tomorrow's promises

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ABSTRACT

The development of new high performance materials faces the challenge of implementing low temperature densification processes to overcome current technological limitations. In this context, the hydrothermal sintering, inspired by the natural processes of geological and biological mineralization, has recently emerged as a major opportunity to develop new and/or optimized materials that respond to today's scientific, technological and related socio-economic issues. The purpose of this viewpoint paper is to present opinions and propose future outlook for hydrothermal sintering based on the most recent achievements.

New materials have always accompanied scientific and technical progress. Currently, research is directed towards materials with new properties, improved performance to cost ratio, limited environmental impact over their entire life cycle. More particularly, ceramics and high performance assemblies have a major impact in automotive, electronic applications, energy and environment, mechanical engineering, medical technology… These materials, due to their exceptional properties, are able to meet the specific requirements of different applications, especially when a high level of functionality and reliability is required. These ceramic-type materials are oxides, sulfates, carbonates, phosphates, silicates, non-oxides and can be crystallized or amorphous.

The development of new high-performance ceramics, but also the design of complex assemblies, requires the mastery of the shaping processes, including suitable sintering processes. Most of advanced ceramic materials are currently fabricated from powders and sintered above 1000 °C to reach at least 95% of their theoretical densities. The decrease in surface free energy, which is the driving force for sintering, might be promoted either by applying pressure or by enhancing diffusional processes using fast heating routes. Thus, intense international research has led to the development of numerous sintering techniques to enhance the performances of conventional sintering (CS) such as two-step (TSS), flash (FS), high pressure (HPS), spark plasma (SPS), rate controlled (RCS), microwave (MWS) sintering [1–6]. If it is well admitted that pressure is beneficial for densification *via* particle sliding and rearrangement, plastic deformation, and pore shrinkage, the high temperatures required by these processes create several technological barriers: (i) advanced materials need to be produced by energy- and cost-efficient processes to ensure the feasibility of industrial scalability, (ii) materials that are metastable or that decompose at low temperature are difficult to sinter with such processes and (iii) co-sintering of multimaterials is hindered by differences in thermal stability, the rate and the onset temperature of shrinkage, and the physical and/or chemical compatibilities between the components [7,8].

To decrease these processing temperatures, the use of nanopowders (with particle size in the range 10–100 nm [9]) as starting materials appears as a key solution since the high surface-to-volume ratio of nanoparticles provides a strong driving force to promote the diffusion process, especially at elevated temperatures [10]. Another advantage of nanostructured ceramics is that, unlike the conventional technical ceramics, the pore volume fraction should be limited below a few tens of ppm [11]. It was shown that oxide nanoparticles with equiaxed morphology and narrow size distribution are a prerequisite to form green pellets with homogeneous density and low pore-to-particle size ratio, and thus to optimize the final relative density of the nanoceramics while preserving the initial nanograin size at full densification [11]. Finally one should consider that the use of nanoparticles is a route to design increasingly performing ceramics, providing a deep knowledge of the impact of the nanoscale structure on bulk properties. The recent advances in processing high quality nanocrystalline powders have favored the design of well controlled functional nanoceramics [12].

However, the decrease of the sintering temperature associated with the use of nanopowders is limited when full densification is targeted and high temperatures are still required to achieve densification. Consequently, one should consider that the competition between densification,

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coarsening processes and agglomeration often yields microstructures with overly coarse grains, which is detrimental to densification [13].

Then it appears clearly that an indisputable breakthrough in the sintering approaches would consist in combining pressure (below 350 MPa) and low temperature (at least below 500 °C). In this way, hydrothermal sintering appears as a powerful technology that surmounts the aforementioned barriers. First, similarly to advanced sintering processes such as SPS and hot pressing, this process uses an applied force to generate an internal pressure to improve particle rearrangement and densification of materials. It combines also the benefit of low temperatures that allow a better control of defects, prevent from solid state diffusion and grain growth and can be suitable for materials exhibiting low transition or decomposition temperatures. In addition, it overcomes the weakness of low temperature regime with respect to reactivity. Indeed, the main feature of hydrothermal sintering is to take advantage of hydrothermal conditions that promote diffusion of chemical species and optimize reactivity considered as an efficient driving force. The nature of solvent, the pH and the addition of mineralizers are then important levers to operate to optimize densification.

1. A brief history on this geologically inspired process

Dense ceramic materials can form in the nature under mild temperatures in the presence of water. As an example, besides biomineralization, the formation of ceramic-dense materials such as limestone also occurs in nature through large scale geological processes. Here the basic physicochemical mechanism may involve dissolution-precipitation process, referred to pressure solution creep, which relies on the mass transport from the contact zone between touching particles to the surrounding liquid phase and eventually to nearby non-contacting surfaces [14–18]. Consequently, the distance between the particle centres decreases, enabling global shrinkage and densification. The motion of ions during pressure solution creep is driven by the high-stress concentration at the contact point when the particle compact is subjected to an externally applied mechanical load. In response to such stress concentration, the ions at the contact point dissolve from the solid particle into the interfacial liquid film and eventually diffuse along the grain boundary before reaching the continuous liquid phase and precipitate on a lower-stressed particle surface. In addition, when the applied pressure is sufficiently high, plastic deformation through dislocation motion and/or viscous flow of the solid phase may participate to the densification process. It was shown that, for a given temperature, the densification rate is increased by reducing the particle size and increasing the applied pressure.

The hydrothermal sintering process is totally inspired from this geological process. It was first developed by N. Yamasaki et al. [19] and was called Hydrothermal Hot Pressing (Fig. 1.a). Here, a powder with water is externally and mechanically compressed in an autoclave, under hydrothermal conditions (100 °C < T < 350 °C; 22.5 MPa < P < 220 MPa) over short periods of time (from a few minutes to a few hours). As expected, the main driving force of such a process is the stress gradient within grains induced by external compression leading to the activation of the dissolution-precipitation phenomena at the solid/liquid interface. Here, water is expelled from the sample during densification and recovered in specific spaces for water retreat. Water acts both as a solvent, as a pressure transmitting medium and as a mass transport medium. Thus, hydrothermal conditions promote the reactivity at the solid/liquid interfaces, as diffusion processes in the solid phase are hindered at such low temperatures. This process was set up to densify metastable materials (anatase) [20,21], materials with mild temperature decomposition ($Ca/SrCO_3$ [22,23], hydroxyapatite [24,25]), porous ceramics (porous hydroxyapatite [26], zeolites [27]), nanomaterials without coarsening ($Sn_{1,24}Ti_{1,94}O_{3,66}(OH)_{1,50}F_{1,42}$ [28]), amorphous nanomaterials (SiO_2 [29,30]), tailored thermoelectric materials ($Ca_3Co_4O_9$ [31,32], $Na_xCo_2O_4$ [33]) or to bond different materials (hydroxyapatite bonded to titanium [34] or to magnesium alloy [35]).

We have recently developed a new apparatus inspired by the hydrothermal hot pressing tool described by Yamasaki and Yanasigawa [19], but with improved performances due to the specific design of both the pistons and the autoclave (Fig. 1.b) [36]. Here, the glass-filled teflon gaskets are maintained below 100 °C, *i.e.* far from their maximum operating conditions (300 °C), thanks to a double system (cooling fins and water cooling circuit), so the tightness of the system is ensured even when samples are submitted to higher temperatures. As a result, temperature and pressure can reach 500 °C and 350 MPa, respectively [36]. Thanks to this optimization of the device, the range of experimental parameters is wide enough to tune the conditions to get either

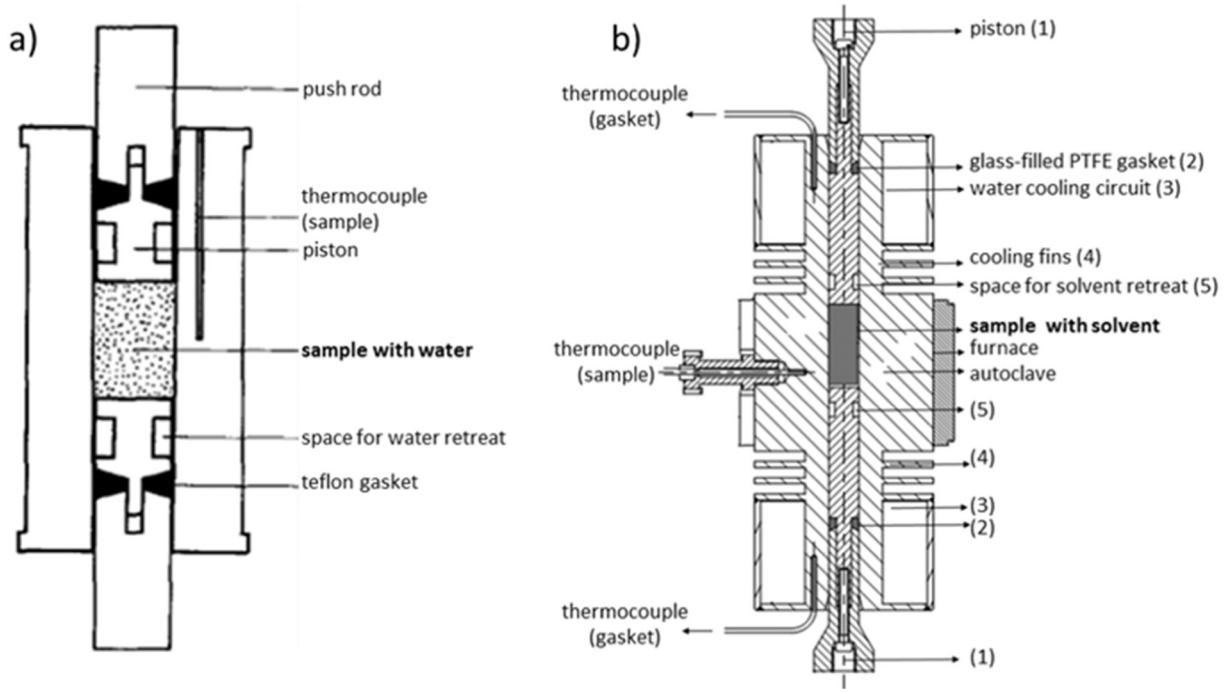

Fig. 1. Hydrothermal sintering apparatus designed by a) Yamasaki et al. [19] and b) Goglio et al. [36]. In b), the design of pistons and specific cooling systems favor improved performances.

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