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A Perspective on Emerging and Future Sintering Technologies of Ceramic Materials

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Novel sintering methods have emerged in the recent past years, which have raised great interest in the scientific community. Relying on electric field effects, high heating rates, the use of mechanical pressure, or hydrothermal conditions, they offer fundamental advantages compared to conventional sintering routes like minimizing the energy consumption and enhancing the process efficiency. This perspective aims at explaining these effects in a general way and presenting the status quo of using them for the processing of high-performing ceramic materials. In detail, this work focuses on flash sintering, ultrafast high-temperature sintering, spark plasma sintering, cold sintering, and photonic sintering methods based on different light sources. The specificities, potentials, and limitations of each method are compared, especially in the light of a possible industrialization.

1. Introduction

Sintering is an extremely old process—the oldest artifacts made out of clay and fired in a kiln are more than 25 000 years old—but has experienced renewed interest in the recent years.

Mastering advanced firing technologies has been determinant for the development of specific, high-quality products like porcelain. Nowadays, the control of the sintering process and the development of sintering methods at both lab and industrial scales are crucial for the manufacturing of high-performance ceramics. Examples of technological progress made possible by sintering are numerous: ceramic capacitors, magnets, cutting tools, extrusion dies, crucibles, furnace refractories, filters and membranes, prostheses of any shape, solid oxide fuel cells, lasers, etc.

Sintering occurs roughly above half the melting temperature of the compound. As ceramics have the highest melting point of all engineering materials, sintering temperatures usually lie between 1000 and 2000 °C. To control the resulting microstructures and properties, key sintering parameters are the heating rate, maximum temperature, holding time, and atmosphere. Additional possibilities are the use of mechanical pressure, electric fields/currents or electromagnetic waves, sintering additives, etc. In industrial batch or continuous furnaces, slow heating rates, long holding times, and followed by again slow cooling rates are standard. Due to the current energy crisis and global climate change, energy-intensive processes like the sintering of metallic and ceramic parts not only increase production costs but also negatively influence their carbon footprint and their life cycle assessments.

The ability to accelerate sintering kinetics, shorten cycle time, and reduce furnace temperature and total energy demand are therefore extremely attractive from a practical point of view. The use of renewable power instead of fossil fuels for firing is another decisive aspect for "green," sustainable manufacturing. A common principle for energy-efficient sintering approaches is to apply the heat only where it is necessary (at best within the specimen only), instead of heating large furnaces which require in addition excellent thermal insulation to reduce heat losses. In addition, the localized and rapid heating and cooling may freeze out-of-equilibrium states and enable new combinations of materials which otherwise are likely to react with each other. To finish with, specific effects induced by external mechanical/electrical loadings can be used on purpose.

The present article gives a perspective on the development of emerging novel sintering technologies, which make specific effects induced by electric fields and currents, high heating rates, pressure, and hydrothermal conditions available for the processing of high-performing ceramic materials. To better understand how these effects lead to improved sintering behavior and at the

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same time minimize energy consumption and enhance process efficiency, the involved physicochemical mechanisms are first briefly reviewed. Second, the emerging (i.e., already introduced in the industry) and possible future (i.e., still in the lab, no commercial equipment available yet) sintering technologies are presented. Finally, we aim at comparing these methods mentioning advantages, limitations, and remaining research and development efforts, as none of them can be seen yet as the holy grail for all cases.

2. Effects Leading to Enhanced Sintering

In the last decade, energy transition and climate change led to a serious re-evaluation of established material processing. In this context, conventional sintering technologies are rated critical because combinations of low heating rates, high sintering temperatures, and long dwell times lead to a limited efficiency and high energy costs. Activation of additional sintering mechanisms not present in conventional sintering is the key to go a step beyond. Most of these mechanisms are already described in patents or scientific literature, but their implementation in modern sintering equipment is—with only few exceptions—still in a premature stage. To better understand how novel sintering equipment must be designed for taking full advantage of such kind of mechanisms, the physics behind is introduced in compact form below.

2.1. Effects Related to Electric Current and Field

The possible phenomena induced by electric fields of different magnitudes and possible current flowing through a sintering body are complex and depend on composition, temperature, field characteristics, time, and environment. **Figure 1** shows the principle experimental setup to apply an electric field to a ceramic powder compact. From a macroscopic point of view, low electric fields (i.e., inducing negligible Joule heating within the sample) increase shrinkage in both axial and radial directions, as shown for ceria.[1] The sintering stress (i.e., the thermodynamic driving force for densification) increases indeed almost linearly with the applied electric field whereas uniaxial, bulk, and shear viscosities decrease. The viscous Poisson's ratio as coupling factor between orthogonal space directions increases with the field strength.[1] When the possibility of current flow is given, internally generated Joule heating can become significant (Figure 1b), leading to

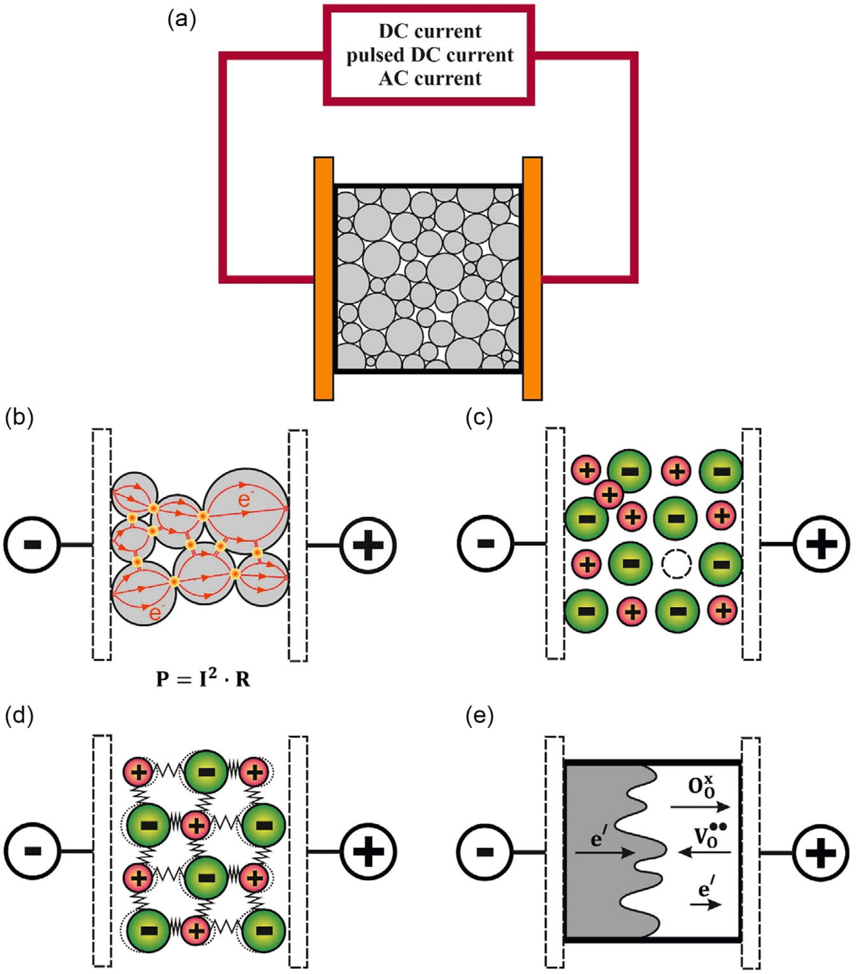

Figure 1. Enhanced sintering by electric current and field effects: a) principle setup to generate such kind of effects; b) Joule heating (P = power, I = current, R = resistance); c) formation of Frenkel defects; d) activation of phonon modes; and e) electrochemical blackening.

temperature increase of several hundreds of degrees compared to the furnace temperature.[2,3] If the balance between electrical power and heat dissipated in the sample is not possible anymore, thermal runaway is observed as in flash sintering (FS).[4] Before onset of the flash event, change of material properties such as drop of electrical resistivity can be observed locally.[5] Not only light emission within the expected frequency range (according to the black body radiation) but also electroluminescence was observed.[6] Sample geometry and boundary conditions have a strong influence on the heat balance and hence conditions for FS. In addition, bulk and grain boundary chemistry, as well as environment such as a reducing atmosphere can drastically modify the sintering behavior and enable a surge of high current through the sample.

At temperatures significantly lower than the conventional sintering temperatures, polarization occurs if an electric field is applied to a dielectric material.[7] If the applied field reaches a threshold value named dielectric strength, outer valence electrons become mobile causing an electric breakdown, which means a localized high current, extreme Joule heating, and in many cases permanent damage. Like the mechanical strength of brittle materials, the dielectric strength is not a fixed material property and lies typically $>10\,\text{MV}\,\text{m}^{-1}$. In oxide ceramics, for ion transport to take place, point defects are required to be sufficiently mobile and to be present at sufficiently high concentrations.[8] Defect formation under electric fields has been proposed as possible reason for enhanced sintering kinetics under electric loading. In the case of Frenkel-pair generation (Figure 1c), a regular ion moves from its lattice site to an interstitial site, leaving a vacancy behind. However, a thermodynamic approach has shown that extremely high fields—far beyond those used in sintering experiments—are required to create such defect pairs in the crystal lattice (e.g., in CeO_2 $E = 10^{10}\,\text{V}\,\text{m}^{-1}$). Phonon modes (Figure 1d) close to the Brillouin zone edge can generate Frenkel defects in oxides.[9] This would provide an alternative mechanism, but at present, it is not clear how a field produces these phonon modes in an ionic crystal. The case of grain boundaries is much more complex and interesting because this is very probably the strongest effect taking place. Possibly, a gradual modification of the grain boundary structure and associated space charge layer or temperature gradients on the microscale may develop. Amorphous films at grain boundaries were observed in pure zirconia after flash-sintering process[10] and it has been postulated that local transient melting of sintering necks may even take place leading to different properties.[11,12]

In any case, electrochemical blackening (Figure 1e) as a result from internal solid-state reactions driven by an electric field has been rationalized for ceria single and polycrystals for example.[13] The observed chromatic alteration of the sample is due to the migration of the positively charged oxygen vacancies that accumulated at the cathode side, while the oxygen ions moved to the anode side. The nonlinear rise in conductivity occurs when the sample is completely blackened. A clear and direct parallel to redox-based switching can be made: ionic motion (leading to concentration polarization, space charge formation) and electronic motion (Joule heating, thermodiffusion/thermochemical reactions) are observed in the reduced filament of a memristive oxide element. The "set time" is equivalent to the incubation time in FS and changes by order of magnitude as function of applied voltage ("voltage time dilemma") and temperature.[14] To finish with, the switching speed is limited by the phonon frequency in the crystal.

Concerning grain coarsening, grain boundary migration is dragged by the diffusion of cationic segregation.[15] As segregation often depends on the oxygen partial pressure, the drag effect of segregation depends on the reduction state. For example, in reduced SrTiO_3, little cationic segregation to the grain boundaries is observed. By modifying the concentration of oxygen vacancies, the electric field indirectly influences grain growth behavior too and grain size gradients are thus observed in specimens submitted to a DC field.[16] **Figure 2** exemplarily explains the change of the cationic diffusion depending on the oxygen vacancy concentration gradient triggered by an electric field.

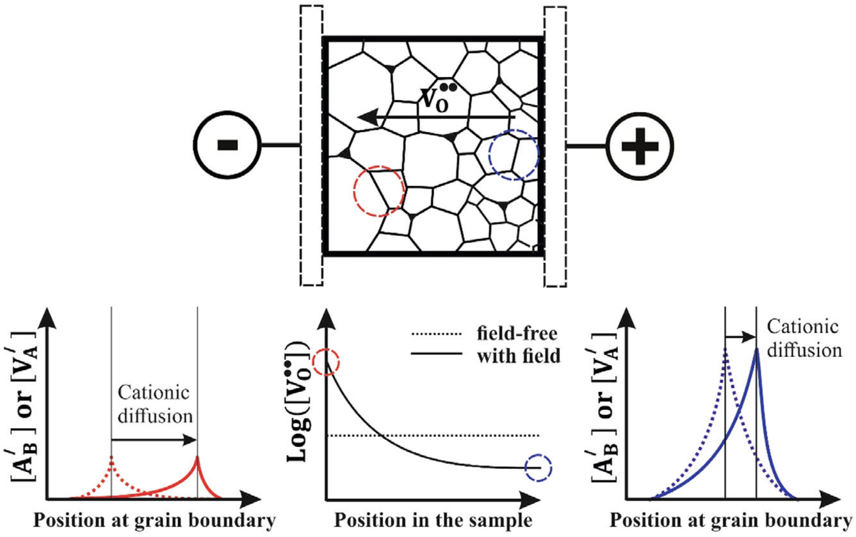

Figure 2. Influence of electric fields on grain boundary motion.

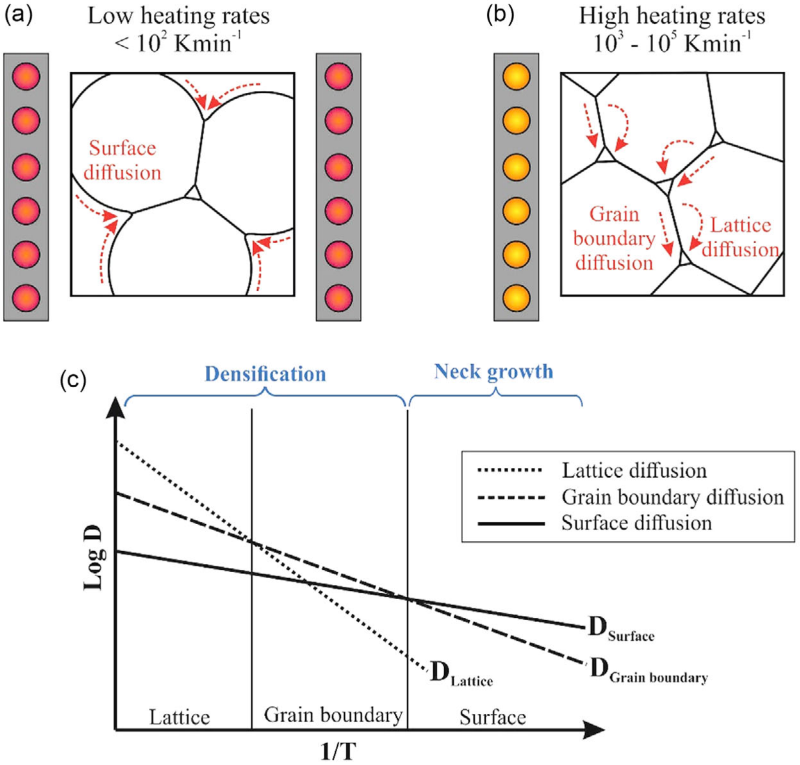

Figure 3. Influence of heating rate on sintering: a) low heating rates trigger surface diffusion leading to neck formation at early stage of sintering and retarded densification afterward; b) high heating rates directly activate grain boundary and lattice diffusion leading to rapid densification; and c) diffusion coefficients as function of inverse temperature.

2.2. Heating Rate Effects

The importance of heating rate effects is known since the 1980s[17,18] and relies on the existence of different mass transport mechanisms at different temperatures. The most relevant transport mechanisms for sintering are surface, grain boundary, and volume diffusion (**Figure 3**). Typically, the activation energy is lowest for surface diffusion and highest for the volume diffusion; accordingly, surface diffusion dominates transport during sintering at low temperatures, grain boundary diffusion at intermediate temperatures, and volume diffusion at high temperatures (Figure 3c).

The driving force during early-stage sintering is provided by the curvature radii and resulting Laplace pressures. Accordingly, any neck growth decreases the driving force for sintering, without resulting in any densification. Densification during sintering requires grain boundary or volume diffusion as mass transport mechanism.[19]

This loss of driving force is minimized by high heating rates because the time spend at lower temperatures (where surface diffusion and neck growth dominate) is minimized. This simple mechanism is the basis of fast firing.[17,18,20,21]

Beyond fast firing, the conservation of high driving forces for sintering plays a significant role for FS. Ji et al.[22] used a model experiment where they achieved very high heating rates by chemical heating. In parallel, they did FS with a similar heating rate and observed similar densification and microstructures. Other high heating rate sintering processes such as microwave sintering, ultrafast high-temperature sintering (UHS), and photonic sintering likely benefit from the same mechanism.[23,24]

2.3. Mechanical Pressure and Hydrothermal Effects

A mechanical stress modifies the densification behavior in the following ways[25,26]: first, at low temperature, it may already break powder agglomerates and induce particle rearrangement. This increases particle packing and reduces pore size, allowing homogeneous densification and grain growth subsequently. Second, at higher temperatures, it enhances the existing densification mechanisms already present in free sintering (such as diffusion through grain boundaries or lattice, viscous flow) while not affecting the nondensifying mechanisms (such as surface diffusion or evaporation/condensation). It can also activate new mechanisms, such as plastic deformation or grain boundary sliding. A compressive stress assists densification (while a tensile stress acts again the intrinsic sintering potential) and can also help removing strength-limiting defects depending on their size and morphology.[27] In addition, the macroscopic applied stress is magnified at the microscopic scale in a porous body. For a low-density body, the contact area between particles where forces are transmitted is small and stresses are locally higher than the macroscopic applied stress. Already in 1972, useful "deformation mechanism maps" have been established by Ashby, showing the controlling densification mechanism as function of temperature, pressure conditions, and grain size.[28] **Figure 4** summarizes sintering mechanisms which are enhanced by applying a mechanical pressure, and sintering mechanisms which are activated by mechanical pressure, i.e., plastic deformation and creep.

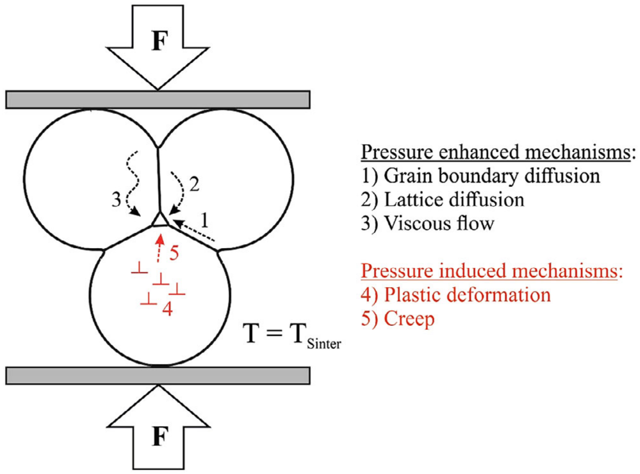

Figure 4. Superposition of pressure during sintering induces additional densification mechanisms supporting densification and enables lowering of the sintering temperature.

On the other hand, the role of water on the formation and evolution of rocks like carbonates, silicates, chloride salts, etc. has been long studied by geochemists.[29,30]

Due to their dynamic character, mechanisms of densification are complex and can be modified by dissolved species like CO_2.[31] Beyond particle rearrangement, partial dissolution of the material followed by Ostwald ripening and recrystallization, precipitation from a supersaturated solution or formation of protonated disorder at the grain boundaries, and plastic flow are considered as main mechanisms of hydrothermal densification.[32–34] Hydrolytic weakening has been observed in quartz and olivine and, i.e., the presence of small quantities of water was found to facilitate plastic deformation.[35] Water itself could also accelerate the self-diffusion of ions and facilitate the nucleation and diffusion of kinks and dislocation climb. To conclude, the role of sintering additives is only known empirically and their mechanisms not completely understood. In principle, water would be a perfect sintering aid due to its abundance, low price, safety, easy handling, and environment-friendly nature. **Figure 5** shows the main steps of low-temperature densification induced by hydrothermal effects.

3. Novel Sintering Technologies

In recent years, a lot of efforts have been devoted to develop novel sintering technologies, which make nonconventional sintering effects accessible for highly efficient processing of ceramic materials. Most of these technologies are only demonstrated on lab scale so far, but their obvious potential toward reduced energy consumption and increased efficiency has already attracted interest from industry. An exception is field-assisted sintering technology/spark plasma sintering (FAST/SPS), which is an established method in industry since more than 50 years, but use of this technology is still limited to niche applications. We believe that FAST/SPS will be one of the key technologies for implementing some of the new sintering concepts. Modern hybrid FAST/SPS devices enable to conduct FS, UHS, and cold sintering by suitable modification of the basic FAST/SPS principle. Also heating via Xe lamps or lasers is already implemented in industrial production of microelectronics. By using industrially established technologies as a basis, accelerated implementation and scaling-up of the new technologies are expected. Below, the most promising emerging and novel sintering technologies are introduced.

3.1. FS

In 2010, FS was discovered by Cologna et al. in the quest of unveiling the mechanisms of FAST/SPS.[36] In FS experiments, simultaneous application of electric field and external heat to a ceramic green body leads a sudden drop of electrical resistivity followed by internal heat generation mainly due to the Joule effect. With optimized FS parameters, densification within a few seconds appears accompanied by a bright glow caused by black body radiation superimposed by electroluminescence.[6] Compared to conventional sintering, FS can be done at significantly decreased furnace temperature and orders of magnitude reduced dwell time. Therefore, the method is highly attractive with respect to efficiency and cost reduction. It has been demonstrated that FS can be applied to almost all oxides including ionic conductors, electronic conductors, insulators, and multicomponent oxides[5] and even synthesis of complex oxides in seconds by reactive FS is another promising kind of application.[37–39] FS of other material classes like nonoxide ceramics like nitrides,[40] carbides,[41–45] and even metals is currently under investigation.

Usually, FS cycles can be divided into three stages.[46] Stage I represents an incubation time during which the current gradually increases. When exceeding a critical value, current flow raises like an avalanche suddenly coupled with rapid heating to sintering temperature within seconds (stage II). To avoid uncontrolled overheating, in stage III the power supply is switched from voltage to current control entering a constant state of flash.

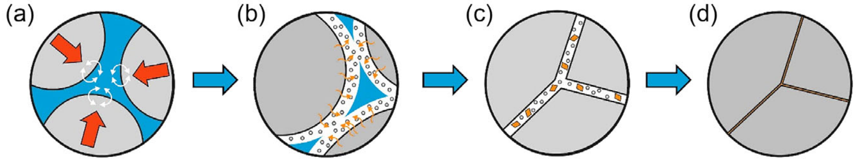

Figure 5. Densification of ceramic materials at moderate temperatures (<500 °C) by hydrothermal treatment: a) compaction of the powder with liquid sintering aid; the liquid phase eases particle rearrangement; b) solution and optional decomposition of the powder starting from the surface; c) removal of the liquid by evaporation and squeezing out of the die. Afterward precipitation of new phases from the supersaturated liquid; d) formation of a dense microstructure at the final stage of treatment. There often remain residuals from hydrothermal treatment at grain boundaries (e.g., amorphous phases or secondary phases).

The three stages are gone through either by applying an electric field and a defined heating rate or by applying an electric field at a given furnace temperature. There is a complex interplay between material properties, sample geometry and homogenity, and FS setup defining at which electric field and temperature the flash event occurs.[47] Recently, systematic parameter studies enabled the definition of FS maps for safe application of FS.[48]

Due to its highly dynamic nature, control of FS is challenging, especially with respect to avoid large thermal gradients. Several types of thermal gradients can be distinguished which range from the macroscopic scale down to microstructural features like grain boundaries and other interfaces.[49] It is not surprising that thermal gradients lead to undesired microstructural inhomogeneity, which can even occur in small samples with a size of only a few millimeters. The main reasons of thermal gradients are: 1) the disparity between Joule heating in the sample and heat loss from the sample surface by radiation, convection, and/or thermal conduction via the electrodes; 2) the geometry of the sample and the attached electrodes; 3) the accumulation of charge carriers at the electrodes, especially if they are fully or partly blocking the ion exchange; 4) density gradients in the sample; and 5) other reasons like secondary phases and impurities. In worst case, amplification of temperature gradients might lead to unstable heating regions, also called hot spots. Formation of such hot spots is often associated with abnormal grain growth or local melting of the sample. In addition to obvious measures like thermal insulation, optimized electrode configuration, or improved powder processing, a promising way to avoid local overheating is current rate or power rate controlled FS. In this case, the FS setup is operated using a low current or power limit reliably avoiding critical current or power peaks.[50] Recently, a computer control system has been developed by Lucideon Ltd., which permanently adjusts current, voltage, or power outputs on a millisecond basis based on a nonlinear algorithm.[49]

Even if there are first attempts to scale up FS to industrial scale,[51] the technique primarily remains at the laboratory scale today.[49] **Figure 6** shows the basic experimental setup for conducting FS of powder compacts. A recent attempt to overcome the drawback of FS being suitable only for simple sample geometries like dog bones or small cylinders is the introduction of contactless FS. In this case, expensive Pt electrodes are replaced either by an electrically conductive gaseous medium generated by electric arc, cold plasma, or conductive flame[49,52,53] or by superimposition of a magnetic field.[54] Contactless FS opens up new opportunities for sintering components with more complex shape and nonuniform thickness, as well as for sintering of functional layers like battery and fuel cell components or environmental barrier coatings.

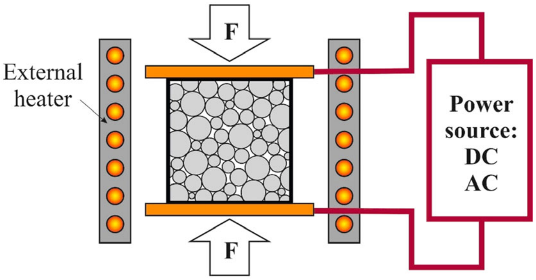

Figure 6. Principle sketch of FS setup for cylinder shaped samples. Optionally, load can be applied to improve the electrical contact. Often, the electrical contact is improved by using a contact paste.

3.2. UHS

UHS was discovered in 2020.[55] This method originally uses graphite felt heaters in direct contact to ceramic green bodies (**Figure 7**). Due to the lack of a large furnace chamber and the low thermal mass of the setup, very high heating rates of several thousands of degrees per second can be achieved. Total cycle times can be below 1 min. Generally, an oxygen-free atmosphere is needed for this method to protect graphite heater from degradation.

UHS was applied to many different ceramics including alumina, zirconia, strontium titanate, glass, various battery materials, and silicon nitride,[23,24,55–58] and has proven to be useful for more complex shapes as well.[55]

Generally, UHS sintering can result in microstructures and properties with similar features as conventional sintering (certainly in much shorter time). For strontium titanate, uniform and fine-grained microstructures were obtained.[24] A TEM investigation documented clean, crystalline grain boundaries with expected chemical composition profiles. The conductivity compared well with conventional sintering. However, for more complex compositions as, e.g., battery materials, homogeneity issues can occur.[59]

The UHS sintering process offers immense potential due to its simplicity and adaptability. For example, other materials such as Tungsten can be used as heater,[60] and thermal insulations can be used to improve the temperature distribution.[23] Upscaling to larger lateral dimensions is also possible.[61]

As with any high heating rate sintering process, UHS sintering comes with uncertain temperature distributions in the sintered material which is experimentally very difficult to access. Modeling techniques were used to estimate temperature distributions.[23,24]

3.3. Cold Sintering

Based on works involving both the presence of water and mechanical pressure (e.g., hydrothermal hot-pressing developed

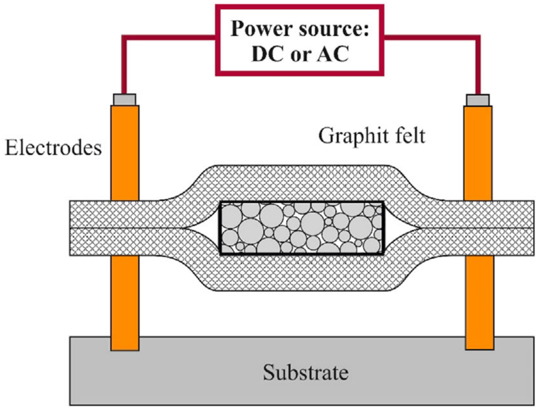

Figure 7. Principle sketch of a UHS setup.

in Japan in the 1970–1980s,[62,63] room temperature densification of water-soluble lithium molybdate,[63] and FAST/SPS of humid zinc oxide,[64,65] the "cold sintering process" was proposed in 2016.[35] This method enables low-temperature (<300 °C) processing of ceramics and composites, and relies on high pressure (up to 600 MPa, much larger than in standard hot pressing) and the addition of a liquid or adsorbed phase (pure water, aqueous solution with dissolved precursors of the solid phase or pH modifiers) acting as a sintering aid. The low temperature is particularly interesting for integration of ceramics with other materials, like temperature-sensitive polymers.[66,67] Cold sintering effect was already observed for over 50 inorganic compositions including binary, ternary, and quaternary oxides, bromides, chlorides, fluorides, phosphates, and carbonates at temperatures where normally no densification is expected. Particle size, morphology, agglomeration grade, and surface chemistry are key factors for the success of the cold sintering process. In some cases, almost theoretical density was reached. Particularly impressive are the results achieved with nanocrystalline ZnO.[68] In other cases, cold sintering is more a compaction process enabling densification (up to ≈80%) but requiring an additional high-temperature treatment for final densification (postannealing) and achievement of desired properties. Most of the time in the as-cold sintered state, dielectric or mechanical properties, as well as electrical conductivity lie significantly below what would be expected for a sintered material of that density.[69] If properties related to grain boundaries are targeted (like the ionic conductivity), then the quality of these interfaces is crucial and most of the time only modified by a high-temperature treatment.[70] Successful processing and tuning of properties of high-performance ceramics by cold sintering require the fundamental understanding of underlying mechanisms down to the atomistic scale. Cold sintering has the potential to enable the processing of new material combinations that are not sinterable by other methods due to temperature degradation. Due to the low temperatures involved, a rather simple setup (i.e., instrumented warm press) can be used (**Figure 8**).

3.4. FAST/SPS

FAST/SPS is a low-voltage, current-activated/assisted, and pressure-assisted sintering process.[71] FAST/SPS thus belongs to the group of "electric current activated/assisted sintering (ECAS)" technologies, enabling enhanced densification by superposition of external pressure and direct heating by applying an electric field. This commercially available technique results in higher heating rates (up to 1000 °C min^{-1}) and shorter cycle times (between 5 and 20 min typically) when compared to conventional sintering, hot pressing, or hot isostatic pressing. FAST/SPS is preferentially suitable for ceramic powders, metal powders, and composite materials, which are difficult to sinter due to their low sintering activity, high reactivity in "normal" environment, poor deformability, nanoscale, or unfavorable particle morphology and size distribution.[72] **Figure 9** shows the principle setup of a standard FAST/SPS device.

FAST/SPS devices are usually instrumented so that temperature (measured by pyrometer and/or thermocouples), applied pressure, and gas pressure in the chamber as well as displacement are recorded during the whole cycle. Possible atmospheres are vacuum, nitrogen, argon (with some addition of hydrogen), and technical air (with temperature limitation). Standard tool material is graphite, which is used as heating element, shaping matrix, and mechanical load transmitting medium. Graphite can be used up to 2400 °C, but only in nonoxidizing atmospheres, and can withstand stresses of 100 MPa at least. If higher pressures are required, alternative tool materials should be chosen (refractory metals, ceramics). By adding sintering additives as defined in 3.3., standard FAST/SPS devices can be used to carry out "cold sintering" experiments with high reproducibility.[64,72] Concerning the possible geometry of specimens sintered by FAST/SPS, discs of 50 cm diameter have been achieved in industrial apparatuses. For the realization of complex shapes, either net-shaped tools or embedding in a sacrificial powder is possible. The latter is also suitable for parts additively manufactured for example.[73]

Hybrid FAST/SPS devices are also on the market which enable the superposition of induction or resistance heating by placing an external heating element around the FAST/SPS tool.[74] This concept can help to further increase heating rates and thermal homogeneity or on the opposite allows for the creation of temperature gradients on purpose. FS can be conducted in a hybrid FAST/SPS equipped with external power source and electrodes,

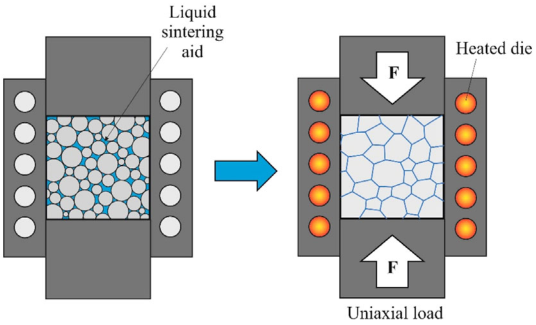

Figure 8. Principle sketch of cold sintering setup based on an instrumented warm press.

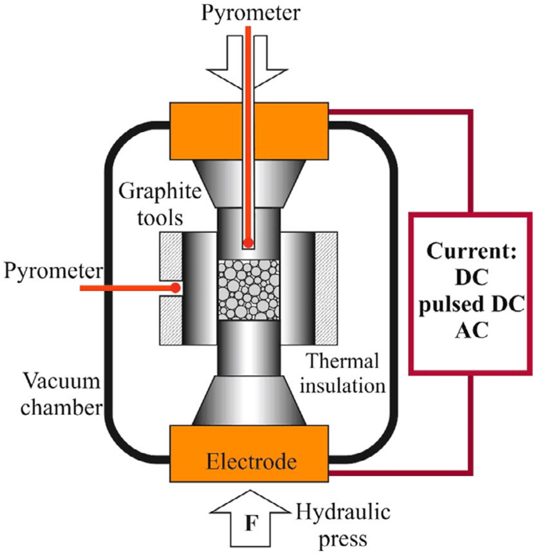

Figure 9. Principle sketch of a standard FAST/SPS device.

which can be placed between punch and sample. What has been often introduced in the literature as "flash SPS" can be mostly considered as pressure-assisted UHS. In this case, a standard FAST/SPS device can be used.[75] Very high heating rates in the range of 10^4–10^6 K min^{-1} and rapid densification rely on a DC current pulse of several 10 kW providing extremely high heating power.

3.5. Photonic Sintering

The term photonic sintering refers to a number of different sintering processes where photons are used to heat powder compacts as sketched in **Figure 10**. The most common process is the densification of metallic inks in the field of microelectronics via Xe flash lamps and is sometimes referred to as flash lamp annealing (FLA).[76–79] For the same reasons summarized in Section 2.2, very fast sintering with heating rates of up to than 10^8 °C s^{-1}[80] and little thermal impact on the substrate can be achieved. The process has been applied to ceramic coatings as well: Gilshtein et al. obtained dense alumina films with a thickness of a few μm on glass substrate.[80] However, such processes are limited to coatings.

Another common photonic sintering process is the use of infrared light (rapid thermal annealing [RTA] or rapid thermal processing [RTP]). Again, very heating rates of up to 10^4 °C s^{-1} can be achieved; however, the maximum temperature is limited to about 1200 °C. Most applications are found in the field of coatings, particularly for sol–gel-derived coatings, and mostly for ferroelectric materials.[81–83] Other applications include cathode materials for solid-state batteries.[84,85] However, this method was also applied to bulk ceramics as, e.g., ZnO.[86]

For metallic materials, the most common photonic sintering process is selective laser sintering (SLS) usually applied for the additive manufacturing of complex shaped parts.[87] SLS of ceramics was attempted as well, again mostly in the context of additive manufacturing.[88,89] However, the success of SLS for ceramic powders is limited for multiple reasons. For example, the particles are sometimes partially melted, causing chemical inhomogeneity and suboptimal microstructures. More problematic are the high-temperature gradients during selective heating and cooling, which result in a high remaining porosity, the formation of cracks, and poor mechanical properties.[90–92] Accordingly, in most cases, a thermal posttreatment is required.[88] Still, reasonably well-densified microstructures can be obtained, e.g., for alumina,[93] zirconia,[94] and porcelain.[95]

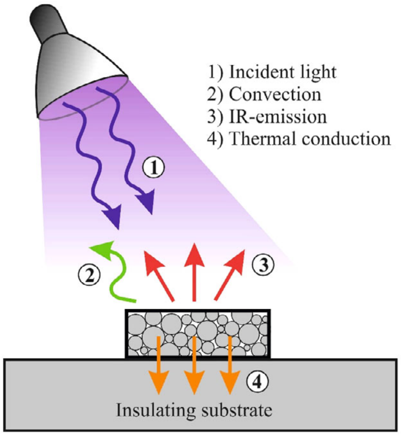

Figure 10. Experimental setup for photonic sintering reproduced from Ref. [96]. Different light sources are used by different photonic sintering methods: focused lasers in scanning mode, defocused laser, Xe flash lamps with single or multiple pulses, or IR lamps with continuous operation. This sketch also includes all relevant heat flow mechanisms.

Blacklight sintering is the latest invention in the field of photonic sintering.[96,97] This process uses blue wavelengths to maximize the optical absorption of the light in the ceramic powder for optimal heating. As light source, Xe flash lamps or blue lasers can be used. Typical irradiation densities are in the range of 100–200 W cm^{-2}. Maximum temperatures easily exceed 2000 °C depending on the used light source and optical absorption.

This sintering process allows cycle times down to 10 s for full densification. Blacklight sintering was used to densify many different ceramics such as alumina, zirconia, titania, zinc oxide, strontium titanate, barium titanate and $Li_{0.33}La_{0.57}TiO_3$. The electric properties are in the range of those for conventional sintering.[97]

Blacklight sintering turns out to be very versatile: very homogeneous microstructures can be achieved, but depending on the parameters and sample support, density gradients and surface textures are possible as well. While this process is naturally most efficient for planar geometries, it is a very flexible sintering process that allows a free design of heating schedule, atmosphere, and sample size.

4. Conclusions and Outlook

For replacing established, energy-intensive sintering technologies in the future, implementation of novel effects leading to enhanced densification is necessarily required. Promising measures for overcoming the limitations of conventional sintering are the realization of high heating and cooling rates, optionally combined with mechanical pressure, the localized heating of the samples, and/or the addition of sintering aids. When applied in a suitable way, these effects minimize the energy requirements by reducing overall cycle time and temperature, therefore enhancing the process efficiency and reducing the risk of interfacial reactions compared to conventional sintering. In recent years, there were strong efforts to make the effects accessible for real application by implementing them in existing sintering devices or by developing novel sintering technologies. Nevertheless, most of these technologies are still investigated only on lab-scale so far. Therefore, realistic benchmark with respect to energy and resources consumption up to industrial level is difficult at current status of development. In this article, the specific characteristics of the most promising sintering technologies are introduced, highlighting their potential use for emerging and future processing of high-performing ceramic materials up to industrial scale. **Table 1** summarizes the main characteristics of these technologies according to materials, sample geometry, sintering parameters like heating rate, pressure, and atmosphere in compact form.

Overall, most emerging sintering technologies aim for higher heating rates and faster process times. This applies to FAST/SPS in the same way as to FS, UHS, and photonic sintering. Out of these methods, FAST/SPS and FS are best investigated. FAST/SPS as the oldest method comes with geometric limitations and

Table 1. Specific characteristics of the sintering technologies considered in the manuscript including status of development (UHS, ultrafast high-temperature sintering; FAST/SPS, field-assisted sintering technology/spark plasma sintering; FLA, flash light annealing; SLS, selective laser sintering; RTA/RTP, rapid thermal annealing/rapid thermal processing).

Technology	Materials	Temperature range	Applied pressure	Heating rates	Sample size demonstrated	Atmosphere	Heating source	Sintering device (including media supply)	Industrial applications
Flash sintering	Oxides Carbides Nitrides	$<1768\ ^\circ\mathrm{C}$[a)]	None[b)]	$\approx 10^3\ ^\circ\mathrm{C\,s^{-1}}$[c)]	⌀ 2 cm	Mostly air	AC/DC power source + external heater	Chamber furnace, roller kiln	Very early state[51]
UHS	Oxides Nitrides Metals	Beyond 2000 °C[d)]	None	$\approx 10^3\ ^\circ\mathrm{C\,s^{-1}}$	2.5 cm	Mostly inert	Graphite felt heated with AC/DC power source	Heating chamber	Not yet
Cold sintering	Oxides	RT–400 °C	200–600 MPa	Any	2 cm	Any	Heated dies	Warm press, FAST/SPS	Not yet
FAST/SPS	All	$<2400\ ^\circ\mathrm{C}$	<400 MPa	Typically a few $100\ ^\circ\mathrm{C\,min^{-1}}$	50 cm	Vacuum, $\mathrm{Ar/H_2}$, Ar, air[e)]	Pressing tool and die	FAST/SPS with water cooling	Diamond tools, sputter targets, brake pads, luxury goods,...
Photonic sintering with lamps or lasers (FLA, SLS, blacklight)	Alumina Zirconia Porcelain Oxides Metals	Beyond 2000 °C	None	FLA: up to $10^8\ ^\circ\mathrm{C\,s^{-1}}$ SLS: $>10^4\ ^\circ\mathrm{C\,s^{-1}}$ Blacklight: $\approx 10^4\ ^\circ\mathrm{C\,s^{-1}}$	FLA: thin layers only SLS: layer by layer, up to several cm Blacklight: 4 cm wide, 0.5 cm thick	Any	FLA: Xe flash lamp SLS: laser Blacklight: Xe flash lamp, blue laser	Furnace equipped with Xe flash lamp or laser	Microelectronics, metallic electrode layers, protective coatings
Photonic sintering with IR emitters (RTA/RTP)	Oxides	$\leq 1200\ ^\circ\mathrm{C}$	None	up to $10^4\ ^\circ\mathrm{C\,s^{-1}}$	Mostly thin layers	Any	IR emitters	IR annealing furnace	Microelectronics

[a)] Melting temperature of Pt electrodes; [b)] For cylinder shaped samples optional pressure possible; [c)] In voltage to current control mode; [d)] Technology enables melting of refractory materials; [e)] Maximum 600 °C in air.

high equipment costs. As such, FAST/SPS is only used so far if conventional sintering fails. However, increasing energy prices and possible incentives for decarbonizing industrial processes (using green electricity) may change this situation. Industrial applications exist in the fields of refractories, armor, cutting tools, sputter targets, and similar. For FS, equipment costs are much lower, but contacting the parts is complicated and might involve noble metals that may stick to the ceramic part. Industrial applications of FS are very rare (the authors are aware of just one tentative). The possibility of having contactless FS would open up new possibilities, if hot spots can be prevented. Possibly, the highest industrial potential can be found among UHS and photonic sintering processes, due to the simplicity of the processes and rather low equipment costs (although special atmosphere needs to be guaranteed for preserving the heating elements in UHS and light source has to be acquired for photonic sintering). Certainly, these processes are for the moment limited to planar geometries. For photonic sintering, some methods (FLA, RTP, and SLS) are already used for a number of applications, mostly for layered structures or surface coatings. Heterogeneity of the sample properties (surface roughness, variations in density for example) coupled to nonlinear absorption of light as function of temperature might also lead in some cases to localized thermal runaway.

The only method that does not use high heating rates is cold sintering. Here, the equipment costs are relatively low as well, and the geometric limitations are the same as for SPS sintering due to the applied pressure, and not all materials can be densified with this process. However, the benefit of this method is the potential of exceptionally low sintering temperatures that allow material combinations that are not possible otherwise (e.g., polymer–ceramic). Still, applications are yet to come.

In principle, all technologies can be applied to oxide ceramics, but transfer to other material classes such as nonoxide ceramics and metals is not excluded in most cases. A common possibility for oxide ceramics is reactive sintering, where precursors are mixed and pressed together. During a short high-temperature treatment both the solid-state reaction and densification take place, leading to lower energy consumption compared to the often lengthy calcination step of the classical mixed oxide route. At the current state of development, most of the technologies are suitable for small and less complex parts as well as for functional layers and layered systems preferentially.

In order to transfer sintering methods from lab to fab, an important criterion to fulfill is the ability to produce not only samples of materials (of limited size and simplified geometry), but real sintered products. Cylindrical pellets of 10 mm diameter or dog bone-shaped specimens cannot be seriously considered as parts to be used in application. Due to the almost complete dissipation of the heating power by the sample, FS is discussed to be very efficient and economic, but scaling-up of this technology is still limited by risk of localized current path formation, especially when enlarging the sample volume. Other methods such as UHS and cold sintering also need to be demonstrated for real parts and large-area layers. For industrial application of these technologies, homogeneity of microstructure over the entire part and the relevant properties must be evaluated carefully. The complexity and cost of the equipment required as well as the processing steps (e.g., binder burn-out, the use of electrodes for electric flow, etc.) which can be automated or not have to be considered carefully as well. Finally, realistic comparison of energy and resources consumption has to be done, and not only on a lab scale but industrial environment. The total balance might be different depending on the materials to be sintered and the geometry of the component.

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Conflicts of Interest

The authors declare no conflict of interest

Keywords

ceramics, cold sintering, electric fields, flash sintering, photonic sintering, sintering, spark plasma sintering

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