



Ultrafast firing effects in Y-doped zirconia nanoparticles: Heating rate matters even under “Conventional” conditions

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ABSTRACT

The development of firing technologies like flash sintering and ultrafast high-temperature sintering has renewed interest in how heating rates influence microstructural evolution during sintering. Herein, we observe an exceptional heating-rate effect during conventional consolidation of 3YSZ nanopowder (20 nm). Increasing the heating rate from 2.5 to 50°C min⁻¹ accelerates sintering by a factor of ~1000, reversing the positions of the sintering curves in dilatometric analysis: the material sinters at a lower temperature when heated faster. We attribute this behavior to “microstructural separation” in which high-density regions of the green body draw mass from lower-density ones via surface-mediated transport, causing the formation of pores significantly larger than the grain size. This observation highlights the importance of the green shaping procedure: sintering of more homogeneous green bodies is less sensitive to the heating rate because the driving force for surface transport between differently packed regions is reduced.

1. Introduction

Although sintering has been practiced for over 25,000 years [1], its theoretical understanding started only in the mid-20th century with the first pioneering works of Burke, Coble, Kingery, and others [2–7]. A major limitation of the original sintering models was their reliance on geometrical assumptions valid only within specific density ranges, thus partitioning the sintering process into three stages: respectively occurring increasing temperature: i. neck formation, ii. densification, and iii. grain growth. A substantial advance took place in 1992 when Hansen and co-workers [8] developed the combined sintering stage model, building on the previous equations by Wand and Raj [9]. It provided a unique equation to characterize the densification pathway through the entire sintering process.

In 1996, building on Hansen's unified approach [8], Su and Johnson extended the concept into a practical framework known as the master sintering curve [10]. They concluded that if the microstructure is only a function of density (i.e., the grain/pore size depends on density and not on the thermal history leading to a certain density value), then one can identify a sintering parameter, $\theta_{(T,t)}$, often referred as the work of

sintering, which correlates with the material density, $\rho = f(\theta)$. The work of sintering is defined as

$$\theta_{(T,t)} = \int_0^t \frac{\exp(-Q/RT)}{T} dt' = \frac{R}{3\gamma\Omega D_0} \int_{\rho_0}^{\rho} \frac{G_{(\rho)}^m}{\rho \Gamma_{(\rho)}} d\rho \quad (1)$$

where Q is the activation energy for the dominant mass transport mechanism, R the perfect gas constant, t the time, T the absolute temperature, G the grain size, γ the surface energy, Ω the atomic volume, D_0 the preexponential constant for diffusion, m is an exponent depending on the densification mechanisms (usually 3 or 4), and Γ a shape factor.

Defining $\theta_{(T,t)}$ within a framework in which the microstructure depends only on ρ leads to an obvious consequence: the sintering curves plotted in the density-temperature domain should shift to the right (at higher temperatures) when the heating rate increases. In other words, faster heating schedules require higher temperatures to achieve the same value of $\theta_{(T,t)}$ (the $\frac{\exp(-Q/RT)}{T}$ function increases with T due to the thermal activation of mass transport).

However, the master sintering curve (MSC) model, often effective under conventional conditions, encounters challenges when applied to

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rapid, non-conventional sintering methods (heating rate $\approx 10^3 - 10^4$ °C min⁻¹). These include, for instance, recently developed technologies such as ultrafast high temperature sintering (UHS) [11,12], flash sintering (FS) [13–15], blacklight sintering (BLS) [16–18], flash-spark plasma sintering (F-SPS) [19–23] and more traditional approaches like fast firing (FF) [24]. In these processes, rapid heating can enhance densification [25–29] through different mechanisms. Among them, the most established are a deviation in the grain size/pore size-density trajectory [30], with fast heating promoting finer microstructures, and the development of out-of-equilibrium grain boundary complexion possessing larger diffusivities [25,26,29,31].

The influence of heating rate on the microstructural evolution at a given density level is based on the fact that coarsening, grain growth, and densification occur through different mechanisms. In particular, coarsening is driven by the chemical potential difference between the surfaces of particles possessing different curvatures. It occurs through surface-mediated mechanisms (evaporation/condensation or surface diffusion), which, possessing a low activation energy, can be activated at low temperatures. On the other hand, densification is mediated by volume diffusion (lattice or grain boundary), which is generally dominant at high temperatures; therefore, fast heating could contribute to reducing particle coarsening in the early sintering stages, resulting in fine-grained materials [30,32–36].

While coarsening is generally thought of as a single pore-pore or particle-particle interaction, Ji et al. proposed that larger-scale transport might occur [27]. In fact, reports suggest that the pore coordination changes with the heating rate in flash sintering [27] and UHS [28]. A possible mechanistic interpretation is based on an extension of the typical length scale assumed for surface diffusion [27]. When substantial surface transport occurs before densification, the hypothesis behind the MSC model does not apply as the right side of Equation 1 depends on the thermal history and not on density only. This can result in incorrect calculation of the activation energy for sintering through the MSC model, which might represent a mere fitting parameter rather than an entity related to a well-defined diffusion pathway [37].

Although heating-rate acceleration phenomena are usually observed in nanopowders [25,38–40], we recently found that for coarser systems, the effect of heating rate in fast-firing technologies was more modest [41] or nearly absent [42]. Hence, powders with similar chemistry but different particle size often appear to have different responses to rapid heating. Moreover, there is a robust literature showing that the *Q* measured by the MSC model can be significantly different for the same powder when shaped through different technologies [37]. While the origin of such an anomaly is not completely clear, one might argue that the “quality” of the particle packing can itself change the ratio between surface-mediated and bulk-mediated transport; thus making the material more or less adherent to the traditional MSC hypothesis.

Emerging questions are, therefore, “When the particle size increases, fast heating appears less effective. What happens at very small length scales, such as nanopowders. Specifically, could the heating rate still influence sintering kinetics even under conventional conditions of a few °C min⁻¹. Moreover, does the green shaping procedure affect the rapid sintering behavior? This manuscript addresses these questions by examining the consolidation of 20 nm 3YSZ nanopowders, with a standard Tosoh 3YSZ as a reference for comparison.

2. Experimental procedures

To prepare the green pellets, a stock solution was first prepared and adjusted to approximately pH 10.5 using ammonium hydroxide (28–30 wt%, J.T. Baker, USA). The 20 nm yttria-stabilized zirconia nanopowder (3YSZ, US Research Nanomaterials, Inc., USA) was then mixed with this solution. Approximately 0.15 g of powder (75 wt%) was homogenized with 25 wt% of the stock solution using a mortar and pestle. The mixtures were uniaxially pressed at 350 MPa into 6 mm pellets, followed by drying.

While the main focus of this manuscript is the US Nano system, some samples were also prepared with a reference YSZ powder for comparison. 3YSZ granulated (3% grade binder) ready-to-press commercial powder with 90 nm particle size (TZ-3YSB-E, Tosoh Corporation, Tokyo, Japan) was also used under the same shaping conditions. The nominal composition of the different impurities in the two powders from the manufacturer are (wt%), Tosoh: Al₂O₃ 0.1–0.4%, SiO₂ < 0.02%, Fe₂O₃ < 0.01%, Na₂O < 0.06%; US Nano: Al₂O₃ 0.0035%, SiO₂ 0.0008%, Fe₂O₃ < 0.0039%, NiO 0.0025%, Cl < 0.03%; TiO₂ 0.0055%, CuO 0.0015%, ZnO 0.0006%, MgO 0.005%. The starting powder were characterized by X-ray diffraction (XRD), using an Italstructures IPD3000 diffractometer equipped with a Dectris Mythen 1 K hybrid pixel detector and a Cu-anode X-Ray source (@ 40 kV, 30 mA).

Some additional samples were also prepared using a colloidal approach to improve the homogeneity of the green body obtained with the US Nano powder (20 nm). Accordingly, the powder was ball-milled for 1 h with an ammonium polyacrylate dispersing agent (Darvan® 821-A, Vanderbilt Minerals, LLC, Norwalk, CT, USA) to reduce particle agglomeration. Ball milling was operated with zirconia spheres and using a Turbula mixer. The mixture was bound using polyvinyl alcohol (PVA; Mowiol® 10–98, Sigma-Aldrich, Mw $\approx$ 61 000) and polyethylene glycol (PEG; Sigma-Aldrich, average Mn $\approx$ 400) as binders, ready for pressing. The amount of water, dispersant and PVA-PEG solutions was 44.4%, 5.5% and 5.5% of the powder weight, respectively. The slip was then cast in a gypsum mold and, after drying overnight at 65°C, was ground. The obtained powder was then used to shape additional pellets following the procedures previously described. Note that these samples are referred to as “slip press” in the manuscript; if not stated, all the other samples are produced just by pressing without any pre-colloidal processing.

The green porosity was characterized by N₂ physisorption after a thermal treatment at 600°C, allowing a full removal of the moisture and binder without significant shrinkage. Gas adsorption-desorption isotherms were collected using a Quantachrome Instrument (Anton Paar, USA) with nitrogen utilized as the adsorbate gas at 77 K. The pore size distribution was computed according to the BJH model. Furthermore, the volume and size of the pores were assessed by mercury intrusion porosimetry (MIP) (Carlo Erba). The total pore volume from the BJH analysis and Hg porosimetry was used to compute the green density assuming a theoretical density of 6.1 g cm⁻³.

Dilatometry analyses were carried out on the pressed green bodies at heating rates of 2.5–50 °C/min up to 1500°C using a heating microscope (EM301, Hesse Instruments, Osterode am Harz, Germany). Some of the analyses were also conducted with an isothermal holding at the selected temperatures (925°C–1225°C) for various dwell times.

The green samples were subjected to either conventional sintering or fast-firing at different temperatures. For the fast firing process, the green pellets were quickly introduced into the hot zone of the tube furnace (Nabertherm P330, Lilienthal, Germany) at temperatures ranging from 1100 to 1450°C and held there for 10 min. The process was carried out in air atmosphere. After the set dwell time, the samples were rapidly taken out of the furnace. The conventional sintering experiments were carried out in the same furnace with a heating rate of 10°C min⁻¹. The same sintering temperature and dwelling time as those applied in FF were employed.

The 3YSZ nanopowder (20 nm) from US Research Nanomaterials was also densified by Spark Plasma Sintering (SPS) at the Plateforme Nationale CNRS de Frittage Flash (University of Toulouse), and using a 632LX model (Fuji Electronic Industrial CO., Japan). As a procedure detailed before, 600 mg (75 wt%) of 3YSZ nanopowder was mixed manually in a mortar for 10 min with 25 wt% of the aqueous stock solution (pH 10.5 adjusted with ammonium hydroxide). The mixtures were then dried in an oven at 110°C for 12 h, before being introduced into an 8 mm diameter graphite SPS die to perform the consolidation of the 3YSZ ceramics. The SPS experiments were conducted in a dynamic argon atmosphere vacuum, after reaching an initial level of 16 Pa in the

chamber with a primary pump. The system's heating is provided via a pulsed direct current with a pattern of 40 ms on 7 ms off, the temperature is monitored and regulated using an optical pyrometer focused on a hole (3 mm in depth) at the external surface of the graphite die. A preheating step at $300^{\circ}\text{C}\cdot\text{min}^{-1}$ until 600°C was performed to reach the pyrometer's detection threshold. The uniaxial pressure of 5 MPa is gradually applied over these 2 min. After a 3-minute dwell at 5 MPa and 600°C , to give the system time to adjust to particle rearrangement and homogenize the temperature across the entire sample, a heating ramp (10 , 50 or $100^{\circ}\text{C}\cdot\text{min}^{-1}$, depending on the experiment) is applied until the target temperature, either 1150°C or 1400°C .

The densification curves of 3YSZ samples during the SPS thermal cycles were deduced from the displacement data acquired using a sensor located on the lower electrode by which the load is applied. Blank experiments (without samples) were also conducted to account and subtract the contribution of the expansion of the entire graphite column. It is therefore possible to determine, from the raw measurements, the vertical shrinkage of the 3YSZ ceramics during their consolidation. The thermal expansion of YSZ nanopowder is also considered, with a thermal expansion coefficient α (YSZ) = 10^{-5} K^{-1} , consistent with the near-complete stabilization of the tetragonal phase. The instantaneous relative density is thus determined based on the vertical shrinkage of the sample during densification by SPS. Given the final thickness of the pellet e_f and its final relative density D_f (measured by three-weighing Archimedes' method), measurements of the instantaneous thickness of the sample e_i are used to infer D_i , $D_i = \frac{D_f}{e_i} e_f$.

The bulk densities of the samples were measured by Archimedes'

method using water as the buoyancy medium. The fracture surfaces were observed by FEG-SEM (SUPRA V40 and Zeiss Ultra Plus, Carl-Zeiss, Germany) after sputtering a conductive coating.

To evaluate the evolution of the powder during sintering, a "quasi in situ" experiment was designed. The YSZ powder was deposited on an alumina wafer on which a scratch was made using a sharp alumina knife. After cleaning the wafer in an ultrasonic bath, a small amount of zirconia powder was placed on the surface and lightly pressed against the surface. The surface was then gently wiped with a tissue and ethanol to remove excess powder, leaving zirconia particles trapped within the scratch. The powder was then observed by SEM after heat treatments at different temperatures for different times.

3. Results

The starting powders are a mixture of the tetragonal and monoclinic polymorphs (Fig. S1). The amount of tetragonal phase is larger in the US Nano system, likely due to the stabilization of this polymorph in small nanopowders. There is a clear broadening of the diffraction peaks in the US Nano system, consistent with a small particle size (20 nm).

The N_2 physisorption isotherm and the BJH pore size distribution obtained from the green bodies after calcination at 600°C are presented in Fig. 1a,b, while mercury porosimetry data are presented in Fig. 1c,d. The relative green density was estimated from the total pore volume (Hg porosimeter and BJH) and was 52.1–52.8% for Tosoh and 47.2–47.3% for US Nano. The US Nano, undergoing pre-colloidal processing before pressing, showed an intermediate green density value, ≈ 49.4 –51.5%. The BJH pore size distribution can be identified for the US Nano, it being

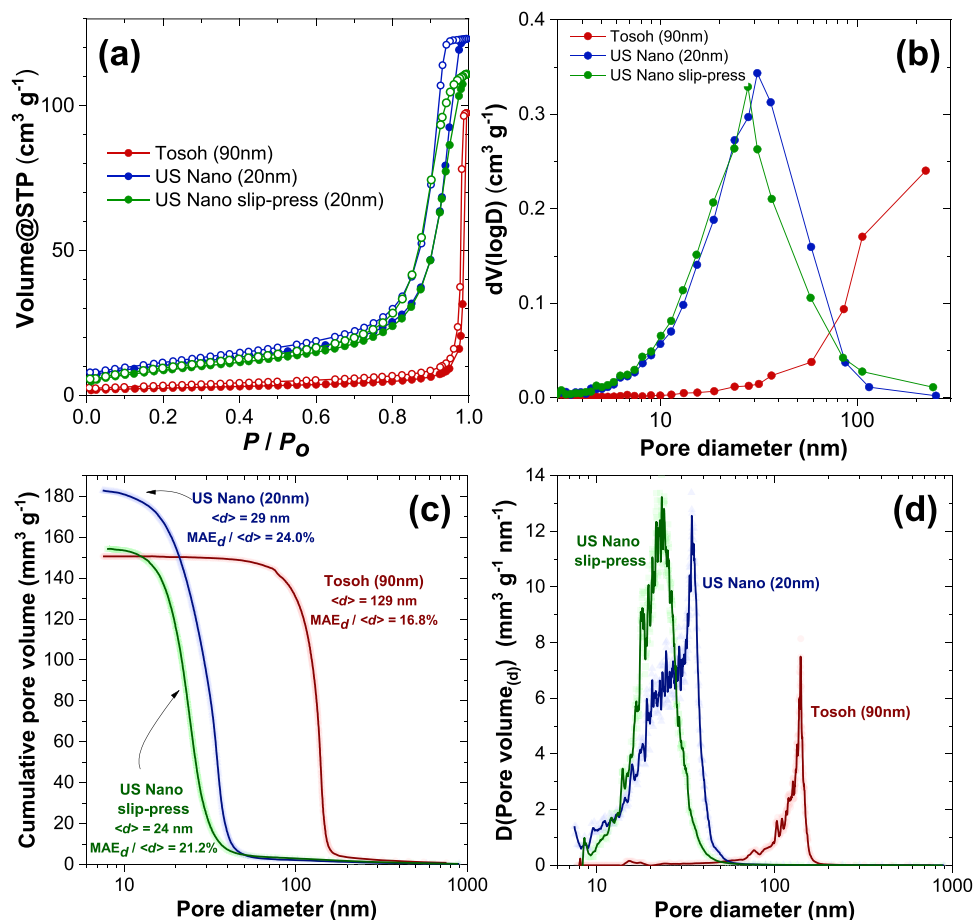


Fig. 1. (a) Nitrogen physisorption isotherms on different green bodies after calcination at 600°C and (b) the corresponding pore size distribution derived through the BJH model. (c) reports the Hg intrusion porosimetry of the green bodies with corresponding statistical variables (average pore diameter, $\langle d \rangle$, and mean absolute error, MAE_d , of the pore size distribution), (d) reports the derivative of the cumulative pore volume data in (c).

mainly below 100 nm; while the Tosoh powder possesses larger pores at the boundary of the detection limit of N_2 physisorption. The pore size distribution appears narrower for the US Nano shaped after pre-colloidal processing than for the as-received and pressed powders. In particular, the US Nano powders not undergoing colloidal processing are characterized by a long tail at larger pore sizes. The specific surface area (SSA) estimated by the BET method was about $8.9 \text{ m}^2 \text{ g}^{-1}$ for the Tosoh powder and $32.3\text{--}36.8 \text{ m}^2 \text{ g}^{-1}$, which falls within the reported SSA data

from the manufacturers.

Hg-intrusion porosimetry allows for observing the pore size distribution with a higher resolution. The Tosoh powder is characterized by a volume-averaged pore size ($\langle d \rangle$) of about 130 nm, the pore size reduces to about 24 nm for the slip-pressed US Nano and about 29 nm for the as-received US Nano. The pore size distribution appears narrow for the Tosoh, while it is clearly larger for the US Nano. In particular, we estimated the mean absolute error ($MAE_d = \sum_i v_i |d_i - \langle d \rangle| / \sum_i v_i$,

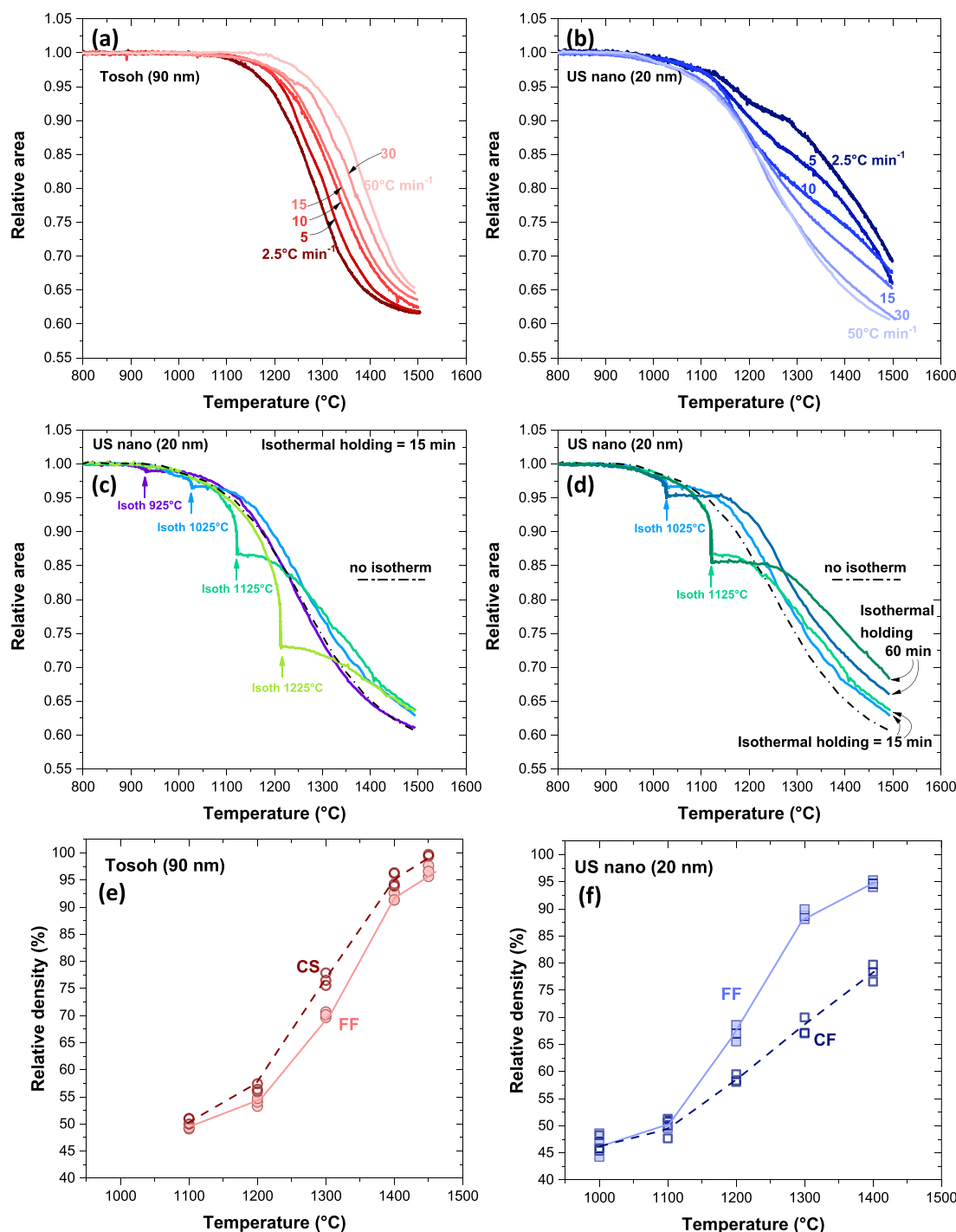


Fig. 2. Dilatometric tests under different heating rates on (a) Tosoh 90 nm and US Nano 20 nm YSZ; (c,d) illustrate the effect of different isothermal holding (15 and 60 min) at different temperatures on the sintering behavior of the US Nano system, the samples in (c,d) were heated at $50^\circ\text{C min}^{-1}$. Note that the deviation in the dilatometric curves right before the isotherm can be explained by an instrumental artifact due to a reduction of the heating rate of the sample when approaching the isotherm. Relative density evaluated by the Archimedes' method after conventional firing ($10^\circ\text{C min}^{-1}$) and fast firing at different temperatures with a holding of 10 min at the sintering temperature for (e) Tosoh and (f) US Nano YSZ.

and d_i being the pore volume and diameter in each class) and normalize it over the average pore size. This quantity is representative of the dispersion in the pore size. It progressively increases moving from the Tosoh (16.8%) to the slip-press US Nano (21.2%) to the “just-pressed” US Nano system (24.0%). In particular, the just-pressed US Nano system shows a clearly bimodal pore-size distribution likely originating from some agglomeration of the nanopowder (Fig. 1d).

The dilatometric response of uniaxially pressed Tosoh (90 nm) powder is typical; as the heating rate increases from 2.5 to 50 °C min⁻¹, the shrinkage curves shift to higher temperatures (Fig. 2a). This is expected, since diffusion-controlled consolidation requires higher temperatures when the available sintering time is reduced by a rapid heating schedule.

In contrast, the trend is reversed for the US Nano (20 nm) powder (note that where not otherwise stated herein we refer to the US Nano powder not undergoing slip processing). In this powder system, fast heating leads to a marked decrease in the sintering temperature (Fig. 2b). This unusual behavior is corroborated by sintering experiments comparing fast firing (10 min dwell time) with conventional sintering (10 °C min⁻¹ up to the sintering temperature, followed by a 10 min dwell). For the Tosoh (90 nm) powder, conventionally sintered samples are consistently as dense as, or slightly denser than, fast-fired

ones. However, for the finer US Nano nanopowder, fast firing produces substantially higher densities (Fig. 2e,f).

We also notice that the dilatometric response of US Nano (20 nm) powder is “irregular” under slow heating; at 2.5 °C min⁻¹ the shrinkage curve shows multiple inflections and changes in concavity. In contrast, under rapid heating (50 °C min⁻¹), the behavior becomes regular and follows an approximately sigmoidal profile. These inflections occur primarily in the 1000–1300 °C temperature range.

To gain insight into the microstructural evolution within this “low temperature” window, we performed dilatometry at 50 °C min⁻¹, while introducing a 15 min isothermal dwell at different temperatures (Fig. 2c). An isotherm at ~925 °C yields a sintering curve that fully overlaps with the reference curve without a hold, indicating no measurable impact on subsequent high-temperature densification. On the other hand, a 15 min hold at ~1025 °C produces a pronounced delay in the shrinkage curve. This delay becomes stronger at 1125 °C and then saturates, or is even slightly reduced, when the hold temperature is increased to 1225 °C. Applying longer isotherms (1 h), further amplifies the sintering delay in the US Nano (20 nm) powder (Fig. 2d).

Based on the dilatometric data, it is possible to extrapolate a master sintering curve (MSC) for the Tosoh (90 nm) powder (Fig. 3a). As expected, when the density (calculated assuming isotropic shrinkage) is

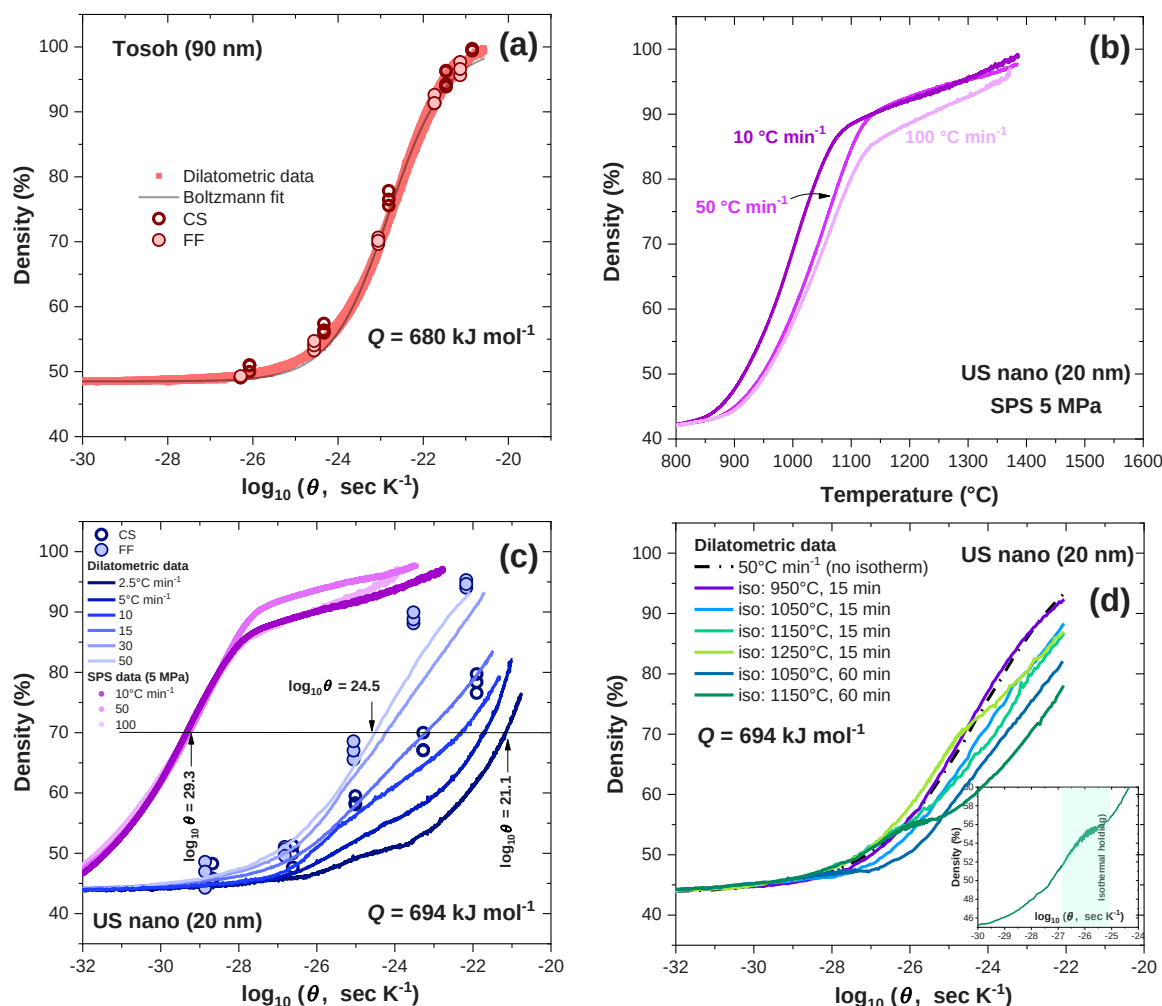


Fig. 3. (a) master sintering curve calculated based on the dilatometric data for the Tosoh powder (from Fig. 2a) with an activation energy of 680 kJ mol⁻¹, the datapoints from conventional firing and fast firing in the tube furnace are also reported (data from Fig.1e). (b) Relative density for US Nano 20 nm system as a function of temperature in SPS under 5 MPa, the relative density was estimated based on the SPS piston displacement. (c) MSC extrapolated from the SPS data of the US Nano, the dilatometric data (from Fig.1b), and conventional/fast firing datapoints are also reported (from Fig.1f). (d) reports the density vs. work of sintering plot for the US nano sample subjected to different isotherms inside the dilatometry (data from Fig.1c,d), the inset shows the deviation from the regular sigmoidal shape during the isothermal holding.