

plotted against $\log(\theta)$, all the dilatometric data points obtained under different heating conditions collapse into a single MSC. The Q minimizing the error was about 680 kJ mol^{-1} . This value is slightly larger than the norm, but it aligns with literature data for the same powder [42]. Remarkably, the data obtained by conventional sintering and fast firing closely follow the dilatometric MSC. To compute the work of sintering in the FF experiment, we assumed an effective sintering time of 9 min (assuming that 1 min was used for heating up the sample and the alumina crucible).

Given the inverse relation between strain and heating rate for US Nano (20 nm) (Fig. 2b), it is not possible to apply the MSC model. As presented below, one of the main assumptions for the MSC model, “the microstructure depends on density only,” is not maintained.

When pressure-assisted sintering is applied using SPS for the US Nano (20 nm) powder, most consolidation occurs below 1100°C (Fig. 3b); that is largely within a temperature range below, or just at the boundary of the conditions that lead to a loss of sintering ability (see the isothermal hold-effect in Fig. 2c). Under these conditions, the density-heating rate relation becomes regular again: increasing the heating rate shifts the dilatometric curves to higher temperatures (Fig. 3b).

These data, therefore, allowed us to derive an approximate master sintering curve. We emphasize that this MSC is approximate, since the actual sample temperature in SPS may deviate from the measured value,

and the displacement-based density measurement is less accurate than in conventional dilatometry. Nevertheless, it is notable that the estimated activation energy is 694 kJ mol^{-1} , which is close to the value previously measured for the Tosoh powder. This finding suggests that densification in both powders is governed by a similar thermally activated process.

Using the activation energy estimated from SPS for the US Nano (20 nm) powder the density evolution from dilatometry (Fig. 2b) and the densities measured after conventional and fast firing experiments (Fig. 2f) can be plotted in the $\log(\theta)$ space (Fig. 3c). In this representation, the curves do not overlap; therefore, an MSC cannot be defined.

Several trends emerge: (i) for a given value of the work of sintering, higher heating rates consistently yield higher densities; (ii) the conventional-sintering data align closely with the dilatometry curves obtained at $10\text{--}15^\circ\text{C min}^{-1}$, consistent with the heating rate used in the tube furnace; and (iii) the fast-firing densities are comparable to the $50^\circ\text{C min}^{-1}$ dilatometry results at low $\log(\theta)$, but exceed the dilatometric data at high $\log(\theta)$ (i.e., at higher temperatures during fast firing).

Similarly, Fig. 3d reports the density evolution for the samples that were isothermally held in the dilatometer (data from Fig. 3c,d). We can clearly observe that the plots in the $\log(\theta)$ space do not follow the regular sigmoidal shape (excluding the dash and dot plot representing the sample without an isotherm). The deviation from the isotherm-less

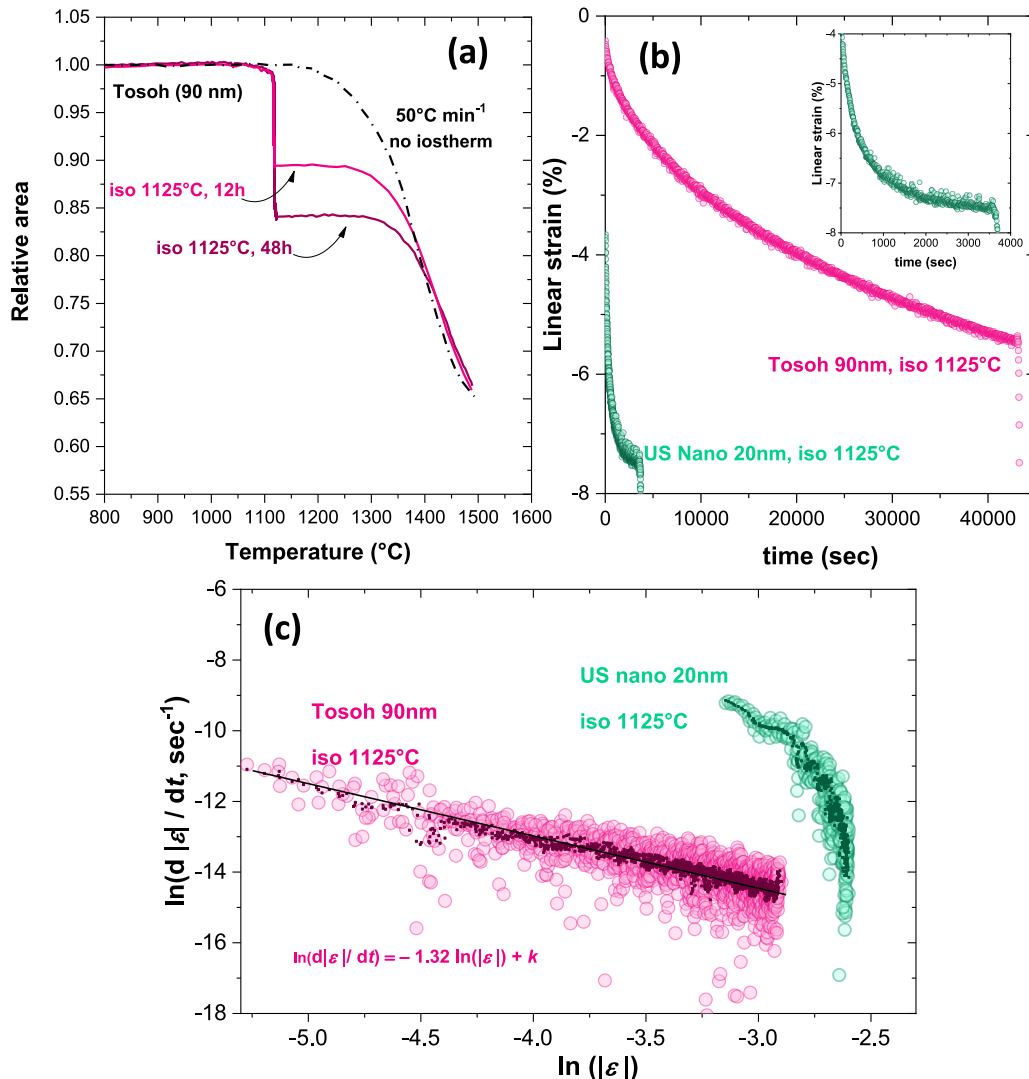


Fig. 4. (a) Dilatometric data obtained at $50^\circ\text{C min}^{-1}$ from the Tosoh 90 nm powder with and without an isothermal hold at 1125°C ; (b) linear strain during the isothermal hold at 1125°C for both Tosoh 90 nm and US Nano 20 nm systems; linearization of the data in (b) according to (c) Eq. 3.

sample occurs during the isothermal step, as shown in the inset in Fig. 3d. During the isothermal hold, the density increases less than would be expected from the acquired $\log(\theta)$ values; indeed, the density data points collected during the isotherm consistently fall below those of the sample processed without an isothermal hold.

While a short isothermal hold (15–60 min) at relatively low temperatures markedly degrades the sintering behavior of the US Nano (20 nm) powder, the same is not observed for the coarser Tosoh (90 nm). In the Tosoh system, even an “extreme” isotherm hold of 12 h or 48 h at 1125°C does not lead to a significant loss of sintering ability (Fig. 4a). In fact, the final part of the dilatometric curves, after the isotherms, nearly overlaps that of the sample processed without any hold.

Examining the linear strain during the 1125°C isotherm hold, we can observe that the strain rate decays for both powders with time (Fig. 4b), however, the decay is significantly faster for the US Nano (20 nm) powder. In summary, the US Nano (20 nm) powder shows a quick loss in its densification kinetics during the isothermal hold. To model this data, we can consider that, in the early sintering stages, the strain rate follows [43]

$$\dot{\varepsilon} = \frac{k_{(T,a,\Gamma)}}{n} \varepsilon^{1-n} \quad (2)$$

where ε is the linear strain, $k_{(T,a,\Gamma)}$ is a function including the thermal activation, a is the particle size, Γ is the sintering mechanism, and n is characteristic exponent depending on the densification mechanism. This can be linearized as:

$$\ln(\dot{\varepsilon}) = \ln\left(\frac{k_{(T,a,\Gamma)}}{n}\right) + (1-n) \ln(\varepsilon) \quad (3)$$

Its integral form is the well-known expression [3]:

$$\varepsilon^n = k_{(T,a,\Gamma)} t \quad (4)$$

or

$$\ln(\varepsilon) = \ln(k_{(T,a,\Gamma)}) + \frac{1}{n} \ln(t) \quad (5)$$

Using Eq. 3 and Eq. 5 it is possible to evaluate the values of n based on the logarithmic representation of strain, time, and strain rate data. Herein, we used only the differential equation (Eq. 3), which is more

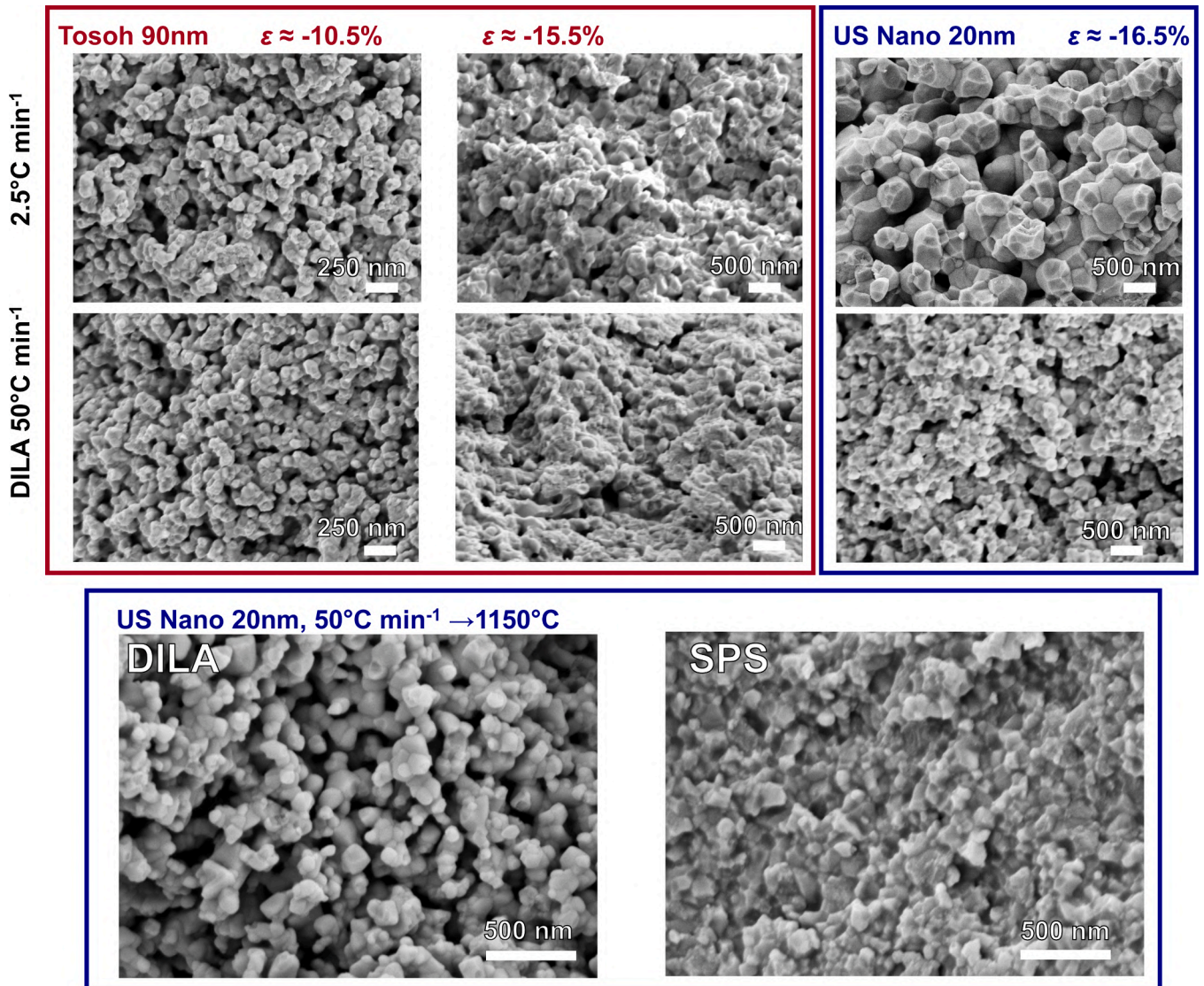


Fig. 5. The top panel presents secondary electron SEM micrographs of the cross-section of US Nano and Tosoh powders sintered in the dilatometer under different heating rates at a similar linear strain level. The bottom panel compares the fracture surfaces of the US Nano YSZ obtained at 1150°C under 50°C min⁻¹ in the dilatometer and SPS (5 MPa).

accurate than the integral form that assumes the strain acquired during the heating ramp is negligible. The analysis is also limited to data points where the strain is below $\approx 7\%$, corresponding to a maximum relative density of about 62%.

The plots in Fig. 4c indicate that the data from the Tosoh (90 nm) powder closely follow a linear trend, as expected by the linearization of the sintering equations. Based on the slopes of the curves and using Eq. 3, can be estimated to be around 2.32, which is in rather good agreement with densification controlled by lattice diffusion ($n = 2.5$, while grain boundary diffusion is associated with $n = 3$). On the other hand, the data for the US Nano (20 nm) powder are not very linear, with a notable decrease in the strain rate as sintering proceeds. Using a linear fit to match the experimental data, the resulting exponent n is extremely high (larger than 5, and in some regions even approaching 10) and has no physical meaning based on the traditional sintering models.

The SEM micrographs (Fig. 5 and Fig. 6) provide microstructural support for the dilatometry data. First, we note that the microstructure at a certain strain level (same density) is weakly dependent on the heating rate used for processing the Tosoh 90 nm powder (Fig. 5). Such an observation is not valid for the US Nano (20 nm) powder system where coarser microstructures are formed with a decreasing heating rate (Fig. 5). The micrographs also confirm that SPS provides effective consolidation at 1150°C under 5 MPa, while the sample sintered in the same conditions inside the dilatometer is still very porous (Fig. 5). The microstructure after SPS appears dense and with a finer grain size,

similar or smaller than the material sintered in the dilatometer.

The US Nano (20 nm) samples treated in the dilatometer up to 1500°C under a slow heating rate ($2.5^\circ\text{C min}^{-1}$) are porous and characterized by large pores and grains. The grain size ranges between ≈ 400 and 800 nm (Fig. 6). On the contrary, the sample sintered under fast heating conditions ($50^\circ\text{C min}^{-1}$) shows a faceted grain morphology and a well-defined microstructure. The grain size is sub-micron, ranging from about 150–400 nm. When the heating rate is fast ($50^\circ\text{C min}^{-1}$), up to 1500°C, but an isotherm is introduced (1 h at 1125°C), the final microstructure is again porous and characterized by abnormal grains (sometimes larger than $1\ \mu\text{m}$) combined with grains smaller than a few hundred nanometers.

During isothermal holding (1 h) at 1125°C, the microstructure (bottom panel of Fig. 6) of the US Nano (20 nm) system largely evolves, even if the shrinkage is relatively limited (linear strain during the isotherm $\approx 4\%$). The isothermal holding induces substantial coarsening with a notable increase in the grain size. The initial microstructure appears rather homogeneous and fine. Such features disappear in the isothermal stage, and regions with substantially different densities develop. We can clearly observe that at the end of the isotherm, large areas (including many grains) are fully dense, while large pores form between these fully-densified regions.

To corroborate the microstructural evidence from SEM, we measured the pore size distribution by Hg intrusion porosimetry in the US Nano samples sintered in the dilatometer at 10 and $50^\circ\text{C min}^{-1}$. The average

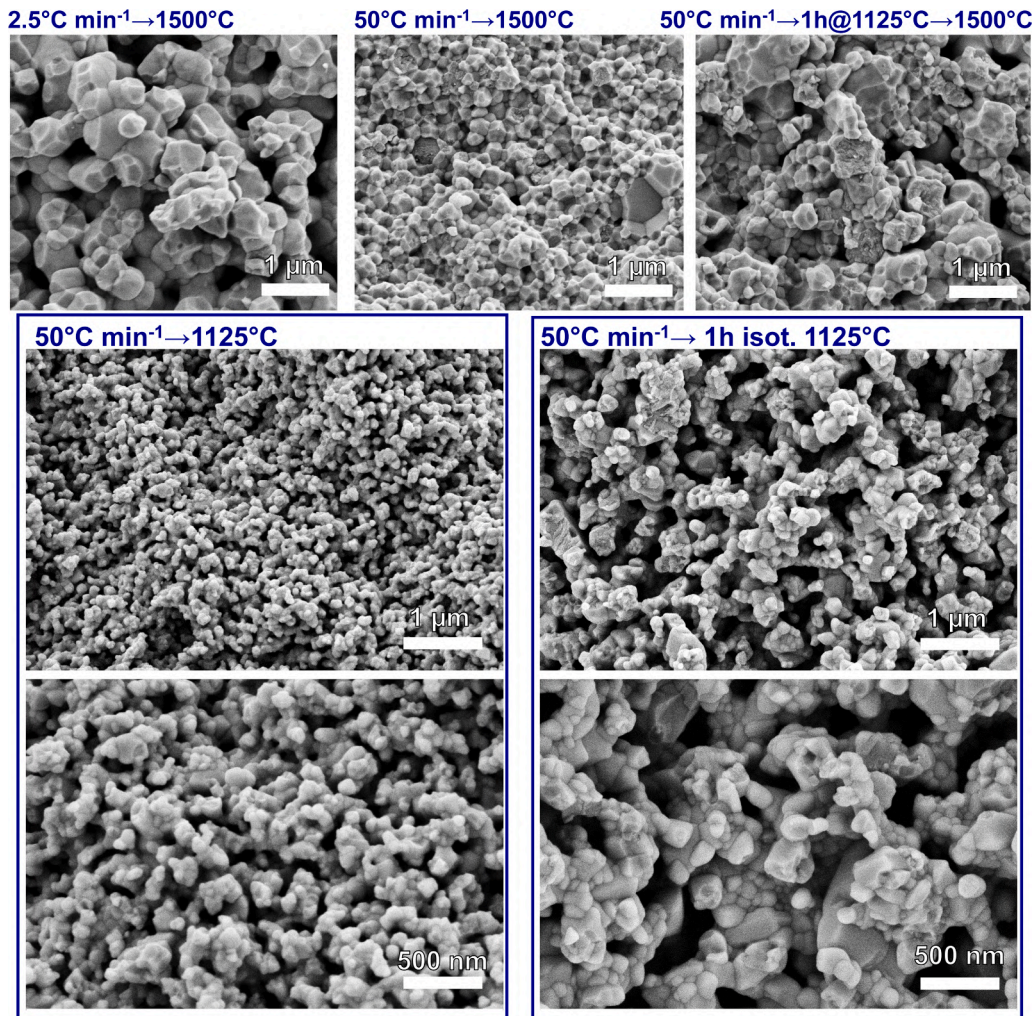


Fig. 6. The top panel presents secondary electron SEM micrographs of the cross-section of US Nano YSZ sintered in different conditions up to 1500°C in the dilatometer. The lower panel compares the microstructures at the beginning and at the end of a 1h-long isotherm at 1125°C.

pore size together with the MAE of the pore size distribution is reported in Fig. 7 and confirms a substantial refinement under fast heating. Note that the data may not fully represent the state during sintering at high temperatures; in fact, samples processed at $50^\circ\text{C min}^{-1}$ can undergo substantial evolution during cooling. Besides this limitation, the data fully support the microstructural evidence previously described.

Fig. 8 reports SEM micrographs obtained on US nano powder deposited on an alumina substrate after different treatments. The regions highlighted by the white arrows point out clear de-sintering phenomena based on the collapse of polycrystalline bridges. Note that the breakage of the polycrystalline bridges can be partially influenced by the constraint exerted by the sintered, rigid alumina substrate. Some regions of the micrographs apparently lose mass during the treatments (magenta circles) while other regions reach near full-density (blue circles). The Tosoh powder treated at the same temperatures shows a much more stable microstructure (Fig.S2).

Fig. 9 presents the dilatometric behavior of the US Nano (20 nm) powder when the green body was formed by uniaxial pressing after a pre-colloidal treatment designed to improve homogeneity. These samples, labeled “slip-press” in the figure, do not exhibit the inversion in the strain curves with heating rate, namely the anomalous decrease in the sintering temperature with increasing heating rate observed in Fig. 2b. With pre-colloidal processing, the US Nano powder heated at $50^\circ\text{C min}^{-1}$ sinters at a slightly higher temperature than when heated at $2.5^\circ\text{C min}^{-1}$ (Fig. 9a).

However, the response is still not fully typical. The dilatometric curves remain very close to one another; they partially overlap, and their shape is not a clean sigmoidal profile. Moreover, when a long isothermal dwell is applied under conditions similar to those used for the Tosoh system (Fig. 4a), then the US Nano powder still loses a substantial fraction of its sinterability (Fig. 9b).

4. Discussion

The main findings of this work are:

- (i) Heating rate affects sintering in YSZ nanopowders (US Nano, 20 nm) even under “conventional” conditions ($2.5\text{--}50^\circ\text{C min}^{-1}$). In other words, ultra-rapid heating methods such as FS or UHS are

not required to observe deviations from the expected sintering behavior.

- (ii) Fast heating can reduce the influence of defects in the green body, such as density fluctuations.
- (iii) In nanopowder systems (US Nano, 20 nm), the effect of heating rate can be amplified or diminished by changing the green body shaping procedure.

Specifically, the heating rate effect is so strong in the US Nano (20 nm) powder that it can reverse the strain-heating rate relation commonly observed in dilatometry (Fig. 2b). These observations are corroborated by the fast firing and conventional sintering experiments in a tube furnace at different temperatures (see the differences between Tosoh 90 nm and US Nano 20 nm in Fig. 2.e,f) and are coherent with previous UHS experiments in the same system [28]. As such, the work of sintering, θ , required to achieve a certain density can increase by 3 orders of magnitude when the heating rate decreases from 50 to $2.5^\circ\text{C min}^{-1}$ for the 20nm-sized powder (Fig. 3c, assuming a constant activation energy Q). This appears largely correlated with the microstructural evolution. In fact, the microstructure of the US Nano powder is not just a function of density, but it also depends on the thermal history: coarser microstructures are obtained (even at lower density levels) when the heating rate decreases (Figs. 5,6). This anomaly is substantially reduced for the Tosoh 90 nm system (Fig. 5).

The said loss in the sinterability of the US Nano under slow heating is related to the prolonged dwell at relatively low temperatures, where surface-mediated transport dominates. In fact, the samples undergoing a short (15–60 min) isotherm between 1025 and 1225°C do not sinter like the material without any dwell (Fig. 2c,d). This effect is not detectable in the Tosoh 90 nm powder, which does not show substantial loss in its sinterability even after a 2-day-long isotherm (Fig. 4a). In summary, a low-temperature dwell of only 15 min in the US Nano system produces effects larger than those detectable after 2 days in the coarser powder.

Such observations suggest a substantial “microstructural decay” for the US Nano system during the isotherm. There are several pieces of evidence for this. The first is the anomalous relationships between strain, strain rate, and time during isothermal holding. In fact, while the “regular” Tosoh (90 nm) system exhibits a linear relationship between these variables on a log scale (Fig. 4c), the US Nano powder does not behave linearly. In summary, the data obtained during the isothermal hold for US Nano powder do not follow traditional sintering equations. Specifically, the strain rate decreases more than would be expected, signaling a “microstructural decay” responsible for a decrease in the sintering kinetics. This leads to a clear deviation of the isothermal data points from the no-hold sintering curve in density versus $\log\theta$ space (Fig. 3d), confirming a loss in the sinterability of the material.

The microstructural decay induced in the US Nano powder during the low-temperature hold impacts the non-thermally activated component of the MSC equations. These can be highlighted by calculating the differential increase in the density induced by a differential change in the work of sintering:

$$\frac{d\rho}{d\theta} = \frac{T \exp(Q/RT)d\rho}{dt} = \frac{3\gamma\Omega\rho D_0\Gamma(\rho)}{RG_{(\rho)}^m} \quad (6)$$

Besides the obvious impact of atomic volume and surface energy, this quantity is sensitive to the sample microstructure, including the grain size, G , and the stress intensity factor, Γ . When the MSC hypotheses are respected (the microstructure depends only on the relative density), all the datapoints should collapse onto a single curve in $\frac{d\rho}{d\theta}$ versus ρ space. Fig. 10 shows that this is not the case for the US Nano system: changing the heating rate from 2.5 to $50^\circ\text{C min}^{-1}$ reduces $\frac{d\rho}{d\theta}$ by 3 orders of magnitude (or even more, assuming a constant activation energy Q). It is worth noting that there is a strong “memory” of low-temperature isothermal dwell until the final sintering stages. For instance, the 1 h isotherm at 1125°C causes a substantial, $\approx x100$ drop, of $\frac{d\rho}{d\theta}$ even at the

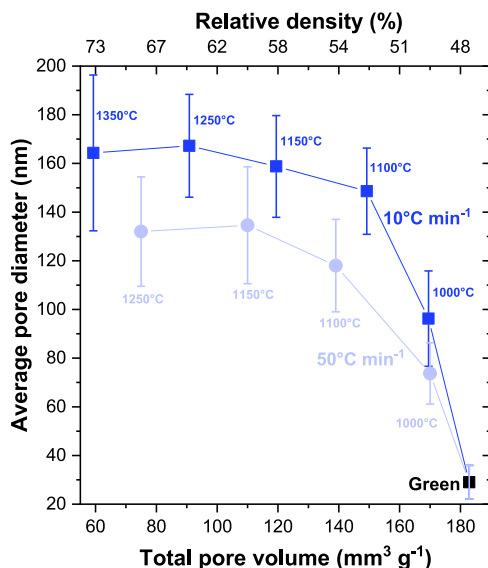


Fig. 7. Average pore size measured by Hg intrusion porosimetry in the US Nano samples sintered in the dilatometer up to different temperatures under 10 and $50^\circ\text{C min}^{-1}$. The error bar reports the mean absolute error of the pore size distribution. The relative density is computed from the total pore volume assuming a theoretical density of 6.1 g cm^{-3} and no close porosity.

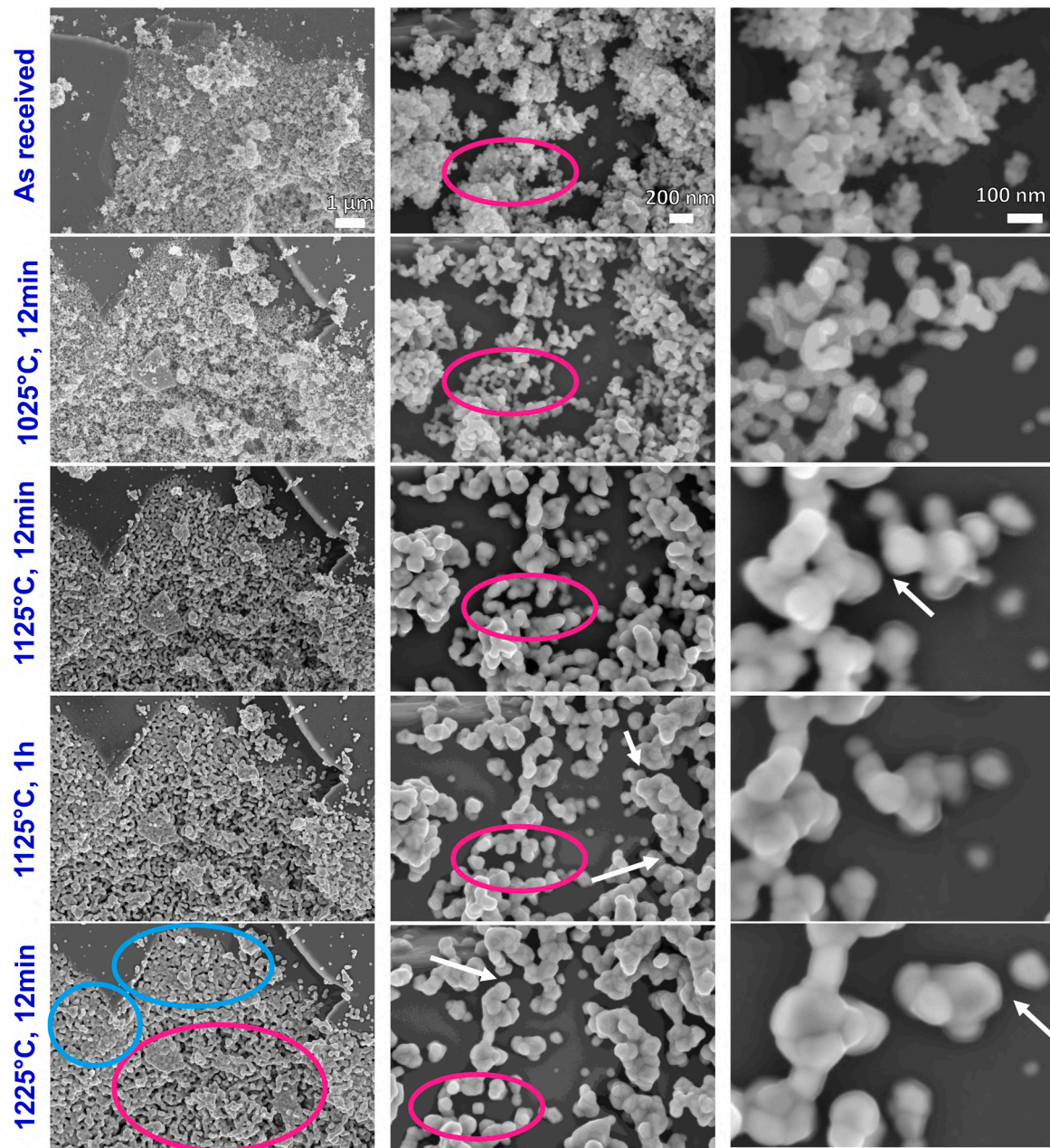


Fig. 8. Microstructural evolution during “quasi in situ” experiments on US nano powder. Each column of micrographs presents, at different magnifications, the microstructural evolution of a given region. The white arrows highlight the regions where the polycrystalline bridges collapse, the magenta circles identify regions that appear to lose mass during the thermal treatments, and the blue ones identify regions that become nearly fully dense. All the micrographs on the same line are taken at the same magnification.

end of the process. This would be coherent with a change in the microstructural scale (G) of about 3–5 times, depending on the densification mechanism. Such a change seems rather coherent with the micrographs before and after the isotherm in Fig. 6.

Taken together, these results show that the US Nano (20 nm) powder is particularly sensitive to the heating rate and this phenomenon is associated with a change in the microstructural evolution during the low-temperature dwell. Indeed, at low temperatures, mass transport mediated by surface phenomena (surface diffusion or evaporation/condensation) is dominant due to the lower energy barrier [3,44].

When we consider surface-mediated coarsening, we often think of a particle-to-particle process in which mass is removed from the smallest particles (higher curvature) and transported to larger ones (lower curvature). We note, however, that in a homogeneous packed mono-

dispersed powder, this mechanism is minor in importance since all the particles would be indistinguishable in terms of curvature, average mechanical stress, and chemical potential. In this scenario, no particle-to-particle mass transport would be expected. On the other hand, if density fluctuation exists within the green body, and in real green bodies, these always exist, a chemical potential difference between different regions of the body is established. In fact, during the early stages of sintering, the neck density, defined as the number of necks per particle, is higher in densely packed regions than in low-density regions. Since the neck is characterized by a lower chemical potential due to the negative curvature ($\Delta\mu = \gamma k\Omega$, k being the curvature), the average chemical potential in the well-packed regions is lower, driving mass to these regions. The same consideration also holds in the intermediate sintering stages, when the dihedral angle and its coordination dictate the

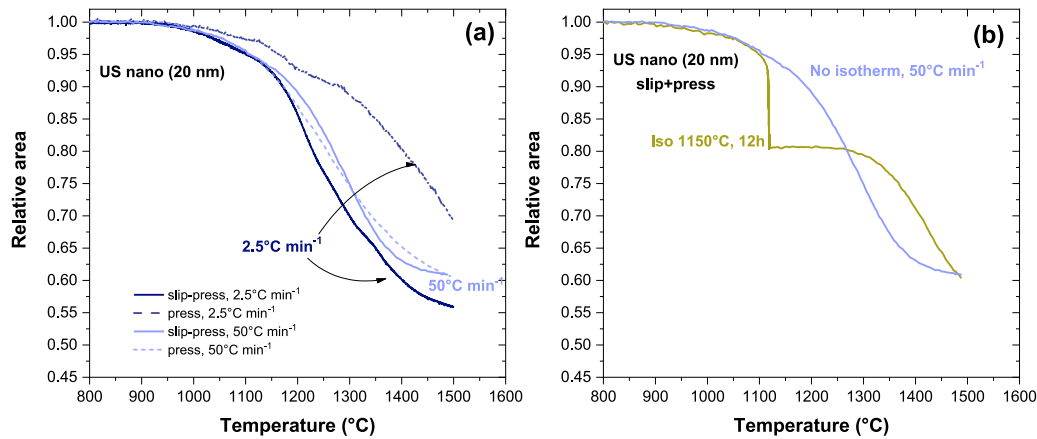


Fig. 9. (a) Dilatometric analysis of the US Nano YSZ under different heating rates with different green shaping procedures: “press” refers to the green body obtained without any colloidal pre-treatment, while “slip-press” refers to the powders that were ball-milled with a dispersant to reduce the degree of agglomeration. (b) reports the dilatometric data of slip-press samples with and without an isothermal holding.

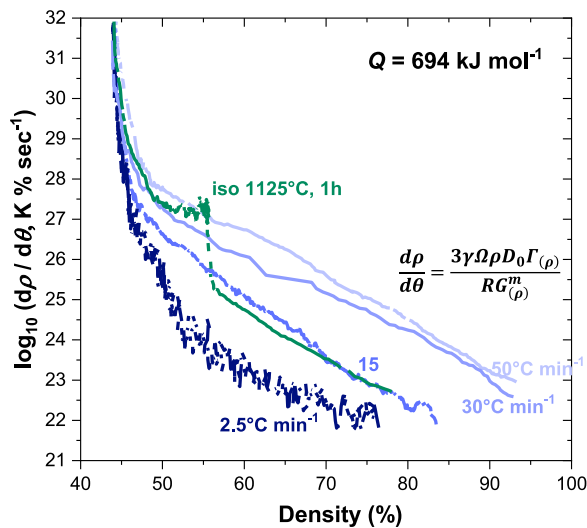


Fig. 10. $\frac{d\rho}{d\theta}$ as a function of the relative density for US Nano 20 nm. The curves were extrapolated using an activation energy of 694 kJ mol^{-1} and using the data in Fig. 2c,d.

pore curvature. In fact, pore coordination is expected to decrease in the well-packed regions. A smaller coordination leads to convex pores, while concave pores form when the coordination exceeds a threshold defined by the dihedral angle [3]. There has been an extended discussion about the thermodynamic stability of these large pores [45–47], with the first seminal works on the topic suggesting that concave pores are stable and even expand. This statement has been largely criticized and is correct only for highly symmetrical pore geometries [45]. However, we can still recognize that the chemical potential on the surface of a concave pore (low-packing regions) is larger than on the surface of a convex one (high-packing regions) due to the curvature difference. As such, the pore surface in the low-packing region can act as a source of atoms, and pores in the highly packed areas as sinks.

This cooperative multiple-particle phenomenon can be deduced from the micrograph in the bottom part of Fig. 6. During the low-temperature isotherm, the US Nano system develops large pores whose size is substantially larger than the grain size. This indeed increases the pore coordination above the critical values, making them (theoretically) stable. The formation of these large pores is coupled with the development of fully dense regions composed of several grains, which can originate from areas in the green body with higher packing density. This results in an

average increase of the pore coordination when the heating rate is slow. The said observation is consistent with previous literature on flash sintering and UHS [27,28], which have been shown to suppress the formation of large pores (significantly larger than the grain size).

There are several pieces of evidence of this cooperative multiple-particle transport. The first is actually the formation of the fully dense areas during the isotherm at 1125°C. Let's assume that due to a certain level of agglomeration, the hard and dense agglomerates present in nanopowder systems form a kind of percolative skeleton during pressing. At the end of the isotherm, the linear shrinkage was only about 7.5% (Fig. 4b). To achieve full densification, with such a strain, the starting green density of those regions should exceed 79%, a value which is well above the ideal theoretical packing of a mono-dispersed system (72%). In other words, the shrinkage does not justify the formation of fully dense areas. The only possible explanation for their existence is that they densify not only by shrinking but also by accumulating additional mass from the low-density regions: the grain centers do not get much closer, but the grains grow within the pores. It is important to note that this local densification mechanism, where pore removal is mediated by coarsening, contributes to keeping the pore coordination low (due to grain coarsening and pore shrinkage) in the packed regions. This keeps the chemical potential of the pore surfaces in these regions below that of the low-packing region, where the opposite effect takes place (the largest pores expand and the grain shrinks).

A second argument against the idea that complete densification in well-packed regions can be achieved solely through volumetric shrinkage, which must be mediated by volume transport, is schematically illustrated in Fig. 11. If bulk mechanisms dominated, the porosity in the low packing region should also shrink and decrease in size at the same rate as in the high density matrix. Experimentally, we did not observe this behavior. Instead, we measured only limited shrinkage (Fig. 4b) and observed the formation of large pores that were significantly larger than the grain size. Such pores cannot form from uniform shrinkage alone. Their formation requires mass transfer between different regions of the green body, which concentrates porosity in areas with the highest chemical potential, namely the low packing regions. This long-range transport is activated at low temperatures and is therefore expected to be governed primarily by surface-mediated processes (Fig. 11). The “quasi in situ” micrographs support this hypothesis, pointing out that certain areas of the sample lose mass while others get denser (Fig. 8).

Interestingly, if the green pressing follows a slip preparation that improves the green density and the homogeneity of the pore size distribution (Fig. 1), then the heating rate impact on densification of the US Nano powder is reduced (Fig. 9). This confirms that the inhomogeneity

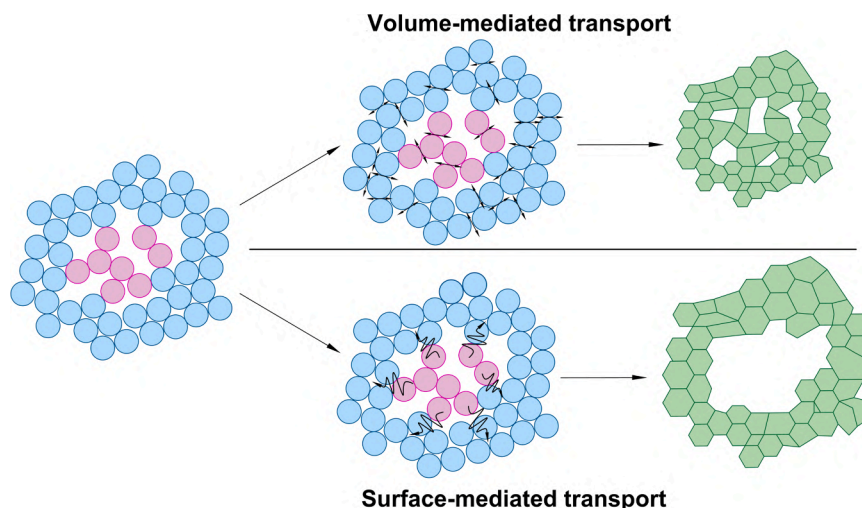


Fig. 11. Schematic representation of the evolution of a green including density fluctuation in the case of transport dominated by bulk and surface phenomena.

in the green bodies is strictly connected to the exceptional heating rate impacts on densification of the nanopowder system.

We cannot rule out that some differences in the sintering behavior between the “regular” Tosoh powder and the “anomalous” US Nano pressed bodies can be partially associated with the powder chemistry (i. e., the impurities present in the two systems might still play a role). In fact, small amounts of impurities might interact with the defect chemistry, grain boundary structure, the thermodynamics of sintering [48–50] and grain growth [51]. Among the elements impacting sintering in YSZ, chlorine is one of the most effective. In fact, it favors vapor transport via evaporation-condensation, coarsening the microstructure and preventing sintering [52–54]. Herein, the nominal composition of the US Nano powder falls below the 0.03 wt% threshold, showing substantial effects on sintering of YSZ [52]. Moreover, slow heating favors chlorine elimination before sintering; therefore, chlorine contamination is known to delay sintering when high heating rates are employed [54]. In this work, the US Nano system shows clearly the opposite behavior, and the results cannot be explained in terms of chlorine contamination. Finally, we remark that a pure microstructural effect is detected by observing the “normalization” of the US Nano behavior when the samples are colloidally processed. In summary, the chemistry alone does not explain the results reported in this manuscript.

The process leading to this “microstructural separation” between fully dense regions and large pores causes an average increase in the pore coordination in the US Nano system, which is consistent with previous observations by Ji, Biesuz and coworkers [27,28]. The increase in the pore coordination is associated with extensive desintering of the low-packed areas where the bridges between particles break, allowing different small pores to join in a new large pore. Clearly, the micrographs at the beginning of the isothermal holding indicate that the material contains throughout all its sections small grains bridged by inter-particle necks (see the bottom panels of Fig. 6). The transition to the microstructure after the isotherm requires the break-up of these bridges existing in the low packed regions opening the new large porosity, as confirmed by the “quasi in situ micrographs” reported in Fig. 8. We note that the observed polycrystalline bridges breakage in Fig. 8 is influenced by the degree of constraint within which the material evolves. The “quasi in situ” experiment can be considered a relatively extreme condition as the powder is constrained by the rigid alumina substrate. However, the material in low-packing regions of the US Nano compacts is also largely constrained by the high-density areas, which become fully dense and form a “rigid” skeleton. In this regard, the “quasi in situ” experiments can be considered still representative of what happens within the green body.

The break-up of necks through desintering is not new and has been

documented using in situ TEM [55] (see also Supplementary Materials of [56]) and an elegant thermodynamic analysis of the stability of polycrystalline bridges [57]. In our specific case, we note necks form throughout all the samples at the beginning of the process, and later they selectively break in the low-density regions. This behavior should not be surprising. In fact, the formation of necks is a necessary condition to activate mass transport between different regions of the body (blue and magenta in Fig. 11). As discussed before, the driving force for such transport is the different curvatures established on the surfaces of pores, which depend on the pore coordination and dihedral angle, and it is established during sintering. The neck formation, eventually leading to the stabilization of the equilibrium dihedral angle, is a mandatory condition required to change the curvature of the particle's surface and the local chemical potential (which in the green state was the same throughout all the samples, assuming a monodispersed powder size).

When the blue regions start to draw mass from the magenta regions (Fig. 11) without substantial shrinkage, the cross-section of the magenta bridges must decrease. Their length cannot change as there is only modest volumetric shrinkage, but their volume is reduced. This triggers a Rayleigh instability [58] and causes the magenta microstructure to break up into a set of particles that attach to the blue skeleton, thereby opening the large pores observed in Fig. 5 (see also the pore size distribution in Fig. 7). The stability of polycrystalline bridges has been modelled by Sundre and Lange [57], showing that the bridge depends on the number of grains in the bridge, the dihedral angle, and the bridge

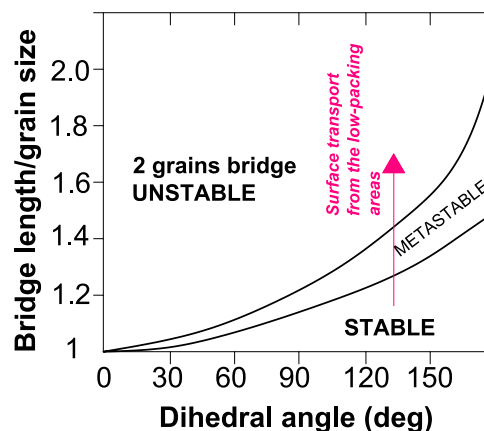


Fig. 12. Two-grain bridge stability map, reproduced after Sundre and Lange [57]. The effect of surface-mediated mass transport from the magenta (low-packing) to the blue (high packing) regions of Fig. 9 is also highlighted.

length normalized by the grain size. Fig. 12 replots their data for a polycrystalline bridge containing only two grains and highlights the regions where the bridge is stable, metastable, or unstable. Surface transport, as schematically depicted in Fig. 11, reduces the grain size in the magenta bridges, thus increasing the relative bridge length and causing desintering of the structure.

SPS provides additional information about the said “microstructural separation” between highly packed and mildly packed regions in the US Nano powder. First, we note that the said microstructural effect is particularly rapid between 1025 and 1225°C. Smaller effects were observed, for instance, during the isotherm at 925°C (Fig. 2c). If the material is substantially densified below those temperatures, removing a large portion of the surface area that is required for surface transport, then the sintering behavior becomes regular. This is the case for the SPS dataset, where increasing the heating rate shifts the sintering curves to the left (Fig. 3c). In summary, if the US Nano powder is sintered by SPS at temperatures lower than those needed to separate the body into fully dense areas and large pores, it behaves regularly, like the standard Tosoh powder. Moreover, the microstructure obtained by SPS at 1150°C is dense, but the grain size is similar or even smaller than that obtained at the same temperature and heating rate in the dilatometer (Fig. 5b). This is relatively surprising since densification in SPS maintains a small grain size, increasing the grain boundary area, which is still very limited in the sample processed in the dilatometer due to its low-density (the linear shrinkage is just a few %). This is consistent with surface-mediated coarsening in dilatometry experiments.

These conclusions are particularly significant. They show that the extent to which the heating rate affects densification depends on the quality of the green body (and therefore on the shaping method used). This insight goes beyond traditional mechanistic explanations focused on powder type, particle size, and chemistry, and instead highlights the importance of shaping in processes such as flash sintering, fast firing, and UHS. Specifically, if the green body is more homogeneous with smaller or longer-range density fluctuations, then fast heating is less effective in improving the densification behavior. This can be deduced from Fig. 9, where the US Nano (20 nm) system was pre-processed to reduce the degree of agglomeration before pressing (see, for instance, the original pore size distribution in Fig. 1). In that case, the said inversion in the sintering curves disappears or is heavily reduced, though a long isotherm at low temperature still causes a delay in the sintering. A corollary of the statement is: fast heating is more effective in improving the densification of bodies where density fluctuations do exist. In other words, rapid sintering can minimize the deleterious effects introduced by an unoptimized green shaping. This conclusion is consistent with some previous results. In 2016, we observed that flash sintering provided dense and homogeneous gadolinia-doped ceria shaped from co-precipitated nanopowders, while conventional firing led to inhomogeneous microstructures [59].

It is worth remarking that the shaping process/green quality interaction with the heating rate during sintering might be the origin of the unusually high activation energies for sintering measured by the MSC approach and reported in the literature [37]. In 2018, Frueh et al. showed in their “critique of master sintering curve analysis” that the MSC model applied to the same alumina powder (Almatis CT3000 LS SG) gives different activation energies for sintering based on the green shaping procedures. It is interesting to note that the bodies showing a higher activation energy are actually those obtained by pressing, while the lowest activation energy is associated with “non-aqueous” slip casting; aqueous slip or tape falls in the middle. It is well known that usually the degree of homogeneity in the green improves as: non-aqueous colloidal processing > aqueous colloidal processing > pressing. Following the reasoning developed in this manuscript, the bodies produced by pressing are likely more prone to the formation of large pores during the early sintering stages, resulting from surface diffusion between regions with different packing density. This might cause a delay in sintering at low heating rates in the pressed samples,

resulting in an apparent increase of the activation energy for sintering (note that when the low heating rates curve shifts at higher temperature, the activation energy used for fitting must increase). In summary, the green shaping procedures are crucial not only when studying the influence of heating rate, but also when considering theoretical and mechanistic models of the sintering process.

We still do not have a definitive answer to whether the anomalous behavior of the US Nano (20 nm) system arises solely from the green body's homogeneity or from an intrinsic effect of particle size. Indeed, small nanopowders are prone to agglomeration and therefore more sensitive to the heating rate, based on the previous considerations. While much experimental evidence is now suggesting that an intrinsic effect (scaling law) exists, it is still difficult to decouple it from effects associated with the green homogeneity.

5. Conclusions

3YSZ nanopowder (20 nm) is particularly sensitive to the heating rate during sintering, even in conventional conditions. A change in the heating rate from 2.5 to 50°C min⁻¹ can boost the densification rate by 3 orders of magnitude. It is inferred that this effect is associated with a “microstructural separation,” in which regions in the green body with lower packing density lose mass to those with higher packing density. This causes the formation of large fully dense areas coupled with large pores. This phenomenon is surface-mediated and is substantially minimized with an increasing heating rate. We emphasize that this mechanism is not particle-to-particle transport but rather cooperative transport between different areas of the green body.

In this regard, green-body homogeneity strongly influences how the heating rate affects sintering. Green bodies with large density fluctuations are more sensitive to heating rate, and a fast heating schedule can significantly improve their densification. This could also affect the measurements for the sintering activation energies through the master sintering curve model, especially when agglomerated green bodies are considered.

CRedit authorship contribution statement

Etienne Martin: Investigation, Formal analysis, Data curation. **Mattia Biesuz:** Writing – original draft, Visualization, Validation, Resources, Formal analysis, Data curation, Conceptualization. **Thomas Hérisson De Beauvoir:** Writing – review & editing, Supervision. **Levent Karacasulu:** Writing – review & editing, Investigation, Conceptualization. **Wayne D. Kaplan:** Writing – review & editing, Supervision, Resources, Methodology. **Rachel Marder:** Visualization, Investigation, Formal analysis. **Claude Estournès:** Writing – review & editing, Validation, Supervision, Resources, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jeurceramsoc.2026.118809.

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