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Flash Sintering of Nanograin Zirconia in <5 s at 850°C

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We show that yttrium-stabilized zirconia can be sintered in a few seconds at ~850°C to full density, starting from a green density of 0.5, by the application of a dc electrical field (nominally, several hours at 1450°C are needed to complete the sintering process). This finding is explained by the local Joule heating at grain boundaries, which, on the one hand, promotes grain-boundary diffusion (a kinetic effect), while at the same time restricts grain growth (a thermodynamic effect). The smaller grain size and the higher temperature at grain boundaries can then act synergistically to enhance the rate of sintering. These results have a bearing in explaining the widespread spark plasma and microwave-assisted techniques for enhanced sintering.

I. Introduction

DENSE ceramic bodies are traditionally produced by sintering green powder compacts at high temperatures. Sintering occurs by solid-state diffusion, which transports matter from grain boundaries into the neighboring pores. Thus, the effective diffusion distance scales with the grain size, while the rate of matter transport is determined by self-diffusion along the grain boundaries (at large grain sizes, the transport may become dominated by lattice diffusion, which is not relevant to the present study). At the same time, the driving force for sintering, which is proportional to the curvature of the pores, is also proportional to the grain size. As a result, the rate of sintering is related to the grain size and to the diffusion coefficient, leading to the following equation for the densification rate, $\dot{\rho}$[1]:

$$\dot{\rho} = \frac{Af(\rho)}{Td^4} e^{\frac{-Q_B}{RT}} \qquad (1)$$

where A is a material constant, Q_B is the activation energy for self-diffusion at grain boundaries, $f(\rho)$ is a function of the density, T is the temperature in K, and d is the grain size. The grain size exponent of 4 applies to boundary diffusion-dominated mass transport. Sintering is nearly always accompanied by significant grain growth, which slows the sintering process.

Recently, new techniques that use electromagnetic and electrical fields, in tandem with time and temperature, have been shown to enhance the sintering rate. These new methods are collectively known as field-assisted sintering techniques (FAST).[2–4] These methods are technologically significant, but a fundamental understanding of the underlying atomistic mechanisms remains clouded.[2] Electrical sparks and plasmas at particle–particle contacts, self-cleaning of particles surfaces, and temperature-gradient-driven diffusion have been proposed as explanations for field-enhanced sintering.[5]

In a recent article,[6] it has been shown that electrical fields of approximately 20 V/cm lower the sintering temperature of 3 mol% yttria-stabilized zirconia (3YSZ) from ~1400° to 1300°C.[6,7] This enhancement in the sintering rate could be successfully explained by a slower rate of grain growth in the presence of an electrical field.[8] These papers document that electrical fields retard grain growth, which, as given by Eq. (1), can enhance the rate of sintering.

The present work makes a huge leap from the work of Yang *et al.*[6]: it demonstrates that 3YSZ can be sintered in a few seconds at temperatures as low as 850°C by increasing the field strength to ~100 V/cm. This unusual finding is explained by local heating at grain boundaries formed at the particle–particle junctions. It appears that this local heating can unleash a runaway process whereby heating reduces the local resistance leading to more intense Joule heating, and so on. The end result is that the sample can be flash sintered in just a few seconds at a furnace temperature of just 850°C.

II. Methods

Commercial tetragonal 3YSZ powders (TZ-3YB, Tosoh USA, Grove City, OH) with a particle size of 60 nm were uniaxially pressed into dog bone-shaped specimens having a relative density of 50.4%. The gage section had a length of 21 mm and a rectangular cross section of 3 mm × 1.58 mm. Sintering was performed in a vertical tubular furnace under the application of a constant dc voltage. The sample was suspended in the center of the tube by means of two platinum electrodes attached to the handles of the dog bone specimens. A CCD camera recorded the sample dimensions through a series of optical filters positioned at the bottom end of the tube.[9] Samples were sintered with the following heating ramp: 2°C/min to 500°C, and then at a constant heating rate of 10°C/min up to 1450°C or less, as needed to achieve full densification. The true (linear) shrinkage strain, given by $\varepsilon = |ln(l/l_o)|$, where l_0 is the initial gage length and l is the time-dependent gage length as the specimen sinters. Because the experiments were carried out at a constant heating rate, time and temperature are proportional to one another. Thus, the results are presented by plotting the shrinkage strain as a function of temperature.

III. Results

The sintering strain measured as a function of temperature, for different values of the initial applied dc field, is reported in Fig. 1. These graphs show two regions: at low fields, <40 V/cm, densification occurs gradually, albeit at increasing rates as the field is increased. This regime is equivalent to the method called FAST sintering. At higher fields, sintering occurs almost instantly as recognized by the nearly vertical slope of the shrinkage
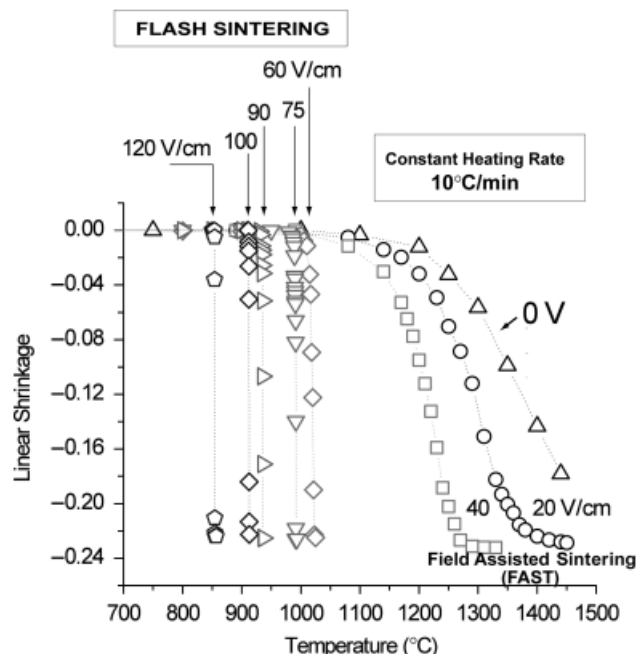
Fig. 1. dc electrical fields enhance the rate of sintering in yttria-stabilized zirconia (3YSZ). However, an instability occurs when the field is greater than a threshold value, estimated to be about 40 V/cm in the present experiments, leading to sintering in just a few seconds at unusually low temperatures. This kind of sintering process is called flash sintering. Note that full sintering occurs, by this new method, at temperatures as low as 850°C, nearly instantaneously, at a field of 120 V/cm.

curves. In this regime, the onset of sintering moves to a lower temperature as the field is increased from 60 V/cm, eventually dropping to 850°C when the field reaches to 120 V/cm. This nearly instantaneous sintering method is being called flash sintering. The rates of sintering given by the slopes of the strain versus time (or temperature, because the experiments were carried out a constant heating rate of 10°C/min) are three orders of magnitude faster in flash sintering regime than in FAST sintering.

A plot of the measured input power as a function of temperature yields an interesting finding that is shown in Fig. 2. In the flash sintering regime (60–120 V/cm), there is an abrupt increase in power dissipation at the temperatures that correspond closely to
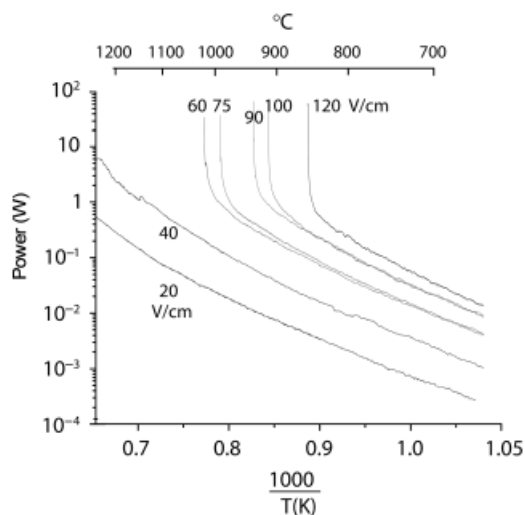
the onset of flash sintering. Furthermore, the onset of the instability occurs at about the same power level, about 1 W, irrespective of the applied field. At fields below 40 V/cm, the power continues to increase monotonically as the temperature increases, as would be expected from the temperature dependence of ionic conductivity.

IV. Discussion

(1) Explanation: Joule Heating at Grain Boundaries

We explore the hypothesis that local Joule heating at the grain boundaries, which form at the particle–particle contacts, is the underlying cause for the onset of flash sintering. In a constant voltage experiment, the power dissipation is given by V^2/R, where V is the applied voltage and R is the electrical resistance of the specimen. In a first-order approximation, the total resistance can be written as a sum of the resistance of the crystal matrix, R_C, and the grain boundaries, R_{GB}. Therefore, the power (Watts) dissipated in the specimen is given by:

$$W = \frac{V^2}{R_C + R_{GB}} \tag{2}$$

If, in Eq. (2), $R_{GB} \gg R_C$ then power dissipation is dominated at the grain boundaries. A local rise in grain-boundary temperature would lower R_{GB}, which, in turn, would impel greater power dissipation, thus leading to the instability shown in Fig. 1. At the same time, an increasing grain-boundary temperature would accelerate grain-boundary diffusion producing ultrafast sintering.

The explanation given above leaves two questions unanswered. First, the instability can be explained as well by Joule heating of the crystal matrix, because a rapid decrease in R_C could have the same consequence as a drop in R_{GB}. The second question is why the effect is seen at higher fields but not at a lower applied field. One point of distinction between the low field and high field behavior is that the onset of flash sintering begins below 1000°C, while field-enhanced sintering (FAST) occurs above this temperature. This is also the temperature where the necks at particle–particle contacts begin to grow.[10] The runaway effect is more likely when Joule heating can be concentrated at the boundaries, which is most likely when the contact area at particles is small and its resistance is high. This effect was confirmed in an experiment where the sintering experiment was started with zero field until reaching 1150°C, at which point a field of 40 V/cm was applied. As shown in Fig. 3, flash sintering occurred when the field was applied after reaching 1150°C, but not if applied from the start of the experiment. The interpretation is that when the field is applied from the start, some

Fig. 2. The phenomenon of flash sintering also manifests in a power surge when the critical sintering temperature is reached, confirming that it is an instability in the process. The onset of the power instability coincides with the onset of flash sintering shown in Fig. 1.
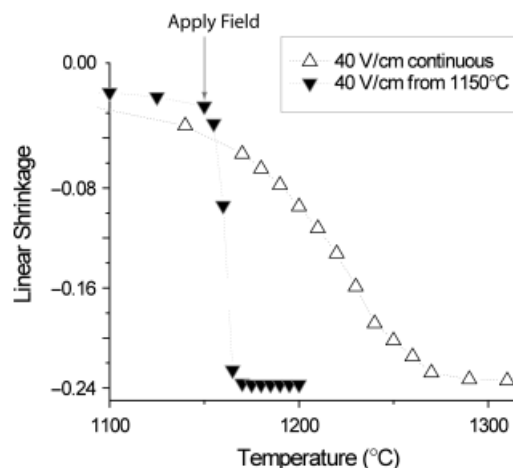

Fig. 3. Flash sintering is not observed when a field of 40 V/cm is applied at the start of the sintering experiment, but it does occur if this field is applied when the furnace reaches 1150°C.

neck growth has occurred at 1150°C (as shown by a shrinkage of ∼4%), which prevents the onset of instability. If the field is applied at 1150°C, then the absence of neck growth means that interface resistance is high, which allows the field to produce the instability.

(2) Estimate of Grain-Boundary Temperature

It is possible to estimate the local temperature at the grain boundaries by comparing the sintering rates (at the same density), by means of Eq. (1). The activation energy for self-diffusion in 3YSZ is well characterized from creep experiments, which, like sintering, are controlled by grain-boundary self-diffusion.[11] Its value ranges from 480 to 533 kJ/mol. We assume an average value of 500 kJ/mol for the following analysis. Note that the sintering rate also depends on the density: this can be factored out by comparing the sintering rates measured at the same density. The grain size in Eq. (1) is assumed to remain constant because grain growth is usually insignificant when the porosity remains interconnected (open porosity), as is the case when relative densities that are <0.8.[12]

We now apply Eq. (1) to estimate the grain-boundary temperatures subject to the constraints described above. If $\dot{\rho}_o$ is the densification rate under zero applied field at temperature T_0, and $\dot{\rho}_E$ is the densification rate measured under an applied field, both densification rates having been measured at the same relative density, then it follows from Eq. (1) that:

$$\ln\left(\frac{\dot{\rho}_E}{\dot{\rho}_o}\right) = \frac{Q_B}{R}\left(\frac{1}{T_E} - \frac{1}{T_0}\right) \quad (3)$$

where the activation energy for self-diffusion, $Q_B = 500$ kJ/mol. The effective grain-boundary temperature, T_E, can now be estimated from Eq. (3). The values for T_E for different densities calculated in this way are given in Table I. The top row gives the values for the furnace temperatures corresponding to five levels of relative density, ranging from 0.55 to 0.75, without an applied field. The values with the applied field refer, on the left, to the furnace temperature, T_0, and on the right to the estimated grain-boundary temperature, T_E. The data are separated into two segments: the upper set referring to FAST sintering and the lower set to flash sintering.

Consider first the FAST sintering data. Here, the estimated grain-boundary temperatures, with an applied field, are close to the furnace temperature without the applied field. For example, for $\rho = 0.65$, the furnace temperature without the applied field is 1334°C, whereas in FAST sintering, the estimated temperature is 1345°C at 20 V/cm and 1365°C at 40 V/cm. The reasonable agreement between the estimated temperature (with the field) and the measured temperature (without the field) is satisfying.

In the case of flash sintering, the estimated grain-boundary temperatures increase drastically. The difference between the

estimated and the furnace temperature increases to 350°C at a field of 60 V/cm, and to 850°C at a field of 100 V/cm.

(3) Estimate of Joule Heating by Power Dissipation and Black Body Radiation

If the specimen is considered as a monolithic body, which heats up uniformly, then the rise in temperature may be calculated by equating black body radiation to the power dissipation in the specimen by the applied field. The analysis leads to the following equation[6]:

$$\frac{\Delta T}{T_0} = \frac{W}{4A\sigma T_0^4} \quad (4)$$

here ΔT is the increase in the temperature of the body due to Joule dissipation of electrical energy, given by W. The total surface area of the specimen (assumed to be the gage section) is equal to A, and σ is the black body radiation constant equal to $\sigma = 5.67 \times 10^{-8}$ W·m²/K⁴. As before, the furnace temperature is given by T_0. For our experiments, A $= 1.9 \times 10^{-4}$ m². Substituting the range of values from the experiments, the increase in the specimen temperature is predicted to be not higher than 10°C, much less than the estimated increase in the grain-boundary temperature.

The discussion above draws a distinction between field-assisted sintering of ceramics and metals. Refractory metals, e.g. Mo and W, are sintered, even today, by electrical resistive heating, as taught in a patent dating back to 1906.[13] In these experiments, the primary function of the applied fields is to heat the entire specimen directly with electrical currents; a mechanism quite different from the proposed local heating of grain boundaries in ceramics.

(4) Closing Remarks

The results in Fig. 1 draw a distinction between FAST sintering, where there is a gradual increase in the sintering rate with applied field, and flash sintering where sintering occurs nearly instantaneously above a threshold value of the applied field, at remarkably low temperatures. The field-enhanced sintering in the FAST regime has been successfully explained in terms of the effect of the electrical field on reduced rate of grain growth.[6] However, the grain size of the sample that was flash sintered at 850°C was measured to be 150 nm (first by SEM and then confirmed by TEM), not remarkably different from the grain size in specimens sintered by the FAST method. The inference is that flash sintering is not due to reduced grain size under the applied field, but due to enhanced kinetics, which has led us to propose a rapid rise at grain boundaries as a possible mechanism for flash sintering. It would be a mistake to discard other possible mechanisms for this unusual behavior, for example, the kinetics may

Table I. Estimates of Grain-Boundary Temperature, T_E, at Different Applied Electric Fields at Different Values of Relative Density

| Field (V/cm) | $\rho = 0.55$ | | $\rho = 0.60$ | | $\rho = 0.65$ | | $\rho = 0.70$ | | $\rho = 0.75$ | |
	T_0 (°C)	T_E (°C)	T_0 (°C)	T_E (°C)	T_0 (°C)	T_E (°C)	T_0 (°C)	T_E (°C)	T_0 (°C)	T_E (°C)
0	1244		1303		1334		1362		1387	
FAST sintering										
20	1195	1247	1237	1315	1265	1345	1288	1388	1301	1421
40	1138	1252	1175	1324	1195	1365	1208	1398	1219	1434
Flash sintering										
60	1014	1358	1017	1454	1018	1494	1020	1541	1020	1577
75	990	1417	991	1532	991	1571	991	1607	991	1641
90	935	1428	935	1561	936	1608	936	1649	936	1689
100	912	1470	912	1636	912	1683	912	1730	912	1770

The temperature T_0 refers to the grain-boundary temperature without an applied field. The top row refers to the zero field case, and the data refer to the furnace temperatures at different values of the density. All experiments were carried out at a constant heating rate of 10°C/min.

be enhanced by the "nucleation" of Frenkel defects (vacancy interstitial pairs) under the driving force of an applied electrical field. Alternatively, the high applied fields may interact nonlinearly with the intrinsic fields present across the space charge layers adjacent to grain boundaries, thereby producing a catastrophic change in self-diffusion at grain boundaries.

It is well to keep in mind that platinum electrodes are blocking, that is they transport electrons, not oxygen ions. At the cathode, the neutral oxygen must be reduced to oxygen ions. If the currents are so large that the oxygen cannot be replenished from the environment, or if the environment is essentially inert, then high fields and currents can produce electrolytic reduction of the oxide, which can be seen as blackening of zirconia near the cathode. In the present experiments, such blackening was not observed.

V. Conclusions

The flash sintering phenomenon is expressed by a sudden sintering event when a certain temperature is reached for a given applied field. In 3YSZ, we find that the fields must be greater than a critical value, above 40 V/cm. As the field is increased, the temperature for the onset of flash sintering becomes lower and lower. In the present experiments, 3YSZ specimens could be sintered in a few seconds at 850°C at a field of 120 V/cm. The proposed mechanism for flash sintering is preferential Joule heating at the grain boundaries, especially when initiated in the early stages of sintering when particle–particle contacts are just beginning to develop. When the relationship between the sintering rate and temperature is applied to the data, then grain-boundary temperature that is 585°C above the furnace temperature is estimated for an applied field of 100 V/cm. The energy input to induce flash sintering is only 1 W, which translates into a temperature rise of 10°C in the specimen as a whole when analyzed by black body radiation, far below the estimated increase in the grain-boundary temperature. Flash sintering can lead to considerable energy savings in the processing of ceramics.

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