Electronic Supplementary Information:

Anisothermal densification kinetics of cold sintering process below 150°C

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Abstract

Cold sintering is an emerging non-equilibrium process methodology that densifies ceramic powders at significantly reduced temperatures. This study proposes a fundamental framework to investigate its densification kinetics. By controlling four densification process variables including transient chemistry, sintering temperature, uniaxial pressure and dwell time, anisothermal sintering kinetics of highly densified ZnO is identified and phenomenologically modeled for its relative activation energetics.

Experimental methods

Instrumentation

In this study, we herein presents a new engineering design of collecting the real–time temperature of the pellet during the cold sintering. A functional plate has a close–ended vertical hole and horizontal slit for a thermocouple insert. It is placed right under the thin bottom punch, which allows to measure the center temperature of the sintering die. Note that two thin bottom punches are intended to serve the following functions: 1) prevent cross–chemical contamination, 2) improve homogeneous pressure distribution and 3) slow punch surface degradation. The materials selection among stainless steel, inconel and nickel

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are based on acidic and basic nature of the transient phase. As the thermal conductivity difference among the die sleeve (W18Cr4V hardened carbon tool steal), bottom punch (stainless steel) and functional plate (A2 tool steal) is less than 30% [1], the temperature reading from the inserted thermocouple was reasonably assumed to be the pellet temperature. Such a simple functional plate design offers the following advantages to the cold sintering experimental setup; 1) the center temperature of the sintering die is used as a feedback to control the input voltage, resulting accurate output temperature; 2) a tight fit of the thermocouple inserted to the functional plate grants highly repeatable heating cycles; 3) a modular part design allows full compatibility to commercially-available sintering dies, and 4) a temperature profile of the center can be comparable to different die sizes, which will be crucial information for a size scale-up process. The heating source was a 200 W mica insulated band heater, which was controlled by a PID loop feedback mechanism with parameter autotuning. For the sintering temperature ranging $100 - 200°C$, the maximum heating rate was $15.0°C/min$. As the sintering die and band heater were placed in an open ambient condition, the temperature fluctuation in the steady state was measured to be $\pm 3.5°C$.
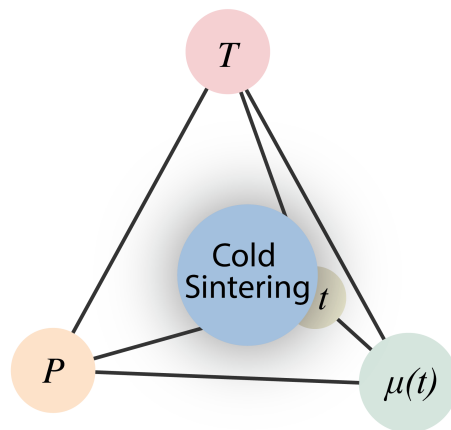

Figure S1: Schematic of four densification process variables including transient chemistry ($\mu(t)$), sintering temperature (T), uniaxial pressure (P) and dwell time (t).
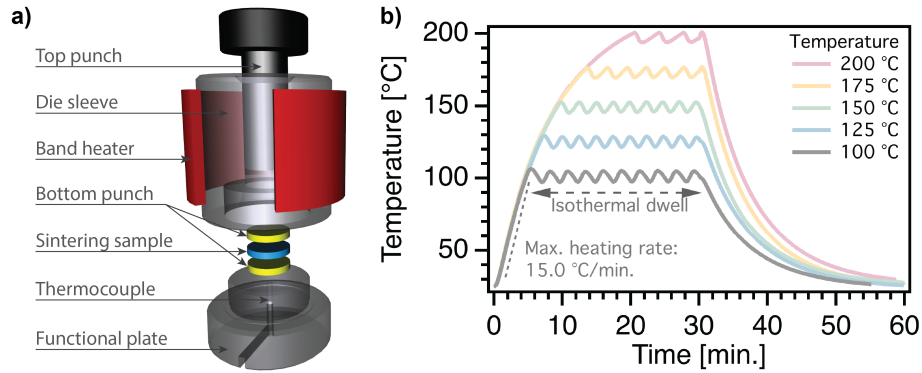
Figure S2: a) Schematic diagram of the cold sintering die with a thermocouple insert placed on the center of a functional plate, and b) sintering temperature profiles of $100 - 200°C$ for the total time of 30 minutes with the maximum heating rate of $15°C/min$. The temperature fluctuation in a steady state was $\pm 3.5°C$, and the dwell time was measured at the beginning of isothermal temperature.

Cold sintering process

1.0 g of the ZnO powder (Alfa Aesar $40 - 100$ nm APS powder) was mixed with 15 wt.% of 2 M acetic acid solution for 5 minutes in an agate mortar. The powder and transient phase mixture were then transferred in a 13.0 mm diameter tungsten alloy steel die and uniaxially pressed at $175 - 350$ MPa for 5 minutes to stabilize any extrusion by the applied pressure. During the ramp, the sintering die was kept pressed under a constant hydraulic press. During the cooling, the uniaxial pressure was released, and the sintering die was fan–cooled down to room temperature. By using a semi–automatic hydraulic pressure with attached digital contact sensor (Keyence GT2–H32),[2] the linear displacement of a green body was monitored with a resolution of 0.5 μm Both temperature and contact sensor had a synchronized sampling rate of 1 second. The linear shrinkage of the pellet was evaluated by subtracting linear displacement caused by sintering die thermal expansion, which can be denoted by:

$$\Delta L_t / L_0 = \frac{(\Delta d_t - \Delta d_0)}{\Delta d_0} \tag{S1}$$

S3

where $\Delta L_t/L_0$ is the linear shrinkage of the pellet at a given time t, Δd_t is the displacement difference between pellet and calibration at a given time t, and Δd_0 is the initial displacement difference at $t = 0$. In this study, $t = 0$ was measured at the end of 5-minute pressure stabilization, in other words, at the start of the heating ramp. Note that the initial die temperature was attentively controlled at $25.0 \pm 1.0°C$ to obtain closely correlated thermal expansions between the calibration and cold sintering experiments, which permits the assumption made in the mathematical derivation with minimized experimental artifacts.

Figure S3: Photograph of the cold sintering setup.

Material characterization

Relative density

The envelop or bulk density of the sintered ZnO pellet was measured using a geometric method. The thickness was measured by position display units (Heidenhain ND 280). The relative density was calculated by dividing the envelop density by the theoretical density of ZnO, which is 5.61 g/cm^3.

X-ray diffraction

Room-temperature X-ray diffraction (XRD) (Malvern PANalytical Empyrean) with Cu$K\alpha_1$ radiation ($\lambda = 1.5406$ Å) and Cu$K\alpha_2$ radiation ($\lambda = 1.5444$ Å)

was used to determine crystal phase purity. A powder or bulk pellet sample was scanned at 45 kV and 40 mA using a PIXcel detector with a step size of 0.02° between 2θ angle of 10 and 70°.

Specific surface area

Brunauer, Emmett and Teller (BET) specific surface area measurements (ASAP 2020 Automated Surface Area and Porosimetry System) of the powder and the pellet were obtained by N_2 gas molecule physisorption after 8 hours of degassing at 80°C. Such a low temperature was chosen to prevent potential additional microstructure change induced during the degassing.

Scanning electron microscopy

Micrographs of the fracture surface were obtained by scanning electron microscope (SEM) (FEI Nova NanoSEM 630). 10-nm iridium sputtering was used to minimize electron charging at the landing energy of 7 keV.

Thermogravimetric analysis

Amount of the transient liquid residue was quantified by thermogravimetric analysis (TGA) (TA Instrument TGA Q5500) operated at the heating ramp of 5°C/min. under air atmosphere.
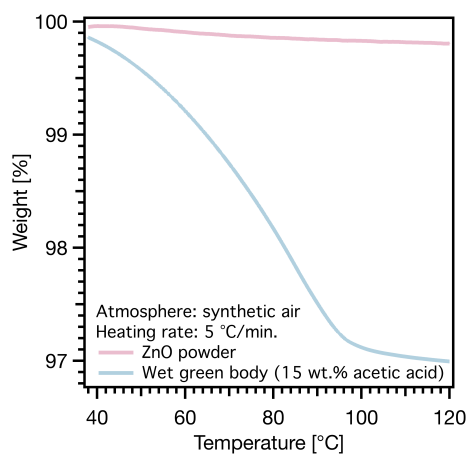
Results

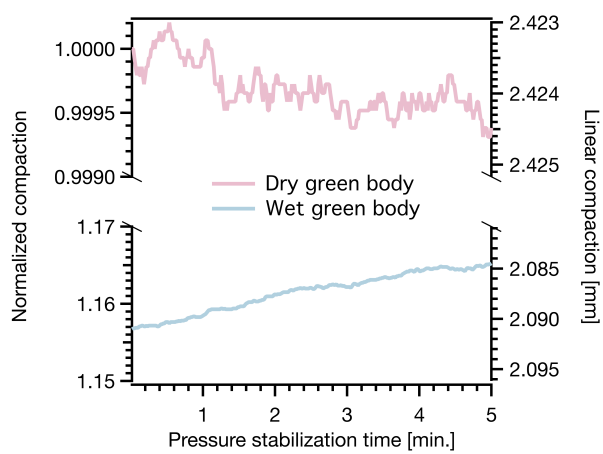Figure S4: TGA of the powder and wet green body pellet under air.

Figure S5: Linear compaction behaviors of 1.0 g of ZnO powder (dry green body) and with 15 wt.% of 2 M acetic acid (wet green body) mixture under 350 MPa uniaxial pressure for 5 minutes.
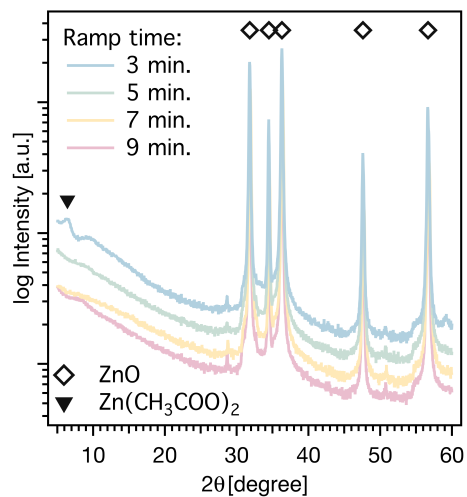
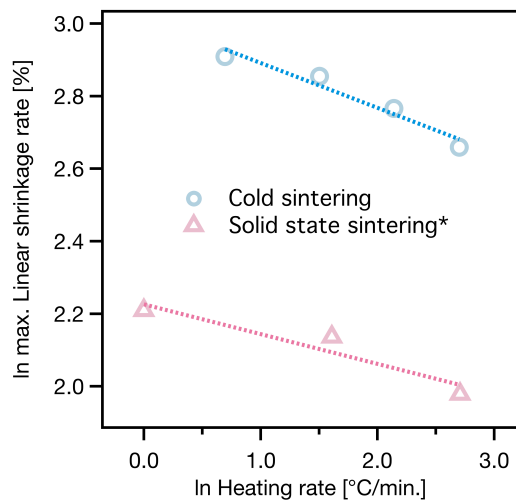Figure S6: XRD of ZnO cold sintering after 3, 5, 7 and 9 minutes.

Figure S7: Determining empirical n from Eq. 4, where the maximum linear shrinkage rate was treated as a characteristic point for each heating rate. ZnO solid state date shrinkage data was extracted from the following reference [3].
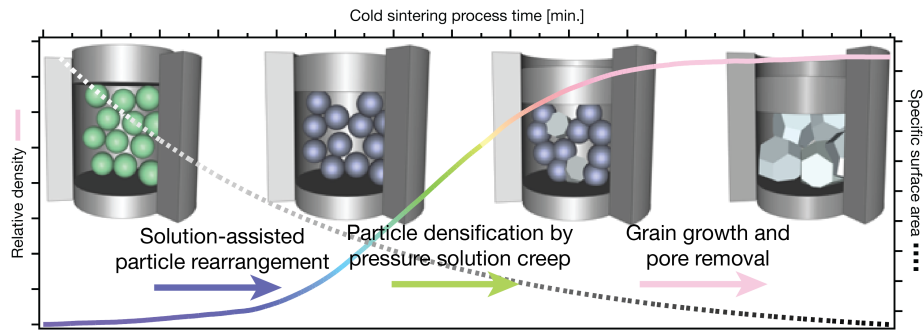
Figure S8: Classifying three possible dominant stages of the cold sintering process in a function of time, where the blue spheres indicates presence of the transient phase.

References

S1. Maity SR, Chatterjee P, Chakraborty S. Cutting tool material selection using grey complex proportional assessment method. Materials & Design (1980-2015). 2012;36:372–378.

S2. Floyd R, Lowum S, Maria JP. Instrumentation for automated and quantitative low temperature compaction and sintering. Review of Scientific Instruments. 2019;90(5):055104.

S3. Neves N, Barros R, Antunes E, Ferreira I, Calado J, Fortunato E, et al. Sintering Behavior of Nano-and Micro-Sized ZnO Powder Targets for rf Magnetron Sputtering Applications. Journal of the American Ceramic Society. 2012;95(1):204–210.