THE EFFECTS OF INTERNAL GAS PRESSURE AND MICROSTRUCTURE
ON THE MECHANISMS OF HOT-PRESSING
AND SWELLING IN CERAMICS

PROGRESS REPORT
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ABSTRACT

The low temperature isostatic pressurization system has been completed, operated successfully and calibrated. The new high temperature TD tungsten vessel and MoSi_2 element furnace system has also been designed and is presently under construction. Porous CoO single crystals have been grown using a "skull melting" process. Automated quantitative microscopy techniques are being developed using the KONTRON system to examine porosity evaluation during hot-pressing and sintering. Initial sintering experiments under variable isostatic pressures from 100 $\mu\text{m Hg}$ to 2000 psi reveal no significant effect of ambient pressure. Nor were differences observed in sintering kinetics when either Helium or Argon were used as the pressurizing gas. Swelling experiments, conducted by reducing the ambient pressure after pore closure, revealed dramatic changes in density. The densification rates also appeared to depend on history, suggesting that mechanical deformation may play a dominant role in hot-pressing, at least during transients.

I. Experimental Techniques

A. Isostatic Pressurization System

The components and detailed design of the isostatic pressurization system have been described in the previous progress report. A schematic of the pressure vessel is shown in Fig. 1 for convenience. Construction of the system has now been completed and it has been operated successfully without significant alteration. Its operating characteristics have been determined and a number of critical calibrations have been performed to optimize system performance and establish the accuracy of the measurements.

1. Temperature Control

Optimization of the temperature controller was complicated by two factors: (1) the rather large thermal mass of the pressure vessel compared to the power output of the furnace, tended to make temperature response rather sluggish, and (2) the desire to conduct experiments near the maximum operating temperature of the wire wound (Kanthal A-1) furnace (approximately 1200°C) precluded large temperature overshoots. The problem was partially solved by using a thermocouple next to the furnace windings for control (rather than the thermocouple used to measure vessel temperature) thereby reducing the effective thermal inertia of the system. With optimum controller settings, a heating rate of $\sim 100^{\circ}\text{C}/\text{min.}$ was obtained, which was viewed as acceptable since the intermediate and final stages of densification are of most concern in the present investigation. Once setpoint temperature is attained, controller gain is increased to achieve control of the pressure vessel temperature within $\pm 1^{\circ}\text{C}$ at 1175°C over ~ 2 hours.

2. Calibration of the Deflection Measurement System

Knowledge of the accuracy of the deflection measurement system is

crucial in the light of the possible errors caused by differential thermal expansion, pressure and friction.

An initial LVDT calibration was done using a special Boeckeler micrometer head with a translating spindle. LVDT signal conditioner output was measured for each 0.001", within the linear range of ± 0.125 ", on recorder scales used in a typical experiment. The resultant calibration, shown in Fig. 2, reveals a linearity deviating less than 0.25% at full range. (The linearity of the recorder is 0.1%.) The slope of the curve is 86.374 mV/.001" which, on the 1mV scale of the chart recorder theoretically allows resolution of $\sim 0.1 \mu\text{in}$ displacement. Temperature and pressure variations, however, limit actual resolution. Temperature variations arise primarily from oscillations in furnace temperature and LVDT cooling water temperature. Fig. 3 shows the difference in response of the system to LVDT temperature changes, as measured by a thermocouple taped to its outer wall, and response when the water jacket is mounted. Although the temperature change is small (10°C), the equivalent displacement is significant. The waterjacket, however, fitting tightly around the vessel nut and sealed with high thermal conductivity grease ("Thermal Compound")* maintains relatively constant LVDT temperature,** causing an equivalent displacement of $\pm 6 \mu\text{in}$. The $\pm 1^{\circ}\text{C}$ variation in furnace temperature has an insignificant affect on the LVDT temperature as shown by the temperature profiles in Section 4.

Sensitivity of the deflection measurement to internal gas pressure is significant and must be accounted for in those experiments involving changes in pressure. At pressures $\gtrsim 0$ psig, changes in pressure are step changes and produce corresponding step changes in displacement as shown in Fig. 4. The measured sensitivity of the system to pressure change at 1090°C was $\sim \frac{600 \mu\text{in}}{1,000 \text{ psi}}$. When vacuum is applied, however, a larger slow transient is observed, Fig. 5, probably

*Wakefield Engineering Inc.

**Cooling water temperature varies $\pm 2^{\circ}\text{C}$ over ~ 10 hours.

due to a thermal transient caused by evacuation.

Differential thermal expansion in the system presents the largest source of systematic error in measuring specimen deflection. It is most troublesome during the initial heat-up of the specimen, and the data must be corrected for the first 25 min. after raising the furnace around the pressure vessel.

Fig. 6 shows thermal expansion during heat-up to several set point temperatures. The signal is observed to first increase due to initial expansion of the pressure vessel in response to its sudden rise in temperature; then the signal decreases as the alumina LVDT extension rod begins to heat up. The variation in LVDT signal caused by both the temperature oscillations of the pressure vessel and the LVDT at steady-state are $<25 \mu\text{in.}$ which is negligible compared to typical specimen deflections of $\sim 30,000 \mu\text{in.}$

Thermal expansion calibrations of the system are done for all experimental conditions by performing a run without a specimen. Thermal contraction, shown in Fig. 7, is much more uniform because of the longer times involved and because the measurement is from setpoint temperature to room temperature. A small transient due to non-uniform cooling of the LVDT rod is observed but it occurs after 30 minutes and does not affect the measurements.

3. Pressure Vessel Temperature Profiles

Temperature gradients inside the pressure vessel were measured for two principal reasons: (1) to determine the temperature variation between the outside of the vessel where the temperature is measured during an experiment, and the inside of the vessel where the sample is situated; and (2) to minimize the axial temperature gradient in the region of the sample, by optimizing the furnace position with respect to the pressure vessel.

To measure temperature gradients, a sliding thermocouple was installed in the pressure vessel. Fig. 8 shows temperature gradients for two setpoint

temperatures at the same furnace position. The temperature drop between the outside and inside of the vessel is 12°C at 1200°C , and the axial temperature gradient in the region of the sample is $\sim 1.1^{\circ}\text{C}/\text{mm}$. Fig. 9 shows the gradients in the region of the sample.

The temperature in the region of the LVDT core stays constant at approximately 30°C , indicating that convective heat circulation contributes little to temperature variations in the LVDT region. The large temperature drop which occurs at the point where the pressure vessel joins the LVDT prevents changes in pressure vessel temperature from affecting LVDT temperature significantly. Fig. 10 shows the cooling rate of the vessel when the furnace power is cut. Initial cooling is rapid, which is desirable for quenching the samples.

4. Miscellaneous Calibrations

The flow rates of the water coolant in the pressure vessel and the oxygen getter furnace were also correlated to their respective drive pressures. These calibrations are presented in Fig. 11. The flowmeter controlling the inert vessel cover gas was calibrated for Helium and Argon (the two gases used for this application) and the effect of the gas flow on vessel thermocouple temperature was noted. This last variation occurs only when the furnace is heating in the down position during the specimen outgassing operation. The inert gas flows through the furnace, transporting heat upwards to the vessel thermocouple located near the top of the furnace.

5. Safety Provisions

Several new safety provisions were incorporated in the pressurization apparatus to minimize the consequences of a pressure vessel rupture. The rapid heat-up and cool-down of the brittle TZM vessel, while pressurized, presented potential dangers of combined thermoelastic and applied stresses. Steel

shields, 4.5 mm thick and hinged at the top, were constructed around the pressure vessel assembly following normal safety practice. Lifting arms were then built to raise and lower the furnace when the shields were in place. The pressure line entering the assembly was also secured with a steel strap to prevent whipping in case of an accident.

A relay was installed in the furnace electrical circuit to keep it de-energized after a power failure. This prevents instances of unsupervised heating when power is re-established. A second latching relay was installed to shut off furnace power and keep it off if water coolant pressure drops below a preset level necessary for efficient cooling of the system. Finally, a powerstat (auto-transformer) was installed in the furnace power lines to limit input power thereby protecting against overloads due to a defective control thermocouple or temperature controller.

6. Proposed Pressure Vessel and Furnace

To extend the experiments to $\sim 1600^{\circ}\text{C}$, the new TD tungsten pressure vessel and furnace have been designed and construction is underway. The pressure vessel, Fig. 12, is similar to the present TZM vessel, but is longer with a slightly larger bore. The length was increased to minimize temperature gradients in the specimen region of the new furnace. It was decided to use the pressurization system presently available with the new vessel and furnace for the initial experiments.

A new 1800°C furnace was designed with Molybdenum Disilicide heating elements and Zircar insulation. The stainless steel outer shell permits raising and lowering of the furnace on two upright steel pipes in a fashion similar to the

wire-wound furnace now in use. A high purity alumina tube surrounding the vessel is used to maintain either vacuum or a reducing flowing atmosphere around the vessel. Consideration is being given to coating the external surfaces with iridium as a further precaution in case of loss of atmosphere.

B. Specimen Preparation and Characterization

1. Specimen Preparation

The particle size distribution, surface area, and desorption behavior of the starting powder have been described in the previous progress report. Table 1 lists the impurity content as obtained from atomic absorption analysis provided by the supplier.*

Green pellets, ~ 5 mm high and ~ 5 mm in diameter, are produced by light compaction (200 psi) in a double-ended punch and die followed by isostatic compaction at 50,000 psi. Green densities are approximately 52% T.D. Despite the light pelletizing pressure, a slight "hour-glass" shape is obtained after isostatic compaction with typically a 1.9% difference between the diameter at the mid-plane and at the ends. This suggests that the low-pressure pelletizing process forms a pellet which is less dense in the center than at the ends; under isostatic compaction, the high pressure tends to make the density more uniform, causing the center section to shrink more than the ends. Preliminary results indicate that even after isostatic compaction and firing, a density gradient persists. An attempt was made to avoid the initial pelletizing step by isostatic pressing only, but a cracking of the pellet led us to abandon this approach.

A depletion of pores has been observed near the outer surfaces of the specimens. In measurements of open porosity, such a dense outer layer impedes

* Atomergic Corp.

penetration of fluids like mercury (in mercury porosimetry) and water (in immersion density tests). Therefore, a lapping procedure was adopted to remove a 0.1 mm layer from the pellet's cylindrical walls using a fine diamond grit dispersed in oil. A similar layer is removed from both ends by mounting the pellet in a drill press and lightly grinding with a fine file. The pellet is then cleaned ultrasonically in hot trichloroethane, acetone, and ethanol. The resulting specimen is very geometrically regular (length $\pm .001$ mm, diameter $\pm .001$ mm) permitting geometric densities to be obtained with high precision and avoiding the "coke-bottle" effect that would arise in Hg porosimetry if the high density surface layer remained.

After measuring the specimen's geometric density, immersion density is then obtained using distilled water. Fig. 13 shows the results of one series of measurements of samples sintered in vacuum at 1020°C . Other representative samples are measured with a mercury porosimeter to obtain open pore volume and open pore size distribution. Some results of this technique were presented in the previous report.

Finally, pellets are mounted in bakelite, polished, and impregnated with epoxy. After a final polishing, the epoxy filled pores provide a high contrast for quantitative metallography.

2. Characterization of Porosity

Information concerning density, pore volume, and pore size distribution is determined by geometric density, immersion density, mercury porosimetry, and quantitative metallography. Previously, manual point counting was used. We are presently using a KONTRON phase integrator* to automatically scan polished surfaces. It consists of an optical microscope with a programmable mechanical scanning stage.

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Lerchenstrasse 8-10
W. Germany

As a specimen is scanned, a photometer generates a signal proportional to the light reflected from a spot $0.7\text{ }\mu\text{m}$ in diameter. The analog signal is then automatically processed to yield pore fractions, pore density, and pore size distribution. The results of this instrument will be correlated with information from the other techniques to determine the specimen morphology during sintering and hot pressing. The $0.7\text{ }\mu\text{m}$ spot size limits resolution of fine porosity using normal optical techniques. Consideration is being given to scanning SEM photographs to increase resolution.

3. Porous CoO Single Crystals

A new technique has been employed by the Purdue Materials Research Laboratory, to grow large pure single crystals of high melting point oxide materials. It makes use of the "skull melting" principle* in which a water cooled copper crucible is charged with material and RF heated. Because of the cooling efficiency of the crucible, the charge only melts in the central region which is surrounded by a "skull" of unmelted powder. This skull thereby prevents contamination from the crucible.

Large polycrystalline aggregates of CoO have been grown with some grains of centimeter size which would be suitable for our investigation. Fig.14 shows the polycrystalline aggregate and a polished section of one of the single crystals.

II. Densification at Various Ambient Pressures

A. Procedure

In the initial experiments, the sintering kinetics and porosity evolution were studied as a function of ambient pressure and ambient gas. In a typical experiment, the pellet is inserted in the pressure vessel and outgassed for

* V. I. Aleksandrov, V. V. Osiko, A. M. Prokhorov, and V. M. Tatarintsev, A New Method for Obtaining Refractory Single Crystals and Fused Ceramic Materials, Vestnik Akad. Nauk, SSSR No. 12 (1973) pp. 29-39.

several hours at 100 μm and approximately 640°C. The system is then flushed several times with the high purity pressurizing gas. To set the desired oxygen potential, the system is evacuated to a predetermined level (typically 2000 μm) then pressurized with ultra high purity Argon. The evacuation pressure is selected such that the oxygen partial pressure exceeds that in the pressurizing gas at the highest pressures used, so that the evacuation process establishes the oxygen potential. During an experiment the specimens lose $\sim 1.75\%$ in weight which is presumably caused by specimen evaporation. However, stoichiometry measurements will be performed to verify specimen stoichiometry after testing.

After pressurization, the vessel is rapidly heated ($\sim 100^\circ\text{C}/\text{min}$) by raising the furnace. The experiment is terminated by lowering the furnace from the vessel while pressurized.

B. Effect of Ambient Pressure

Fig. 15 shows the results of sintering specimens in Argon atmospheres ranging from vacuum to 2000 psi at 1175°C. All are characterized by a very rapid initial densification rate followed by a much slower rate. The n values (in the $\Delta\ell/\ell_0$ vs. Kt^n relation[†]) range from 1.39 to 1.70 in the initial stages and 0.37 to 0.54 in the later stages. The similarity in curves indicates that an ambient isostatic pressure does not affect densification rates significantly. This is in contrast with Coble's analysis* which contains a theoretical error.

[†]F. Thummler, W. Thomma, "The Sintering Process", Met. Rev. 12 (1967) pp. 69-108.

*R. L. Coble, "Diffusion Models for Hot Pressing with Surface Energy and Pressure Effects as Driving Forces", J. App. Phys. 41 (1970) pp. 4798-4807.

C. Effect of Ambient Gas

Although gases are known to alter surface energies to varying degrees,^{*} sintering experiments run in atmospheres of Argon and Helium indicate no significant change in densification behavior in different atmospheres. Fig. 16 shows a comparison of two experiments conducted at 100 psi Helium and 100 psi Argon at similar conditions of oxygen potential and temperature. In most experiments, however, Argon was used because of its presumed lower solubility in CoO.

In the initial sintering experiments, an anisotropic densification behavior was thought to have been observed.¹ To test for this effect, one sample was placed horizontally in the pressure vessel. Fig. 17 shows a comparison of fractional diametral contraction, $\Delta d/d_o$, with length contraction, $\Delta l/l_o$, as a function of time for two samples sintered under identical conditions. The densification rates based on diameter and length, are observed to be identical. Subsequent experiments confirmed this result. It was concluded that an error in measurement of green samples had probably occurred in the initial experiments.

III. Hot Pressing and Swelling

Preliminary experiments have been obtained for hot pressing and swelling by sintering at a fixed pressure, then applying either a higher pressure or lower pressure at a point where a large fraction of the pores are closed. Some results are depicted in Figures 18 and 19. Fig. 18 shows the densification of a sample sintered to approximately 81.5% TD in 2000 psi Argon at 1075°C. When the pressure

^{*}M. H. Tikkanen, S. Ylasaari, and K. Blomster, Phys. Sintering 3-1: 1-27 (1971).

P. Kumar and D. L. Johnson, J. Am. Ceram. Soc. 56-7: 389-90 (1974).

is reduced to 1 atmosphere, the density is observed to rapidly decrease to approximately 76%. Upon application of pressure, there is a rapid increase in density at a much higher rate than the initial densification

This behavior was completely unexpected. If the swelling and hot-pressing involves the expansion and contraction of a fixed number of closed pores, one would expect the rate of dimensional change to be a function of density and the pressure difference between external and internal pressure only. The apparent history effect suggests that deformation mechanisms with anelastic elements dominate at least the transient behavior.

Figure 19 shows the swelling behavior of a sample which was sintered at 1750 psi Argon at 1175°C. At 86.4% TD, the ambient pressure is released and the sample swells to 81.7% TD. When 2000 psi Argon is reapplied, the sample again densifies but at a rapid rate and to a higher density.

IV. Work to be Performed in Balance of FY 1977

The major task that will be completed in this period will be the purchase and assembly of a quadrupole mass analyzer. This will enable us to measure the gas species that are released while sintering and during a swelling experiment when there is a driving force for gas release. Gas release kinetics are extremely important for nuclear fuels under steady state and transient conditions.

It was decided that the purchase of the ultra high vacuum pump and several smaller items originally proposed for FY 1977 should be deferred until FY 1978 in the interest of obtaining the quadrupole mass analyzer earlier.

COMMUNICATIONS IN FY 1977

1. R. A. Abbott, C. W. Tally and A. A. Solomon, "The Effects of Internal Gas Pressure on the Dimensional Stability of Ceramics", Intl. Materials Symposium on Ceramic Microstructures, Aug. 24-27, 1976, Berkeley, California.
2. R. A. Abbott and A. A. Solomon, "A Technique for Examining the Dimensional Stability and Microstructure of Ceramics", Bull. Amer. Ceram. Soc. 55:9 Sept. 1976. Presented at the 29th Pacific Coast Regional Meeting of the American Ceramic Society.
3. R. A. Abbott and A. A. Solomon, "Swelling and Densification of a Ceramic with Internally Pressurized Pores". To be presented at the 79th Annual Meeting of the American Ceramic Society, April 23-27, 1977.

TABLE I

Impurity Content of CoO Powder

<u>Impurity</u>	<u>ppm</u>
Si	470
Al	160
Fe	250
Mi	160
Ca	1290
Na	120
K	130

Figure 1. Pressure Vessel Assembly

Figure 2. LVDT Linearity

Figure 3. Temperature Sensitivity of LVDT

Figure 4. Effect of Pressure on LVDT Signal

Figure 5. Effect of Evacuation on LVDT Signal

Figure 6. Thermal Drift of System During Heat-Up

Figure 7. Thermal Drift of System During Cooling

Figure 8. Axial Temperature Gradients Within Pressure Vessel

Figure 9. Axial Temperature Gradients in the Specimens

Figure 10. Vessel Cooling Rate at Termination of Experiment

Figure 11. Water Flow Calibrations

Figure 12. TD Tungsten Pressure Vessel

Figure 13. Ratio of Open Porosity, to Total Porosity During Sintering

(a) CoO Boule and Ruler Divided in Inches

(b) Polished Section of Single Crystal

(Probable Second Phase: Co_3O_4)

Figure 14.

Figure 15. Sintering Curves at Various Ambient Pressures

Figure 16. Effect of Ambient Gas on Sintering

Figure 17. Relative Changes in Specimen Length and Diameter

Figure 18. Densification and Swelling Behavior at Various Ambient Pressures

Figure 19. Densification and Swelling Behavior at Various Ambient Pressures