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

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ABSTRACT

The pressurization system components for studying the hot-pressing and swelling behavior of CoO have been built including the displacement transducer, inert gas pressurization system, refractory metal pressure vessel with platinum liner, vacuum system and high temperature furnace. In addition, an elevated temperature refractory metal vacuum furnace has been modified so that specimen dimensional changes can be continuously monitored during sintering under high vacuum. Characterization of the CoO starting powders has been initiated in terms of surface area (BET absorption isotherms) particle size distribution (sedimentation/ non-fractionation and scanning electron microscopy) adsorbed gases (residual gas analysis) and surface contamination (ESCA). A technique has been developed to form geometrically uniform pellet compacts of high green density using low pressure punch and die pressing followed by high pressure isostatic compaction to obtain uniform green density. Preliminary sintering experiments have been carried out at one atmosphere pressure in air, inert gas and under vacuum with specimen deflection continuously monitored. The resulting microstructures following sintering have been characterized using mercury porosimetry and quantitative optical microscopy. The sintering experiments have shown drastic differences in sintering rates in vacuum and air. The results are being examined to determine if this difference is a stoichiometry effect or is associated with surface contamination on the starting powders. Single crystals of CoO have been grown by the arc transfer process and have been obtained from outside sources.

I. First Nine Month's Progress

A. Isostatic Hot-Pressing System

The hot-pressing apparatus has been designed with operating limits of 10,000 psi pressure at a temperature of 1200°C. Where possible, components have been used from available facilities at Purdue University and modified for the present application. Thus, certain aspects of the system were designed to conform to existing equipment while still preserving maximum flexibility for experiments.

The available Rene 41 pressure vessels imposed severe temperature and pressure limitation on experiments (~3000 psi at 1200°C). In addition, preliminary sintering studies on CoO in these vessels indicated that the specimens were being reduced to free Co metal. Therefore, it was found necessary to design a more creep and oxidation resistant pressure vessel. The hydraulic pressurization system that was available was also rejected because conversion from its liquid pressurizing capability to gas would have been costly but still less reliable, less efficient, and less versatile than a system specifically designed for gas pressurization. The furnace and vacuum equipment presently being used have been obtained from existing university resources. However, to extend the experiments to ~1400°C, the Kanthal A-1 furnace will be modified to use MoSi₂ elements. The design of the furnace is completed and parts are now on order.

1. Pressurization System and Pressure Vessel

The pressurization system, shown schematically in Figure 1, consists of four main functional components - the compressor, the accumulator, or gas receiver, the pressure vessel and a diffusion pumped vacuum system. The compressor is driven by compressed air and has a maximum output pressure

of 30,000 psi. A double-acting diaphragm type pump was selected to prevent specimen contamination by the compressing medium. The compressed gas is fed via an isolation valve to the accumulator which stores the gas supply at a pressure higher than the chosen working pressure for the experiment. From the accumulator, gas may be metered to the pressure vessel manually by an output valve for accurate control of working pressure. Another metering valve is used to release gas from the pressure vessel when desired. This system, while simple, requires manual adjustment and experience will dictate whether a closed-loop servo-controlled system is necessary. One gauge is used to monitor accumulator pressure, and a high precision Heise gauge is used to monitor pressure vessel pressure. Both parts of the system are protected by means of rupture discs.

An alternative (to the diaphragm pump) that is presently being used to perform preliminary experiments at relatively low pressure is a 6000 psi argon cylinder with a high pressure regulator.

A liquid nitrogen trapped diffusion pump is used to outgas the system and to perform swelling experiments in vacuum. Because the pressure vessel cavity is rather long and thin, a special, larger, diameter, sintering chamber will be constructed for sintering in ultra-high vacuum.

The pressure vessel, shown schematically in Figure 2 is made of TZM alloy (molybdenum - .5% titanium - .05% zirconium) which has the required high temperature strength and creep resistance. It can readily withstand temperatures above 1300°C at stresses considerably above 10,000 psi without failure. To prevent high temperature oxidation of the molybdenum, the vessel has been coated with molybdenum disilicide (MoSi_2) and further protected by a flowing inert gas jacket. On the interior, the vessel is protected by a .020" thick platinum liner which also allows suitable oxygen potentials in the specimen

cover gas. One potential problem with this arrangement is interdiffusion of platinum and molybdenum; therefore a technique is being developed to flame spray an alumina coating on the exterior surface of the liner as a diffusion barrier. The liner is to be brazed at the opening of the vessel with a gold alloy braze to prevent oxidation of the interior of the vessel.

The linear - variable - differential - transformer (LVDT) has been specially designed and built for a maximum temperature of 600°C and is capable of withstanding pressures up to $\sim 12,000$ psi. The LVDT core is mechanically linked to the sample at the bottom of the pressure vessel by means of an alumina rod. Cooling of the LVDT housing is accomplished by a copper water jacket.

The furnace is situated in a counterbalanced transport system that allows the pressure vessel to be exposed for inserting specimens and quenching them after testing. Although the stored energy in the pressure vessel is quite small, refractory metals are notoriously brittle at low temperatures so a $3/8$ inch thick, 10 inch diameter barrier has been incorporated in the transport system so that an operator is never exposed to the pressurized vessel.

Photographs of the pressure vessel components and the entire pressurization system are shown in Figures 3 and 4 respectively.

2. Heating System

Power is supplied to the furnace by means of a solid state power supply and controller. Temperature control signals are furnished by means of a thermocouple inserted in a well at the bottom of the pressure vessel.

3. Instrumentation

A summary of the instrumentation is depicted schematically in Figure 5. Normally three signals, representing temperature, pressure, or vacuum, and specimen deflection will be fed to a recorder. Pressure is

continuously monitored using a transducer[†] and electronics specially designed and built at Purdue.

Single crystal CoO has been grown by the arc transfer process in which an arc is struck between a cobalt rod and a substrate. Crystals the size of $\sim 1/2$ cm on an edge have been grown from relatively low purity material. These crystals are presently undergoing analysis. Porous CoO crystals grown by the Verneuil Process, have also been obtained from Argonne National Laboratory.* The porosity in these crystals is not homogeneously distributed, however, and it is not known whether it is possible to obtain a uniform distribution.

Methods are presently being considered for specimen encapsulation for hot-pressing or swelling experiments.

B. Powder Preparation and Characterization

The characterization of the starting material** has involved the use of several techniques and processes. Initial particle sizing by sieving and scanning electron microscopy indicated the need for particle size reduction in order to obtain high green densities. Dry ball milling was employed, followed by mechanical sieving to -325 Mesh.

The surface area of the prepared powder was measured using BET adsorption isotherms[†] and a sedimentation/non-fractionation test employing the Andreasen Pipette technique was used to determine particle size distribution; Fig. 6. Finally, scanning electron microscopy was used to determine general particle morphologies. In addition, residual gas analysis was used to determine the adsorbed gases on the powder, Fig. 7.

[†]Standard Controls Model 211-35-120

*Courtesy of W. K. Chen, Argonne National Laboratory

**Atomergic Corp. 99.9% CoO

[†]11.14 m²/gm for a received powder

C. Specimen Fabrication

The goal of our sample fabrication was to achieve a cylindrical pellet of high but uniform green density with a minimum of contamination. This was accomplished by the use of a light initial punch and die pressing pressure (approximately 100 psi) followed by isostatic compaction to 50,000 psi. This procedure offers the advantage of requiring no binder or lubricant and yields a rugged pellet with green density above 50% TD.

Initial attempts were made to sinter these pellets in air using available pressure vessels constructed of Rene 41; however, as mentioned earlier, specimen reduction to metallic Co was observed. An alumina tube insert placed between the vessel and the specimen failed to prevent reduction. Sintering was then attempted in air in a standard box furnace over a range of temperatures and for time spans up to 96 hours. Neck formation did take place, but without significant densification. Attempts were then made to sinter in vacuum and extensive outgassing was observed followed by densification to >90% TD. This outgassing appears to be essentially complete well below the sintering temperatures $\sim 1100^{\circ}\text{C}$ and work is presently underway (using ESCA and desorption analysis) to determine if the differences are due to stoichiometry or impurity variations.

D. Vacuum Sintering

To monitor sintering experiments in vacuum, a specimen support structure was modified to allow a displacement sensing rod to transfer specimen length changes to an LVDT transducer inside the vacuum system. In this way the densification of the pellet could be continuously measured during sintering to obtain kinetics data. This modification was just recently completed and the system is presently being tested. The fast response time of the refractory metal furnace will also permit the determination of temperature dependencies of sintering by thermal cycling experiments.

E. Specimen Characterization

Of the various analytical techniques being applied to specimen characterization, mercury porosimetry has required the most preparation. A computer program has been developed to correct for mercury and trapped air compression during pressurization and the classical "ink bottle effect" (due to small interconnections between pores). As indicated in Table 1, the porosimetry technique yields pore size distributions, pore surface areas, as well as the fraction of open porosity.

Quantitative microstructural analysis is performed using a Wild Heerbrug quantitative metallograph and photomicrographs taken with scanning electron microscopy. This allows the use of efficient counting techniques on samples with pore sizes down to 0.2 microns. Point counting for volume fractions and chord length measurements for size distributions are being used. The coordination of these two techniques permits the determination of the fraction of open porosity and the pore size distribution at any stage during sintering.

II. Work Expected to be Completed During Remainder of First Term

During the remaining three months, it is expected that the first sintering experiments will be conducted at elevated temperature and pressure under controlled atmosphere, with continuous measurement of densification rates. The sintering experiments at high vacuum and at 1 atm will be continued. Our first study will be to compare quantitatively the microstructural development during sintering as a function of pressure. This forms the basis of one M.S. thesis (see below) and should be essentially complete in the next three months.

The important measurements of the open porosity fraction will dictate the density at which it will be necessary to encapsulate the specimens.

Several methods are being considered for encapsulation including electron beam welding of formed capsules, chemical vapor deposition and flame spraying.

These methods will be investigated in the next three months.

III. Time Spent by Principal Investigator

The principal investigator has spent 15% of his time during the academic year and 100% of his time in the summer session during the first year.

This program is currently the principal investigator's sole research support for his time.

IV. Publications and Communications

- (1) "Microstructural Evolution of CoO during Sintering of Powder Compacts. M.S. Thesis, C. T. Tally. Expected completion date: May 1976.
- (2) "Effects of Internal Gas Pressure on the Microstructure of Ceramics", C. W. Tally, R. A. Abbott and A. A. Solomon, Sixth International Materials Symposium, August, 1976; abstract has been submitted which, if accepted, will be presented orally at the symposium; the paper will be reviewed for publication in the Proceedings.

Table 1. Typical Mercury Porosimetry Results

Mercury Gauge Press, psi	Cum. Pore Volume, %	Pore Radius Microns	Total Pore Area m ² /gm
5.2	0.00	57.381	0.00
10.0	4.30	14.029	.00
14.7	5.88	8.073	.00
100.0	7.65	.806	.00
300.0	9.58	.288	.01
400.0	14.32	.218	.03
450.0	25.90	.194	.09
500.0	44.25	.175	.20
550.0	52.45	.159	.26
600.0	59.14	.146	.30
700.0	67.26	.126	.37
800.0	72.76	.110	.42
1000.0	78.10	.088	.48
2000.0	88.67	.044	.68
3000.0	90.59	.030	.74
6000.0	92.22	.015	.83
10000.0	93.14	.009	.93
15000.0	94.48	.006	1.13

Note: Fraction of open porosity = 0.936 (This was a powder compact.)

Fig. 1 Pressurization System

Fig. 2 Pressure Vessel Assembly

Fig. 3a. Pressure vessel components. Shown left to right, (1) cooling jacket, (2) clamping nut, (3) LVDT, (4) platinum liner and (5) TZM pressure vessel.

Fig. 3b. Pressure vessel mounted in furnace assembly

Fig. 4 Pressurization System

Fig. 5 Schematic of Electronics

Fig. 6 Particle Size Distribution by
Sedimentation/Nonfractionation