MASTER

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

FINAL REPORT

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ABSTRACT

The results of the study of the effects of internal and external gas pressures on ceramics are summarized. The new experimental systems for studying these phenomena are described.

The study has shown that the rate of volume change in ZnO is linearly related to the total pressure driving force. Swelling and hot-pressing can be described on a consistent basis in terms of this driving force. For ZnO, Ni and UO_2 the rate of volume change is dependent on bulk diffusion. The porosity evolution during swelling is described and the resintering phenomenon is identified. Various models for pore growth and shrinkage are considered and related to the behavior of the different systems.

Suggestions for future work are made.

I. Experimental

A. Hot-pressing and Swelling System

In the course of this investigation, a new technique was developed to study an important group of problems involving the response of porous media to external and internal pressures at temperatures up to 1600°C . A description of the system is given in Appendix A.

Many problems had to be solved, including the design and selection of the refractory metal pressure vessel and materials. For testing low melting point ceramics, high equilibrium oxygen potentials are required which necessitated the use of a platinum liner and an alumina diffusion barrier between the liner and pressure vessel. The lined vessel worked well up to $\sim 1200^{\circ}\text{C}$, but above $\sim 1400^{\circ}\text{C}$, Al_2O_3 tends to be reduced by Mo or W and the differential thermal expansion between the liner and pressure vessel causes failure of the bond. A new flexible joint was designed to accomodate the differential expansion and an MgO coating is being investigated. Plasma coating of pure MgO has not been achieved, heretofore, and we are working with the Union Carbide/Linde Division to accomplish this. We have used an unlined TD tungsten vessel or low oxygen potentials, at $T > 1200^{\circ}\text{C}$.

B. Gas Release Mass Spectrometer System

The quadrupole mass spectrometer system was designed and built to measure release of entrapped gases in metals and ceramics. This system has required extensive calibration to correlate the release of gases from the specimen with the measured signal at the spectrometer.

A stainless steel tube which had the same length and inside diameter as the pressure vessel was used to simulate the pressure vessel. A valve was connected to the lower end of the tube, and the other end of the valve was plugged to simulate a typical specimen pore volume.

Different known quantities of argon gas were trapped in the valve cavity by closing the valve at different pressures to simulate variable amounts of gas in a sintered specimen. The pressure was measured by an MKS Baratron pressure transducer. The cavity volume was determined by comparing the resulting pressure when the entrapped gas is expanded into a bigger volume, with the pressure from a standard known volume expanded into the same volume.

A typical quadrupole response for an instantaneous burst of gas is shown in Figure 1. The figure shows that the experimental system has a time resolution of better than 3 seconds. The amount of released gas measured by the mass spectrometer is the area under the curve in Figure 1. Figure 2, shows that the system response is linear over the pressures investigated which correspond to instantaneous release of gas in a typical specimen with internal pressures of 1.4 to 0.004 MPa. Initial experiments have been conducted on ZnO and Ni which confirm the earlier swelling results, Appendix B. In particular, the release is gradual, but eventually terminates corresponding to a rapid decrease in the swelling rate.

The remainder of the system has been described in previous progress reports. Other calibrations and testing involved the new LVDT transducer system; the new MoSi₂ furnace designed and

built at Purdue; and testing of the high pressure and ultra-high vacuum systems so that compatible operation is obtained from 35 MPa to 10^{-9} TORR (over 14 orders of magnitude in pressure!)

In order to handle all of the temperature, pressure and quadrupole data, an automatic data acquisition system was designed and built as described in the next section.

C. Automatic Data Acquisition System

An automatic data acquisition system was designed and built, using the Purdue PDP 11/70 computer, a Keithley digital multimeter with BCD digital output, and an Iveron Pacific programmer with programmable relay control outputs.

This system converts channels of measured analog signals into digital signals which can be accepted by the computer for tabulation, printout and manipulation. Thus, the raw data can be sent directly to the computer without manual recording. The system makes the data collection very fast, accurate, and complete.

The block diagram of the data acquisition system is shown in Figure 3. Data channels in DC volts, are connected into a switching relay box. The switching box is controlled by the relay control signals from the Iveron Pacific 2100A programmer. It is programmed so that at each instant a proper channel is connected to the digital multimeter. The output of the digital meter is in BCD format which means they are parallel signals. The parallel signals are then converted by the "BCD to RS232 interface" into serial signals in ASCII code which conforms with

the RS232 I/O requirement for the PDP 11/70 computer. A computer program was written to the time the signals and identify which channel each signal belongs to and then store them properly.

D. Quantitative Microscopy

A semi-automatic system and software were developed for examining polished surfaces of ceramics. This system, described in Appendix C, was used in the study of ZnO swelling and gas release. Although it has good resolution, its use is cumbersome and does not allow operator discernment and selection of features. We have therefore ordered a Zeiss Viodeoplan to supplement our previous capability.

II. Experimental Results

A. Swelling and Gas Release:

1. ZnO

Our study of ZnO swelling and gas release (Appendix B) represents the first time swelling has been measured under controlled conditions. The temperature, pressure driving force dependencies and microstructural evolution were all characterized, and related to theories of hot-pressing, fracture, and swelling theories (Appendix D).

2. CoO

Attempts to measure hot-pressing and swelling in CoO were not successful, primarily because facetting limited the final densities achievable with a Pt-lined TZM pressure vessel. This ceramic system still appears attractive otherwise. The proposed hot-pressing experiments on porous CoO single crystals could not be performed because sufficient crystals were not available.

3. Nickel

Swelling of nickel metal was studied to verify that the activation

energy for swelling in a very well-characterized system, followed the same kinetics as creep and diffusion. Activation energies for swelling were found to agree very closely to those reported for dislocation creep and bulk diffusion in pure nickel. The stress dependence is presently being examined.

4. UO_2

Experiments were initiated on swelling and gas release in UO_2 using a thoria-dispersed tungsten pressure vessel. UO_2 is found to swell and release gas much like ZnO and this is presently being characterized.

Although hot-pressing experiments have been performed on nearly stoichiometric UO_2 under NRC sponsorship, the final results, Appendix E, have suggested important extensions to swelling and gas release. The hot-pressing is again found to be linear with pressure driving force. Although the pressure, temperature, grain size and porosity dependencies and even the predicted strain rates are in reasonable agreement with Nabarro-Herring creep, the microstructure did not appear consistent with such a model. This should also be examined for swelling in UO_2 .

III. Recommendations for Future Work

We feel that our new program involving the rupture of single phase ceramics at elevated temperatures is the most logical, relevant and potentially fruitful extension of our previous study. That such work is needed both scientifically and technologically hardly requires emphasis. In particular, we feel that the quantitative and statistical nature of the microstructure needs to be related to the measured properties. Cavity and pore growth depend very sensitively on their mutual interactions when they approach each other. Well-controlled experiments need to be performed on relatively well-understood ceramics especially in

terms of defect structure and kinetics. CoO is accordingly, a better material for study than ZnO . In general, there is a strong need in the study of ceramics for well-controlled critical experiments. In the area of rupture, any one of perhaps 6 or 7 models might apply, and we have very little definitive basis on which to narrow the choice.

In the area of mechanical properties of ceramics, it would be highly desirable if a centralized source of high purity material were available, so that related experiments could be performed on the same source of material by different laboratories. Characterization of the grain boundaries and mechanical property studies are two examples, as has been so vividly shown for two phase glass/ceramics. It appears to us that elevated temperature deformation of polycrystalline engineering ceramics has become neglected in the last few years in favor of the single crystal TEM studies. There are many important questions that remain unanswered. We hope to make a contribution in this area.

Figure 1. Mass spectrometer response following a simulated instantaneous burst of gas from specimen.

Figure 2. Measured total gas release using mass spectrometer vs. actual gas released

Fig. 3. BLOCK DIAGRAM OF THE DATA ACQUISITION SYSTEM