MASTER

Contract Report #C00-2408-4

PRESSURE SINTERING AND CREEP DEFORMATION

-- A JOINT MODELING APPROACH

Progress Report

for period

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Abstract

The joint modeling of creep deformation and pressure sintering, previously developed for the final and intermediate stages, has now been refined to include a "transition stage" that accounts for a decreasing "connectivity" for the cylindrical-open porosity and a smooth transition to spherical porosity as pinch-off occurs. As in the final and intermediate stages, this transition stage takes into account three major contributions to densification: lattice diffusional flow, grain boundary flow, and power law deformation; effects of grain growth have also been included. The model has been extensively tested and compared to experimental results on hot-pressed CoO, and is now being tested against earlier experimental data that we have obtained on MgAl_2O_4 .

Work has continued on creep studies of NiO and CoO, comparing the similarities and differences in creep behavior and relating these to dislocation structures observed in TEM.

Finally, work has been completed on the grain growth of CoO as a function of porosity level, and also the effects of impurities (Cr, Li) on the creep and densification rates of CoO and NiO. These studies have provided specific information required for the intermediate stage modeling. They have also led to initial work on grain boundary segregation effects studied by STEM that we hope to continue and extend to a quantitative approach during the next year.

I. Project Scope and Significant Results

The purpose of this research is to compare, or jointly model, the densification during the later stages of pressure sintering and creep deformation, for a number of ceramic oxides, as a function of stress level, temperature, grain size and porosity. In order to obtain all the material parameters required for a good quantitative model, this has necessitated experimental studies in six separate areas as outlined in Figure 1. During the previous years of this project, the work has emphasized the final, closed-pore, stage of densification and the intermediate, cylindrical open pore stage of densification; hot pressed specimens were fabricated, both densification and creep kinetics were measured, and steady state multimechanism models were developed. These multimechanism models combined both linear and non-linear plastic flow elements and "densification maps" were developed assuming each mechanism to contribute in an independent manner. As described in previous progress reports, these results were first reported in 1975 [1,2] and formed the basis for an Invited Opening Address at an international meeting that is soon to be published [3]. In conjunction with this work a number of studies were also previously carried out concerning the creep-rate behavior and TEM (Transmission Electron Microscope) examination of a variety of ceramic materials [4-9].

During the course of the present contract year, three major areas of work have been emphasized: first, the development of a model for hot-pressing that includes the transitional microstructural changes between intermediate and final stage densification; second, the improvement of our understanding in creep behavior and the relation between creep rate

and dislocation spacing, so that more dependable mechanical property data can be inputted to the hot-pressing model; and third, initial studies with STEM (scanning transmission electron microscopy) and in-situ X-ray analysis to examine grain boundary segregation effects in impurity doped oxides and their effect on boundary diffusion.

A. Hot Pressing Studies--Modeling and Experiment

During the past year, a multimechanism model, previously developed for the intermediate and final stages of hot pressing, has been refined to include transitional-microstructure effects. As before, this model takes into account three major contributions to densification: lattice diffusional flow (Nabarro-Herring), grain boundary diffusional flow (Coble) and power law deformation. In addition, the effects of grain growth and pore-redistribution have now been included; this includes a "transition stage" that accounts for decreasing "connectivity" for the cylindrical-open porosity and a smooth transition to spherical porosity as pinch-off occurs [10-13]. The results may be displayed, directly by computer output, either in the form of densification maps (plots of stress vs. temperature with lines of constant densification rate contours shown superimposed) at a given constant, but changeable, porosity level, or as plots of densification rate vs. porosity at a fixed applied stress and temperature in conjunction with a tabulated output listing the contribution made by each mechanism to the total densification rate. Plots of porosity vs. time, and grain-size vs. time are also readily obtainable from the computer model. The model has been extensively tested and compared to experimental results on hot-pressed CoO, and is now being tested against earlier experimental data that we have obtained on MgAl_2O_4 .

B. High Temperature Creep Deformation

Creep studies during the past year have centered on the examination of dislocation structures in both pure and Li doped CoO by TEM, and the effect of both impurity doping and stress level on dislocation spacing. An accurate means of measuring dislocation spacing from TEM thin foils has been developed [14] and this technique has been used to develop quantitative relationships as a function of impurities for Li doped CoO [15]. It has been shown that Li impurity additions increase the dislocation spacing, and reduce the steady state stress exponent, n , from 4.4 to 3.1; independent results obtained both by stress increment tests and by direct TEM examination are in excellent agreement. The results of these studies have provided a significant improvement in ability to choose appropriate constitutive equations for use in the generation of deformation and densification maps for ceramic materials.

C. STEM and Microchemical Analysis of Grain Boundaries

Most recently, we have initiated studies of grain boundary segregation effects in impurity doped oxides (NiO, MgO, Al_2O_3) using a newly developed analytical procedure combining scanning transmission electron-microscopy and X-ray microchemical analysis. This technique offers spatial resolution as small as $100\text{\AA}$ and we have examined boundary regions in specimens of MgO-25 w/o NiO, NiO-.1 w/o Cr_2O_3 , NiO-3 w/o Al_2O_3 . The preliminary results are quite encouraging and we plan extensive studies in this area during the next year.

D. Summary

It is the intent of this research to combine the refined understanding of high temperature creep behavior with the multimechanism hot-pressing model in order to develop an approach whereby the densification kinetics

can be predicted if creep results are available for a given material, or vice-versa, to use densification behavior under a given set of conditions to predict creep behavior under use-conditions.

II. Scientific Personnel Performing Research on This Current Project

1. M. R. Notis, Principal Investigator, Associate Professor in the Department of Metallurgy & Materials Science and Senior Staff Member of the Advanced Materials Laboratory of the Materials Research Center--2.25 man-months as of June 30, 1977; estimated 3.25 man-months total at the end of the contract year.
2. D. B. Williams, Faculty Associate, Assistant Professor in the Department of Metallurgy and Materials Science, Director of the Electron Microscopy Laboratory; estimated 1 man-month total at the end of the contract year. Professor Williams has initiated work on TEM and STEM on the structure and composition of grain boundaries in hot pressed ceramics.
3. V. Krishnamachari, Postdoctoral Research Assistant--7.0 man-months total as of July 31, 1977. Dr. Krishnamachari has concentrated on the measurement of high temperature creep properties during the past few months and has guided the production of hot pressed specimens to be used in creep testing and has spent considerable time on computer analysis of hot pressing data.
4. P. Wingert, Graduate Student--6 man-months as of June 30, 1977. Mr. Wingert has completed his Master's Degree in Metallurgy & Materials Science and is responsible for the development of the multimechanism intermediate stage hot pressing model.

5. A. Miro, Graduate Student; estimated 5.5 man-months as of the end of the contract year. Mr. Miro has just joined the Department and will be continuing the modeling work of Mr. Wingert. Mr. Miro has recently graduated from Alfred.
6. Barry Bender, Graduate Student. Mr. Bender has recently graduated from V.P.I. and will be a graduate student in the Department of Metallurgy and Materials Science as of September 1, 1977. He is supported by a Hornor Fellowship through the Graduate School. His research work for his M.S. thesis will be directly related to this project.

III. Papers Published During the Current Contract Year

1. "Subgrain Boundary Formation in Single and Polycrystalline CoO"
V. Krishnamachari, M. R. Notis, D. M. Shah
J. Mat. Sci., 12, 666-669 (1977).
[Appendix 3 of Progress Report C00-2408-3]
2. "Interpretation of High-Temperature Creep of SiC by Deformation Mapping Techniques"
V. Krishnamachari, M. R. Notis
Mat. Sci. & Eng. 27, 83-88 (1977).
[Appendix 6 of Progress Report C00-2408-3]
3. "Advances in Ceramic Hot Forming and Pressing--Theory and Practice"
in Advances in Ceramic Processing, P. Vincenzini, ed., National Res. Council of Italy, in press.
[Appendix 1 of Progress Report C00-2408-3]

IV. Papers Accepted or Submitted for Publication

1. "Effect of Dislocation Spacing on High Temperature Creep of Pure and Li Doped CoO"
V. Krishnamachari, M. R. Notis and D. M. Shah, accepted for publication
Mat. Sci. & Engineering.
[see Appendix III of this Progress Report]
2. "High Temperature Deformation of Polycrystalline NiO"
V. Krishnamachari and M. R. Notis, accepted for publication in Acta. Met.
[Appendix 4 of Progress Report C00-2408-3]

3. "High Temperature Deformation of Polycrystalline CoO"
V. Krishnamachari and M. Notis, submitted to J.A.C.S.
[Appendix 2 of Progress Report COO-2408-3]
4. "Densification Mapping for the Intermediate and Final Stages of Hot Pressing"
M. R. Notis and P. Wingert, submitted to Science of Sintering
[see Appendix I of this Progress Report]
5. "Measurement of Intrinsic Boundary Dislocation Spacing from Electron Micrographs"
D. Shah, V. Krishnamachari, M. R. Notis, submitted to Scripta Met.
[see Appendix II of this Progress Report]

V. Manuscripts in Preparation

1. "Grain Growth and Porosity in CoO," M. R. Notis, P. Wingert and C. Gasdaska, to be submitted to J. A. C. S.
2. "Modeling of Transition Microstructural Effects During Hot Pressing," P. Wingert and M. Notis, to be submitted to J. A. C. S.
3. "Impurity Effects on Creep in NiO and CoO," V. Krishnamachari and M. Notis, to be submitted to J. A. C. S.
4. "Hot Pressing and Creep of $MgAl_2O_4$," R. Smoak and M. Notis, to be submitted to J. A. C. S.
5. "Emerging Areas in Hot Pressing," R. M. Spriggs and M. R. Notis, to be submitted to Science of Sintering.

VI. Lectures and Presentations

1. "Joint Modeling of Creep and Hot Pressing of Ceramics"
Penn. State Univ., March 24, 1977.
2. "Densification Mapping for Final and Intermediate Stage Hot Pressing"
P. Wingert and M. Notis, Paper No. 13-B-77.
Paper presented at 79th Annual Meeting, Am. Ceramic Soc., April 25-27, 1977, Chicago.
3. "Densification Mapping for Final and Intermediate Stage Hot Pressing"
M. R. Notis and P. Wingert, Paper No. 1.28, Fourth Int'l. Round Table Conference on Sintering, Sept. 5-10, Dubrovnik, Yugoslavia.
4. "Role of Interfacial Processes in High Temperature Deformation of Ceramics"
M. Notis, Gordon Research Conf. on Solid State Studies in Ceramics, Tilton, N. H., August 1-5, 1977.
5. "Emerging Areas in Hot Pressing"
R. M. Spriggs and M. R. Notis, Paper No. 4.3, Fourth Int'l. Round Table Conference on Sintering, Sept. 5-10, Dubrovnik, Yugoslavia

References

- [1] M. R. Notis, R. H. Smoak, and V. Krishnamachari, "Interpretation of Hot Pressing Kinetics by Densification Mapping Techniques," in Sintering and Related Phenomena - Proceedings of a conference held at Notre Dame, Indiana, June 1975, G. C. Kuczynski, ed.
- [2] M. R. Notis, "Deformation Mechanism Maps--A Review with Applications," p.1-123 in Deformation of Ceramic Materials, R. C. Bradt and R. E. Tressler, eds., Plenum (1975).
- [3] M. R. Notis, "Advances in Ceramic Hot Forming and Pressing--Theory and Practice," in Advances in Ceramic Processing, P. Vincenzini, ed., Nat. Res. Council of Italy, in press. (Appendix 1 of Progress Report C00-2408-3).
- [4] V. Krishnamachari and M. R. Notis, "High Temperature Deformation of Polycrystalline CoO," submitted to J. Am. Ceram. Soc. (Appendix 2 of Progress Report C00-2408-3).
- [5] V. Krishnamachari, M. R. Notis, and D. Shah, "High Temperature Deformation of Polycrystalline NiO," accepted in Acta. Met. (Appendix 4 of Progress Report C00-2408-3).
- [6] V. Krishnamachari, M. R. Notis, and D. Shah, "Subgrain Boundary Formation in Single- and Polycrystalline CoO," J. Mat'l. Sci. 12, 666-669 (1977). (Appendix 3 of Prog. Rept. C00-2408-3).
- [7] V. Krishnamachari, "Creep Recovery of CoO Single Crystals," J. Mat'l. Sci. 11, 1031-1035 (1976). (Appendix 5 of Prog. Report C00-2408-3).
- [8] V. Krishnamachari and M. R. Notis, "Interpretation of High Temperature Creep of SiC by Deformation Mapping Techniques," Mat'ls. Sci. and Eng., 27, 83-88 (1977). (Appendix 6 of Prog. Report C00-2408-3).
- [9] V. Krishnamachari and M. Notis, "High Temperature Creep of Impurity Doped NiO and CoO," to be submitted for publication, J.A.C.S.

- [10] P. Wingert and M. R. Notis, "Densification Mapping for the Intermediate and Final Stages of Hot-Pressing," submitted to Science of Sintering (Appendix I, this report).
- [11] P. Wingert and M. Notis, "Modeling of Transition Microstructure Effects During Hot Pressing," to be submitted J.A.C.S.
- [12] M. R. Notis, P. Wingert and C. Gasdaska, "Grain Growth and Porosity in CoO," to be submitted J.A.C.S.
- [13] R. Smoak and M. Notis, "Interpretation of the Hot Pressing Kinetics of MgAl_2O_4 by Densification Mapping Techniques," to be submitted for publication.
- [14] D. Shah, V. Krishnamachari, and M. R. Notis, "Measurement of Intrinsic Boundary Dislocation Spacing from Electron Micrographs," submitted to Scripta Met. (Appendix II, this report).
- [15] V. Krishnamachari, M. Notis and D. Shah, "Effect of Dislocation Spacing on High Temperature Creep of Pure and Li Doped CoO," accepted for publication, Mat. Sci. and Eng. (Appendix III, this report).

JOINT - MODELING RESEARCH

CoO

MATERIALS STUDIED

1. CoO
2. NiO
3. MgAl₂O₄
4. Yb₂O₃
5. CoO + Li
6. NiO + (Li, Al, Cr, Mg)

GOALS

1. FUNDAMENTAL STUDIES IN EACH AREA ON WELL CHARACTERIZED SPECIMENS.
2. HOW BULK AND INTERFACIAL (PORES, BDRYS) PROPERTIES INFLUENCE BEHAVIOR.
3. INDEPENDENT SETS OF MEASUREMENTS USING SAME SPECIMENS.
4. DEVELOPMENT OF MODEL RELATING EACH OF FUNDAMENTAL AREAS TO PROCESSING AREAS.

Figure 1: Schematic Flow System of Experimental Areas for Joint Modeling of Creep and Densification During Hot Pressing