LBL-17547
Preprint

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY
JUL 6 1984
LIBRARY AND
DOCUMENTS SECTION

Materials & Molecular Research Division

Submitted to the Journal of the American Ceramic Society

PARTICLE REARRANGEMENT IN EARLY SINTERING

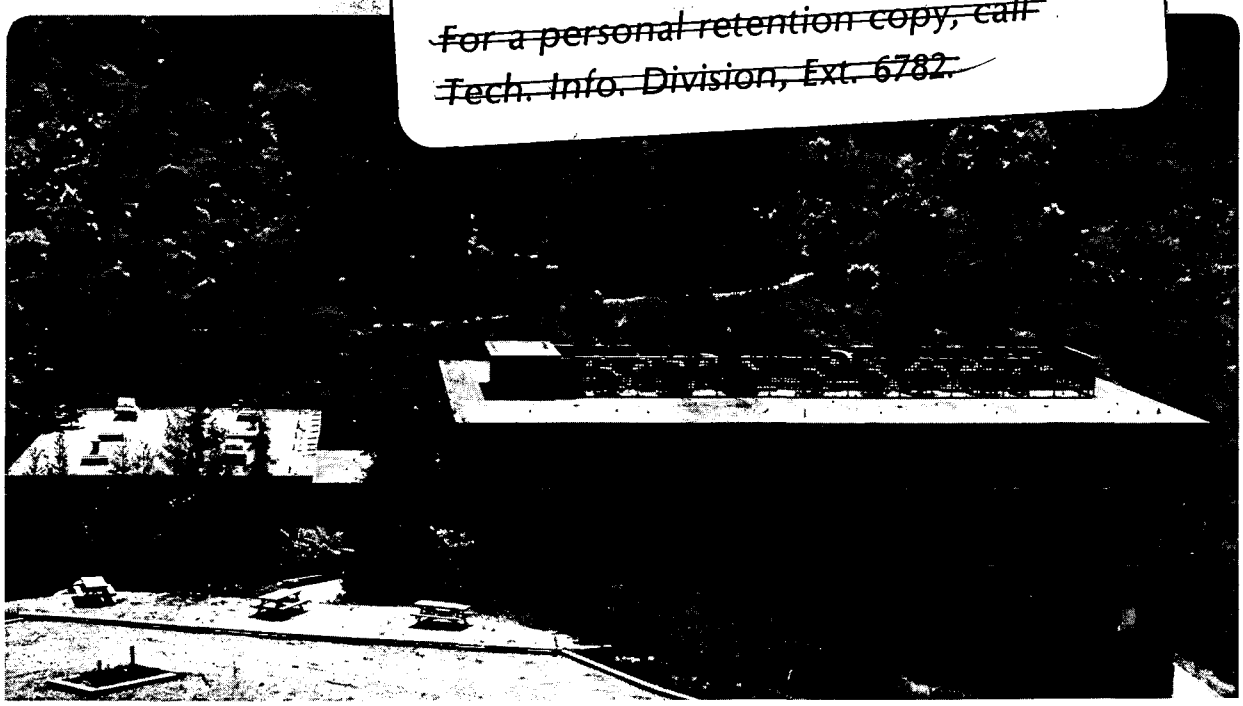
C.-H. Hsueh and L.C. De Jonghe

March 1984

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks.

~~For a personal retention copy, call Tech. Info. Division, Ext. 6782.~~



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-17547

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

PARTICLE REARRANGEMENT IN EARLY SINTERING

CHUN-HWAY HSUEH and LUTGARD C. DE JONGHE

Lawrence Berkeley Laboratory
Materials and Molecular Research Division
and
Department of Materials Science and Mineral Engineering
University of California, Berkeley
Berkeley, California 94720

Abstract

Shrinkage and rearrangement during the early stages of sintering is considered. In such rearrangement the sintering particles can experience both additional center to center stresses, as well as bending moments, arising from multiparticle interactions and asymmetrical neck formation. The response of a particle pair to the simultaneous action of these stresses is solved analytically in a cylindrical geometry.

Introduction

The densification processes that occur as a result of mass transport from interparticle grain boundaries to adjacent surfaces has been modeled extensively for the early stages of sintering for symmetrical (1-4) as well as for asymmetrical neck formation (5-7). Such asymmetrical neck formation can arise when three or more particles interact during the densification, and is believed to be a major cause of rearrangement (8). It is, however, apparent that differential densification in heterogeneously packed powder compacts can have a substantial effect on the particle rearrangement and the microstructural evolution of the sintering body (9). Quantitative modeling of densification processes in non-homogeneous multiparticle powder compacts requires consideration of the applied stresses and bending moments caused by differential densification. The intent of the present paper is to develop

an analysis for the simultaneous shrinkage and particle rotation, by considering an asymmetrical neck subject to an applied stress and bending moment.

Development of the model

A model is considered that consists, for simplicity, of a two-dimensional asymmetrical neck, with radii of curvature R_1 and R_2, between two equally sized cylinders. The neck is subjected to a bending moment M (see Fig. 1a). The resulting stress distribution on the grainboundary gives the gradient in the chemical potential which, in turn, gives the driving force for matter transport. Only the case of grainboundary diffusion is treated.

Consider a small element δx on the grainboundary, within an incremental time interval δt. The total amount of material removed from this element is δm. It can be considered as consisting of two components: a uniform layer of material, δm_s, responsible for the center-to-center approach, and an amount δm_r, accommodating the rotation. The geometry of the rotating particles is shown in Fig. 1a; during particle rotation material must be transported from area A to area B. δm_r depends on position and is readily found by considering the geometry sketched in Fig. 1b to be

$$\delta m_r = \delta\theta \left(\frac{X_0}{2} - x\right) . \delta x \qquad \text{Eqn.1}$$

The meaning of the variables is as indicated in Fig.1b.

Conservation of matter requires that

$$\delta J . \Omega . \delta t = - \delta m \qquad \text{Eqn.2}$$

Combination of Eqns. 1 and 2 yields

$$dJ/dx = -[\dot{\theta}(\frac{X_0}{2} - x) - \dot{S}]/\Omega \qquad \text{Eqn.3}$$

Using the convention that a compressive stress is negative, so that

$$\mu = -\sigma\Omega \qquad \text{Eqn.4}$$

one also has that

$$J = (D_b \delta_b / kT)\, d\sigma/dx \qquad \text{Eqn. 5}$$

The stress distribution on the grainboundary will thus be

$$\sigma(X) = C_1.X^3/6 + C_2.X^2/2 + C_3 X + C_4 \qquad \text{Eqn. 6}$$

where

$$C_1 = kT\theta/D_b \delta_b \Omega \qquad \text{Eqn. 7}$$

and

$$C_2 = -kT\,(\frac{X_0}{2}\dot{\theta} - \dot{S})/\, D_b \delta_b \Omega \qquad \text{Eqn. 8}$$

The rotation rate, $\dot{\theta}$, the shrinkage rate, $\dot{S}$, and the constants C_3 and C_4 are determined by the boundary conditions. The boundary conditions are:

$$\sigma(X=0) = \gamma_s / R_1 \qquad \text{Eqn. 9}$$

and

$$\sigma(X=X) = \gamma_s / R_2 \qquad \text{Eqn. 10}$$

where R_1 and R_2 are taken to be positive quantities for the geometry shown in Fig. 1a.

In addition the force and moment balance requires that

$$\int_{X=0}^{X=X_0} \sigma dx + 2\gamma_s = \sigma_a X_0 \qquad \text{Eqn.11}$$

and

$$\int_{X=0}^{X=X_0} \sigma\,(X - \frac{X_0}{2})\,\sigma dx + M \qquad \text{Eqn.12}$$

Application of the boundary conditions to Eqn.6 yields:

$$C_1 = 60\gamma_s \left(\frac{1}{R_2} - \frac{1}{R_1} - \frac{12M}{X_0^2\gamma_s}\right) / X_0^3 \qquad \text{Eqn.13}$$

$$C_2 = 12\gamma_s \left(\frac{-2}{R_2} + \frac{3}{R_1} + \frac{2}{X_0} - \frac{\sigma_a}{\gamma_s} + \frac{30M}{X_0^2\gamma_s}\right) / X_0^2 \qquad \text{Eqn.14}$$

$$C_3 = 3\gamma_s \left(\frac{2\sigma_a}{\gamma_s} - \frac{4}{X_0} - \frac{3}{R_1} + \frac{1}{R_2} - \frac{20M}{X_0^2\gamma_s}\right) / X_0 \qquad \text{Eqn.15}$$

$$C_4 = \gamma_s / R_1 \qquad \text{Eqn.16}$$

so that

$$\dot{S} = 6\, D_b \delta_b \Omega \gamma_s \left(\frac{1}{R_1} + \frac{1}{R_2} + \frac{4}{X_0} - \frac{2\sigma_a}{\gamma_s}\right) / kT\, X_0^2 \qquad \text{Eqn.17}$$

and

$$\dot{\theta} = 60\, D_b \delta_b \Omega \gamma_s \left(\frac{1}{R_2} - \frac{1}{R_1} - \frac{12M}{X_0^2\gamma_s}\right) / kT\, X_0^3 \qquad \text{Eqn.18}$$

while

$$\sigma/\gamma_s = 10 \left(\frac{1}{R_2} - \frac{1}{R_1} - \frac{12M}{X_0^2\gamma_s}\right) X^3/X_0^3 + 6 \left(-\frac{2}{R_2} + \frac{3}{R_1} + \frac{2}{X_0} - \frac{\sigma_a}{\gamma_s} + \frac{30M}{X_0^2\gamma_s}\right) X^2/X_0^2$$

$$+3 \left(\frac{1}{R_2} - \frac{3}{R_1} - \frac{4}{X_0} + \frac{2\sigma_a}{\gamma_s} - \frac{20M}{X_0^2\gamma_s}\right) X/X_0 + 1/R_1 \qquad \text{Eqn.19}$$

Discussion

The expressions for the center-to-center approach rate, Eqn. 17, and for the rotation rate, Eqn. 18, show that $\dot{S}$ depends linearly on σ_a, and is independent of M, while $\dot{\theta}$ depends linearly on M and is independent of σ_a. One also notes that the expression for $\sigma(X)$ is identical to the one derived by Exner and Bross (7) for the case of asymmetrical necks, if the applied stress and the bending moment are put equal to zero. Some examples of the stress distributions, and of $\dot{S}$ and $\dot{\theta}$, for various values of σ_a and M, have been calculated in Fig. 2-4.

The magnitudes of the applied stresses and bending moments that act on interparticle necks is difficult to estimate, since they will strongly depend on the density gradients and packing arrangements in the powder compact. Such forces and moments can be large, as can be surmized from the work of Lange (10) on the effects of agglomerates on the microstructure of densifying compacts. It is, in fact, thought that the bending moments and stresses due to differential sintering arising from density gradients may dominate the rearrangement process, rather than the asymmetrical neck formation, contributing significantly to the difference in densification kinetics between two particle models and multiparticle compacts. This is currently being verified further by computer modeling of the evolution of multiparticle powder compact rearrangement and comparing this calculated evolution with experimentally observed rearrangement.

Symbols

C_1, C_2, C_3, C_4 :parameters defining stress distribution on grain boundary

D_b :grainboundary diffusion coefficient

J :atom flux

k :Boltzmann factor

m :total mass removed from boundary at X

m_r, m_s :component of m accomodating particle rotation or approach

M :applied bending moment (the sign is negative in the present case).

R_1, R_2 :radii of curvature at X=0 and X=X

S :center-to-center approach rate

t :time

T :absolute temperature

X	: distance along the grainboundary
X_0	:neck width
γ_s	:surface tension
δ_b	:effective grainboundary thickness
$\dot{\theta}$	:rotation rate
μ	:chemical potential of the atoms
$\sigma(X)$	:stress on grainboundary at X
σ_a	:applied stress
Ω	:atomic volume

Acknowledgements

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy, under contract No. DE-AC03-76SF00098.

References

1. R. L. Coble, "Initial Sintering of Alumina and Hematite", J. Amer. Ceram. Soc., 41, 55-62 (1958).

2. D. Lynn Johnson and T. M. Clark, "Grainboundary and Volume Diffusion in the Sintering of Silver", Acta Met., 12, 1173-79 (1964).

3. D. Lynn Johnson, "New Method of Obtaining Volume, Grainboundary and Surface Diffusion Coefficients from Sintering Data.", J. Appl. Phys., 40, 192-200 (1969).

4. R. L. Eadie, D. Wilkinson, and G. C. Weatherley, "The Rate of Shrinkage During the Initial Stage of Sintering", Acta Met., 22 1185-95 (1974).

5. G. Petzow and H. E. Exner, "Particle Rearrangement in Solid State Sintering," Z. Metallk., 67, 611-618 (1976).

6. H. E. Exner, G. Petzow, and P. Wellner, in "Sintering and Related Phenomena", edited by G. C. Kuczynski, 351-362., Plenum Press, New York (1973).

7. H. E. Exner and P. Bross "Material Transport Rate and Stress Distirbution During Grainboundary Diffusion Driven by Surface Tension", Acta Met., 27, 1007-12 (1979).

8. H. E. Exner, "Principles of Single Phase Sintering," Rev. Powder Met. Phys. Ceramics, 1, 1-4 (1970) p. 114.

9. L. K. Barret and C. S. Yust "Progressive Shape Change of the Void During Sintering", Trans. Met., Soc. AIME 239, 1172-80 (1967).

10. F. F. Lange and M. Metcalf, "Agglomerate Motion and Cracklike Internal Surfaces Caused by Differential Sintering"., J. Amer. Ceram. Soc., 66, 398-398-407 (1983).

Figure Captions

1a. Geometry of the rotating particles subject to an applied stress, $_a$, and a bending moment, M. During rotation material must be transported from A to B. XBL 843-8357

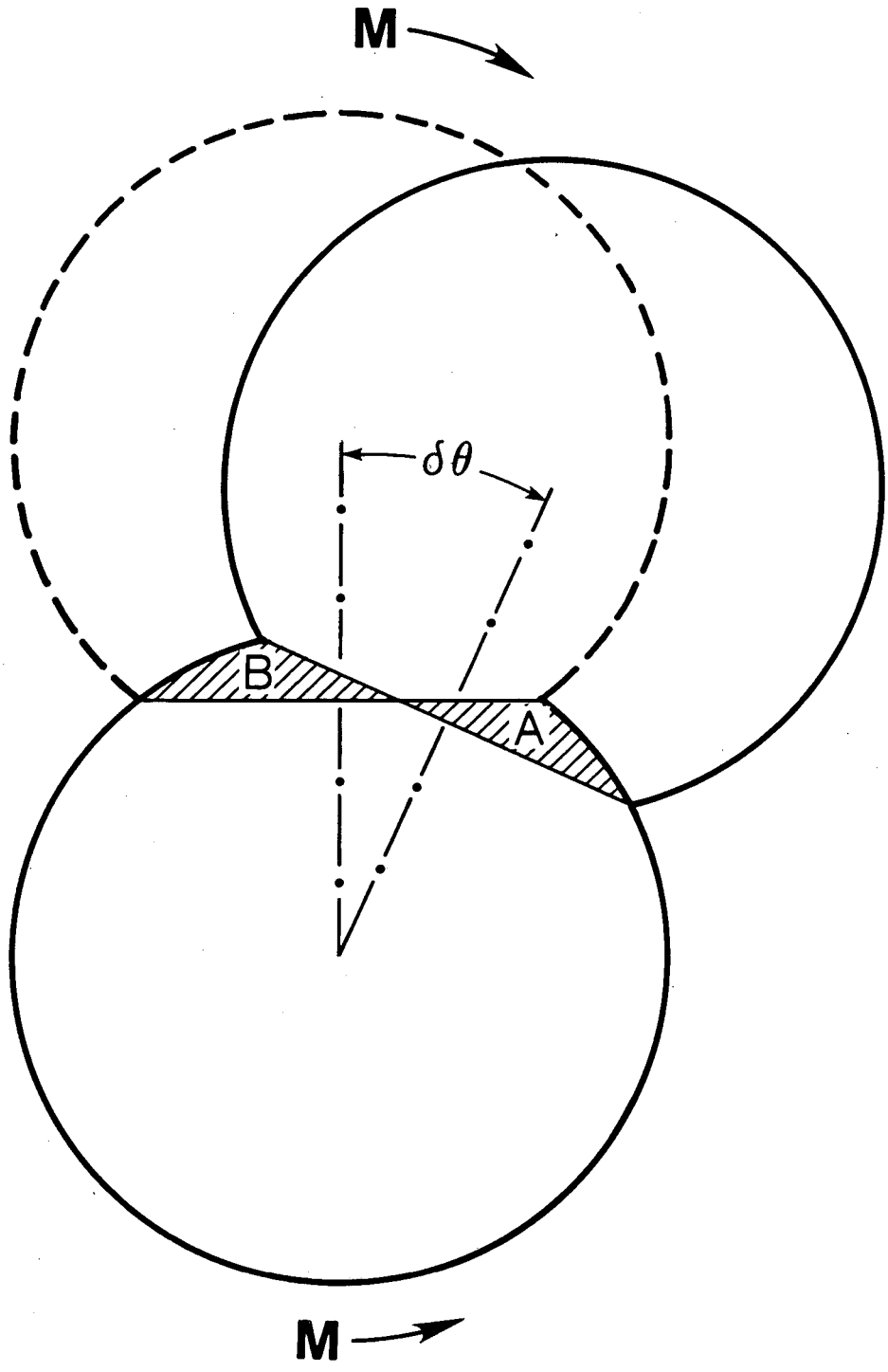
1b. Geometry of grainboundary material removal or addition for an incremental particle rotation. δm_r is equal to the area ABCD, which in turn is equal to the area ACED. Since $\delta m_r = \delta\theta r\ \delta r$, and $\delta X/\delta r = r/DK = r/(\frac{X_0}{2} - X)$, Eqn. 1 follows. XBL 843-8361

2a. Normalized stress distribution on the grainboundary, symmetrical neck case, with applied bending moment, in the absence of an applied stress. XBL 843-8360

2b. Normalized rotation rate and normalized shrinkage rate in the absence of an applied stress, for a symmetrical neck, as a function of bending moment. XBL 843-8358

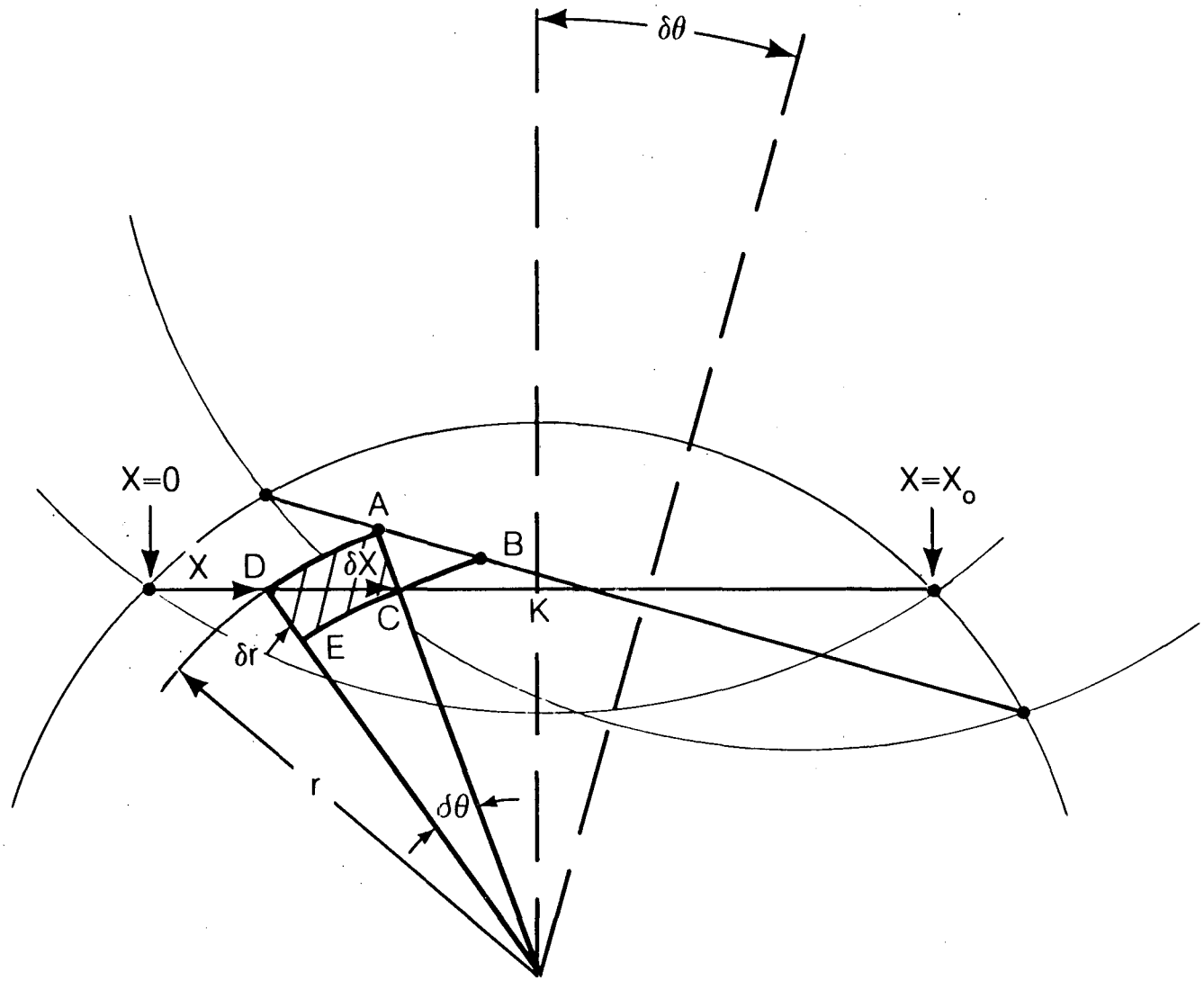
3a. Normalized stress distribution on the grainboundary, in the presence of a fixed bending moment, as a function of applied stress. XBL 843-8356

3b. Normalized rotation rate and normalized shrinkage rate in the presence of an applied moment for symmetrical neck, as a function of applied stress. XBL 843-8359



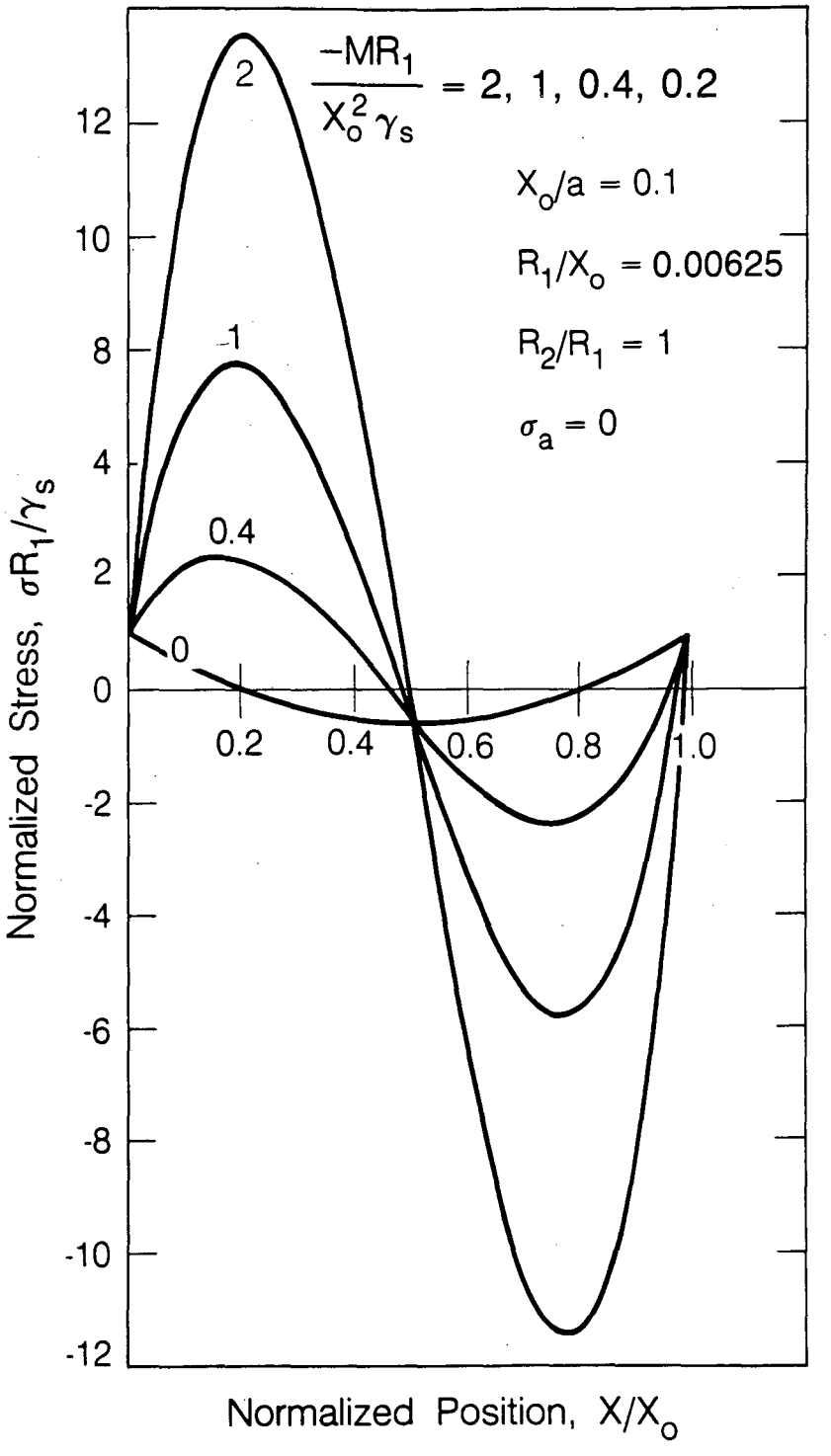
XBL 843-8357

Fig. 1a



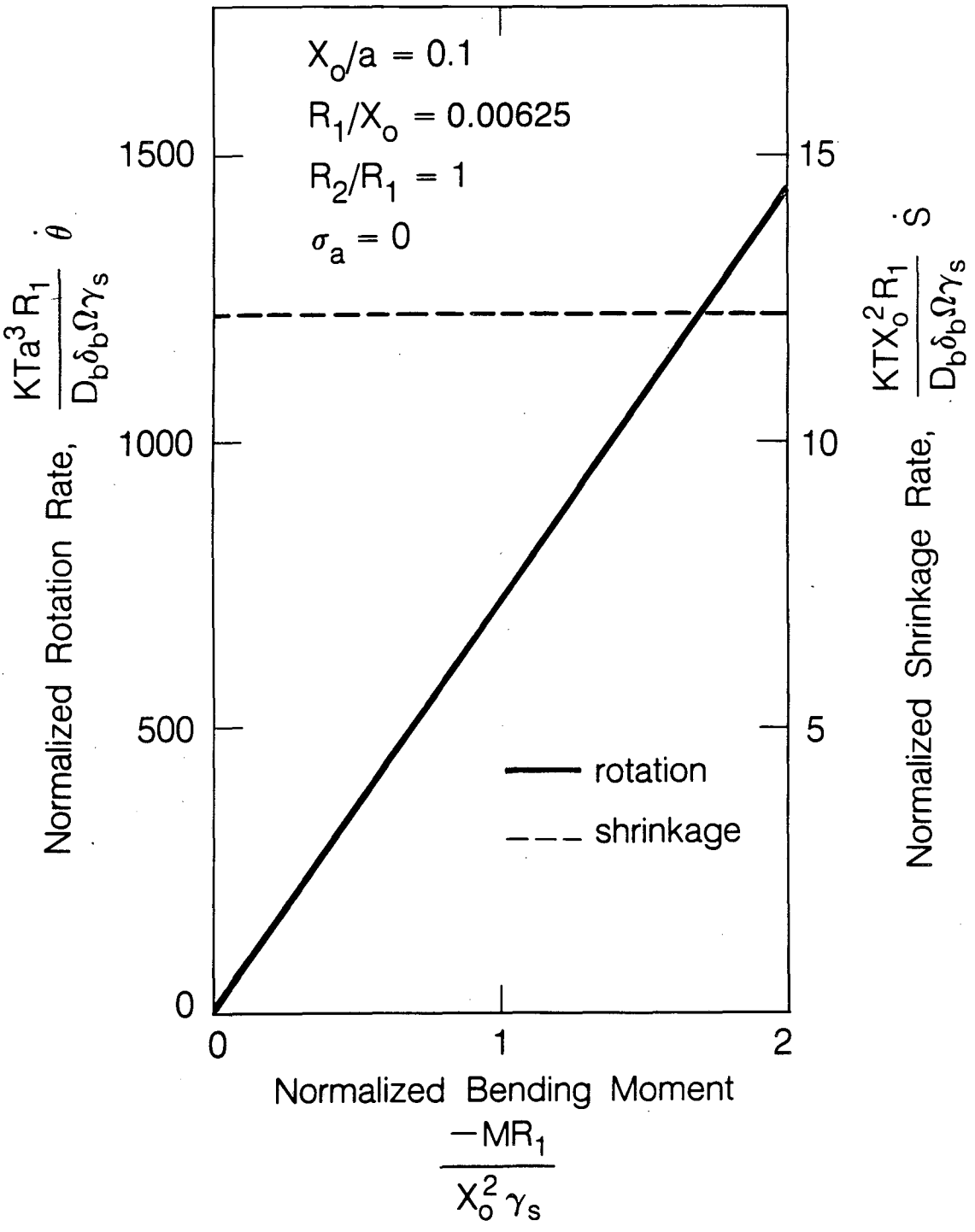
XBL 843-8361

Fig. 1b



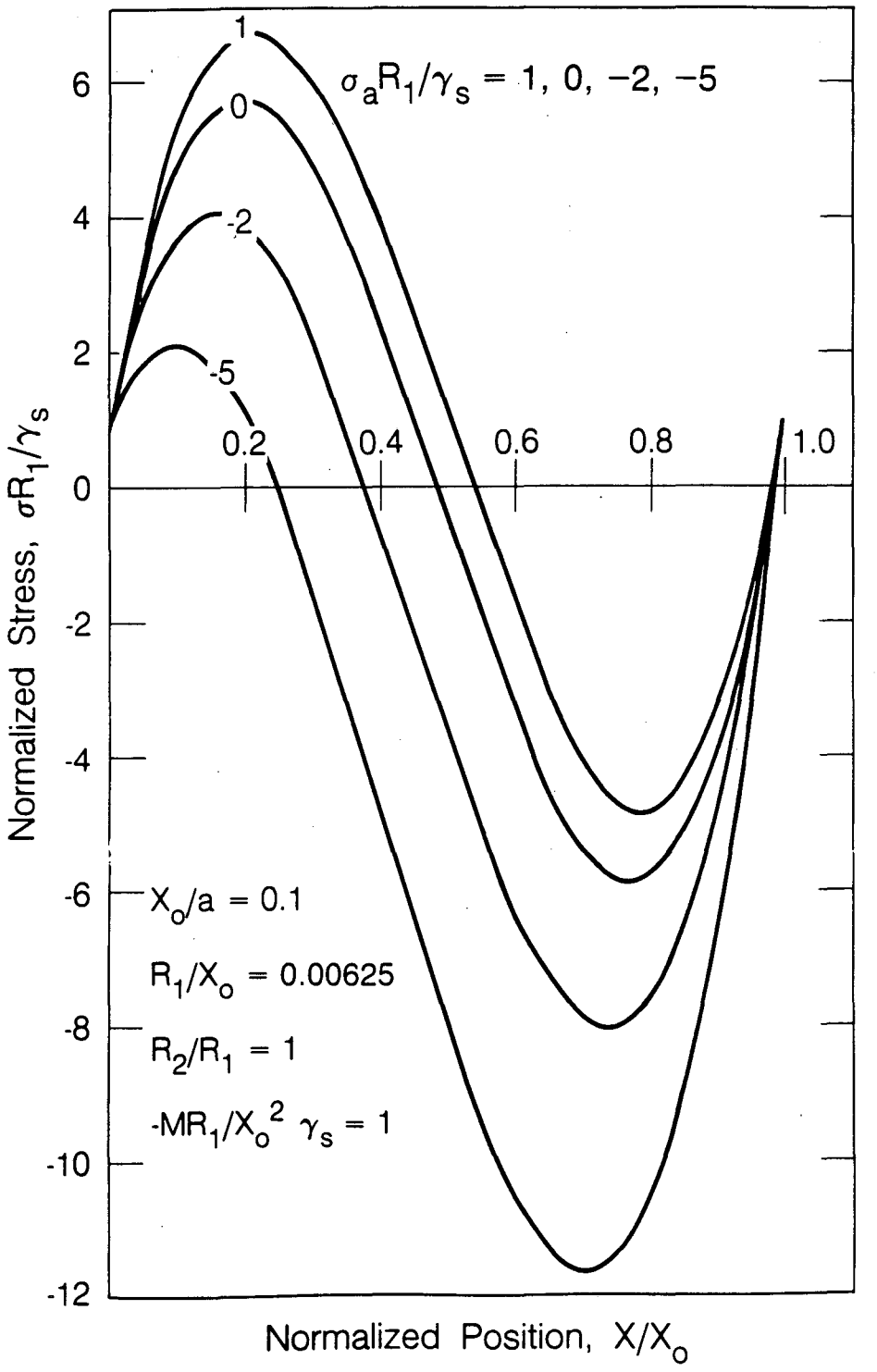
XBL 843-8360

Fig. 2a



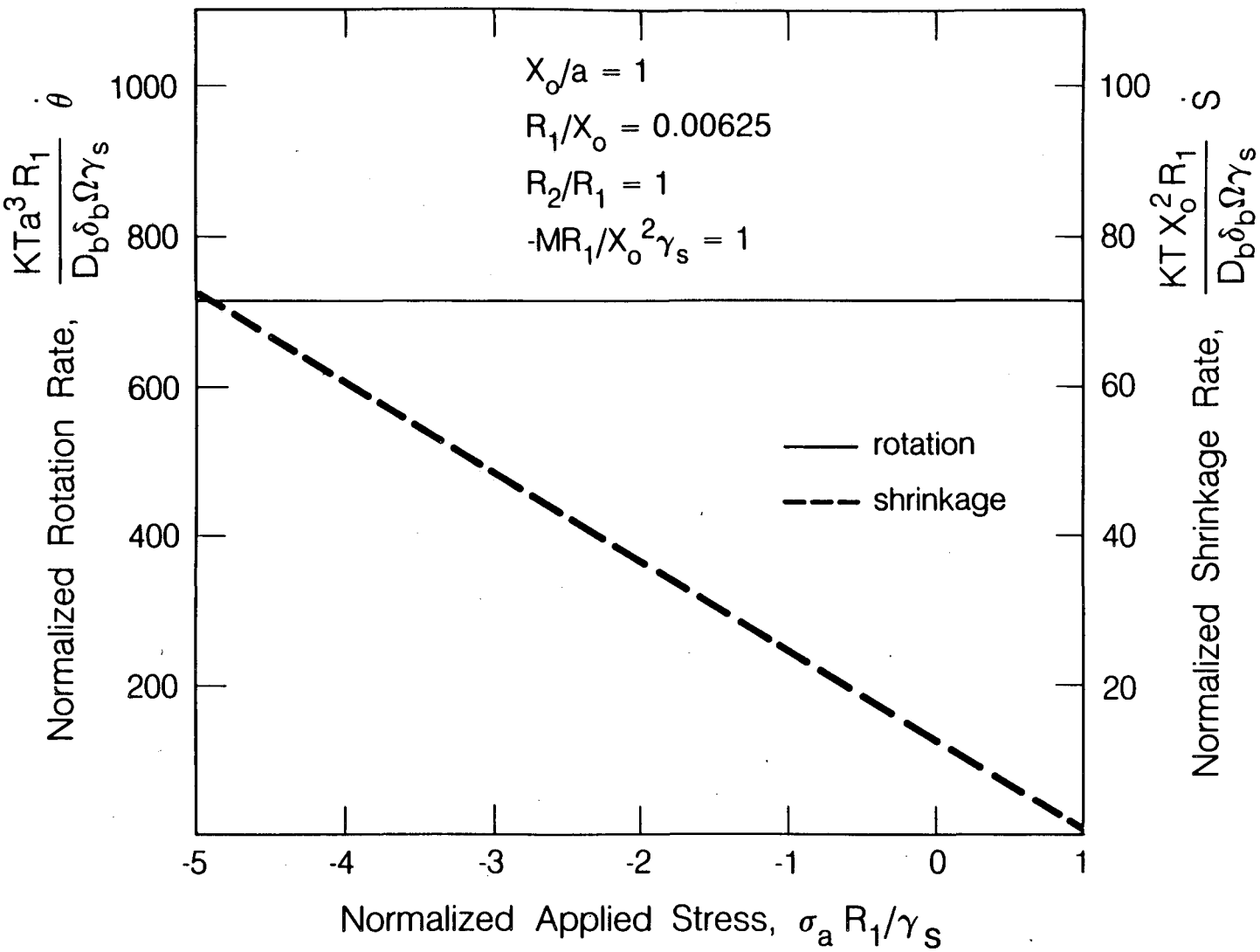
XBL 843-8358

Fig. 2b



XBL 843-8356

Fig. 3a



XBL 843-8359

Fig. 3b

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720