Title

PORE SIZE DISTRIBUTION DURING COMPACTION AND EARLY STAGE SINTERING OF SILICON NITRIDE

Permalink

https://escholarship.org/uc/item/5hb94229

Authors

Naito, N.
Rahaman, M.N.
DeJonghe, L.C.

Publication Date

1989-02-01

LBL-26849 c.2
Preprint

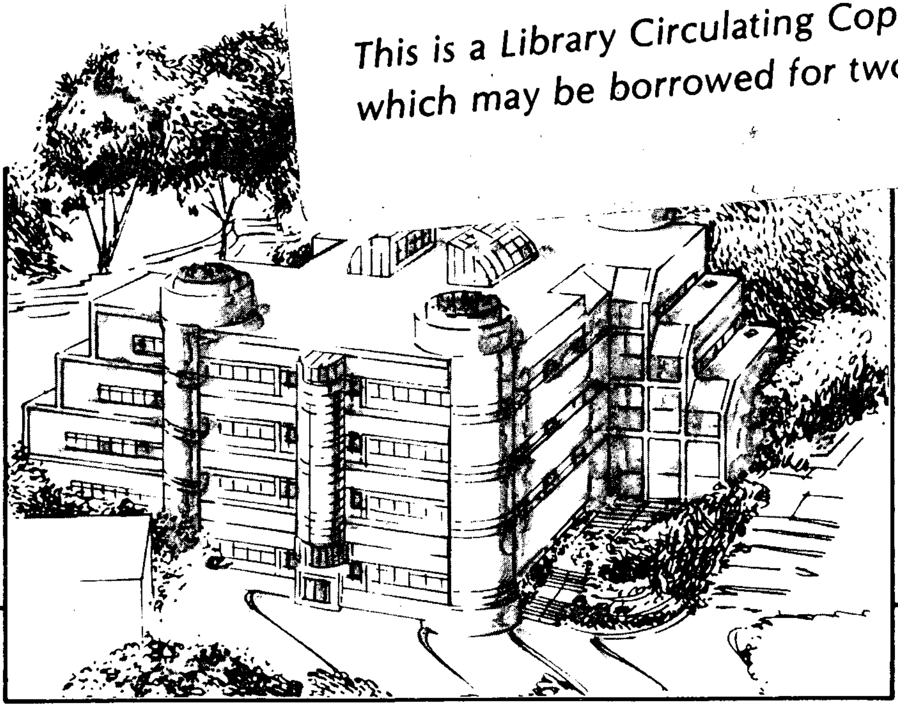
Center for Advanced Materials
CAM

Submitted to Journal of Materials Science

Pore Size Distribution during Compaction and Early Stage Sintering of Silicon Nitride

N. Naito, M.N. Rahaman, and L.C. De Jonghe

February 1989



LBL-26849 c.2

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory • University of California

ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

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

DISCLAIMER

LBL # 26849

PORE SIZE DISTRIBUTION DURING COMPACTION AND EARLY STAGE SINTERING OF SILICON NITRIDE

Naomi Naito*, M.N. Rahaman[#], and L.C. De Jonghe[$]
Center for Advanced Materials
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720

This work was supported by the Division of Materials Sciences, Office of Basic Energy Sciences, United States Department of Energy, under Contract No. DE-AC03-76SF00098.

---

*Present address: GTE Laboratories, Waltham, MA 02254

[#] University of Missouri-Rolla, Ceramic Engineering Department, Rolla, MO 65401

[$] Also with the Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720

Abstract

The effect of a number of compaction parameters on the pore size distribution in silicon nitride powder compacts has been investigated by mercury porosimetry. The powder was compacted in a uniaxial die and the parameters of interest included uniaxial load, loading rate, polymer additives and stress relaxation. The use of a low-viscosity polymer solution as a lubricant, the allowance of stress relaxation following loading, and heat treatment above the glass transition temperature of the polymer lead to a more uniform pore size distribution in the green samples. The more uniform green samples, in turn, showed a more uniform pore size distribution after initial stage sintering. The potential of the present techniques for improving the microstructural uniformity in ceramic bodies is discussed.

1. Introduction

When ceramic powders are formed into green bodies, heterogeneities may be produced as a result of poor powder characteristics or non-uniform compaction. Large pores and agglomerates are among the most difficult heterogeneities to deal with since they may remain or produce other defects during the sintering process and these may then act as sources of failure in the final body. Considerable efforts have therefore been devoted to processing techniques that are capable of producing a more uniform green microstructure [1].

While colloidal processing and sol-gel techniques have been the subject of much research in recent years, the formation of green bodies by powder compaction in a uniaxially loaded die is one of the oldest and still one of the most widely used operations in the ceramics industry. As a result, it has been the subject of extensive study [2-12]. In die compaction, the packing density of the green body is controlled by a number of parameters, including the powder characteristics, intra-particle friction, the applied stress and the constraining forces that the die wall imposes. The uniformity of the compact depends on the stress distribution and the extent of shear produced within the system during forming. It is common practice to prepare the green body with a combination of additives, usually called binders or lubricants, that influence the stress transmission and rearrangement processes during compaction. Several authors have reported the effects of binder properties on green compact formation during dry compaction [13-16]. Use of the binder poly(vinyl alcohol), PVA, with different degrees of absorbed moisture which acts as a plasticizer, or binders with a low glass transition temperature resulted in softer granules for alumina powder. The improved deformability of the compact leads to more reproducible pressing.

Since stresses can be relaxed by viscoelastic deformation, materials with lower viscosity might be expected to relax stresses within the green compact faster. This might be expected to lead to a more uniform distribution of stress and hence to a more uniform green microstructure. The intent of this work was to investigate whether viscous flow during uniaxial die compaction can lead to improved uniformity of the green compact microstructure. Silicon nitride powder was mixed with a lubricant consisting of a low-viscosity polymer solution and the mixture was pressed in a die; the excess lubricant was drained during the pressing. The parameters that were varied included the viscosity of the compact, the load, the loading rate, and stress relaxation at maximum load.

2. Experimental Procedure

A powder system consisting of a mixture of silicon nitride (90 w%) and yttrium oxide (10 w%) was used in the present study. The silicon nitride powder (SN502, GTE, Waltham, Massachusetts, USA; average surface area 4 m^2/g) consisted of an amorphous phase (40%) and a crystalline phase (60%); the crystalline phase contained of 91.4% α-Si_3N_4 and 8.6 β-Si_3N_4. The yttrium oxide (Alpha Chemicals, Danvers, Massachusetts, USA) had an average grain size of 0.5 μm. The powder mixture was prepared by initially mixing the dry powders in a twin-shaft blender for ≈24 hours, followed by stirring in ethanol, and then by drying in a vacuum oven at 30°C.

The mixture was treated with the lubricants to give three different types of powders for the compaction and sintering studies. The first type of powder (referred to as sample A) was ground lightly in a mortar and pestle and compacted dry and without additives. The second type (sample B) was coated with 10 v% of an organic binder (carbowax) by mixing the powder in a solution of carbowax and chloroform, after which the mixture was dried and ground lightly. Finally, the third type of powder (sample C) was prepared as a slurry by mixing in a highly viscous solution of a polymer (polystyrene) in chloroform. The concentration of the polymer in the solutions ranged from 0.05 to 0.4 g/cm^3.

The powders were compacted at room temperature in a uniaxial die (≈12 mm in diameter) using an Instron testing machine. Two different types of compaction experiments were performed. In one type, the powders were pressed at a constant strain rate and the load was removed when the maximum load was reached. In the other type of experiments, the shrinkage strain of the sample was held constant after the same maximum load was reached and the stress was allowed to relax. In both types of experiments, the maximum shrinkage was the same in order to produce samples with the same green density.

For investigations into the effect of pore size distribution on early stage sintering of these materials, compacts prepared from powders A and C were pressed to the same density (1.35 g/cm^3) and sintered for 1-10 min at 1750°C. The compacts were packed in powder beds of the same composition and sintering was performed in nitrogen at atmospheric pressure.

Continuous-scan mercury porosimetry (Autoscan 60, Quantachrome Corp., USA) was used to measure the pore size distribution of the green and the sintered powder compacts. The density of the samples was determined from their mass and dimensions and verified by the cumulative pore volume data obtained from mercury porosimetry. The microstructure of selected samples was monitored by scanning electron microscopy.

3. Results and Discussion

Figure 1 shows the pore size distribution, defined as the volume per unit radius of pores, as a function of pore radius for the three types of powders, A (dry powder without binder), B (dry powder with carbowax as binder), and C (slurry with polymer lubricant). The samples were obtained by pressing the powders at the same loading rate (1 mm/min) to the same density (i.e. same sample length) after which the load was quickly removed. Sample C had a slightly smaller average pore size and a slightly more uniform pore size distribution compared to A. The volume of large pores in sample C is also smaller compared to A. The data for B generally lies between those for A and C; therefore, for the remainder of this paper the data for A and C will be considered in detail and those for B will only be referred to where appropriate.

The effect of stress relaxation on the pore size distribution for powders A and C after compaction to the same density is shown in Figs. 2 and 3, respectively. Stress relaxation is seen to produce smaller, more uniform pores and a preferential elimination of larger pores for powder A. For powder C, the peaks of the curves are almost identical but the important feature is the significant reduction in the volume of the large pores. A comparison of the pore size distribution for powders A and C after compaction and stress relaxation is shown in Fig. 4. The data show that sample C has a narrower pore distribution as well as a smaller volume of large pores.

For sample C that contained a polymer lubricant, the effect of the viscosity of the compact on the pore size distribution was investigated by compacting the powder below and above the glass transition temperature of the polymer (polystyrene, $T_g \approx 130°C$). Above the glass transition temperature, the viscosity of the polymer is expected to decrease by a few orders of magnitude which leads to a reduction in the compact viscosity [17]. Figure 5 shows the data for samples of powder C compacted below and above the glass transition temperature of polystyrene. The sample compacted above the glass transition contains a lower volume of large pores.

Higher compaction load leads to a decrease in the average pore size and narrower pore size distribution of the small pores but does not cause any significant reduction in the volume of the large pores for powder A compacted in the dry state (Fig. 6). The data indicate that higher load did not cause any appreciable breakdown of the agglomerates in the dry-pressed powder. Slower compaction rate also leads to a reduction in the average pore size of the small pores (Fig. 7) without causing any significant reduction in the volume of large pores.

It would be interesting to examine whether the improved green microstructure produced in the samples containing the polymer binder leads, in turn to improvements in the sintered microstructure. Figure 8 shows the pore size distribution for powders A and C that were compacted to the same density and sintered to 1750°C for 10 min. It is seen that the improved microstructure of sample C is retained even after sintering. The samples show pronounced α/β phase transformation but little densification; for the sintering conditions used, the β phase content was $\approx$ 92%.

The data outlined earlier showed that both the use of a polymer lubricant and stress relaxation following compaction lead to improvements in the homogeneity of the green compact microstructure. The polymer lubricant is believed to lead to improvement in the powder flowability, decrease in powder friction and increase in agglomerate breakdown. The effect of viscosity appear to support this conclusion. The lower sample viscosity produced by heat treatment above the glass transition temperature (Fig. 5) leads to an increase in the volume of pores near the mean pore radius and a reduction in the volume of large pores through increased flow which allows increased rearrangement.

For compaction with stress relaxation where the load is allowed to relax viscoelastically, the more uniform pore size distribution may be attributed to the attainment of a more uniform stress distribution within the die. Instead of immediate stress release after loading, the sample is kept under a constant compressive strain thereby allowing the applied stress to relax through rearrangement of the grains. This leads to an increase in the volume of pores with a radius centered near the average, and more significantly, to a marked decrease in the volume of large pores (Figs. 2 and 3). The small pores are expected to exist between the primary particles while the large pores exist between the agglomerates [18]. The reduction in the volume of large pores might be due to isostatic breakdown of the agglomerates, and would be expected to be more pronounced in the powder containing the polymer lubricant in which stress redistribution is more effective (Fig. 4).

In the early stage sintering experiments, the pronounced α/β phase transformation accompanied by negligible densification of the silicon nitride lead to coarsening of the microstructure and an increase in the average pore size distribution. However, as seen from Fig. 8, after the sintering stage the pore size distribution of sample C (compacted with a polymer lubricant) is still more uniform than sample A (compacted in the dry state). Later stage sintering cannot be well characterized by mercury porosimetry but it is reasonable to expect that the improved uniformity of sample C would persist throughout the densification process.

4. Conclusions

The present work shows that the microstructural homogeneity of the green body may be achieved substantially through improvement in the compaction procedure during uniaxial pressing in a die.

The use of a viscous polymer lubricant and stress relaxation following compaction are most effective for improving the green body homogeneity. For the powders compacted with the polymer lubricant, heating above the glass transition temperature of the polymer can also lead to similar advantages.

The microstructural modification produced by the polymer lubricant, stress relaxation and heat treatment above the glass transition temperature is consistent with a mechanism that involves more uniform stress distribution in the compact in addition to increased rearrangement processes.

Enhanced homogeneity of the green body was reflected in increased homogeneity of the sintered body in the early stages of densification.

Acknowledgement

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

5. References

1. F. F. Lange, J. Am. Ceram. Soc., 72 (1989) 3.
2. S. Strijbos, Powder Technol., 18 (1977) 187.
3. S. Strijbos, pp. 415-27 in Science of Ceramics, Vol. 8. Edited by P. Popper. British Ceramic Research Association, Stoke-on-Trent, England (1979).

4. R. Thompson, J. Am. Ceram. Soc., 60 (1981) 237.

5. R. Thompson, J. Am. Ceram. Soc., 60 (1981) 244.

6. R. Thompson, J. Am. Ceram. Soc., 60 (1981) 248.

7. F. F. Lammers, C. Styuck, F. A. Varkeussa, J. Dolderman, and C. J. deBlary, Powder Technol., 28 (1981) 147.

8. A. Broese Van Gronenou and R.C. Lissenburg, J. Am. Ceram. Soc., 66 (1983) C156.

9. G. Y. Messing, C. J. Markhoff, and L. G. McCoy, 61 (1982) 857.

10. G. Isik and P. F. Messer, pp. 39-50 in Fabrication Science 3. British Ceramic Research Association, Stoke-on-Trent (1983).

11. H. F. Fischmeister and E. Alzc, J. Powder Metall., 26 (1983) 82.

12. R. G. Frey and J. W. Halloran, J. Am. Ceram. Soc., 67 (1984) 199.

13. J. A. Brewer, R. H. Moore, and J. Reed, Am. Ceram. Soc. Bull., 60 (1981) 212.

14. R. A. Dimilva and J. Reed, Am. Ceram. Soc. Bull., 62 (1983) 84.

15. R. A. Dimilva and J. Reed, J. Am. Ceram. Soc., 66 (1984) 667.

16. C. W. Nies and G. L. Messing, J. Am. Ceram. Soc., 67 301 (1984).

17. C-H. Hsueh, J. Am. Ceram. Soc., 69 (1986) C48.

18. F. F. Lange, J. Am. Ceram. Soc., 67 (1984) 83.

Figure Captions

Fig. 1. Pore size distribution function versus pore radius for samples of the same green density that were compacted from powders A, B and C. (A - dry powder; B - dry powder with carbowax binder; and C - powder mixed with viscous polymer lubricant)

Fig. 2. Pore size distribution function vs pore radius for powder A compacted with and without stress relaxation.

Fig. 3. Pore size distribution function vs pore radius for powder C compacted with and without stress relaxation.

Fig. 4. Pore size distribution function vs pore radius for powders A and C compacted with stress relaxation.

Fig. 5. Pore size distribution function vs pore radius for powder C compacted at room temperature and above the glass transition temperature of the polymer lubricant.

Fig. 6. Pore size distribution function vs pore radius for powder A compacted at different loads (in MPa).

Fig. 7. Pore size distribution function vs pore radius for powder C compacted at different rates (in mm/min).

Fig. 8. Pore size distribution function vs pore size for powders A and C compacted to the same green density and sintered for 10 min at 1750°C.

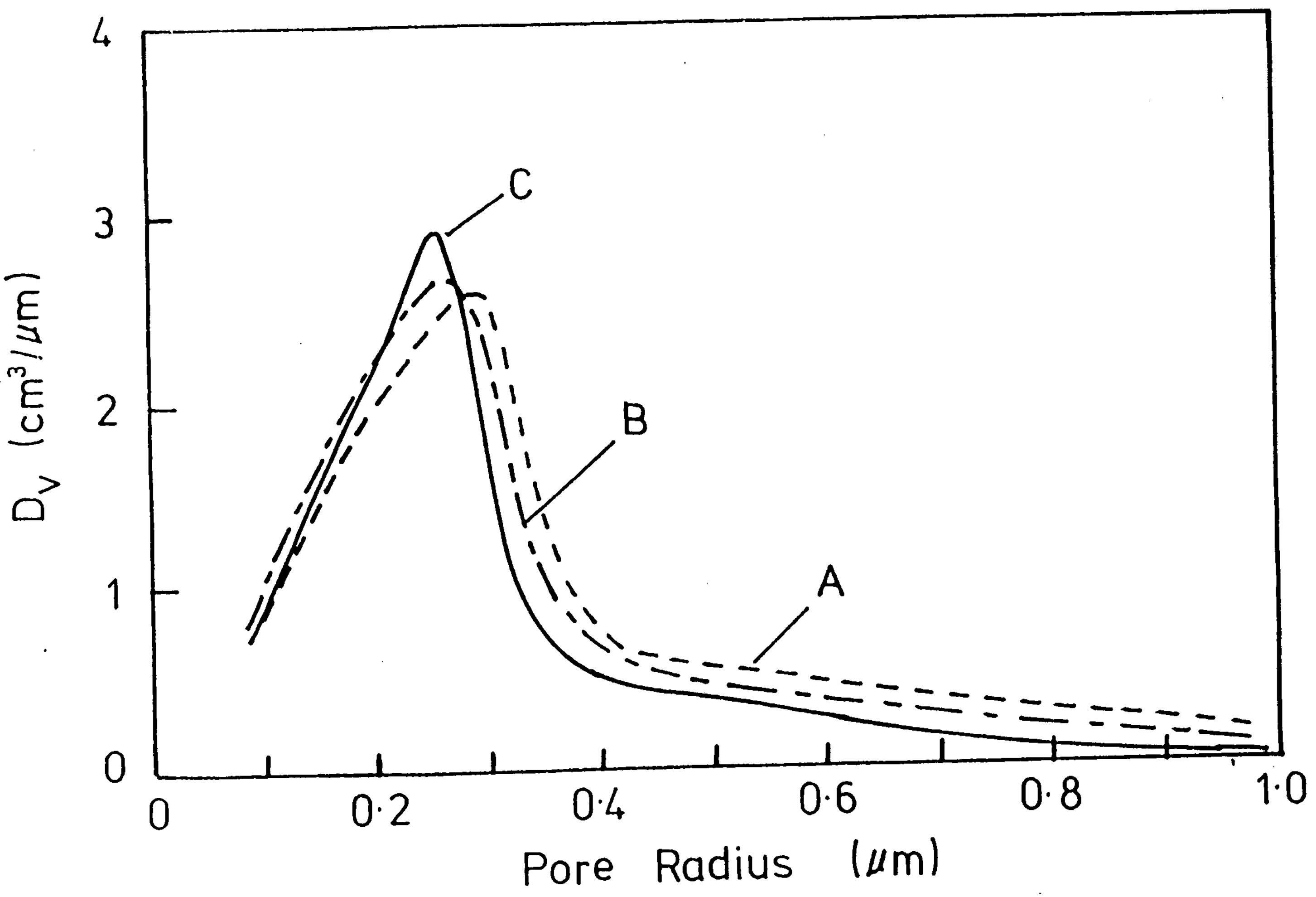


Figure 1

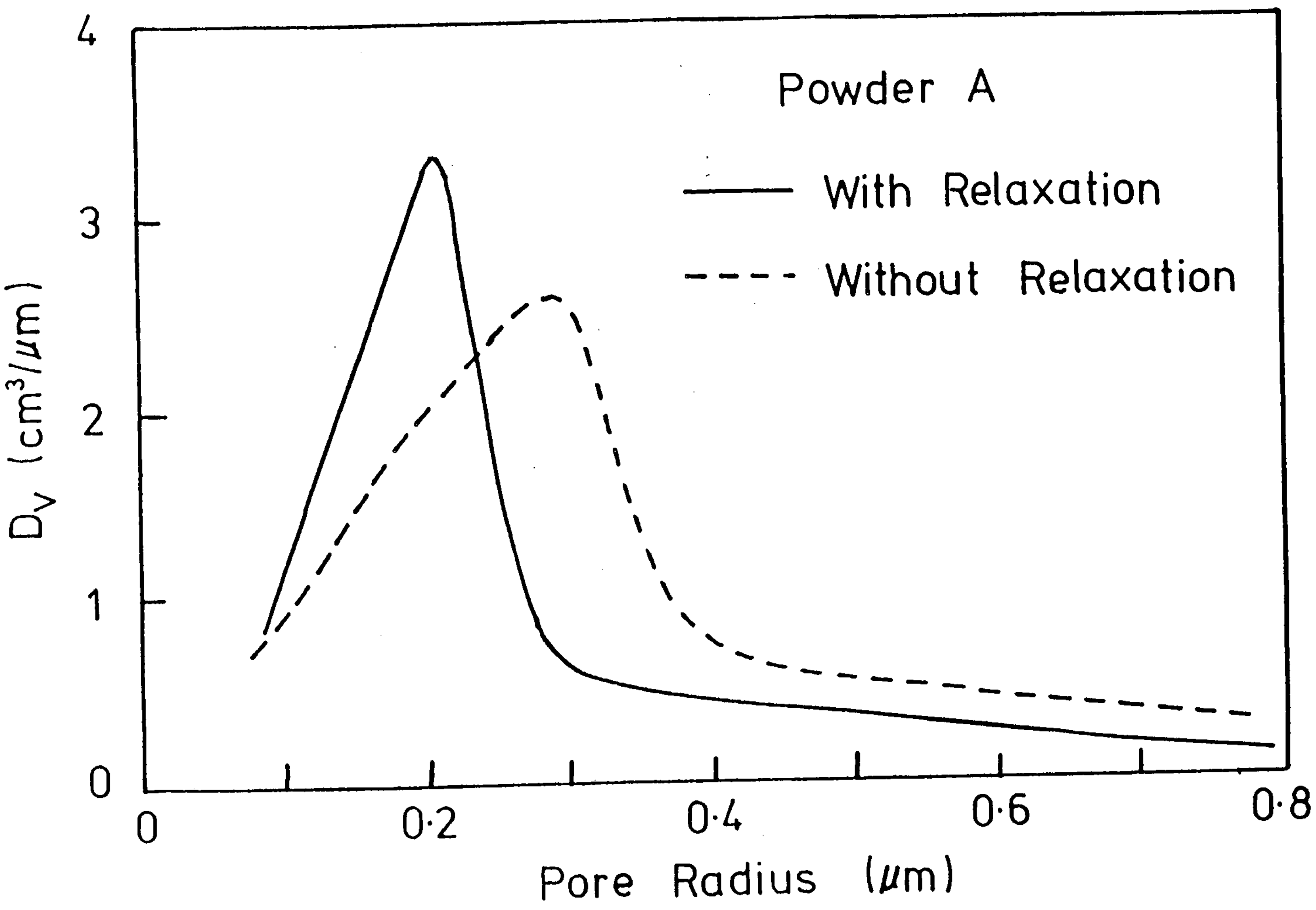

Powder A
With Relaxation
Without Relaxation
D_v (cm^3/μm)
4
3
2
1
0
0
0·2
0·4
0·6
0·8
Pore Radius (μm)

Figure 2

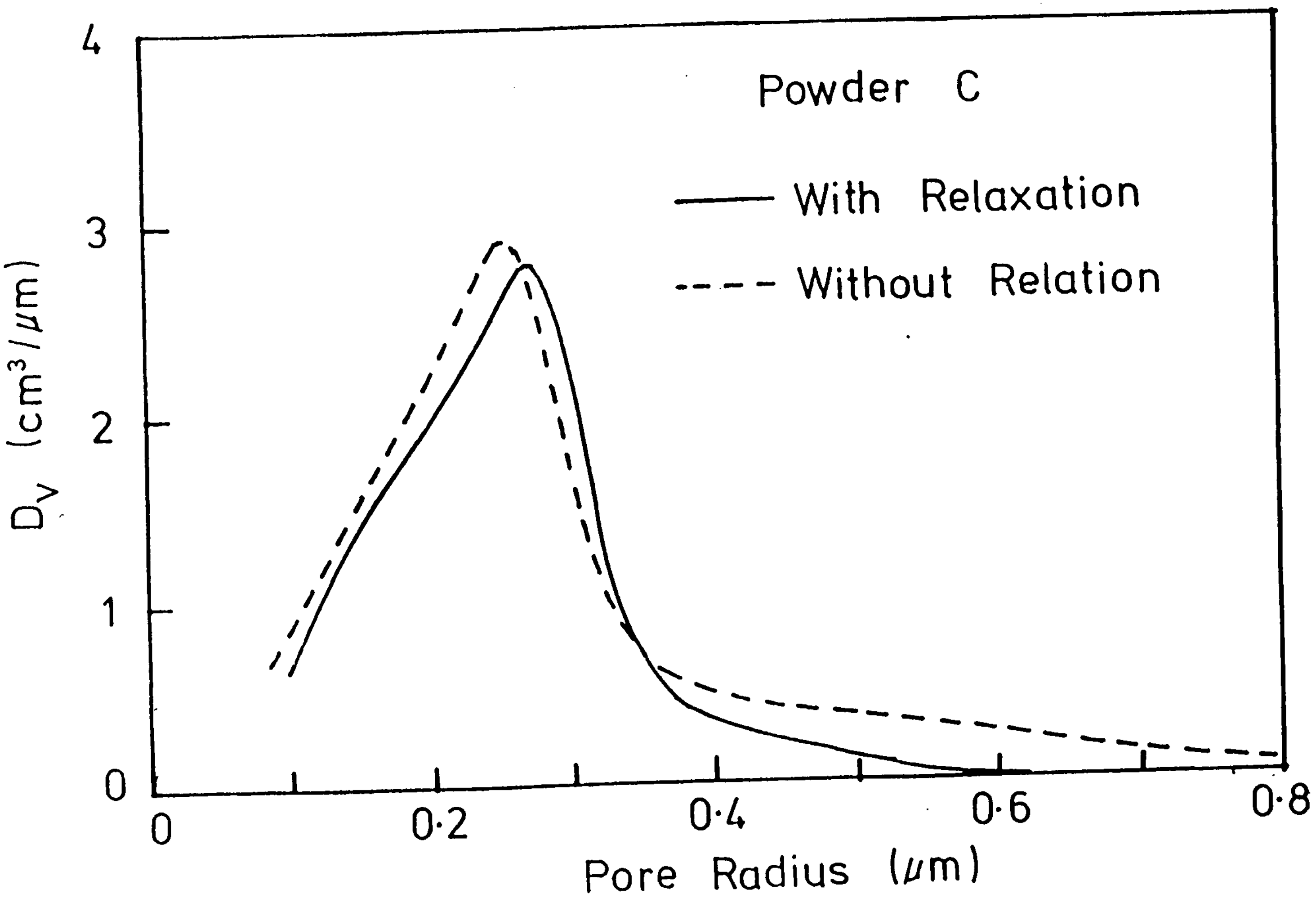

Powder C
With Relaxation
Without Relation
D_v (cm³/µm)
4
3
2
1
0
0
0·2
0·4
0·6
0·8
Pore Radius (µm)

Figure 3

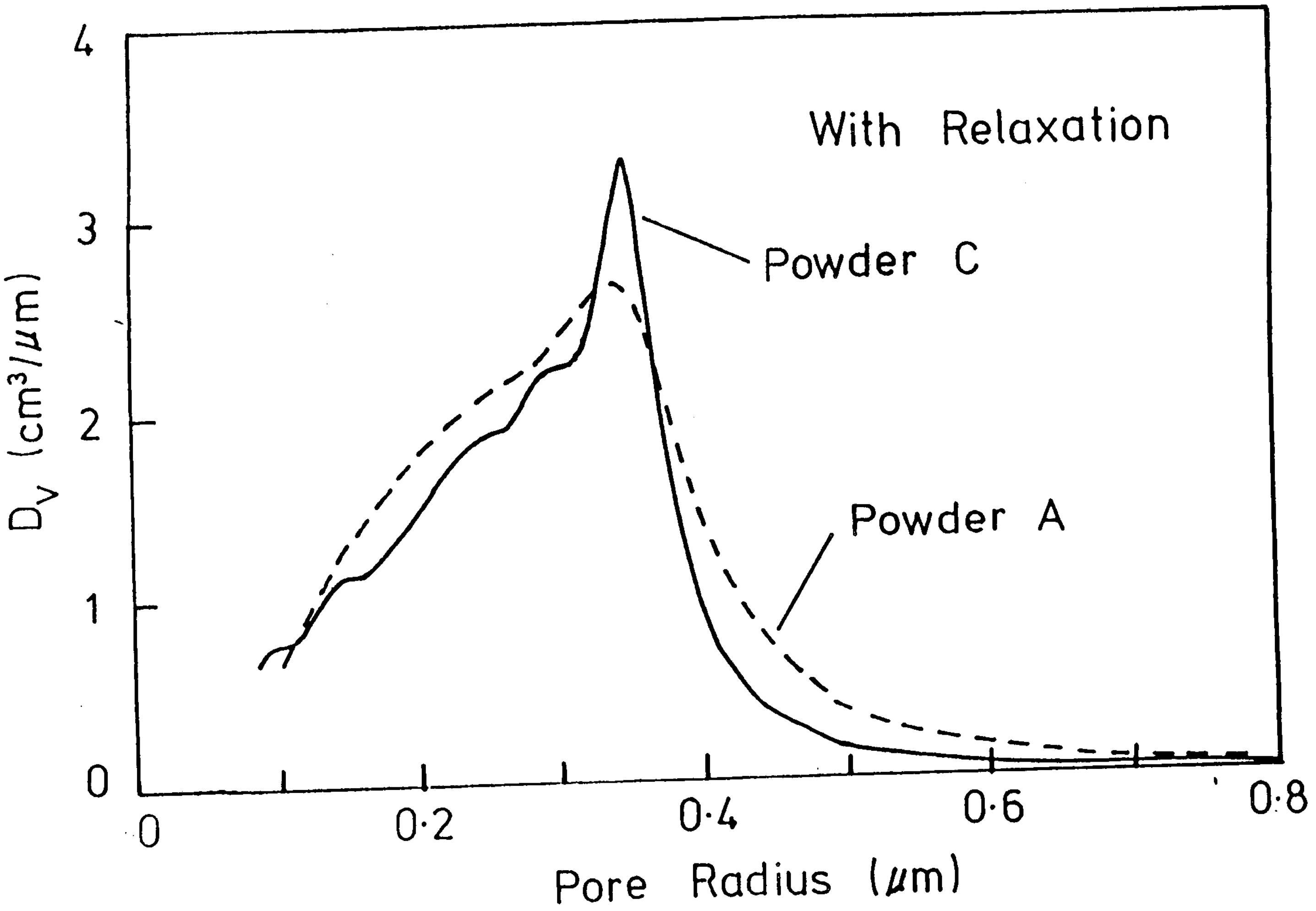

With Relaxation
Powder C
Powder A
D_v (cm^3/µm)
Pore Radius (µm)
0
1
2
3
4
0
0·2
0·4
0·6
0·8

Figure 4

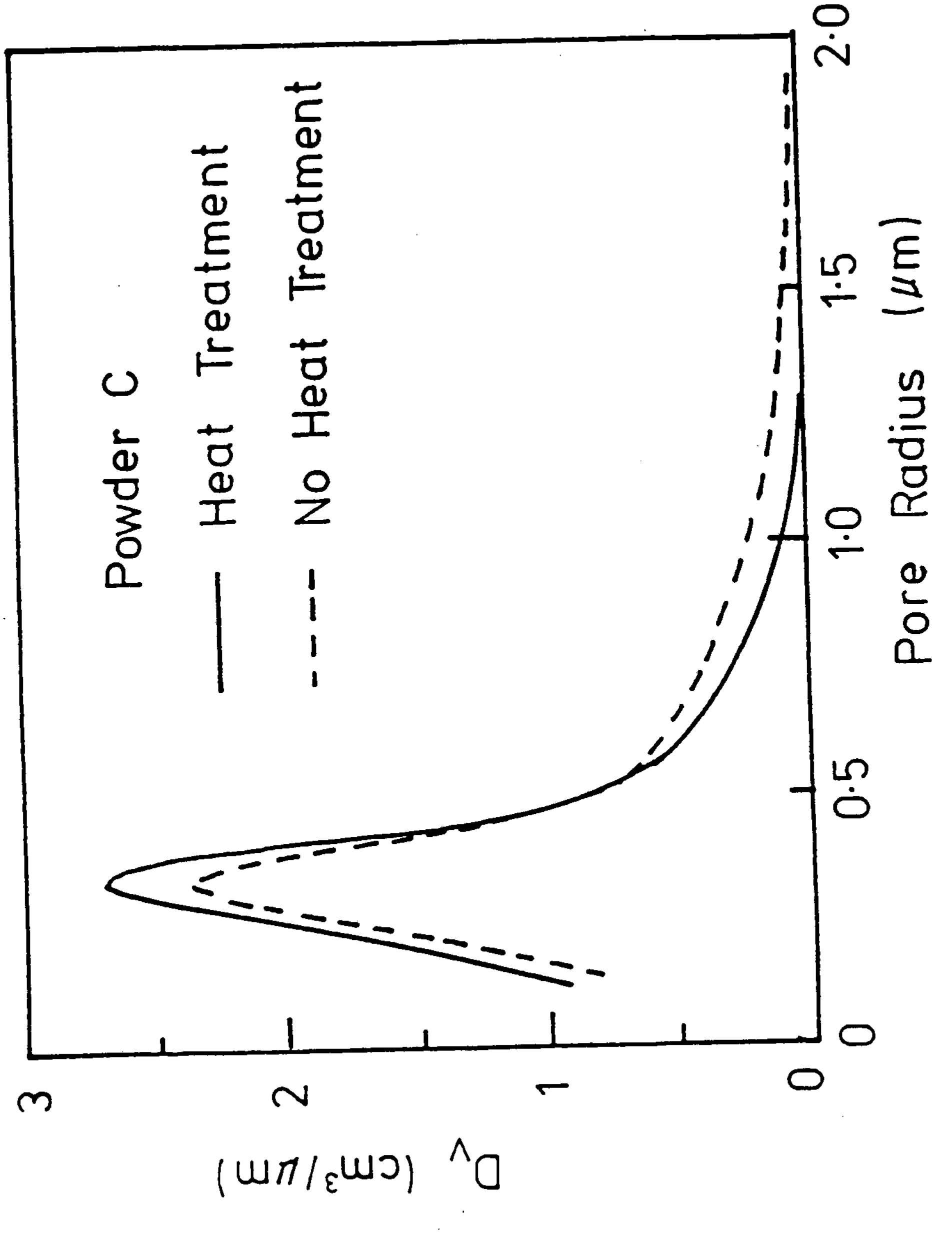

Powder C
Heat Treatment
No Heat Treatment
D_V (cm^3/μm)
3
2
1
0
0
0·5
1·0
1·5
2·0
Pore Radius (μm)

Figure 5

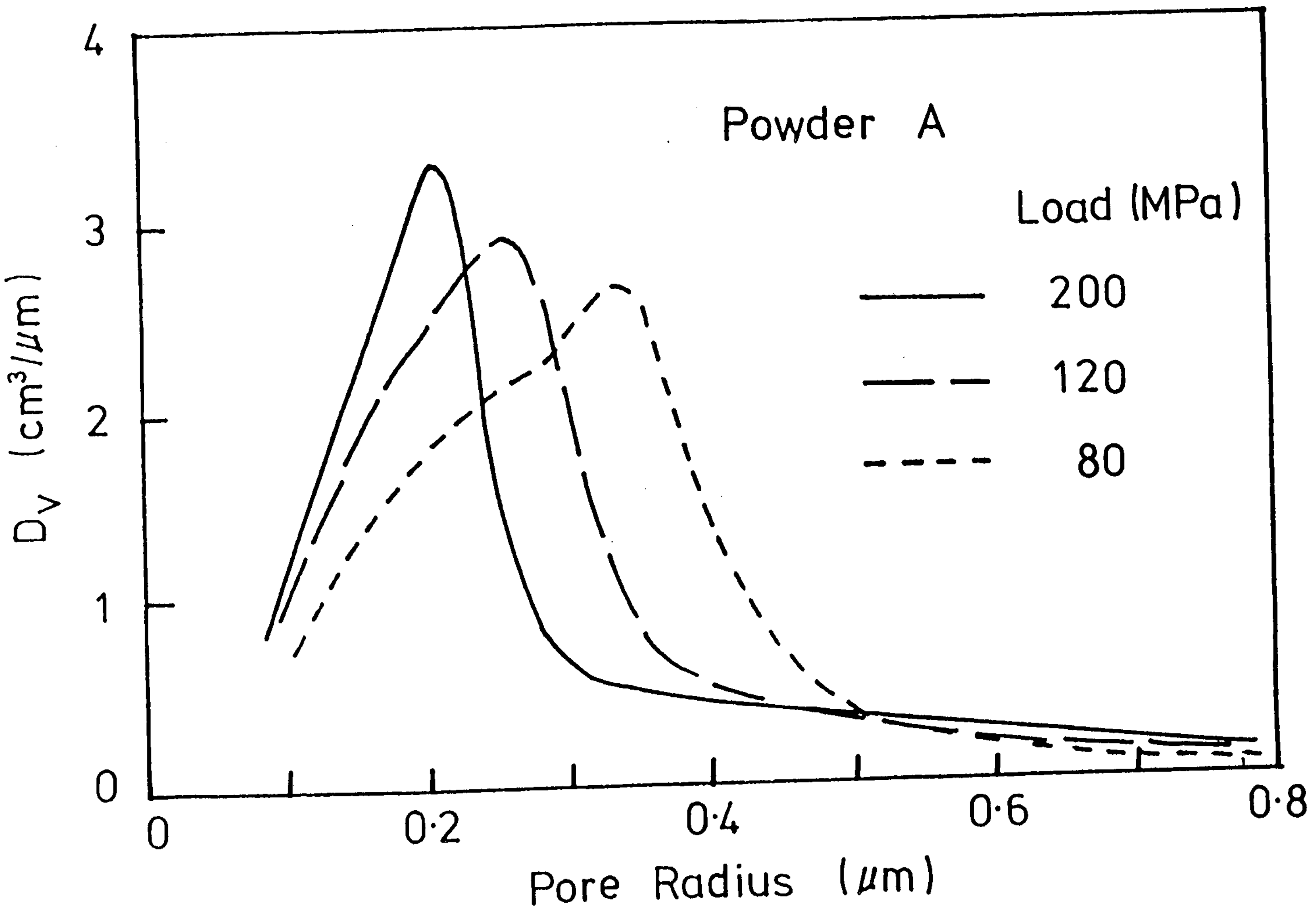

Powder A
Load (MPa)
200
120
80
D_v (cm^3/µm)
4
3
2
1
0
0
0·2
0·4
0·6
0·8
Pore Radius (µm)

Figure 6

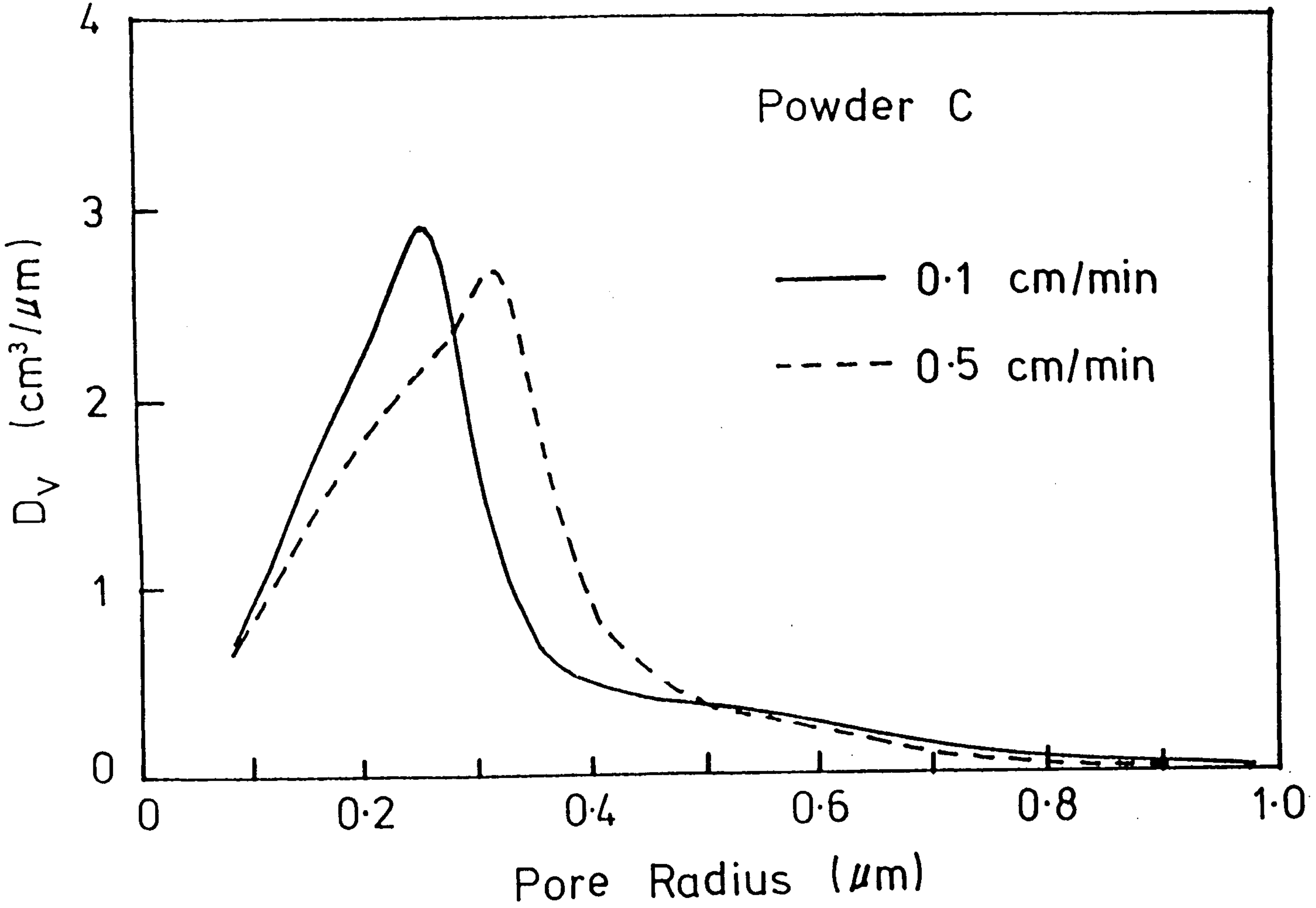

Powder C
0·1 cm/min
0·5 cm/min
D_v (cm³/µm)
4
3
2
1
0
0
0·2
0·4
0·6
0·8
1·0
Pore Radius (µm)

Figure 7

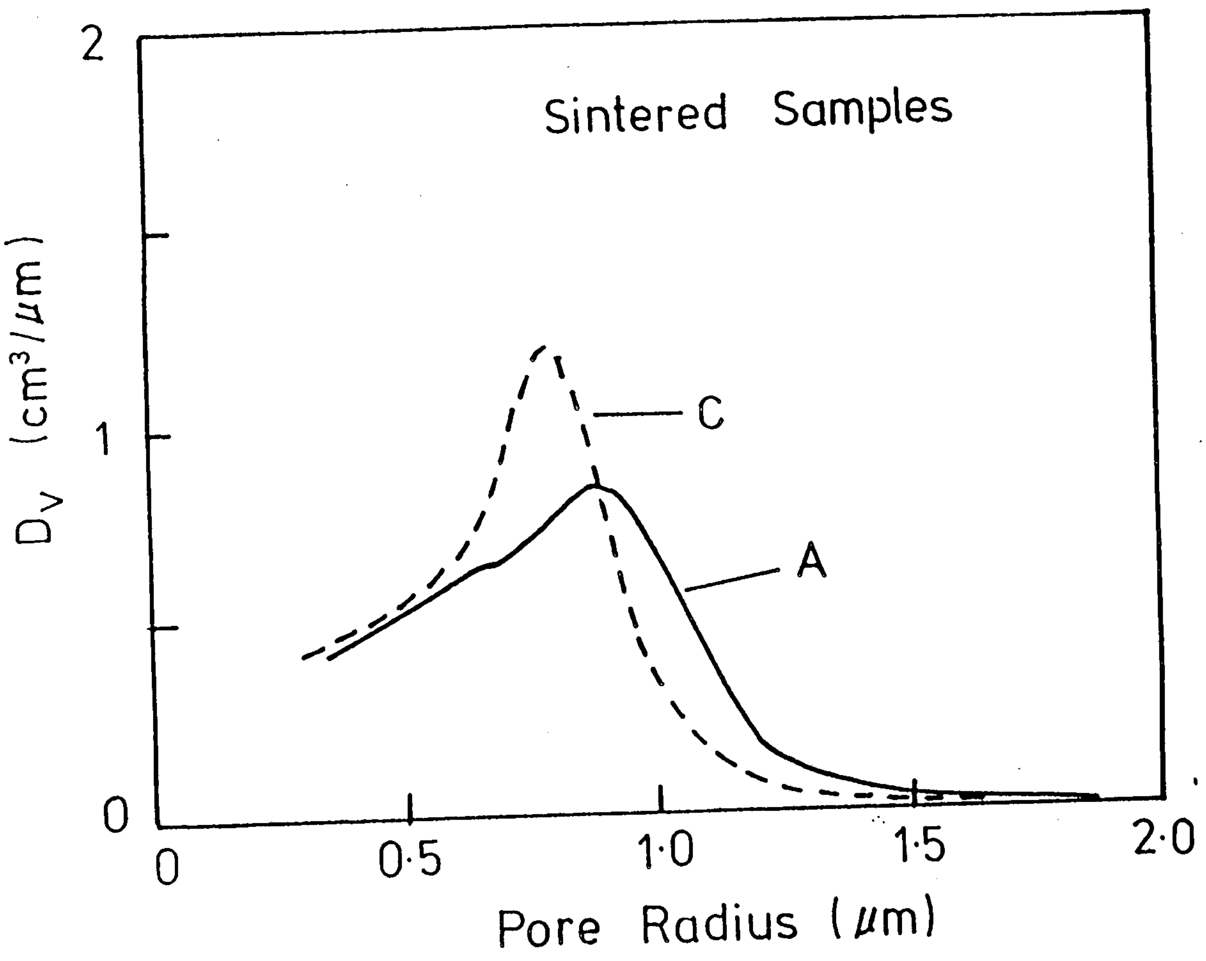


Figure 8

LAWRENCE BERKELEY LABORATORY
CENTER FOR ADVANCED MATERIALS
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720