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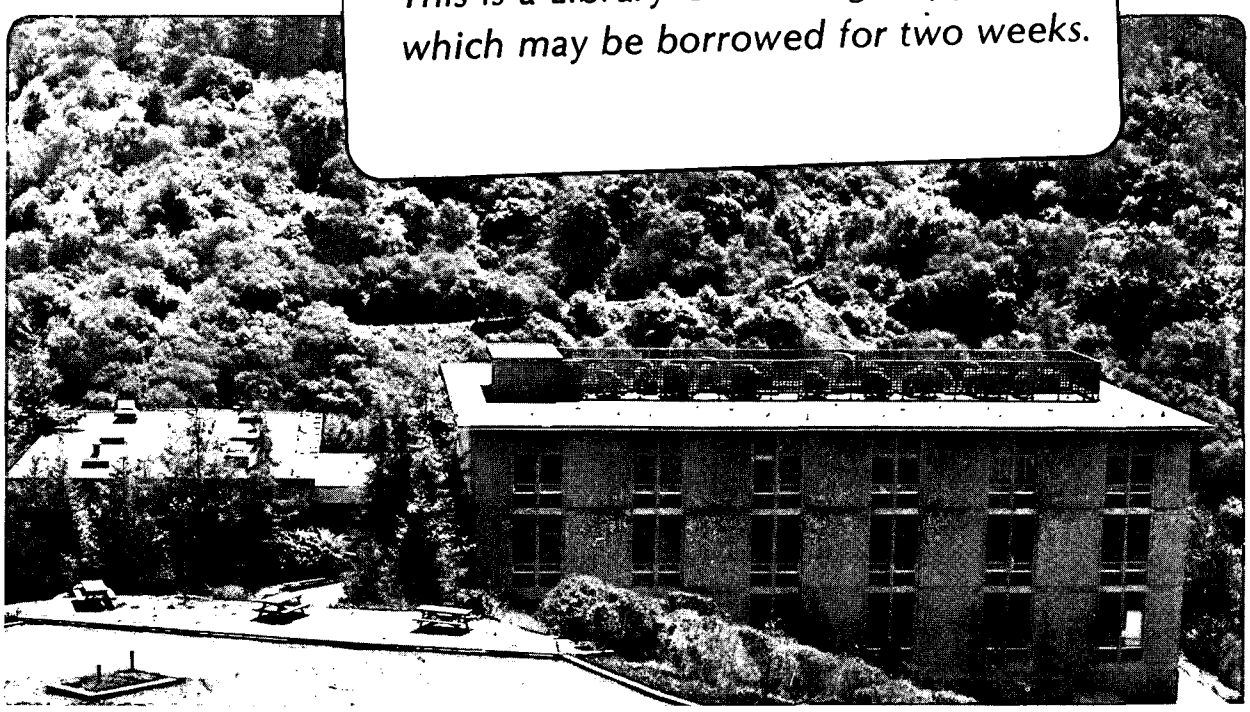

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THE ROLE OF POWDER PACKING IN SINTERING

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

ABSTRACT

The densification of powder compacts, containing larger pores in a fine grain, homogeneous matrix, is considered. Homogenization of the porous microstructure is possible in the intermediate stage of densification due to grain growth driven coalescence of the finer pores, while the coarser pores grow less. The conditions are identified for which homogeneity can be achieved at the end of the intermediate stage. It is found that for finer powders the initial packing perfection, normalized to the grain size, has to increase rapidly. The effects of temperature and the relative merits of monodispersed versus multidispersed powders are also discussed.

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INTRODUCTION

A variety of factors can interfere with the densification of ceramic powder compacts so that potentially advantageous properties are not realized in the the final product . These factors include heterogeneities in initial powder packing, such as large pores, unfavorable particle size distributions, and chemical heterogeneities, that are not eliminated during densification. In principle, all porosity should eventuallly disappear, provided the materials are heated for a sufficiently long time at a high enough temperature. What makes the ceramic unacceptable then is that grain growth will have led to a microstructure where the grains are so large that the mechanical, electrical, optical, or other properties are no longer useful. Practically, it is impossible to produce perfect powder compacts. An important question is not only how closely the perfect green state can be approached, but also which imperfections can be tolerated. Understanding the effect of the initial particle arrangement on the microstructural evolution during densification must therefore be in terms of packing defects that can be eliminated while the system remains below some upper limit on the grain size, set by property requirements. This involves the consideration of the interrelationship of grain growth and densification rates, as discussed by Brook (1), and Lange (2). These aspects are now reconsidered in a somewhat different context. The emphasis is on the absorption of isolated larger pores in a homogeneous, fine pore matrix in which grain growth occurs

densification. If some simplifying assumptions are made, predictions become possible of what is required of the packing perfection when initial grain sizes, densification rates and grain growth rates are modified.

HOMOGENIZATION OF MICROSTRUCTURES IN THE INTERMEDIATE STAGE OF SINTERING.

When densification and grain growth occur simultaneously, pores will on the one hand shrink due to densification, and on the other hand grow as a result of coalescence due to grain growth, provided the pores remain at grain boundaries (3). This condition is most likely satisfied in the intermediate stages of densification, but may persist into the final stages when break-away grain growth is not a problem. In the intermediate stage, large pores tend not to shrink until the grain size is sufficiently large (4). Thus, small pores will tend to grow while decreasing in number, by grain growth-driven pore coalescence, while large pores do not change much. This simple phenomenon constitutes a mechanism for homogenization of the microstructure, opposing the Ostwald ripening process that tends to coarsen large pores at the expense of smaller ones (5). Provided the proper combination of grain growth rate, densification rate, and inititial pore distribution prevails, a powder compact will proceed towards homogeneity in the intermediate stage. The reality of this process is dramatically illustrated in the evolution of the

microstructure of some MgO compacts containing large pores. Fig.1 shows a sequence of microstuctures of MgO sintered at 1250°C, initially containing clearly identifiable large pores in a fine grained matrix. As sintering proceeds, pore coalescence due to grain growth causes the microstrucuture to become more homogeneous. While such homogeneity is not the only requirement for achieving full density, it is an important one. If the microstructure is not reasonably homogeneous towards the end of the intermediate stage of densification, then the end stage is likely to consists of large, widely spaced pores that can only be eliminated at the expense of extensive grain growth.

In developing the model, a number of assumptions will be made. Some of these assumptions may limit the applicability of the model to all systems, but they provide a significant simplification of the calculations, while retaining trends that should be of some practical value.

MODEL CONSIDERATIONS

The model considers an intermediate stage of densification under grainboundary diffusion control, and assumes that "homogeneity" should be achieved towards the end of the intermediate stage. This is arbitrarily set at 80% density. By that time, the pores of the fine grained material should at least have been as large as the largest pore in the system, otherwise these large pores cannot be eliminated easily

in subsequent densification.

For grainboundary diffusion controlled densification, the densification rate, $\dot{\rho}$, may be written as:

$$\dot{\rho} = K\Sigma\phi/G^3 \qquad (1)$$

where K is a kinetic constant, G is the grain size, Σ is the sintering stress, and ϕ^{-1} is the stress intensification factor. Densification rates described by this relation were observed for materials such as ZnO and CdO (6,7)

The grain growth rate is assumed to be independent of the porosity and to be described by a cubic rate dependence

$$G = G_0 \ (1 + B.t)^{1/3} \qquad (2)$$

where G is the initial grain size, B is the grain growth rate constant, and t is the time.

In general, Eqn (2) would be a strong simplification of grain growth in porous systems, although it has been found in CdO (5). Such cases may arise when pores are highly mobile so that they remain on the grainboundaries, when grain growth is controlled by intrinsic grainboundary processes. The density follows from the integration of,

Eqn (1). Significant simplification can be achieved by using an approximate relationship of the form

$$\exp(aP)/(2aP/3) = C \qquad (3)$$

where C is a constant depending on a, if a is about equal to 2 and the porosity is between 0.4 and 0.8. A value of 2 for a was found for the sintering of CdO (6). For other materials the simplification offered by Eqn. (3) might not be possible, and iterative procedures would have to be used to find the porosity as a function of time. In itself, this introduces only some computing complexity without changing the general nature of the results.

The sintering stress, Σ, can be written as (6)

$$\Sigma = 2\gamma/r \qquad (4)$$

where γ is the surface tension. The pore radius, r, may be expressed as

$$r = \alpha P^n G \qquad (5)$$

α is a factor that remains constant at constant pore shape. For a Zener-like relationship (6) n = 1; for the case of strictly constant pore shape n = 1/3, when the number of pores per grain remains constant, and abnormal grain growth is absent. In general n and α could be functions of time (13).

After some algebra Eqns. 1-5 lead to

$$P(t) = \left(P_0^m - m K \gamma \alpha \int_0^t (1/G^4)\, dt \right)^{1/m} \qquad (6)$$

with P_0 = initial porosity and $m = 1 + n - 2a/3$. The integral in this expression is easily evaluated from Eqn. 3:

$$\int_0^t (1/G^4)\, dt = -3\, (1/G(t) - 1/G_0) / B\, G_0^3 \qquad (7)$$

It is immediately clear that P(t) cannot be expressed simply as a function of the densification rate constant, K, over the grain growth rate constant, B, only.

To illustrate the relationship of the homogenization process to the various parameters, n and a were put equal to 1. Different values for n and a do not affect the general trend of the results. In the calculations the parameter $\dot{\rho}_0$, equal to $mK\gamma\alpha$ was used.

The calculated pore radius at the fixed density of 80% is strictly proportional to the grain size if is assumed to be constant. One can now examine r (or G) at 80% , r_{80}, as a function of the parameters of interest. These parameters are the initial grain size, G_0, the grain growth rate constant, B, and the densification rate constant, K or $\dot{\rho}_0$.

Fig. 2 shows a plot of the pore radius at 80% density, r_{80}, normalized to the initial pore size, r_0, versus the grain growth rate constant B. From this graph it is clear that if homogeneity is to be achieved through pore growth of the matrix, for large pores with a

radius $r_1 = 5\ r_o$, the grain growth rate constant, B, must be equal or larger than B_1. With this, a minimum grainsize, G_{min} is associated. If a maximum grain size G max can be tolerated from the properties point of view, then G_{max} puts an upper limit on B, B_2. Of course, if the isolated pores have a radius that would require $G_{min} > G_{max}$, then no satisfactory microstructure can develop unless the green state homogeneity, relative to its particle size, is improved. It is also evident from Fig. 2 that the more perfect the green state packing, the wider the range of grain growth rate constants that can produce homogeneity.

One might recognize two different types of packing imperfections: those that scale with the particle size, the intrinsic ones, and those that are independent of the particle size, the extrinsic ones. In Fig. 3, r_{80}/r_o is plotted for two different starting grain sizes, versus the grain growth rate constant B. Both types are indicated; r_L = constant corresponds the extrinsic defect of constant size, while the intrinsic defect is indicated by r_L/r_o = constant. The effects of changing grain size in relation to the packing perfection can also be discussed simple with the aid of Fig 3. As expected from Eqn.1 the densification rates, and hence the values of G_{80} or r_{80} depend strongly on the initial particle size. For the intrinsic defects with e.g. $r_L/r_0 = 3$, as indicated, the minimum acceptable grainsize is $G_o = 0.8 \times 10^{-4}$, at the fixed grain growth rate constant B_3. A smaller grainsize would not have sufficient grain growth to permit

homogenization at $r_L / r_0 = 3$ at $\rho = 0.8$, and the relative powder packing perfection where the size of the heteropores is decreased relative to r_0, would need to be improved, or the grain growth rate must be increased through the use of appropriate additives. The strong dependence of $\dot{\rho}$ on G_0 will require that the packing perfection be improved rapidly with decreasing grainsize, or the benefits derivable from the use of small grains cannot be realized. This is in agreement with the observations of Rhodes (8). One may expect, in fact, that at some low grain size the required packing perfection may not be practically achievable in ceramic bodies of a useful size. The situation is even more critical for the extrinsic defects, as can be deduced from Fig. 3 for r_L = constant, and the lower limit on the grain size will prevent homogenization at higher grainsizes than for intrinsic defects that have the same r_L / r_0 at some reference grain size (here chosen to be $G_0 = 1 \times 10^{-4}$). Fig 4 also indicates that the maximum grain size limit is not a constraint on going to smaller initial grain sizes. Fig. 3 thus indicates, while homogeneity can be achieved even for rather imperfect packings, that it is a only some rather critical initial grainsize domain that will be "forgiving" for a particular set of factors which include the grain growth rate constant, the pore mobility, the initial grain size, and the densification rate constant $\dot{\rho}_0$.

It is clear that, at a fixed grain growth rate constant, B, the tolerance for packing imperfections decreases with increasing

densification rate. In fact, if the densification rate is increased it is again necessary to improve simultaneously the perfection of the green state, even relative to the particle size, if homogeneity is to be achieved before the end of the intermediate stage, as was the case for the grain size decrease.

Fig. 4 shows the possible effects that a combined reduction in grain size and temperature can produce. At temperature T_1, with an associated grain growth rate constant B_4, a reduction in grain size from G_{o1} to G_{o2} would not permit the absorption of pores larger than $r_L = R_L$. A reduction in temperature, producing $\dot{\rho}_{o1} > \dot{\rho}_{o2}$ and $B_5 < B_4$ can again lower the system's sensitivity to packing imperfections. For the combination shown, pores of a fixed size $r_L = R_2$ could still get absorbed. It is evident that for this to occur the grain growth rate constant B has to have a lower activation energy than the kinetic constant. If B decreases compared to B_5, say to B_6, then for the situation shown here, a satisfactory microstructure could not be achieved by changing the sintering temperature.

As a last comment, one might consider the uniformity of the grain size. While the above examples do not permit to make similar predictions on the grain size distribution requirement, it does bring out the sensitivity of the microstructure to variations in grain size. A detailed consideration of such heterogeneities has to take into account additional complexities (9,10), but Fig. 3 suggests strongly

that the systems is more sensitive to grain size variations at constant packing geometry than to packing fluctuations at constant grain size.

A foremost requirement will therefore be that the spacial variations in grain size, averaged over some small spacial domain, remains within very narrow limits. It cannot be specified yet how large this spacial domain should be, but one could tentatively put it on the order of the size of the largest permissible grain. Thus, packing uniformity requirements are less critical for monodispersed powders (11) compared to multidispersed ones (12) although good results could be obtained with the latter if homogeneity in the spacial distribution of grain sizes is carefully controlled. It would therefore seem possible to trade the difficulty of making narrow powder size-distributions for more stringent control of spacial uniformity of grain size in multidispersed systems.

ACKNOWLEDGEMENTS

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.

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FIGURE CAPTIONS

Figure 1: Microstructural evolution of a heterogeneous, sintered at 1250°C, at various densities. Note the trend towards homogenization.

Figure 2: The size of pores in a uniform compact at 80% density, relative to their initial size, r_{80}/r_o, as a function of graingrowth rate constant B.

Figure 3: Dependence of r_{80}/r_o as a function of B on the initial grainsize, G_o.

Figure 4: Dependence of a r_{80}/r_o as a function of B on temperature and G_o.

Figure 5: Comparison of microstructures of heterogeneous MgO compacts as in Fig. 1, at 80% density, sintered at 1500°C and at 1250°C. The 1250°C microstructure is considerably more homogeneous.

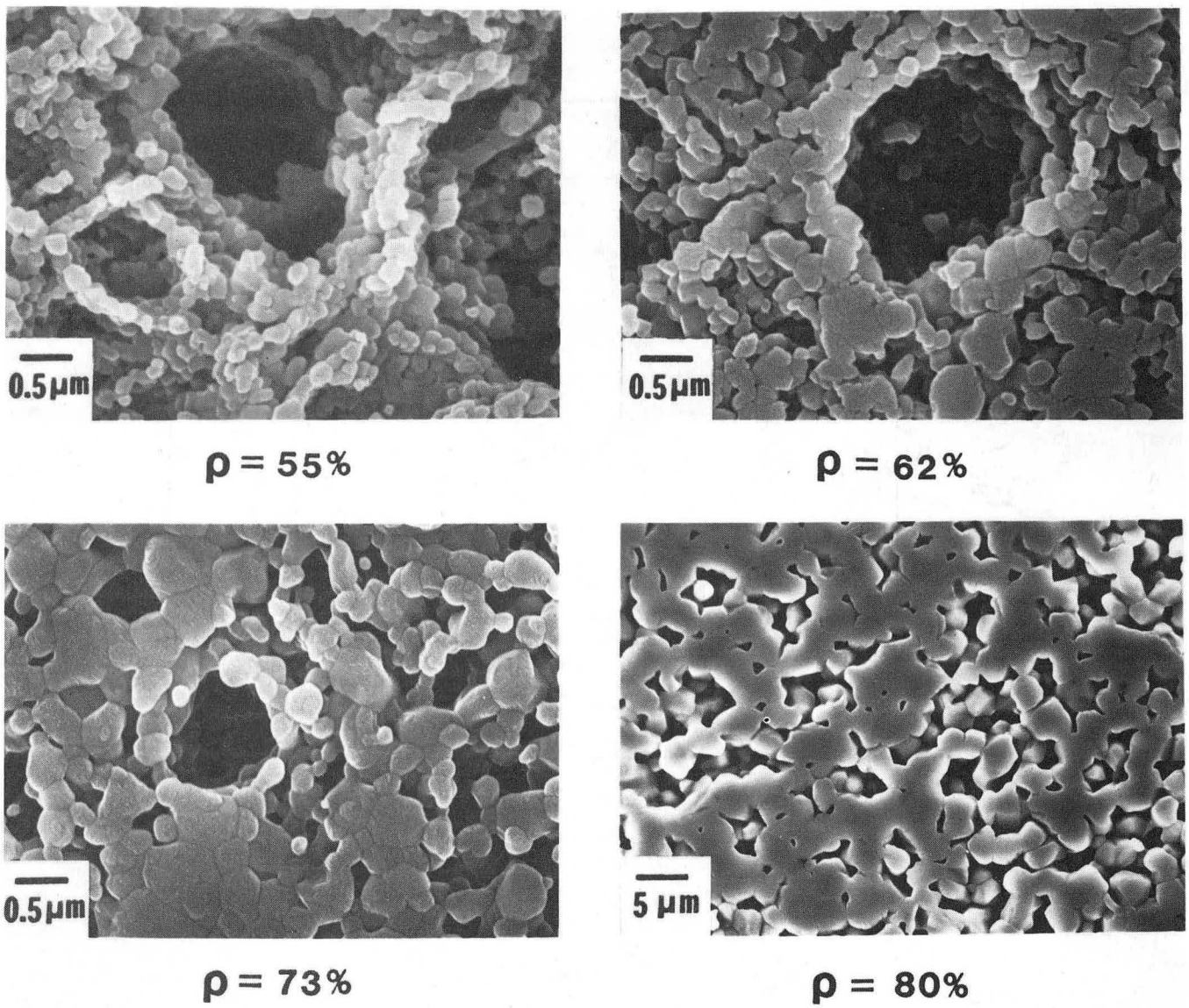

Fig. 1 XBB866-4517

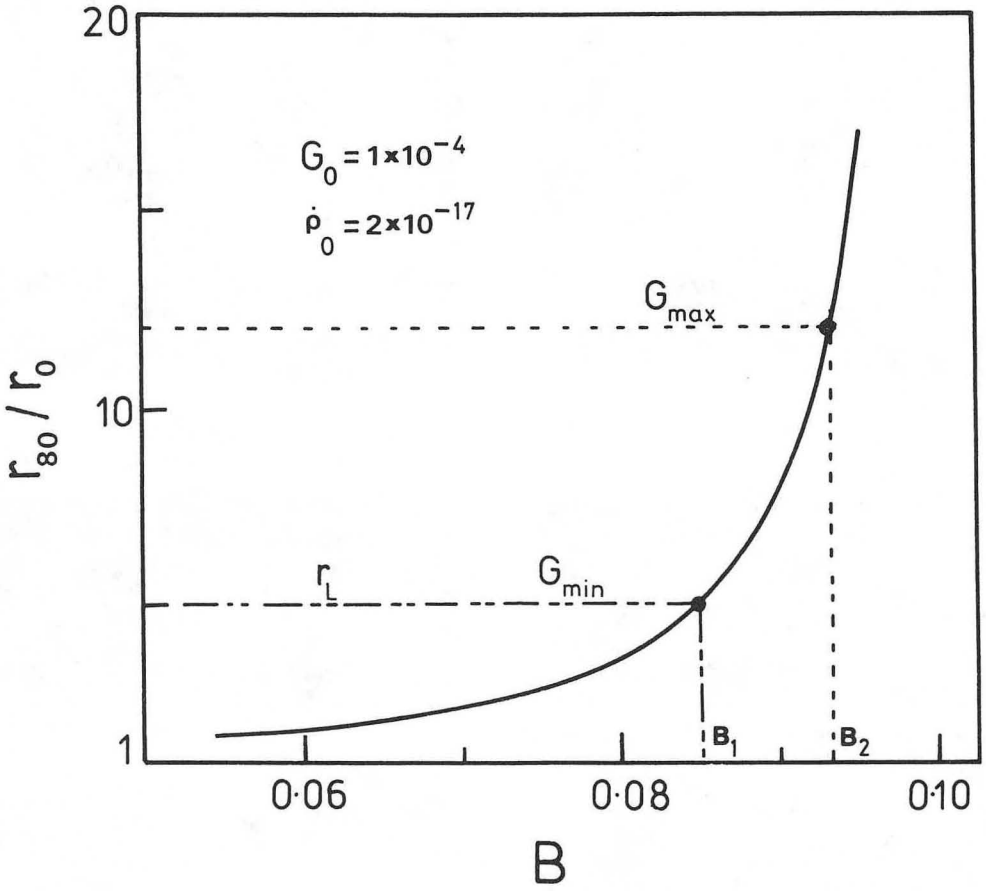

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Fig. 2

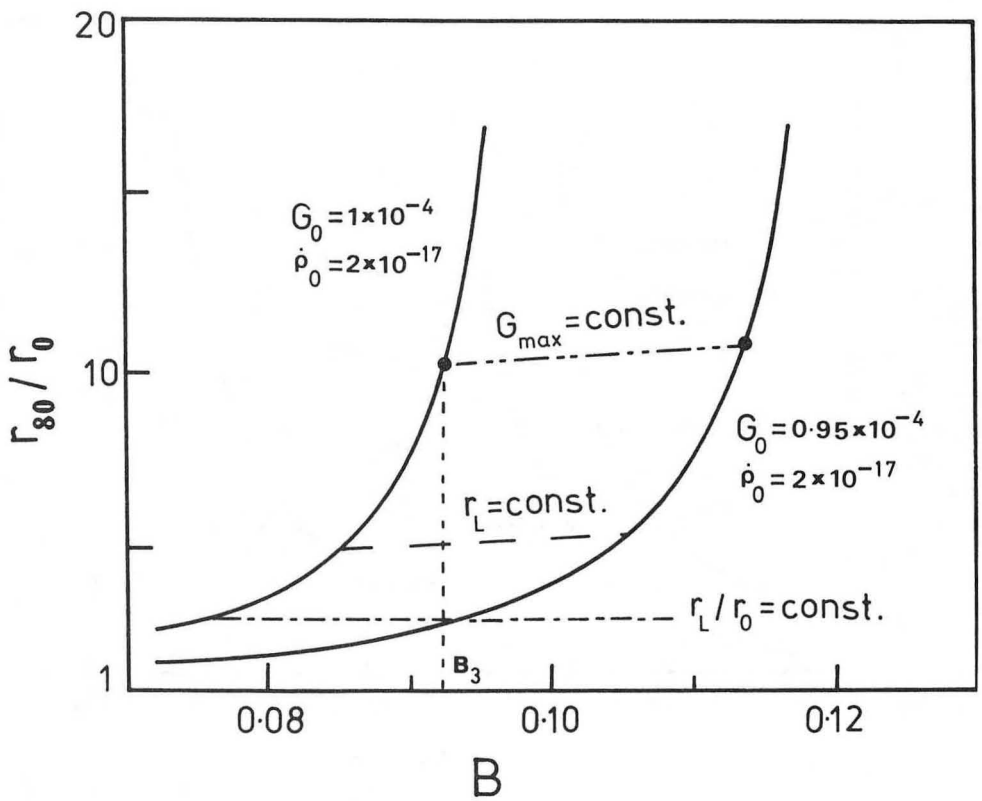

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Fig. 3

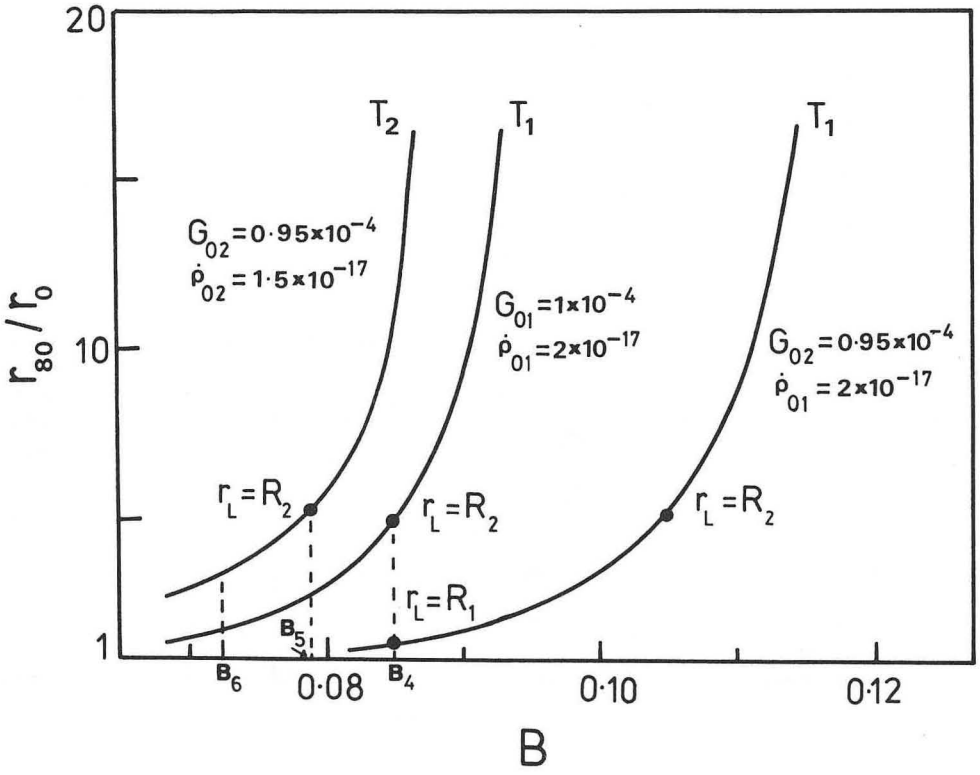

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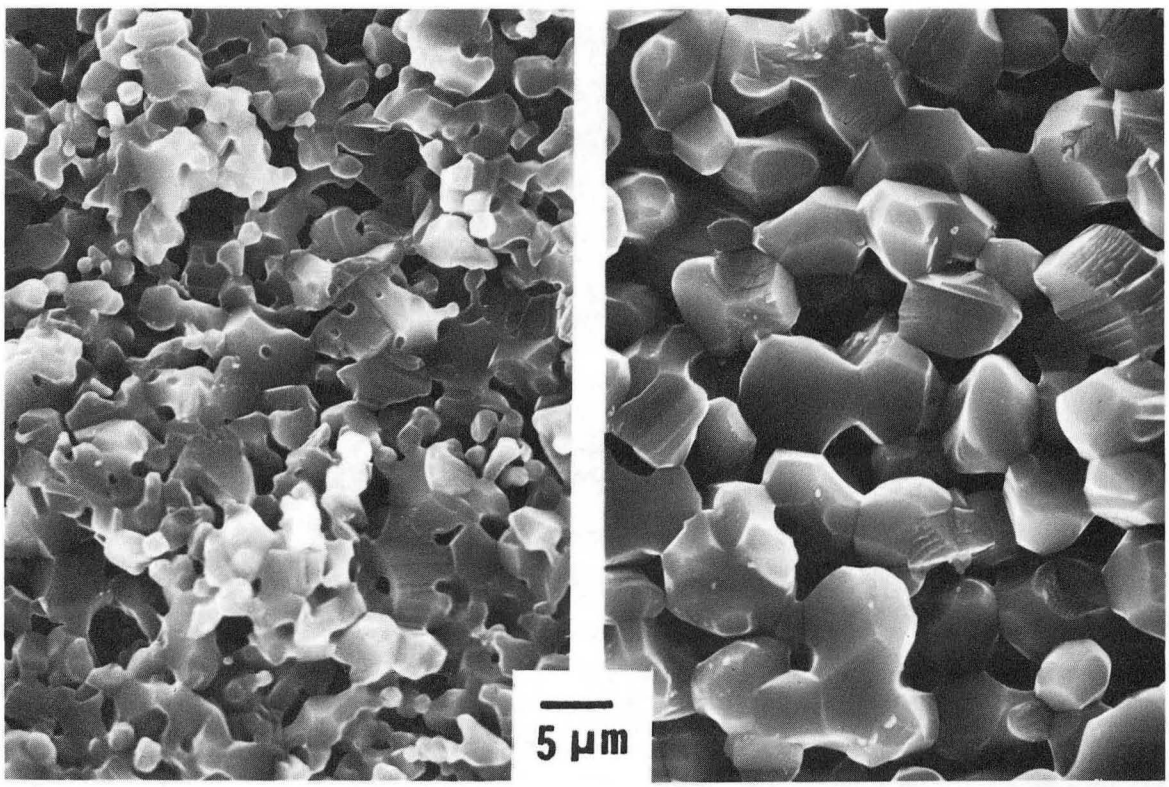
Fig. 4



ρ = 80%

1500°C 1250°C

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Fig. 5

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