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Sintering of the Heterogeneous MgO Compacts

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Ph.D. Thesis

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April 1988

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Kin - Fu Lin

Abstract

This study explores the optimum sintering schedule for an agglomerate compact. Various pertinent models have been proposed to assess the influence of the multimodal pore size distributions on the overall densification kinetics and the effect of temperature on the sintered microstructure. A thorough investigation of the sintering behavior and microstructural evolution for the heterogeneous MgO compact has been performed. The enhancements of the densification rate, the grain growth rate, and the increase in inter-pore spacing while sintering the heterogeneous compacts have been observed in this study. High-temperature sintering tends to produce a heterogeneous structure, and many pores are trapped within the grains. Low-temperature sintering is advantageous to produce a more homogeneous structure. 2-step sintering, combining a pre-treatment at low temperature (i.e. the homogenization treatment) with subsequent high temperature sintering, is proposed as an optimum sintering schedule for the agglomerated compact.

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1. Introduction

Sintering is a thermally activated process which can transform a porous powder compact into a dense product. The evolution of the microstructure during sintering is determined by many processes: densification, coarsening (due to surface diffusion or evaporation and condensation), rearrangement, and grain growth (through grain boundary migration). The resultant microstructure of a sintered product is mainly influenced by three factors: 1. characteristics of the initial powders, 2. the state of powder packing within the green body, and 3. the sintering schedule.

During recent years, the influence of the agglomerated nature of the raw powders on the sintering behavior has been extensively investigated.¹⁻¹⁰ Rhodes¹ has studied the effects of agglomeration on sintering and made the important finding that the full potential of fine powders can only be realized when agglomerates are eliminated. Dynys and Halloran² have reported that the densification rate decreases with increasing agglomerate content in the green compact. Stresses which will develop in association with local differential densification within the agglomerate compact have been analyzed.³⁻⁸ Different types of sintering damages which might be generated due to these unfavorable stresses have also been investigated.^{9,10} Although much work has been devoted to understanding the effect of agglomerates on sintering behavior, little effort has been made to explore a better sintering schedule for the agglomerate compact.

The effects of grain growth on sintering are generally believed to be detrimental due to the increase in the diffusion path length.¹¹ However, it has been proposed that grain growth can be beneficial for sintering by assisting the shrinkage of large pores.¹² F.F.Lange¹³ has

further pointed out that grain growth is necessary in order to eliminate large pores within the agglomerate compact. The contribution of grain growth to densification has been implicitly demonstrated.¹⁴ Nevertheless, direct observation which can explicitly illustrate this grain growth assisted densification has never been done.

The intention of this study is to investigate the relationship between local differential densification, grain growth, and the overall shrinkage behavior of the agglomerate compact. Based on the above investigations, a sintering schedule which can fix the initial heterogeneous structure of an agglomerate compact into a homogeneous state is of great interest. An optimum sintering route which can produce better ceramic products is the ultimate goal of this study.

Due to its practical importance, MgO powder has been chosen as the material of study. The usual sintering experimental methods have been used to examine the densification behavior. The evolution of the microstructure has been investigated by observing fracture surfaces or polished and thermally etched sections with the scanning electron microscope (SEM). Grain size, interpore spacing, pore coordination number (N), dihedral angle, and the triple line length of different types of boundaries have been measured from SEM micrographs of the sintered specimens.

A heterogeneous pore cluster system has been proposed as a 2-D model to simulate the sintering behavior of an agglomerate compact. The shrinkage curves of the "decoupled case" (i.e. no interaction between different pores with different sizes) has been calculated to compare with the experimental results. The shrinkage behavior of the "strong coupling case" has also been analyzed.

Models which clarify the influence of variations in densification rate, i.e. differential densification, on the microstructure evolution have been proposed. The relation between interpore spacing and grain size has been predicted and verified experimentally.

A theory for coarsening has been combined with differential sintering theory to model the temperature dependence of the final sintered microstructure. The model predicts that high temperature sintering will tend to enhance the heterogeneity of pore sizes.

Microstructures of the specimens produced by many different heating schedules have been compared with those prepared by conventional isothermal sintering. An optimum process, *2-step sintering*, for sintering the agglomerate compact has been found.

2. Background

In the past few years many studies have been conducted to understand the influence of agglomerates on the sintering behavior of ceramic system.^{1-10,15,16} The adverse effects of agglomerates have the following aspects:

1. They limit the attainable green density,¹⁵ and make the microstructure heterogeneous by introducing different types of interior pores which are formed by distinct mechanisms.¹⁶
2. They induce differential sintering rates which in turn will produce stresses.³⁻⁸ These stresses will impede the densification kinetics and generate defects.^{9,10}
3. They limit the final density of the sintered products, and also are responsible for the resultant heterogeneous microstructure.^{1,2}

Most commercial ceramic powders are agglomerated to some extent. The agglomerates can be categorized into two types according to the different bonding mechanisms between the primary particles.¹⁷ When the primary particles are held together by the surface adhesion forces (e.g. Van Der Waal's forces, electrostatic attractions, etc.), the bond strength between the particles is weak, and the agglomerate is "soft". The "soft" agglomerate is easy to smash by an external applied load while forming the green compact. In a "hard" agglomerate, the primary particles are bonded with solid bridges (e.g. due to micro-sintering, plastic deformation, chemical reaction, etc.), which are difficult to

break up under the action of the externally load applied in producing the prefired body. When raw powders are agglomerated, the microstructure and the packing density of the green compact are destined to be heterogeneous because of different types and sizes of pores. The sintering behavior of the agglomerate compact is therefore very complicated because: 1. The shrinkage rates of pores with unequal sizes are not the same. 2. Large pores can not shrink in the early stage of sintering. 3. Grain growth kinetics in the dense area and the porous area is different.

2.1 Shrinking of Pores

The sintering behavior of an agglomerate compact is influenced by the characteristics (especially the size) of the interior pores. Figure 1 depicts two distinct types of pores within the heterogeneous system; they behave differently during sintering.

Intra-agglomerate pores, i.e. those embedded within the multiple particle domains, will be preferentially eliminated during the sintering process. The inter-agglomerate pores are introduced as a consequence of bridging across agglomerates; therefore, their size varies with the degree of perfection in packing the agglomerates. The shrinkage behavior of these pores is dependent upon their size.

It has been pointed out that, instead of shrinking, large pores which are surrounded by large numbers of grains (the total number of the surrounding grains is defined as the pore coordination number), will grow during sintering.^{18,19} A more recent and rigorous analysis made by Cannon¹² shows that the large pores would initially shrink toward an equilibrium size at which their shrinkage then would stop. He also proposed that grain growth without growth of the large pores would

reduce the coordination number and eventually promote further densification.

Lange¹³ has studied the sintering behavior of agglomerated compacts, and concluded that the multi-grain dense domains are preferentially densified and then support grain growth. This, in turn, decreases the coordination number of the remaining large pores and makes them shrinkable. Evans and Hsueh²⁰ have analyzed the sintering behavior of large pores in a fine-grained matrix and predicted that an enhancement of the densification rate will occur when the pore size becomes of the order of the grain size.

2.2 Grain Growth

Grain growth kinetics have been studied extensively both in fully dense and in porous systems.²¹⁻²⁹ In fully dense oxides, both the square law (i.e. the grain size increases at a rate proportional to $t^{1/2}$) and the cubic law (i.e. $G \propto t^{1/3}$) have been found. The dragging effect of impurities would be responsible for the slower grain growth kinetics.²¹ For porous compacts, the cubic law fits most of the data.²²

There are some discrepancies regarding the kinetics of grain growth in ceramic systems:

1. The cubic law, because it was derived assuming that the retardation effect of porosity on the grain boundary movement is similar to that of second phase particles,²³ should be only applicable to the final stage of sintering when the pores are few and closed. Nevertheless, numerous studies in porous systems over a wide range of densities have reported that the results satisfied a cubic law.^{22,26,27}

2. Brook²⁴ has suggested that the grain growth kinetics ($G \propto t^{1/n}$) are determined by the dominant mass transport mechanisms for both the pore movement and grain boundary migration, and the characteristic exponent (n) can range from 1 to 4.

3. After considering all of the possible mass transport processes for moving pores, Nichols²⁵ argued that the kinetics could be $G \propto t^{1/3}$, $G \propto t^{1/4}$, or $G \propto t^{1/5}$.

4. Greskovich et al.²⁶ have studied porous Al_2O_3 compacts and reported that grain growth kinetics are different for different sintering temperatures. They proposed that filling up the neck between adjacent particles is the first step of the grain growth mechanism for porous compacts, and that G would vary with $t^{1/3}$ (if surface diffusion is predominant), or $G \propto t^{1/2}$ (for volume diffusion).

5. In studies of the MgO system, the square law was reported to be a satisfactory fit for both dense²¹ and porous systems.^{27,28} Whittemore et al.²⁹ have found that the grain growth kinetics follow a cubic law for sintering at several water vapor pressures (from 2.3 to 101.3 KPa).

In addition, since the heterogeneous microstructure of sintered agglomerate compacts consists of fully dense and of porous areas, the grain growth kinetics must be very complicated due to the different time dependence for these two regions. Up to now, this complication has not been studied.

2.3 Sintering Schedule

The microstructure of the sintered product is mainly controlled by

two concurrent and competitive processes: grain growth and densification. Thus, different sintering schedules, i.e. the choice of the firing temperature, the heating rate, and the firing duration, will produce different microstructure.³⁰ A strategy which can adjust the relative contribution of densification and grain growth and make one of them dominant is commonly known as "ratio control sintering".^{31,32} For instance, for Al_2O_3 sintering, higher sintering temperatures will increase the ratio of the densification rate to grain growth rate due to the higher activation energy for densification than for grain growth. Therefore, a higher sintering temperature is beneficial for producing the high density product with finer grain size.³³ However, for some solids, like MgO , the choice of sintering temperature for controlling the ratio is ambiguous due to the uncertainty and some overlap of the reported activation energy data for these two processes.^{31,34}

There are two other unconventional sintering schedules which have been reported. Ultra-rapid sintering^{35,36} has been proven to be able to produce the products with finer grain size due to the rapid transition through the temperature regime where the coarsening mechanisms prevail. Rate-controlled sintering³⁷ has also been reported to be able to produce microstructures with finer grain size which was presumed to be due to minimizing possible gas entrapment and preventing excessive grain growth.

For the agglomerate compacts, none of the above strategies is suitable. The fast-firing method has already been proven not applicable in the heterogeneous MgO system.³⁸ Rate-controlled sintering has no theoretical basis and the phenomenological model³⁹ needs at least ten numerical factors in order to preset the sintering schedule. Due to the difficulties in achieving accuracy in choosing the numerical factors and to its complicated procedure, rate controlled sintering will not be

considered in this study. A newly developed sintering process, i.e. *2-step sintering*, has been explored and found helpful in producing better microstructure while sintering the agglomerate compact. The model approach, the procedure, and the merits of *2-step sintering* will be discussed in the following sections.

3. Experimental Procedure

3.1 Sintering Behavior and Microstructure Investigation

3.1.1 Specimen Preparation

A commercial magnesium oxide powder* was used in this study. These powders have a very uniform particle size of about $0.06\ \mu\text{m}$, but are agglomerated with a wide agglomerate size distribution (As shown in figure 2). The powders were uniaxially pressed at $\approx 20\ \text{MPa}$ into cylindrical specimens (6mm diameter by 5 mm) with relative densities of 0.40 ± 0.01 . The scanning electron microscope (SEM) micrographs in figure 3 show the fracture surface of the green compact. They illustrate a heterogeneous microstructure with a large fraction of interagglomerate pores formed by bridging between agglomerates.

The specimens were sintered in air at five different temperatures, i.e. 1250°C , 1300°C , 1400°C , 1500°C , and 1600°C . For low temperature studies (1250°C), the experiments were performed in a dilatometer⁴⁰ which continuously recorded the shrinkage. Due to the temperature limitation of the dilatometer, high temperature sintering studies were performed in another furnace.

*. Regent grade, J.T.Baker Chemical Co., Phillipsburg, NJ. (loss on ignition 0.24 wt%, MgO after ignition 98.3%, Cl 0.03%, NO_3 0.005%, heavy metal (as Pb) 0.004%, Fe 0.04%)

3.1.2 Low Temperature Sintering

The green compacts were first placed in the tube furnace entrance of the dilatometer. After the furnace had reached the working temperature, the specimens were quickly introduced into the hot zone. Experiments ranged from 10 minutes up to 4 days.

The axial shrinkage and the temperature were continuously recorded and $t = 0$ was assigned to the moment at which the specimen was heated up to the isothermal sintering temperature. The specimens typically reached their temperature in about 8 minutes.

The initial density of each sample was determined from the measurement of its weight and dimensions. The final density of the sintered specimen was measured in 1-Butanol using Archimedes' principle. The same methods were also applied to measure densities in the high temperature experiments.

3.1.3 High Temperature Sintering

High-temperature isothermal sintering was conducted in static air using a bottom-loading furnace.** Specimens were put in an Al_2O_3 boat situated on top of a refractory pedestal which was then raised into the center of the hot zone. The heating procedures were preset and controlled by a Eurotherm type 211 programmer. The samples were heated to 850°C at a rate of $10^\circ\text{C}/\text{min}$, held for 15 min., and then heated to the different temperatures at various rates (up to $75^\circ\text{C}/\text{min}$. for 1600°C).

** CM1500 Series Rapid Temperature Lab. Furnace with MoSi_2 heating elements and Pt 6%Rh vs Pt 30%Rh (type B) thermocouple.

This sintering schedule, including the holding at 850°C and subsequent rapid heating, was used to simulate the heating process of the dilatometer experiments. After sintering, the power was switched off and the specimens furnace-cooled in air to room temperature. Sintering temperatures of 1300°C, 1400°C, 1500°C, and 1600°C were used. The duration of sintering covered the time of 10 min. to 2 days.

3.1.4 SEM Work

Both the fracture surfaces and polished and etched sections of all the specimens were examined using a scanning electron microscope. The preparation of polished surfaces involved vacuum impregnation with an epoxy resin to prevent grain pull-off during the polishing. After the resin was burned off at 400°C, the samples were thermally etched at 1100°C for 30 minutes.

From the SEM micrographs of the polished surfaces, many important characteristic parameters were measured using the standard quantitative stereology techniques.^{41,42}

Grain size information was obtained by counting the number of grains intercepted by testing lines of a known length. The average grain size was taken as 1.5 times the average measured length.⁴³ The "95% confidence interval" for the measured sample mean⁴² (i.e. $\pm 2\sigma_m$, where σ_m is the standard deviation of the mean value) was calculated as 0.4 μm . The distribution of grain size was determined from measuring the section areas of the studied grains by counting the points covered by each grain on the point-counting grid.

The interpore spacings were measured using the linear intercept method by counting the number of pores traversed by the straight line.

The measurements were made on the SEM micrographs of both the as-polished and polished then thermally etched surfaces. The calculated average value of $2\sigma_m$ is $0.12\mu\text{m}$.

More than 300 pores were counted to find the distribution of the planar coordination number of the remaining pores. Equilibrium dihedral angles were measured from the etched surfaces of the specimen sintered to a relative density of 80% of the theoretical density. In total, 100 measurements were made.

Two types of three-phase lines were measured. L^{ss} is the triple line length of the grain boundary which is connected to other grain boundaries. L^{ssp} stands for the length of the grain boundary which intersects the interior pore. The measurements were done by counting the number of the intersections within a counting area. More than 1000 points were counted for every investigated specimen.

3.2 2-Step Sintering

The *2-step sintering* process consists of an isothermal hold at low temperature to obtain a homogeneous structure followed by a high temperature sintering to achieve high density. A schematic diagram of the schedule for *2-step sintering* is shown in figure 4.

3.2.1 Homogenization Treatment

The purpose of this phase is to find a sintering condition which can convert the initial heterogeneous state into a more homogeneous one. The choice of the sintering temperature and sintering time for homogenization treatment was based on the results of structural investigations in previous sintering studies. Many combinations of the

treatment temperature (i.e. 1250°C, 1300°C, and 1400°C) and soaking duration (from 24 hr. to 72 hr.) were tested. After sintering, the fracture surfaces of the samples were examined with the scanning electron microscope. The best condition (i.e. 1250°C, 48hr.) was found after a set of preliminary tests and was used to homogenize the heterogeneous green compact for subsequent high temperature sintering.

3.2.2 High Temperature Sintering

After the homogenization treatment, the specimens were sintered at 1600°C for various times. The sintering procedure is the same as that described in previous high temperature sintering experiments. (see section 3.1.3) Both the final density and the microstructure were examined and compared to those of specimens sintered at 1600°C without homogenization.

4. Results and Discussion

4.1 Sintering Behavior of a Heterogeneous Compact

Since 1945, after Frenkel⁴⁴ had presented his viscous sintering concept, continuous progresses in understanding the sintering behavior of a porous body has been made. Kuczynski⁴⁵ was first to propose the diffusion mechanism and derived mathematical expressions describing the sintering kinetics of a spherical particle sintered to a metallic plate. Kingery and Berg⁴⁶ studied the initial stage of sintering by considering many mechanisms using the idealized two spheres model. The model has been extended by numerous authors to investigate the kinetics of sintering in many different geometrical shapes.⁴⁷⁻⁴⁹ Most of the effort was focused on the dimensional change of the contact region between adjacent objects. Nichols and Mullins⁵⁰⁻⁵² chose surface diffusion as the mass transport route and made a more accurate prediction, using a digital computer, of the morphological changes proceeding at the neck between spheres. Bross and Exner⁵³ considered the simultaneously acting mechanisms of surface and grain-boundary diffusion. Important models designed to describe the overall densification kinetics without considering the detailed geometrical evolution in the neck region have been proposed by Coble,⁵⁴ Johnson,⁵⁵ Eadie et.al,⁵⁶ and Pask⁵⁷ respectively.

While most of the above studies were made to describe

quantitatively the sintering behavior of a homogeneous system, many investigations pertinent to the heterogeneous case have also been reported. Coble⁵⁸ considered the effects of the particle size distribution and calculated the shrinkage rate by taking into account an additional effective stress on the grain boundary. The extra stress was considered necessary in order to avoid the discontinuity in surface curvature at the grain boundary between particles of unequal sizes. Many possible arrays of different sized particles were considered in Coble's study, but the neck between the particles is symmetrical and connects two identical pores.

The investigation of the shrinkage behavior across an asymmetric neck is physically analogous to the examination of the effects of heterogeneous pore size distribution on the sintering process. Scherer⁵⁹ has considered the behavior of a glass system with a bimodal pore-size distribution. The local stress generated by differential shrinkage rates of small and large pores has been found to produce a substantial effect on the shrinkage rate of large pores during the different stages of sintering. Exner and Bross⁶⁰ have analyzed the stress distribution and mass transport rate along an asymmetric neck in a crystalline system. A more rigorous treatment was made by Hsueh and De Jonghe⁶¹ taking into account both the center to center stress and bending moments generated by the differential sintering stress. The shrinkage rate, $\dot{S}$, they derived can be modified as

$$\dot{S} = C \left(K + \frac{2\sigma_a}{\gamma_s} \right) \quad (1)$$

where K is the mean curvature of the considered pore surfaces, σ_a the mean applied stress on the grain boundary (the effective stress), γ_s the

surface tension, and the kinetics constant C is expressed by:

$$C = \frac{6 D_b \delta_b \Omega \gamma_s}{k T X_o^2} \quad (2)$$

where D_b : grain boundary diffusion coefficient
 δ_b : effective grain boundary thickness
 Ω : atomic volume
 X_o : neck width
 k : Boltzmann constant

4.1.1 2-D Model Simulation

The complication in the sintering kinetics in an agglomerate compact are mainly due to the heterogeneous pore size distribution. However, by adopting the shrinkage equation derived by Hsueh and De Jonghe⁶¹ on a specific 2-D model, the shrinkage kinetics of a heterogeneous system with a wide distribution of pore size can be simulated. Two extreme cases have been considered separately for describing the differential sintering stress acting in the model system. Scherer⁸ has proposed a self-consistent model to calculate the densification rate of a composite system (powder matrix with uniformly dispersed non-sinterable inclusions). He argued that when the volume fraction of the inclusions is considerable (i.e. $V_f \geq 0.16$), a contiguous network is present in which the stress fields of neighboring inclusions will overlap significantly. Following this idea, in the "strong coupling case" the additivity of the stress generated by differential densification around each agglomerate is assumed and the gross effect of all the stresses is considered to be uniformly distributed throughout the whole heterogeneous system. This assumption is appropriate for isotropic shrinkage. Another condition was also considered

taking into account that the area affected by the differential sintering stress may be limited to the immediate neighborhood of the agglomerate and is not transmitted through the whole system. In this extreme case, the "*decoupled case*", each pore shrinks at its own rate without interaction with the neighbors.

4.1.1.1 Strong Coupling Case

To simulate the shrinkage kinetics of an agglomerate compact, a 2-D model system was constructed as shown in figure 5. The clusters of the smallest pores are physically equivalent to an agglomerate and the other large voids can be viewed as the interagglomerate pores. There are two approaches to derive the sintering equation as shown schematically in figure 6. The densification rate can be obtained by either estimating the rate of porosity removal from a predetermined unit cell^{54,56,57} (figure 6(a)) or investigating the rate of approach of the centers of two particles joined across the boundary⁵⁵ (figure 6(b)). In this analysis the family of pores in the model system was first divided into different size hierarchies, then a unit cell was selected and the shrinkage equation was derived by investigating the approach rate across one of the cell boundaries.

As shown in figure 5, the square region which is enclosed by the dotted line with four medium sized pores on the corners is the smallest cell which can be used for studying the densification rate of the heterogeneous system. The cell is physically identical to an agglomerate surrounded by the interagglomerate pores. Assuming that the stress state and the material's characteristics (i.e. bulk viscosity and shear viscosity, which govern the behavior of the material when under the action of stress) are isotropic in this two dimension model, then the shrinkage behavior of the selected cell is equal to that of any neck

region or array of necks. Therefore, the densification kinetics of the unit cell can be assessed by investigating the sintering rate along one neck or array of necks. This methodology is similar to the second approach in deriving the densification equation of a compact by studying the approach rate of two centers across the neck as illustrated in figure 6(b). After the sintering kinetics of this unit cell are solved, the same procedure will be extended to a more complicated system, e.g. the one that is outlined in figure 5 with three hierarchies of pores.

Instead of analyzing the shrinkage rate across a single neck area, the analysis considered the simultaneously shrinkage of several aligned necks. The number of the necks on the cell boundary is dependent upon the unit cell dimension, which is equivalent to the size of the agglomerate. Figure 7 shows the selected neck array, which is composed of two different sized pores connected by a certain number of necks, each has the same length, X_0 . De Jonghe and Rahaman⁶² have used a similar model to explore the sintering stress of the heterogeneous powder compact.

Starting from equation (1), the shrinkage rate of each neck is given by:

$$\dot{S} = C \left(K + \frac{2\sigma_a}{\gamma_s} \right)$$

For the neck regions connected by two equal sized pores, the effective stress is δ_c . On the other hand, necks between two different sized pores will experience a different effective stress, $\delta_c - \delta_t$, where δ_t is the additional stress exerted on the boundary by the bending moment which would happen on an unconstrained, asymmetric neck. By assuming a rigid boundary which stays flat during sintering, the force balance

requirement along the entire cell boundary will be satisfied when

$$2 X_o \delta_t = n X_o \delta_c \quad (3)$$

and the relation between δ_t and δ_c is simply

$$\delta_t = \frac{n}{2} \delta_c \quad (4)$$

where n is the total number of the densifying necks.

Under the "strong coupling" consideration, the mean effect of all the various stresses is equally active on each neck. This is the same as saying that when a quasi-steady state prevails, the material will be removed uniformly from all boundaries. After setting the shrinkage rate equal for all necks, the overall shrinkage rate of the cell boundary can be calculated; it has the following form

$$\dot{S} = C \left(K + \frac{4}{X_o} \right) \quad (5)$$

$$\text{now } C = \frac{6D_b \delta_b \Omega \gamma_s}{k T} \quad (6)$$

again D_b : grain boundary diffusion coefficient
 δ_b : effective grain boundary thickness
 Ω : atomic volume
 k : Boltzmann constant

and K , the weighted arithmetic mean of the curvatures of all the pores, is given by

$$K = \frac{2 \left(\frac{n_1}{r_1} + \frac{1}{r_2} \right)}{n_1 + 1} \quad (7)$$

in which n_1 is the total number of the small pores of radius r_1 , and r_2 is the large pore's radius.

Following the same technique, equation (5) can be applied to more complicated systems (like those shown in figure 8) by simply changing the mean curvature, K , into a general form

$$K = \frac{2 \sum_i \left(\frac{n_i}{r_i} \right)}{\sum_i n_i} \quad (8)$$

where n_i is the number of the i th hierarchy pore with radius r_i .

The shrinkage behavior of many heterogeneous systems has been investigated in this study using equations (5) to (8) and some interesting results of the model analysis are presented here.

First, the presence of the large pores always has an adverse effect on the sintering process and the densification rate will be retarded. Figure 8 shows five continuously magnified systems, each system has its own shrinkage rate $\dot{S}_i$ ($i=1$ to 5). The homogeneous case (the top system) simulates the densifying behavior within an agglomerate and the associated shrinkage rate, $\dot{S}_1$, was selected as a base to compare with other cases. The other enlarged systems were constructed to simulate real powders compact system and the large pores are the interagglomerate pores. From the calculations it was found that as the types of pores

within the system is increased, the shrinkage rate is decreased. The effect is most pronounced when system two is compared with the top system (notice that $\dot{S}_2 = 0.8658\dot{S}_1$) and further expansion of the system has very limited influence. (e.g. the difference between $\dot{S}_5$ and $\dot{S}_2$ is only $0.00071\dot{S}_1$)

Second, as the size of the interagglomerate pore increases, the overall shrinkage rate of the system decreases. The effect is illustrated in figure 9, which shows that after a period of fast decline, the decrease of the relative shrinkage rates with the pore size ratio m for the investigated systems then flattens out. This implies that if the agglomerates were not packed perfectly, the poorer the packing the lower the shrinkage rate. However, beyond a certain degree of imperfection (i.e. when $m \approx 6$ in figure 9), the system becomes less sensitive to further im-perfections.

The effect of the agglomerate size has also been analyzed by changing the number of small pores on the cell boundary. Figure 10 shows that as the number of small pores increases, the densification rates ratio, R , increases; implying that if the agglomerate is larger the shrinkage rate is higher. When the system is composed of only two large pores (i.e. when $\Delta n = -3$ and the number of the small pore is zero), the shrinkage rate is only 54% of the reference system (with $r_2 = 4r_1$, and $n_1 = 3$). This is due to the lower curvature of the large pores.

The retardation effect of the large pore on the overall densification rate can be interpreted in two ways: The first explanation was given by Rhines et al.⁶³ They proposed that the large pore with its smaller curvature and lower chemical potential can serve as a vacancy sink for the neighboring small pores. As a result, not only is the overall shrinkage rate retarded, but also the large pore grows. (Whether

the large pore will eventually shrink or grow depends upon many factors: the coordination number of pore, the ratio of coarsening rate to densification rate, and the sintering temperature, etc. The influence of sintering temperature on the evolution of the microstructure during sintering of a heterogeneous system will be discussed further in section 4.3.1.)

Another way of explaining the lower densification rate is from the "sintering stress" idea developed by De Jonghe and Rahaman.⁶² The "sintering stress" is equivalent to the externally applied stress acting on the porous system that has the same effect as surface tension. During sintering, the "sintering stress" acts as an effective mean grain boundary stress driving the matter removed from the neck regions onto the pore surfaces. In a heterogeneous system, the additional stress introduced by differential shrinkage rates will reduce the effective grain boundary stress exerted on the boundary, thereby decreasing the overall shrinkage rate.

The assumption that the excess differential sintering stresses are additive and distributed equally over the whole system makes the calculated overall shrinkage rate insensitive to the scale of the system after certain points. Based on empirical knowledge, it is thought that the "*strong coupling*" assumption will be suitable only after the neck regions have grown strong enough to transmit stresses across the whole system through the solid skeleton.

In the early stage of sintering, however, many experimental observations strongly indicate that the excess stresses caused by a non-uniform sintering rate can be dissipated by breaking the weak necks and can cause pore opening.⁶⁴⁻⁶⁶ Ross et al.⁶⁷ have proposed a "chain straightening" mechanism which proceeds in the loosely packed area as

another possible way to consume the excess stresses. Weiser and De Jonghe⁶⁶ used computer methods to investigate the rearrangement problem and concluded that differential densification is the major cause of the de-densifying phenomenon. Their statistical approach to understand the evolution of the particle arrangement produced two important results related to the "*strong coupling*" assumption.

First, the densification rates were found widely distributed in the early stage and become fairly uniform in the later stage of the process. The explanation they provided is that larger necks have developed and are able to transmit the differential sintering stresses. Second, there is no correlation between the local densification rate and the local density, therefore, any model which neglects either short range influences (e.g. rearrangement,^{66,68} chain straightening,⁶⁷ or pore space opening⁶⁵ etc.) or long range interaction (i.e. the *strong coupling* assumption) will not sufficiently predict the influence of differential sintering stress on the shrinkage kinetics in a heterogeneous system. Considering stress dissipation in the practice of sintering has led to a study of the other extreme — the "*decoupled case*".

4.1.1.2 Decoupled Case

In the "*decoupled case*", it is assumed that the effect of the differential sintering stress is completely relaxed. Different sized pores are now densified at their own rates and the accumulated porosity change of the whole system is given by

$$\Delta P = \sum_i \Delta P_{i,inter} + \sum_i \Delta P_{i,intra} \quad (9)$$

where $\Delta P_{i,inter}$ is the porosity removed from the interagglomerate pores and $\Delta P_{i,intra}$ the contribution due to the intra-agglomerate pores. When considering the sinterability of the pores, the time-dependent porosity change in the above argument can also be expressed by the following form:

$$\Delta P = \sum_i \Delta P_{i,sinterable} + \sum_i \Delta P_{i,non-sinterable} \quad (10)$$

The densification kinetics of a model system can be calculated using the above equation provided that an adequate densification equation is applicable. Many model simulations qualitatively describing the sintering kinetics have been done,^{53,67,69-71} but not one has taken into account the inactivity of large pores.

To explore the influence of the sinterability of the interior pores on sintering kinetics of the heterogeneous system containing inactive pores, this study has calculated the densification curve of an arbitrarily chosen system using appropriate equations, i.e. equations (10)-(12). Figure 11 schematically illustrates the number distribution of pore vs both size and pore distance for the studied system. Both the pore radius and interpore spacing have the unit of G_0 (i.e. the initial grain size). The choice of this unit is based on the grain size during sintering which can always be expressed as the initial grain size times some constant (see equation (12)), and is convenient in further calculation in which all of the factors can be set to the same units. The selected heterogeneous system has five hierarchies of pores with linearly increasing numbers. The resultant porosity distribution is

shown in figure 12(a).

Instead of using equation (1), calculations were done using the following equation derived for a homogeneous system⁷²

$$\dot{\rho} = \frac{B D \Omega}{k T} \frac{1}{G X_0^{m-1}} \Sigma \quad (11)$$

where B : a geometrical constant,

D : diffusion coefficient of rate-controlling species,

Ω : atomic volume,

k : Boltzmann constant,

T : absolute temperature,

G : grain size,

X_0 : pore spacing,

m : exponential characteristic of the densification mechanism

(m=2 for lattice diffusion, m=3 for grain boundary diffusion)

and Σ is the thermodynamic driving force for sintering. As shown by De Jonghe and Rahaman⁶², Σ contains surface free energy γ_s , grain boundary free energy γ_{gb} , and also the information of grain size and pore radius. In this "decoupled" calculation, a simplified form of Σ is used

$$\Sigma \sim \frac{\gamma_s}{r}$$

where γ_s is the surface tension and r the mean pore radius. This relation has also been used by many investigators in studying the sintering kinetics.^{7,73}

The grain growth kinetics are assumed to follow a cubic time

dependence:

$$G = G_0 (1 + B t)^{1/3} \quad (12)$$

where G_0 is the initial grain size, B is the kinetic factor, and G is the resultant grain size after t . The kinetics of porosity removal have been calculated for grain boundary diffusion, i.e. $m=3$, using equations (10)-(12) for various kinetic factors. These factors include: B , for grain growth and K for densification. The densification kinetic constant is given by

$$K = \frac{B D \Omega}{k T}$$

The calculation starts by taking the large pores, with radii larger than 4 times of the grain size - i.e. $r \geq 4 G$, to be non-shrinkable. From the geometrical consideration¹⁹, the large pore with $r = 4 G$ can be considered as a 2-D regular polygon which has the dihedral angle of 164° and 25 straight sides with the same length as G . A pore with straight pore surfaces is proposed to be non-sinterable in the classical sintering theory which considered the diffusion mechanism is the rate controlled process.^{19,74} Recently, Searcy⁷⁵ has proposed a random fluctuation theory, which is able to explain the sintering behavior of small MgO particles (~ 2 nm in cross section) with the interior pores which have straight surfaces.⁷⁶ In this calculation, the classical theory is followed and a pore with straight pore surfaces will be considered to be inactive during sintering. The main purpose of this calculation is to evaluate the influence of the inactive pores on the sintering kinetics without specifying a system, so the result will be suitable for the general case. Therefore, the choice of large pores with $r \geq 4 G$ as non-sinterable is arbitrary. Under this assumption, only the first term on the right hand side of equation (10) makes a contribution

to the densification kinetics at the early stages. Later in the calculation, grain growth will assist large pores in becoming active and contributing to the overall shrinkage of the system.

Figure 12(b) illustrates a densification curve plotted as calculated relative density vs logarithm of time for the conditions $B = 1.5 \times 10^{-2} \text{ min}^{-1}$ and $K\gamma_s = 0.04(G_0 X^2) \text{ min}^{-1}$. The kinetic constant (K) combined with surface free energy (γ_s) has the units of $G_0 X^2 \text{ min}^{-1}$, and X was set to have the units of G_0 ; therefore, $K\gamma_s$ has units of $G_0^3 \text{ min}^{-1}$. This choice of units is for the convenience of calculation and makes the calculated result applicable for any heterogeneous system to predict the general trend of sintering kinetics, without worrying about the exact values of B , D , Ω and γ_s . The densification rate was obtained by taking the first derivative of the sintering curve with respect to time. Figure 13 is the smoothed curve showing the logarithm of calculated densification rate vs relative density for the selected system sintered under the conditions $B = 1.5 \times 10^{-2} \text{ min}^{-1}$ and $K\gamma_s = 0.04(G_0 X^2) \text{ min}^{-1}$. It is seen that the densification rate increased with density in the density range from 0.45 to 0.49. This is due to grain growth, so the restrictive condition of non-shrinkage, i.e. $r \geq 4 G$, is no longer valid for all of the pores in the system, and the additional contribution provided by the initially inactive pores increases the densification rate. This result supports grain-growth assisted densification models proposed by other authors.^{12,13,22}

4.1.2 Experimental Results

4.1.2.1 Low Temperature Sintering

Figure 14 shows the relative density, ρ vs time, t , for the MgO specimens sintered at 1250°C . The logarithm of the observed

densification rate, $\log \dot{\rho}$, and the logarithm of the grain-size-compensated densification rate, $\log (G^2 \dot{\rho} / G_0^2)$, vs ρ are shown in figure 15. It is seen that $\log (G^2 \dot{\rho} / G_0^2)$ first decreases with ρ and then increases with ρ between $\rho \approx 0.6$ and 0.75 . Plotting $\log \dot{\rho}$ vs ρ is consistent with the methodology applied in the creep-sintering experiment,^{72,77-80} which is able to measure both the densification and creep kinetics simultaneously during sintering. From these, data of the sintering stress and the effective viscosities of densification and creep can be found.⁷⁹⁻⁸⁰ The compensating factor G^2 / G_0^2 was found after the following consideration: The general form of the densification rate was shown before (i.e. equation (11)) as

$$\dot{\rho} = \frac{B D \Omega}{k T} \frac{1}{G X_0^{m-1}} \Sigma \quad (11)$$

In which X_0 is the interpore spacing which, provided all grain triple junctions are pores, is related to the grain size G by the equation⁷²

$$X_0 = G (A_e / A)^{1/2} = G / \Phi^{1/2}$$

where A is the total cross-sectional area of the specimen and A_e is its actual, internal load-bearing area. The quantity Φ is usually referred to as the stress intensification factor.^{81,82} Equation (11) may be simplified to give

$$\dot{\rho} = K_1 \Sigma \Phi^{(m-1)/2} / G^m$$

where K_1 is a kinetic constant at a fixed temperature. Compensation for grain growth can be made by plotting $\log (G^m \dot{\rho} / G_0^m)$ vs ρ , where G is the grain size corresponding to the density, ρ , m is the exponential characteristic of the densification mechanism. For MgO , the mass

transport mechanism has been reported to be lattice diffusion,^{28,83,84} with $m = 2$. The compensating factor is therefore G^2 / G_0^2 .

Figure 16 shows scanning electron micrographs of the polished and thermally etched surfaces sintered for densities of (A) 0.55, (B) 0.62, (C) 0.73, and (D) 0.80. During the first phase of densification, most of the microstructural changes occur within the small pore matrix and the large pore remains relatively unaffected. The rapid local densification of small grain clusters caused the opening of the nearby pores and also allowed rapid grain growth in the densified area. These two features are pronounced in micrograph (c). After $\rho=0.73$ the grain and pore sizes of the matrix have increased to the point where they are becoming comparable in size to the large pores initially embedded in the matrix. Thus, the microstructure has evolved to a more homogeneous state.

The densification rate enhancement predicted by Hsueh and Evans²⁰ and implicitly demonstrated by Lange and Davis¹⁴ is explicitly observed in figure 15. The grain-size-compensated densification rate begins to increase at densities ranging from 0.6 to 0.65. From the SEM micrographs, it appears that grain growth decreased the coordination number of the large pores considerably, allowing them to shrink and thereby increase the densification rate. The pore is non-sinterable when its coordination number is larger than a critical value,¹³ which is determined by the pore size, grain size and the dihedral angle.¹⁹ To investigate the sinterability of pores from the microstructural studies, the values of the dihedral angle have been measured on the polished cross section of specimens sintered to $\rho = 0.80$. Figure 17 shows the histogram of dihedral angle distribution with the mean value of 100° . From the value of the dihedral angle of 100° , it is expected that large, spherical pores will begin to shrink when the coordination number is about 8 in the 3-D consideration.¹⁹ From the statistical approach,⁸⁵ the

most frequent value of the coordination number on a planar section of a polyhedron with 8 sides is about 4. This means that the pores with the coordination number larger than 4 in the SEM micrographs are non-shrinking. Based on this, the microstructural observations are not in good agreement with the observation of the enhancement of the densification rate. For instance, the microstructure corresponding to the increase in the densification rate (i.e. figure 16(b), when $\rho = 0.62$) still contains many large pores with the planar coordination number which is greater than 4, although its value has been dramatically reduced when compared with the microstructure of very early state, i.e. figure 16(a). However, higher values in the distribution of dihedral angles (shown in figure 17) will increase the critical coordination number (for the dihedral angle of 150° , a large pore is expected to begin shrinking at a coordination number of about 20 in a three dimensional study¹⁹). Also the dihedral angles in figure 17 were measured on the specimens with $\rho = 0.80$, Handwerker⁸⁶ has found that for lower density the apparent dihedral angle is higher, so the critical coordination number should be even larger. This may account for the increased activity of large pores at the larger cross-sectional coordination numbers evident in the SEM micrographs.

Both the model calculation of the "decoupled case" and the 1250°C sintering show the enhancement of densification rates during sintering (see figure 13 and figure 15). Since the increase in shrinkage rate in the model calculation is due to the additional contributions from the large pores which are initially inactive, it is therefore believed that this is the most plausible explanation for the experimental observation.

4.1.2.2 High Temperature Sintering

Figure 18 shows the density, ρ vs the logarithm of sintering time

for specimens sintered at 1300°C, 1400°C, 1500°C, 1600°C and 1250°C. The phenomenon of increasing densification rate was also observed in the 1300°C and 1400°C studies. For 1500°C and 1600°C sintering, the sintered density increased rapidly within 20 minutes, then the densification rate decreased monotonically with time and no further densification rate enhancement was seen in the densification curves. The microstructural investigation results will be discussed together with grain size and interpore spacing measurements in next section.

4.2 Relation Between Local Differential Densification and Grain Growth

4.2.1 Models and Theories

Up to now, no suitable parameters have been defined which are able to describe quantitatively (or even qualitatively) the microstructural change while sintering an agglomerated powder compact. As mentioned in the background section, almost all fine powders form agglomerates and the sintering process is complicated by local differential densification. Also, the grain growth kinetics are complicated by the coexistence of porous and dense areas. Therefore, it is necessary to find the pertinent material parameters so that the evolution of the microstructure during sintering can be quantified. Furthermore, these parameters could also be used to determine the optimum sintering procedure.

Pore space opening due to differential sintering, observed in sintering studies at 1250°C has led to the choice of interpore spacing as the first parameter to be investigated. To explore the grain growth kinetics in both the dense and porous areas, it is necessary to examine two distinct boundaries: boundaries which are totally embedded within the dense area and boundaries which intersect the pores.

Interpore spacing is believed to be strongly related to the local differential densification. This idea stemmed from considering the three distinct model systems shown in figure 19. For the idealized model (i.e. figure 19.a), it is assumed that the grain size is invariant and the position of each pore is fixed, therefore, the interpore spacing will be

unchanged during sintering. In the desirable (i.e. most useful) case, figure 19.b, the sintering process is controlled in such a way that the pores remain on grain boundaries and increase in size due to grain growth driven pore coalescence. The evolution of this structure resembles the process of photographic enlargement. Therefore, although interpore spacing increases as the sintering proceeds, the relationship between its value and the grain size should remain the same as in the original state. However, in an agglomerate compact, figure 19.c, the number of pores within the agglomerates will be dramatically reduced during sintering due to preferential pore elimination. The interpore spacing will increase at a rate which is faster than that of grain growth. When the local differential densification occurs more rapidly, the distinction between the increased rates of the interpore spacing and the grain size must be greater.

The kinetics of increasing interpore spacing can be predicted based on the microstructural evolution for different model systems. In the perfect condition (figure 19.b), the interpore spacing increases due to pore coalescence. In order to keep the pores on the grain boundary, the pores must migrate with the same velocity as the grain boundary, therefore

$$v_p = v_{gb}$$

where v_p is the pore velocity and v_{gb} the velocity of grain boundary migration. Thus, the increase in interpore spacing will have the same time dependence as the grain growth process, i.e. if $G \propto t^{1/3}$, then $X \propto t^{1/3}$ is predicted.

For the mechanism driven by local differential densification, i.e. figure 19.c, the increase in interpore spacing is directly related to

the rate of porosity removed from the small pores within the agglomerate. As illustrated in figure 19.c, the pore structure enclosed within the agglomerate is homogeneous and the densification rate is given by equation (11), i.e.

$$\dot{\rho} = \frac{B D \Omega}{k T} \frac{1}{G X_o^{m-1}} \Sigma$$

the symbols have the same meanings as before. X_o is the interpore spacing and, provided all grain triple junctions are pores, is related to the grain size G by the equation⁷²

$$X_o = G / \Phi^{1/2}$$

The quantity Φ is the stress intensification ratio^{81,82} and is equal to the ratio of A / A_e , in which A is the total cross sectional area of the specimen and A_e is the actual, internal load-bearing area. Combining the above two equations, the densification rate can be simplified as

$$\dot{\rho} \sim \frac{K (\Sigma / \Phi^{1/2})}{X_o^m}$$

From the previous study,⁷⁷ it is found that the densification kinetics follow a semi-logarithm relationship⁸⁷ which can be expressed as

$$\dot{\rho} \sim \frac{1}{t}$$

From the above two relations, the time dependence of the kinetics of increase in interpore spacing is determined by the densification

mechanism: $X_o \propto t^{1/3}$ will be satisfied for grain boundary diffusion, $X_o \propto t^{1/2}$ when lattice diffusion prevails.

4.2.2 Experimental Results

4.2.2.1 Microstructure Studies

Figure 20 shows the SEM micrographs of specimens sintered at 1300°C to various densities. Another set of pictures at higher magnification (10,000X) is shown in figure 21. The evolution of the microstructure is basically similar to what is observed in 1250°C sintering (figure 16). The initial structure is heterogeneous with a large fraction of non-sinterable pores. After sintering 220 minutes, the locally densified regions have developed distinctly from other porous areas. The grains have grown to a size of the same order of the initial large pores and the coordination number of the non-sinterable pores has obviously decreased. The resultant microstructure of 24 hr. sintering is more homogeneous as reflected in the narrower pore size distribution compared to the original state.

The microstructural developments during sintering at 1400°C and 1500°C are shown in figure 22 and 23 respectively. Dense and porous areas are indistinguishable after 1500°C, 20 minutes sintering. Since the grains have already grown to about the same size as the large pores, grain growth assisted densification is not observed in the sintering curve (figure 18). Many pores are also trapped within the grains. This is an important feature which was not observed in 1250°C and 1300°C sintering.

4.2.2.2 Grain Growth

Figure 24 shows the grain size, G versus $t^{1/3}$ for different sintering temperatures. The grain growth rate is best fitted by a cubic growth relationship. This is different from the quadratic growth law observed by Gupta²⁸ but is consistent with the grain growth time dependence influenced by impurities or porosity. In general, the grain growth rate increases as temperature increases. Sintering at 1500°C has the highest grain growth rate in the first 3 hours treatment; thereafter, the grain growth rate decreases. This is commonly found in the late stage of sintering.²⁸ From the microstructure (figure 23), most of the pores are isolated and can exert a drag on the movement of the grain boundaries.²³⁻²⁵ Thereby, decreasing the grain growth rate. The grain growth rate was found enhanced during sintering at 1250°C, 1300°C and 1400°C. The time at which the grain growth rate starts to increase is about 40 minutes for 1400°C sintering. It takes about 15 hours for 1250°C to see the enhancement of grain growth rate.

Two different types of grain boundaries coexisted within a porous system, this is seen in the SEM micrographs (e.g. figure 21.2). A grain boundary which intersects the interior pore provides a fast channel for mass transport and contributes most to the densification. The contribution to densification made by grain boundaries engulfed in the fully densified region will be less than the former type. Nevertheless, the boundary in the dense area will play a more active role in grain growth than the boundaries intersecting the interior pore due to the absence of any retardation effect from the pores. This fact can be verified by the observation that a dense region has a much larger grain size. Based on the proceeding discussion, a possible explanation for the enhancement of the grain growth rate has been explored by measuring L^{sss} and L^{ssp} . L^{sss}

is the length of the grain boundary which connected to other grain boundaries. L^{ssp} stands for the length of grain boundary which intersects the remaining pore. Shaw and Brook⁸⁸ have investigated the contribution of MgO dopant to the densification of Al_2O_3 compacts by studying these two quantities. The value of L^{sss} was found higher for the Al_2O_3 compacts doped with MgO than that for the compacts without MgO additives. They concluded that the MgO dopant retards the grain growth kinetics in the dense regions, prevents abnormal grain growth, and is helpful in producing a finer grain size microstructure.

Figure 25 shows the triple line length, L^{sss} vs density, ρ for 1250°C, 1300°C and 1400°C respectively. The change of L^{ssp} with ρ is shown in figure 26. From the plots, it is seen that both L^{sss} and L^{ssp} first increase with density to different maximum points, after which the values decrease with further sintering time. The increase of these two quantities results from densification; and further densification and grain growth decreases them. Since both types of grain boundaries contribute to grain growth, the fraction of $L^{sss} / (L^{sss} + L^{ssp})$ should be directly related to any variation in the grain growth kinetics. Figure 27 illustrates the change of the ratio with density for different sintering temperatures. It is seen that the fraction of the grain boundaries embedded within the dense region reaches a maximum value when the density is in the range of 0.75 to 0.80 for all three sintering temperatures. When the maximum fraction is attained, the grain growth rate starts to increase correspondingly. After grain growth at a higher rate, the ratio of $L^{sss} / (L^{sss} + L^{ssp})$ decreases.

As mentioned in the background section (section 2.2), no one has studied the grain growth kinetics by taking into account the heterogeneous nature of the microstructure with the coexistence of the dense and porous regions which are commonly found in a porous system.

The measurements of L^{sss} and L^{ssp} separately illustrate the contributions to grain growth from two different types of grain boundaries: i.e. those in the dense regions and the others which intersect with pores. Since the grain boundaries within the dense region contribute more to the grain growth rate than the other type, it is proposed that measuring the fraction $L^{sss} / (L^{sss} + L^{ssp})$ will provide a means of characterizing the grain growth kinetics of a heterogeneous compact in a more fundamental sense. Combining the experimental measurements of grain growth and $L^{sss} / (L^{sss} + L^{ssp})$, the enhancement of grain growth rate can be explained as follows: During sintering of an agglomerate compact, locally densified regions are developed, and two types of grain boundaries are created. The overall grain size change of the system is attributed to these two different categories of grain boundaries. As the sintering proceeds, the density of the system increases (i.e. the porosity is decreased) and so does the value of L^{sss} . The value of L^{ssp} will decrease because fewer pores exist. Thus, the fraction of $L^{sss} / (L^{sss} + L^{ssp})$ will increase as the density increases. The grain growth rate will be subject to change when the dense region grain boundaries contribute dominantly to the grain growth kinetics. This is what observed for sintering at 1250°C, 1300°C and 1400°C. After the grains grow at a higher rate, both the values of L^{sss} and $L^{sss} / (L^{sss} + L^{ssp})$ decrease due to the elimination of the grain boundaries within the dense regions. For the 1500°C sintering, the microstructure has evolved to the final stage of sintering within 10 minutes, and no dense regions are formed in further sintering; the value of L^{sss} decreases instead of increasing in the subsequent heat treatment. Therefore, no enhancement of grain growth rate was found.

4.2.2.3 Interpore Spacing

Figure 28 shows that interpore spacing increases at a rate

proportional to $t^{1/3}$ and that the rate is enhanced after a certain period of time in 1250°C and 1300°C sintering. At higher temperatures, i.e. 1400°C and 1500°C, the interpore spacing increases very rapidly at the beginning at a rate which is higher for 1500°C than for 1400°C sintering. Then, instead of an increase, the rate decreases.

As discussed in section 4.2.1 (model and theories), the interpore spacing increase is driven by two mechanisms: pore coalescence and local differential densification. In an agglomerate compact, the mechanism of local differential densification dominates, especially in the early stage of sintering, and the rate is proportional to the sintering temperature. Separation of the relative contributions of these two mechanisms is difficult; however, the evolution of the interpore spacing can be interpreted from the microstructure studies.

The SEM micrographs clearly demonstrate the pore growth around the dense regions (figure 20.1 and 22.1), and the increase in interpore spacing is predominately driven by local differential densification. As sintering proceeds, large dense regions develop after an incubation time, which decreases with the temperature. For instance, in 1300°C sintering, the locally dense regions are seen after about 220 minutes ($\rho \approx 0.76$), while it takes only about 40 minutes at 1400°C sintering to produce the locally dense regions. After sintering at 1500°C for only 10 minutes, the structure has evolved to a totally different structure with large grains and the coexistence of large and small pores. These microstructural investigations strongly suggest that the rate of increase in interpore spacing by preferential elimination of the small pores within the agglomerates is determined by the rate of porosity removal from the agglomerates. As the sintering temperature increases, the shrinkage rate increases. Therefore, the higher the sintering temperature, the greater the interpore spacing increase rate. (compare

the distance between any two neighboring pores in the microstructures of different temperature sintering, i.e. figure 20, 22 and 23).

The contribution to the increase in interpore spacing due to the pore coalescence mechanism has also been considered. The movement of pores driven by grain boundary migration can only happen when the pore has a relatively small size.^{25,89,90} The large pores and the connected pore channels are immobile and will have no contribution to the increase in the interpore spacing by grain boundary drag. It is believed that the small pores pointed out by the arrows in figure 21.2 can be displaced by moving grain boundaries as grain growth proceeds. The pores will either combine with other pores or totally shrink away. The effect of the pore coalescence mechanism is therefore strongly dependent upon the grain size in the dense region and the pore size in the surrounding porous region. When the grain size in the dense region is large and the neighboring pores are small, the additional contribution provided by the pore coalescence mechanism will become greater. This is a possible explanation for the enhancement of the increase rate in interpore spacing observed in 1250°C and 1300°C sintering.

As the sintering temperature increases, the competition between the grain growth and densification will alter the microstructural evolution, and break-away of pores from the grain boundary occurs.⁹¹⁻⁹³ For a MgO compact, a higher temperature increases the tendency for pore separation from the grain boundary.⁹⁴ In figure 22 and 23, pore break-away is clearly shown. Once the pore is left behind the grain boundary and is trapped within the grains, it becomes inactive. The immobile pores (i.e. those trapped within the grains), however, tend to keep the interpore spacing insensitive to the microstructural evolution. Thus, the rate of increase in interpore spacing decreases in the later period for 1400°C and 1500°C sintering.

4.2.2.4 Interpore Spacing vs Grain Growth

Figure 29 shows the evolution of interpore spacing vs grain size for the specimens sintered at 1250°C, 1300°C, 1400°C, and 1500°C. There is a linear relationship between these two quantities and a large portion of the data follows a straight line with a slope greater than one. As discussed in section 4.2.1, the increase in interpore spacing will have the same time dependence as the grain growth process when the interpore spacing is increased due to pore coalescence. The kinetics of grain growth (figure 24) and the increase in interpore spacing (figure 28) can be expressed by the simple equations

$$G = K_1 t^{1/3}$$

$$\text{and } X = K_2 t^{1/3}$$

where K_1 and K_2 are the kinetic factors which will be constants at a fixed temperature. The relationship between X and G is therefore given

$$X = (K_2 / K_1) G = K G$$

The above equation implies that X and G are intimately related by a linear relationship at a fixed temperature because now the hybrid kinetic factor, K , is a constant. This is what observed in figure 29. Additional contributions attributed to the local differential densification (which introduced an excess compressive stress to shrink the small pores, see section 4.1.1.1 and reference 62) and also to the coarsening mechanism (due to large pores acting as vacancy sinks to small pores⁶³) will drive the interpore spacing increasingly at a rate higher than the grain growth rate. Three different model systems have

been compared in section 4.2.1 to find the parameters best describing the microstructural change during sintering of an agglomerate compact. The grain growth rate is predicted to be slower than the rate of increase in interpore spacing. The straight line in figure 29 with a slope greater than one supports the model prediction that interpore spacing increases faster than grain growth due to local differential densification while sintering an agglomerate compact.

Some data in the small grain size region deviated from the characteristic line in figure 29. This deviation can be explained by strongly preferential pore elimination within the agglomerate, which is illustrated by the SEM micrographs. After this initial pore elimination, the interpore spacing will increase dramatically while only a small amount of grain growth occurs. Scattering of data in the larger grain size region implies that the rate of increase in interpore spacing has decreased. This has been mentioned while discussing the kinetics of interpore spacing growth, (section 4.2.2.3) and pore break away from the grain boundary is responsible.

4.3 Two Step Sintering

4.3.1 Model - Influence of Sintering Temperature on The Structural Evolution

A homogeneous structure is required to achieve better sintering results. Yan et al⁹⁵ have demonstrated that the sintering density can be increased from 0.90 to 0.99 by use of a narrow initial grain size distribution. Carpay⁹⁶ has shown that a broad pore size distribution will increase the tendency for exaggerated grain growth (pore-break-away grain growth). The knowledge accumulated up to this point includes: the results of sintering studies, of microstructure examination, of investigations of kinetics for grain growth and evolution of interpore spacing and their relationship. These results, taken together, have pointed at a possible and promising way to change the initial heterogeneous state into a homogeneous structure - i.e. the homogenization treatment.

Figure 30 compares the microstructures, for specimens sintered to the same density ($\rho=0.83$), resulting from different sintering schedules: 1. 1300°C, 24 hr., 2. 1400°C, 2 hr., 3. 1500°C, 20 min.. It is seen that the higher the sintering temperature, the smaller the final grain size. However, pore break-away from the grain boundary is more likely to occur at high temperatures. The grain size distributions of the final microstructures for 1300°C and 1500°C sintering are shown in figure 31. For low temperature sintering, the average grain size is larger ($G_{\text{mean}} \sim 3.02 \mu\text{m}$) with the distribution following the criteria for normal grain growth⁹⁷ and narrow grain size distribution⁹⁵ (i.e. $G_{\text{max}} \leq 2 G_{\text{mean}}$). On the other hand, high temperature sintering produces a smaller average grain size ($G_{\text{mean}} \sim 2.05 \mu\text{m}$), but with a wide grain size distribution

with a maximum grain size ($G_{\max} \sim 6.0 \mu\text{m}$) which is larger than $2 G_{\text{mean}}$. Thus, abnormal grain growth (pore-break-away grain growth) happens under this sintering condition and results in a heterogeneous structure unfavorable for further sintering.

Sinterability is the greatest concern in studying the sintering behavior of an agglomerate compact. The change in distribution of pore coordination number after sintering has been investigated. Figure 32 shows the plane section distribution of the pore coordination number for specimens sintered at 1300°C for 20 minutes and 24 hours. The microstructure after 20 min. sintering is heterogeneous, with a very broad pore size distribution and with very big, non-shrinking pores with large coordination numbers. After 24 hr. sintering, the distribution has narrowed, and the most frequent coordination number is $3 \sim 4$, which means that the pores are polyhedra with $6 \sim 8$ sides⁸⁵ and can shrink. Therefore, the homogenization treatment reduces the coordination number of large pores through normal grain growth. Most importantly, all of the pores remain on the face or at junctions of grain boundaries and are shrinkable.

The influence of sintering temperature on the microstructure reported above can not be explained by local differential densification alone. Locally differential densification causes the development of a dense region which supports grain growth, decreasing the coordination number of the large pores and making them sinterable. However, as the temperature increases the rates of all processes increase and the final structure should be the same for the same final sintered density. The difference in structure implies that another process which affects the pore size distribution is taking place concurrently.

In section 4.1.1.1 ("*strong coupling*" model), it is pointed out that a

large pore can serve as the vacancy sink for neighboring small pores, which may give the large pore a chance to grow. This is the most probable coarsening process. Figure 33 shows the model system considered in this study. The solid arrows indicate the vacancy flux for densification and the dotted arrows are the possible routes for the coarsening of the large pore. Following the "strong coupling" idea, the overall shrinkage rate for this system is expressed as

$$\frac{d V_d}{d t} = - K_d \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

where dV_d/dt is the rate of total volume change caused by densification, K_d is the kinetic factor which includes the parameters described before, and R_1 and R_2 are the radii for small and large pores, respectively. The total volume change comes from both the small and large pores, so

$$d V_d = d V_{d,1} + d V_{d,2}$$

Under the quasi-steady condition, the densification rate is the same for both pores; therefore:

$$d V_{d,1} = d V_{d,2} = 1/2 d V_d$$

Assuming spherical shapes, the rate of the radius change are

$$\frac{d R_{1,d}}{d t} = - K_d \left(\frac{1}{R_1^3} + \frac{1}{R_2 R_1^2} \right)$$

and

$$\frac{d R_{2,d}}{d t} = - K_d \left(\frac{1}{R_2^3} + \frac{1}{R_1 R_2^2} \right)$$

with K_d now containing the shape factor.

The driving force for the coarsening process is the difference of the chemical potential between the different pore surfaces. The volume change rate can be expressed as

$$\frac{d V_c}{d t} = K_c \left(\frac{1}{R_1} - \frac{1}{R_2} \right)$$

The radius change rates due to this coarsening process are

$$\frac{d R_{1,c}}{d t} = - K_c \left(\frac{1}{R_1^3} - \frac{1}{R_2 R_1^2} \right)$$

and

$$\frac{d R_{2,c}}{d t} = - K_c \left(\frac{1}{R_2^3} - \frac{1}{R_1 R_2^2} \right)$$

The radius of the large pore will increase due to the coarsening effect and decrease due to the densification process. The net changes in the rates for the different pores are

$$\frac{d R_1}{d t} = \frac{- R_2 (K_c + K_d) + R_1 (K_c - K_d)}{R_1^3 R_2}$$

and

$$\frac{d R_2}{d t} = \frac{- R_1 (K_c + K_d) + R_2 (K_c - K_d)}{R_2^3 R_1}$$

It is difficult to analyze the kinetics for these two pores separately without further knowledge of the relation between K_c and K_d .

However, the ratio of the radius change rates provides a possible way to investigate the influence of sintering temperature on the behavior of these pores, and is found to have the following form

$$\frac{\dot{R}_2}{\dot{R}_1} = \left(\frac{R_1}{R_2} \right)^2 \frac{\left(\frac{K_d}{K_c} \right) \left(1 + \frac{R_2}{R_1} \right) + 1 - \frac{R_2}{R_1}}{\left(\frac{K_d}{K_c} \right) \left(1 + \frac{R_2}{R_1} \right) - 1 + \frac{R_2}{R_1}}$$

The ratio of the kinetic constant has the following temperature dependence:

$$\frac{K_d}{K_c} \propto e^{-\Delta Q / R T}$$

where $\Delta Q = Q_d - Q_c$, is the difference of the activation energies for densification (Q_d) and coarsening (Q_c). As temperature increases, when Q_d is greater than Q_c , the ratio of the kinetic constants also increases. K_d / K_c therefore can be used as a temperature index to explore the sintering behavior of this heterogeneous system.

Figure 34 shows the computed curves describing the shrinkage rate ratio ($\dot{R}_2 / \dot{R}_1$) influenced by the temperature index (K_d / K_c) for three systems with different size relations, i.e. $m = R_2 / R_1$. The dotted line of zero shrinkage rate ratio separates the figure into two parts. The positive value of $\dot{R}_2 / \dot{R}_1$ indicates that both pores shrink and the lower part ($\dot{R}_2 / \dot{R}_1$ is negative) indicates large pore growth while small pores shrink. The condition for the zero shrinkage rate ratio is that the number of vacancies lost by densification of large pores is balanced by the supply from neighboring small pores created by the coarsening

mechanism. As the size of the large pore increases, the rate ratio decreases. This is primarily due to the enhancement of $\dot{R}_1$, since now the large pore serves as a vacancy sink and the driving force for vacancy migration is enhanced when the curvature difference increases. For different pore size relations (i.e. different m), the curve intersects the zero line at different values of K_d/K_c while evolving from negative to positive value. These results indicate that the large pore will eventually grow at lower temperature and will shrink when the temperature is higher than the intersective value.

The explanation is two-fold: First, as the "strong coupling" calculation predicted, i.e. figure 9, the greater the size difference, the lower the overall shrinkage rate due to the adverse effect of the differential sintering stresses. Nevertheless, the greater size difference implies a higher driving force for the coarsening process. Second, the activation energy for densification was assumed higher than that of coarsening, so a higher temperature will be more favorable for the densification. Based on this interpretation, the influence of the sintering temperature on the evolution of the pore system in a heterogeneous system can be predicted.

The considered heterogeneous system is composed of four different sized pores with the radii: R_1 , $2 R_1$, $3 R_1$, and $5 R_1$. At low temperature sintering (e.g. $K_d/K_c=0.3$), all pores except for the smallest one, will grow by consuming the small one. It is interesting to find that the medium sized pore, i.e. $m = 2$, grows at a rate which is relatively larger than that of the other two types. The result implies that the system has a chance to smooth out the difference in size between different pores. In contrast, when the sintering temperature is very high, e.g. $K_d/K_c \geq 0.8$, all of the pores in the system will shrink at different rates depending on the size difference of the neighboring

pores. The medium sized pores (i.e. $m = 2$ or $m = 3$) shrink faster than the larger ones. This effect tends to increase the size difference and enhance the heterogeneity of the pore size distribution. This strongly suggests that high temperature sintering is not favorable for sintering a heterogeneous system and that a suitable low temperature sintering can produce a more homogeneous structure.

4.3.2 Experimental Results

Figure 35 shows the SEM micrographs of the specimens sintered to the same density ($\rho=0.8$) using different sintering schedules (1250°C , 48 hr. and 1500°C , 10 min.). It is clear that low temperature sintering produces a narrower pore size distribution than a high temperature treatment. Although the resulting average grain size is larger after the homogenization treatment, the grain size distribution is narrower. Most importantly, all of the remaining pores stay on the surfaces or the junctions of the grain boundaries after 1250°C , 48 hr. sintering and all of the interior pores are sinterable due to the reduction of the coordination number. On the other hand, some large pores remain inactive and many pores which are difficult to eliminate in further treatment are found trapped within the grains in the 1500°C sintered specimens.

As mentioned in the above section, it is desirable to have a narrower pore size⁹⁶ and grain size⁹⁵ distribution to decrease the tendency for pore break away from grain boundary. These are the objectives of the homogenization treatment and their contribution to the subsequent 1600°C sintering is demonstrated by comparing the microstructures shown in figure 36. Although the grains have already grown to the size which is about 60 times of the primary dimension after the homogenization treatment, the merits of the homogenization treatment are then successfully regained in the subsequent high temperature

sintering. After the same treatment of 1600 °C, 1 hr. sintering, both the 1-step and 2-step sintered specimens have the same final density of $\rho = 0.93$. However, the pre-treated specimen achieved a finer and more uniform grain size than that produced by directly sintering the untreated (green) sample.

The function of the homogenization treatment is summarized in figure 37 using the usual plot of ratio-control-sintering^{31,32} to describe the relative contribution of densification and grain growth. The homogenization treatment takes advantage of grain growth to reduce the coordination number of large pores, so the trajectory it follows has smaller ratio of densification rate / grain growth rate than that of high temperature sintering. However, the homogeneous structure it introduces is more favorable for the subsequent high temperature sintering. The followed trajectory has higher ratio of densification rate / grain growth rate due to the reduced tendency for pore break-away grain growth. Thus, the final product has finer grain size than that produced by the conventional 1-step process.

5. Conclusions

This study has explicitly illustrated grain-growth assisted densification phenomena in sintering heterogeneous MgO compacts. An unusual enhancement of the densification rate during sintering at temperatures lower than 1400°C was caused by the additional contribution to densification from larger pores. The initially non-sinterable large pores are later able to shrink due to the reduction in their coordination numbers as a result of grain growth.

Interpore spacing and grain size are the parameters selected to describe qualitatively the microstructural evolution during sintering of an agglomerate compact. In the early stages of sintering, local differential densification causes interpore spacing to increase faster than grain growth and a heterogeneous microstructure consisting of porous and dense areas develops. In the subsequent treatment, 1250°C and 1300°C sintering, the experimental results of interpore spacing and grain size follow a characteristic straight line, and the resultant microstructure shows narrower pore size and grain size distributions. Most importantly, all of the pores remain on the surfaces or junctions of grain boundaries and can shrink. For the specimens sintered at 1400°C and 1500°C , at longer times the interpore spacing increased comparatively slower than grain growth. This slower growth was due to the separation of pores from the grain boundary. Consequently, many pores were trapped within the grains, producing an undesirable structure.

To assess the grain growth kinetics in a heterogeneous system containing both porous and dense regions, it is proposed that the kinetics are supported by two distinct grain boundaries: i.e. those

embedded within the fully dense regions (the length is expressed as L^{sss}) and grain boundaries intersecting interior pores (L^{ssp} is the length). The measurements of $L^{sss} / (L^{sss} + L^{ssp})$ showed a maximum value at the same density at which the grain growth rate starts to increase. These measurements explain the observed enhancement of the grain growth rate during sintering. Thus, the investigations of L^{sss} and L^{ssp} provide a deeper understanding of the grain growth kinetics of an agglomerate compact.

The "strong coupling" simulations allow closer investigation of the influence of inhomogeneities on the overall shrinkage rate of a system containing various sized pores. The calculated results show that the large pores retard the overall densification rate and the retardation effect increases as the sizes of the large pores increase. By taking into account the sinterability of pores and the simultaneous grain growth process, the shrinkage curve of a selected multiple sized system was calculated in the "decoupled case". The calculated densification rate was also shown to be enhanced. The message which the "decoupled" calculations delivers supports the claim that the grain growth assisted densification observed in the sintering experiments is due to the additional contribution of the initially inactive large pores.

The coarsening of large pores is driven by the differential chemical potential between them and other surrounding small pores, and is crucial to the sintering of an agglomerate compact. Combining the coarsening effect with the differential densification theory allows assessment of the effect of the sintering temperature on the sintered microstructure of a system with a heterogeneous pore size distribution. The calculated curves indicate that high temperatures are not beneficial for sintering an agglomerate system in regards to the resultant microstructure. In contrast, low temperature sintering is advantageous in

transforming the initially heterogeneous state into a more homogeneous structure.

It has been reported that a wide distribution in either pore size or grain size tends to increase the tendency for pore break away grain growth. Therefore, a homogeneous starting structure with narrow grain and pore size distributions is desirable for producing better ceramics. In a usual ceramic agglomerate compact, the inherently wide distribution of pore size is the major factor causing the unsatisfactory microstructure. Homogenization treatment at 1250°C, 48 hr. successfully reduced the range of pore size distribution and delivered a homogeneous structure for subsequent high temperature sintering. Two-step sintering, which consists of a lower temperature homogenization followed by a high temperature treatment, has been shown to be useful in producing a microstructure with more uniform and finer grain size than would be attainable by conventional 1-step sintering. Without resorting to hot pressing, *2-step sintering* is thought to be the optimum sintering route for an agglomerate compact.

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Figure captions

Figure 1 Two types of pores within an agglomerate compact.

Figure 2 SEM micrographs of MgO powders.

Figure 3 SEM micrographs of green compact's fracture surface.

Figure 4 A schematic time-temperature schedule for the two step sintering.

Figure 5 2-D model system contains three hierarchies of pores.

Figure 6 Two approaches to obtain the shrinkage rate of a porous compact: (a) considering the volume change of a unit cell (b) investigating the central approach rate across a neck region.

Figure 7 The cell boundary for "strong coupling" analysis.

Figure 8 Five continuously enlarged cell boundaries with different shrinkage rates.

Figure 9 The influence of the differential pore size on the overall shrinkage rate.

Figure 10 The influence of the small pore's number on the overall shrinkage rate.

Figure 11 The selected heterogeneous system in "decoupled" calculation

- (a) The number of pore vs pore radius.
- (b) The number of pore vs pore distance.

- Figure 12 (a) Distribution of porosity vs pore radius.
(b) Calculated shrinkage curve for the selected system under the "decoupled" consideration.
- Figure 13 Calculated densification rate from figure 12(b) vs density.
- Figure 14 Relative density vs logarithm of time for 1250°C sintering.
- Figure 15 Observed densification rate and grain-size-compensated densification rate vs density of 1250°C sintering.
- Figure 16 SEM micrographs of polished and thermally etched surfaces of specimens sintered at 1250°C for various densities: (A) 0.55, (B) 0.62, (C) 0.73, (D) 0.80.
- Figure 17 Histogram of dihedral angles measured from the 1250°C sintering specimens with the density of 0.80.
- Figure 18 Relative density vs logarithm of time for five different sintering temperatures.
- Figure 19 Three model systems selected to compare the evolution of interpore spacing and grain size during sintering.
- Figure 20 SEM micrographs at 5,000X for 1300°C sintered specimens
1. 20 minutes, $\rho = 0.62$

2. 220 minutes, $\rho = 0.76$

3. 24 hours, $\rho = 0.83$

Figure 21 Figure 19 at 10,000X.

Figure 22 SEM micrographs at 5,000X for 1400°C sintered specimens

1. 20 min., $\rho = 0.70$

2. 2 hr., $\rho = 0.83$

3. 10 hr., $\rho = 0.87$

4. 24 hr., $\rho = 0.90$

Figure 23 SEM micrographs for specimens sintered at 1500°C

1. 20 min., $\rho = 0.83$

2. 1 hr., $\rho = 0.87$

3. 5 hr., $\rho = 0.90$

Figure 24 Grain size, G vs $t^{1/3}$ for 1250°C, 1300°C, 1400°C and 1500°C, respectively.

Figure 25 Triple line length for the grain boundary embedded within the dense region, L^{sss} vs density, ρ for 1250°C, 1300°C and 1400°C sintering, respectively.

Figure 26 Triple line length for the grain boundary intersects with interior pore, L^{ssp} vs density, ρ for 1250°C, 1300°C and 1400°C, respectively.

Figure 27 $L^{sss} / L^{sss} + L^{ssp}$ vs density, ρ .

Figure 28 Interpore spacing, X vs $t^{1/3}$ for 1250°C, 1300°C,

1400°C and 1500°C, respectively.

Figure 29 Interpore spacing, X vs grain size, G .

Figure 30 SEM micrographs of specimens sintered to the same density, $\rho=0.83$, by

1. 1300°C, 24 hr.

2. 1400°C, 2 hr.

3. 1500°C, 20 min.

Figure 31 Histogram of grain size for specimens sintered to the same density, $\rho=0.83$, by

(a) 1300°C, 24 hr.

(b) 1500°C, 20 min.

Figure 32 Histogram of plane sectional pore coordination number and the correlative microstructures for 1300°C, 20 min. and 1300°C, 24 hr. sintering.

Figure 33 Model system for the investigation of temperature influence on the structural evolution. The solid arrows are the vacancy flux for densification and dotted arrows the routes for the coarsening of large pore.

Figure 34 Calculated ratio of radius change rates, $(\dot{R}_2 / \dot{R}_1)$ vs temperature index, K_d / K_c .

Figure 35 SEM micrographs of fracture surface of specimens with same density, $\rho=0.80$, sintered at

(A) 1500°C, 10 min.

(B) 1250°C, 48 hr.

Figure 36 SEM micrographs of fracture surfaces of

1. Green compact, $\rho = 0.40$, $G = 0.06 \mu\text{m}$.
2. Homogenized specimen, $\rho = 0.80$, $G = 3.5 \mu\text{m}$.
3. Green compact after sintering at 1600°C for 1 hr.,
 $\rho = 0.93$, $G = 10.6 \mu\text{m}$.
4. Homogenized specimen after sintering at 1600°C , 1 hr.
 $\rho = 0.93$, $G = 5.6 \mu\text{m}$.

Figure 37 Grain size vs density plots for the conventional sintering and 2-step sintering.

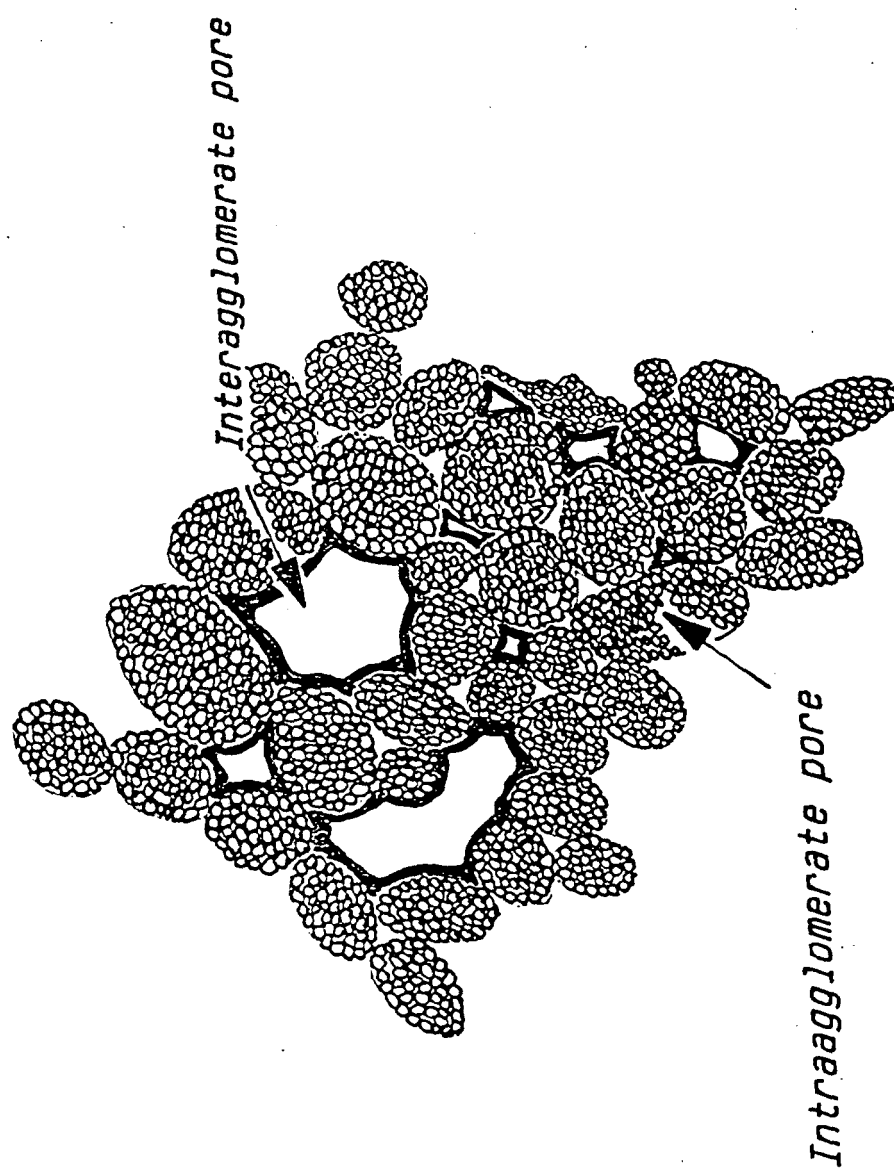


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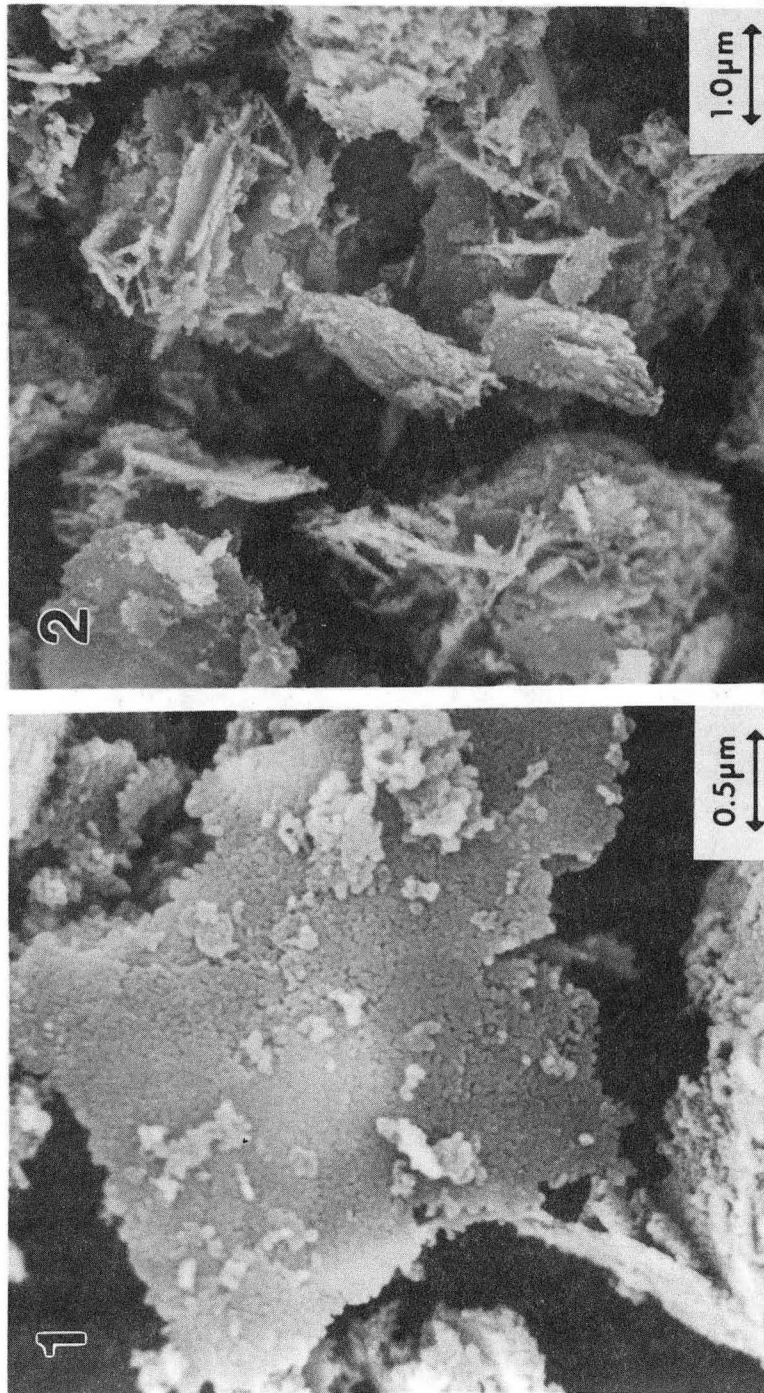


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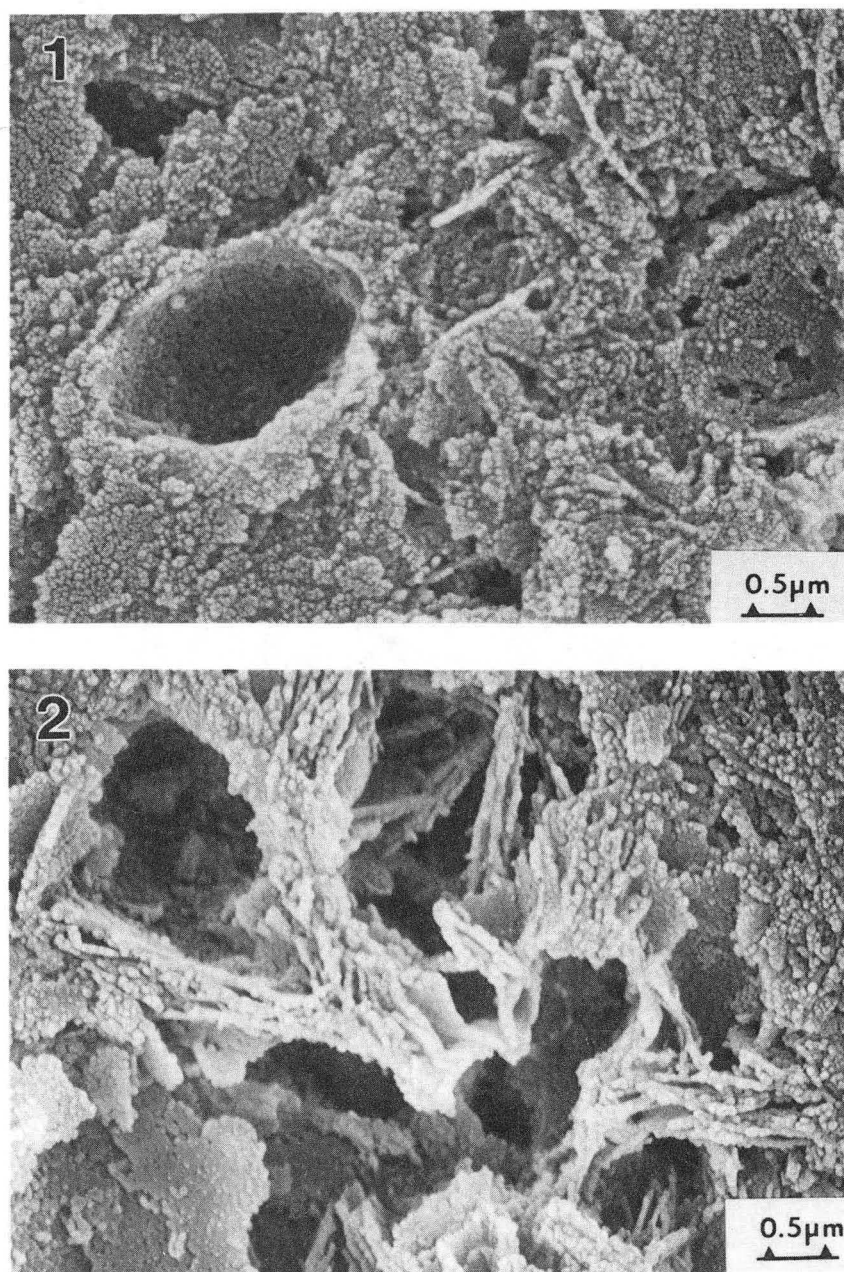


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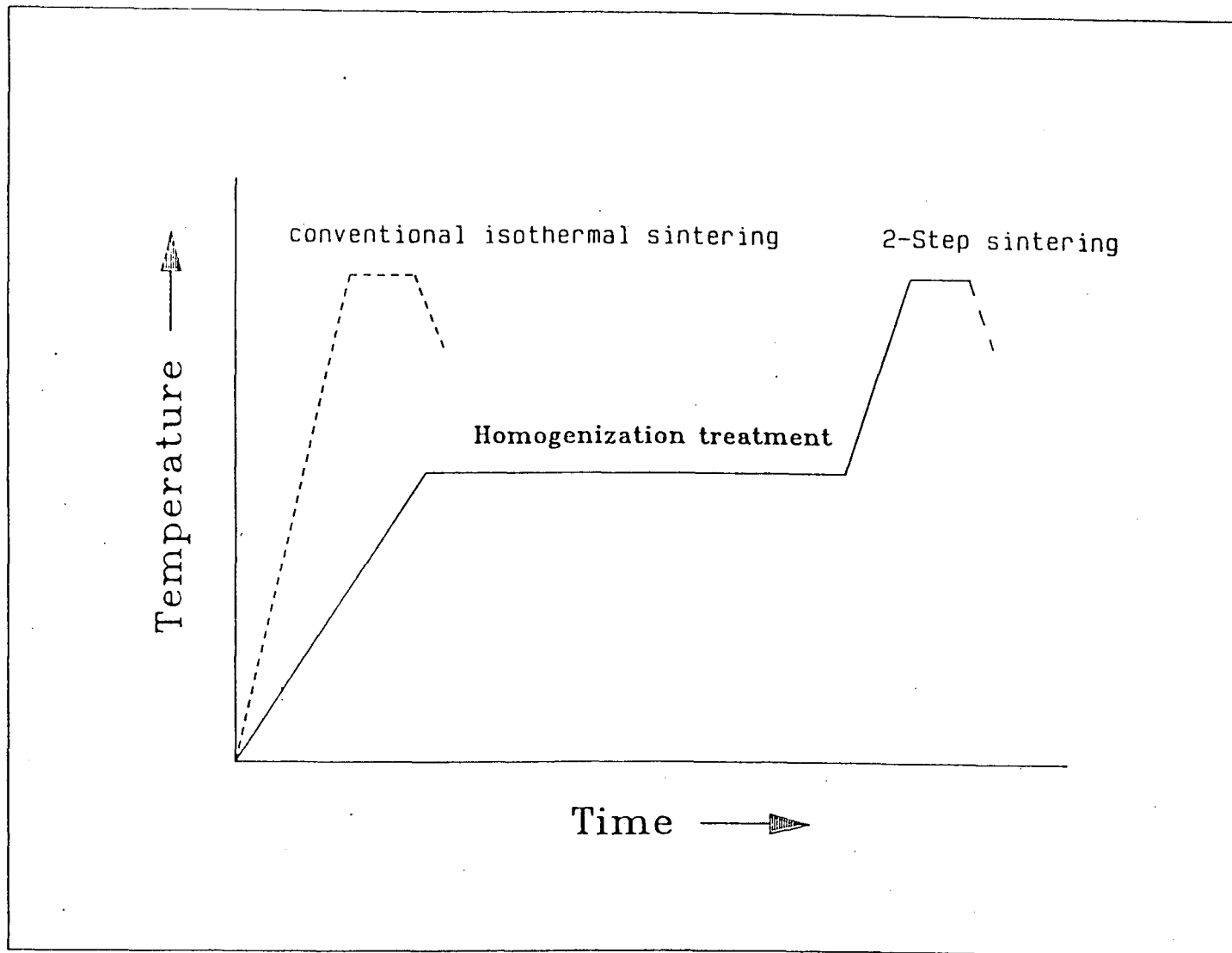


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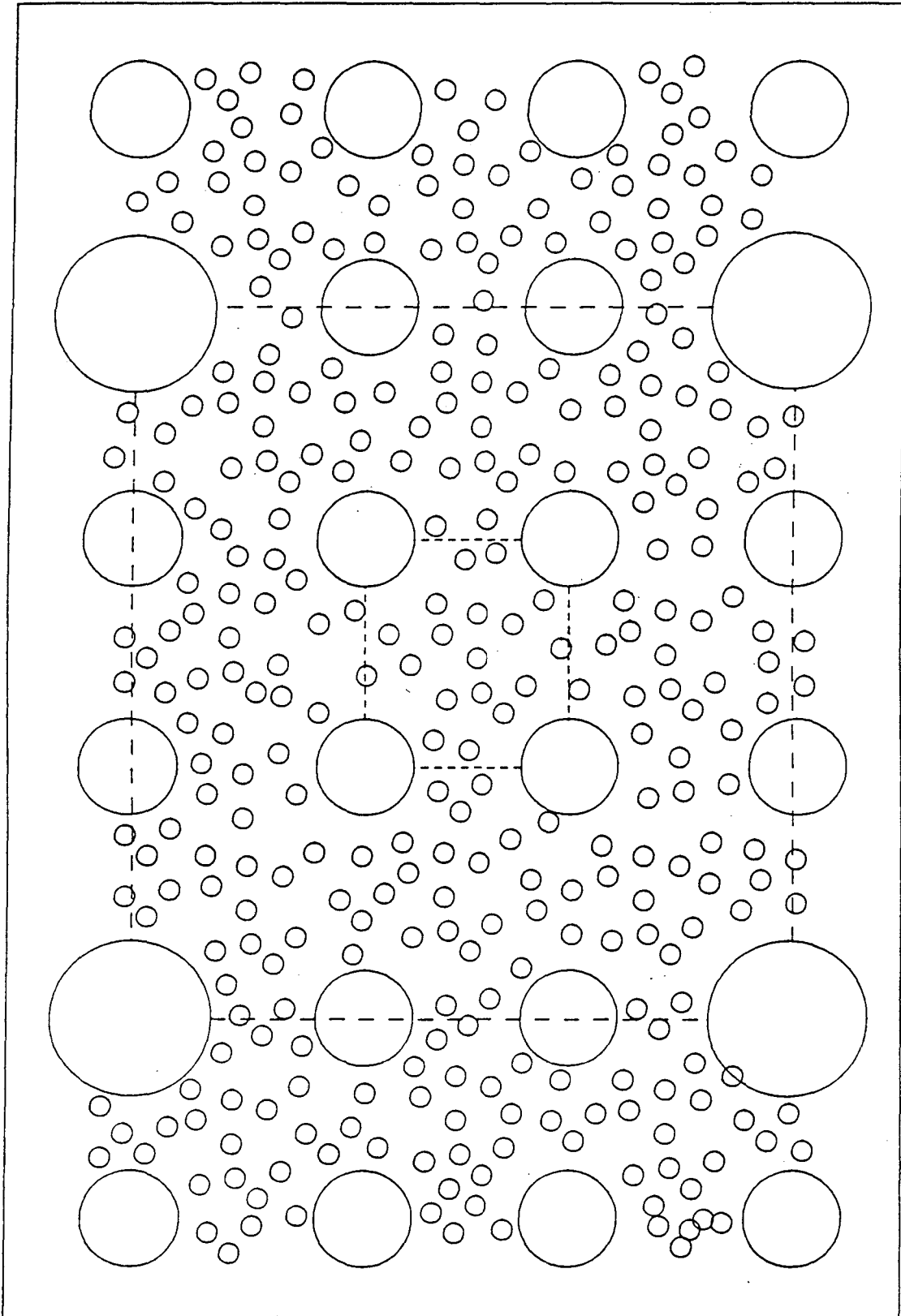


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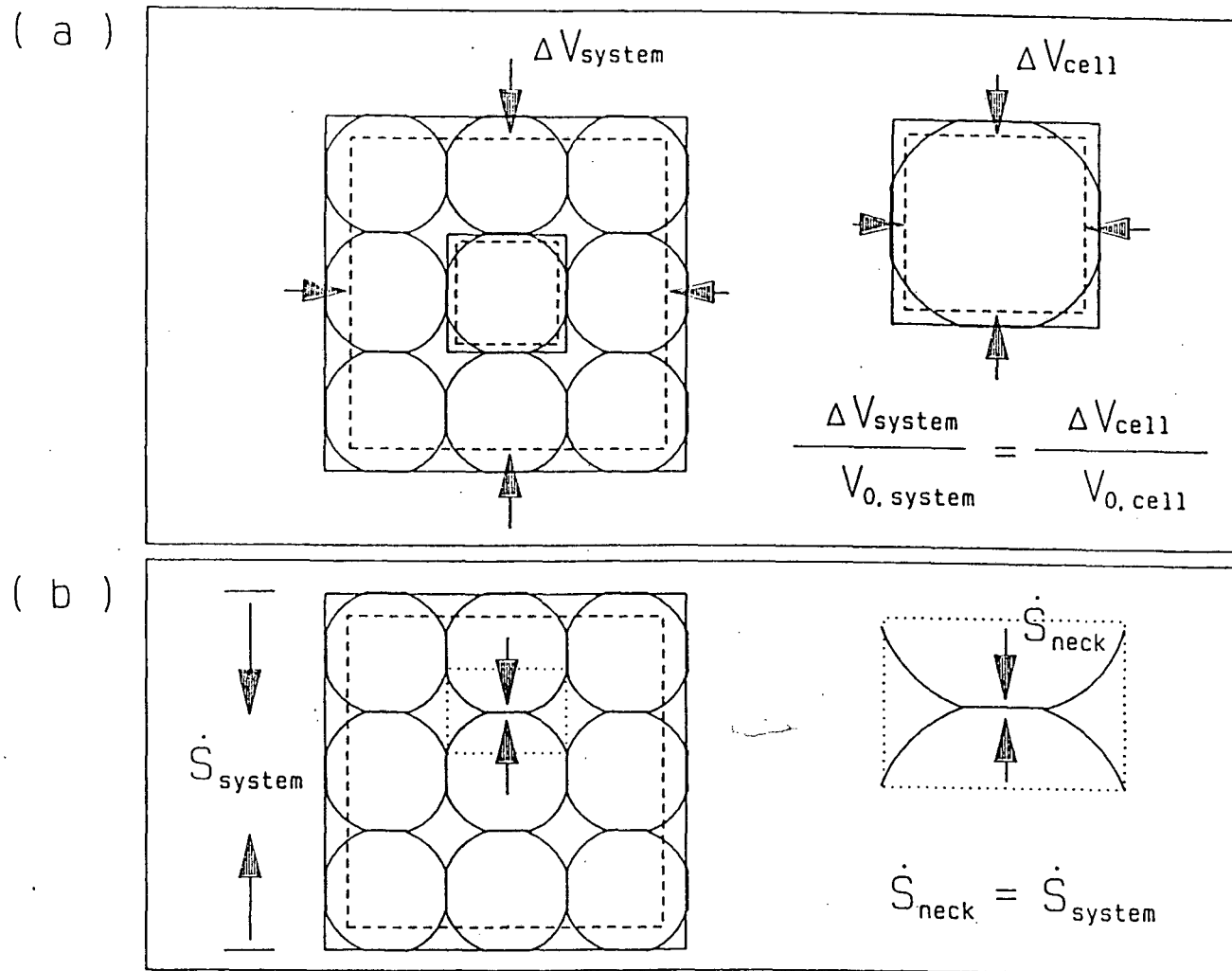


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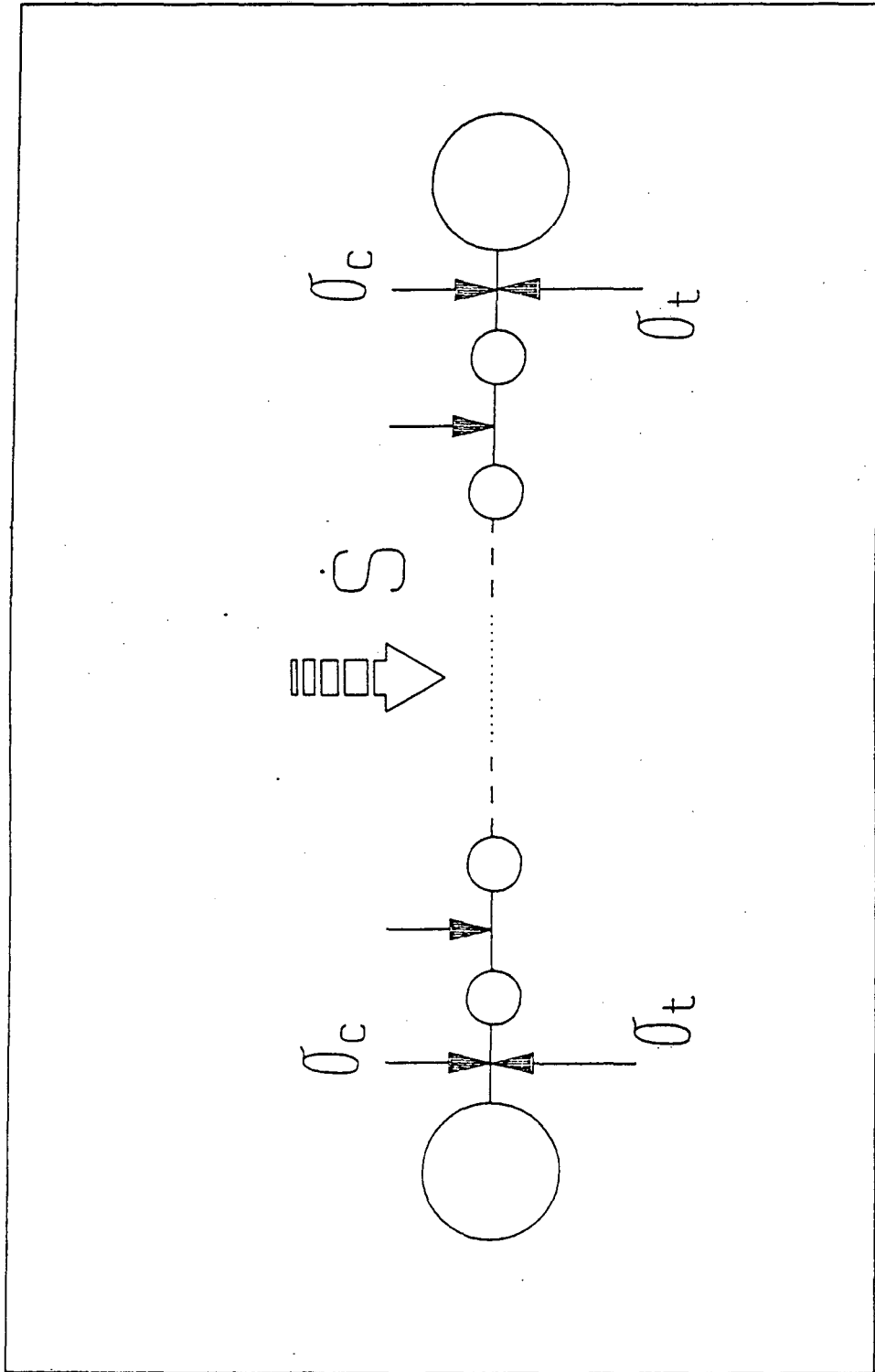


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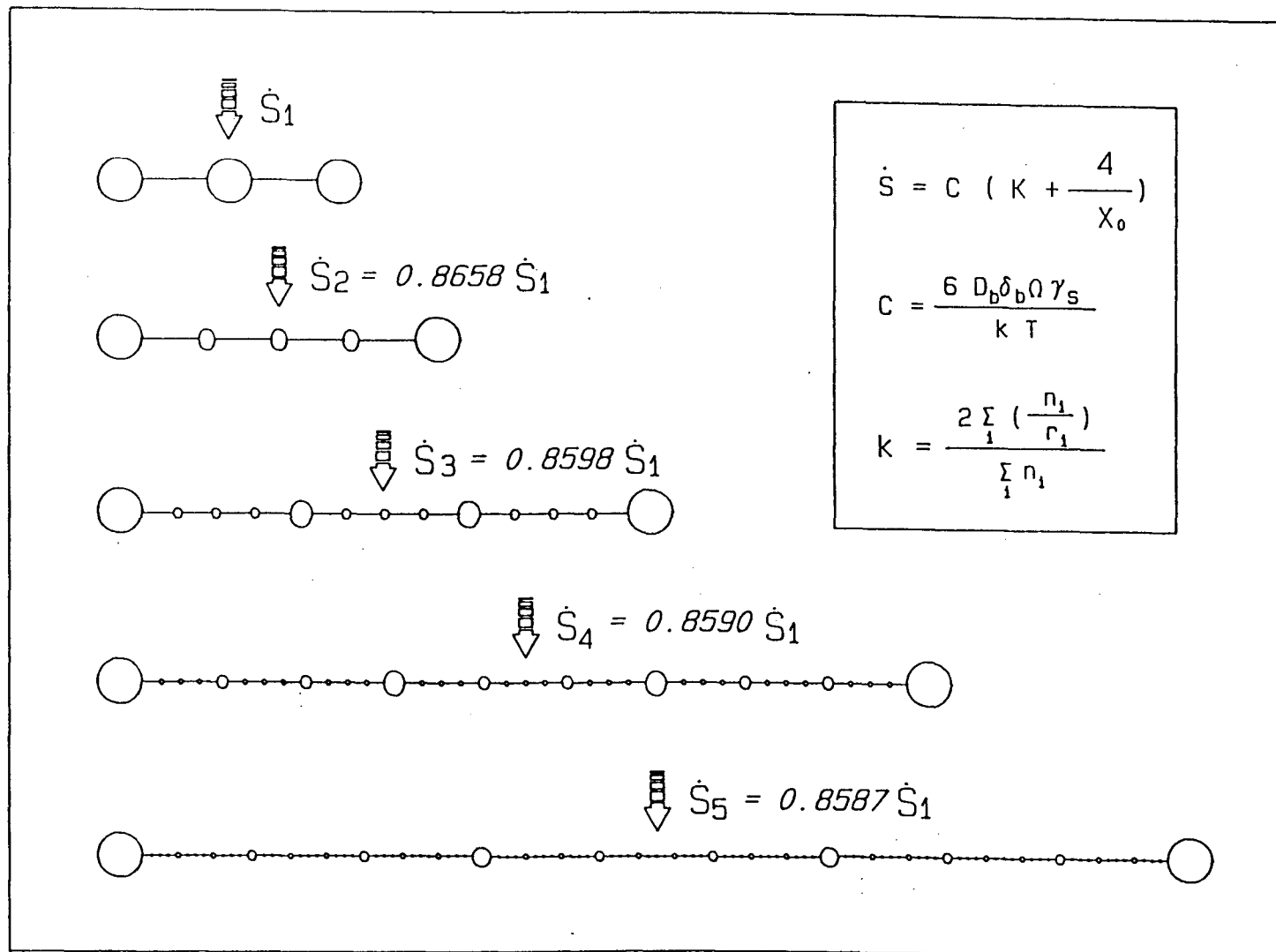


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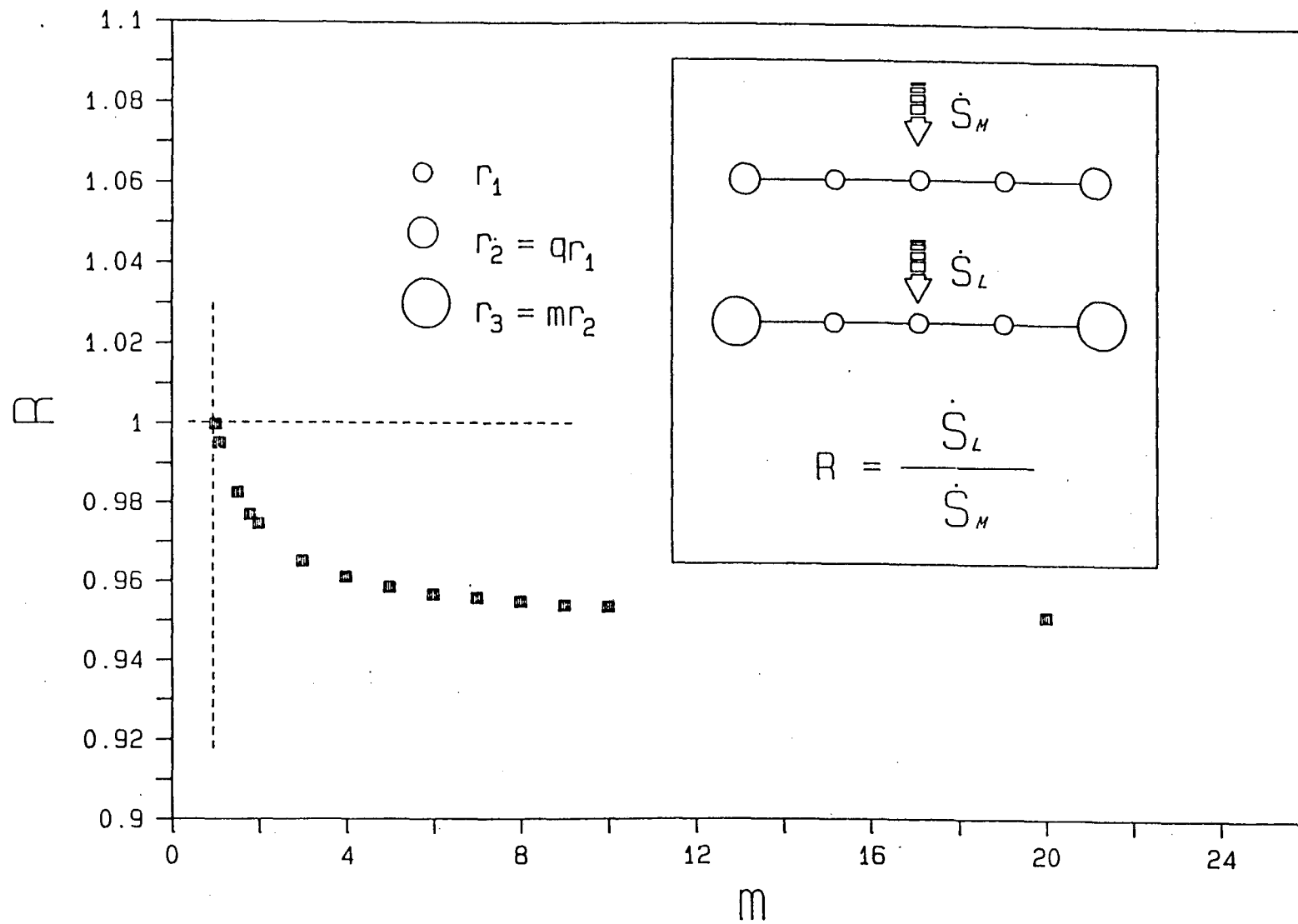


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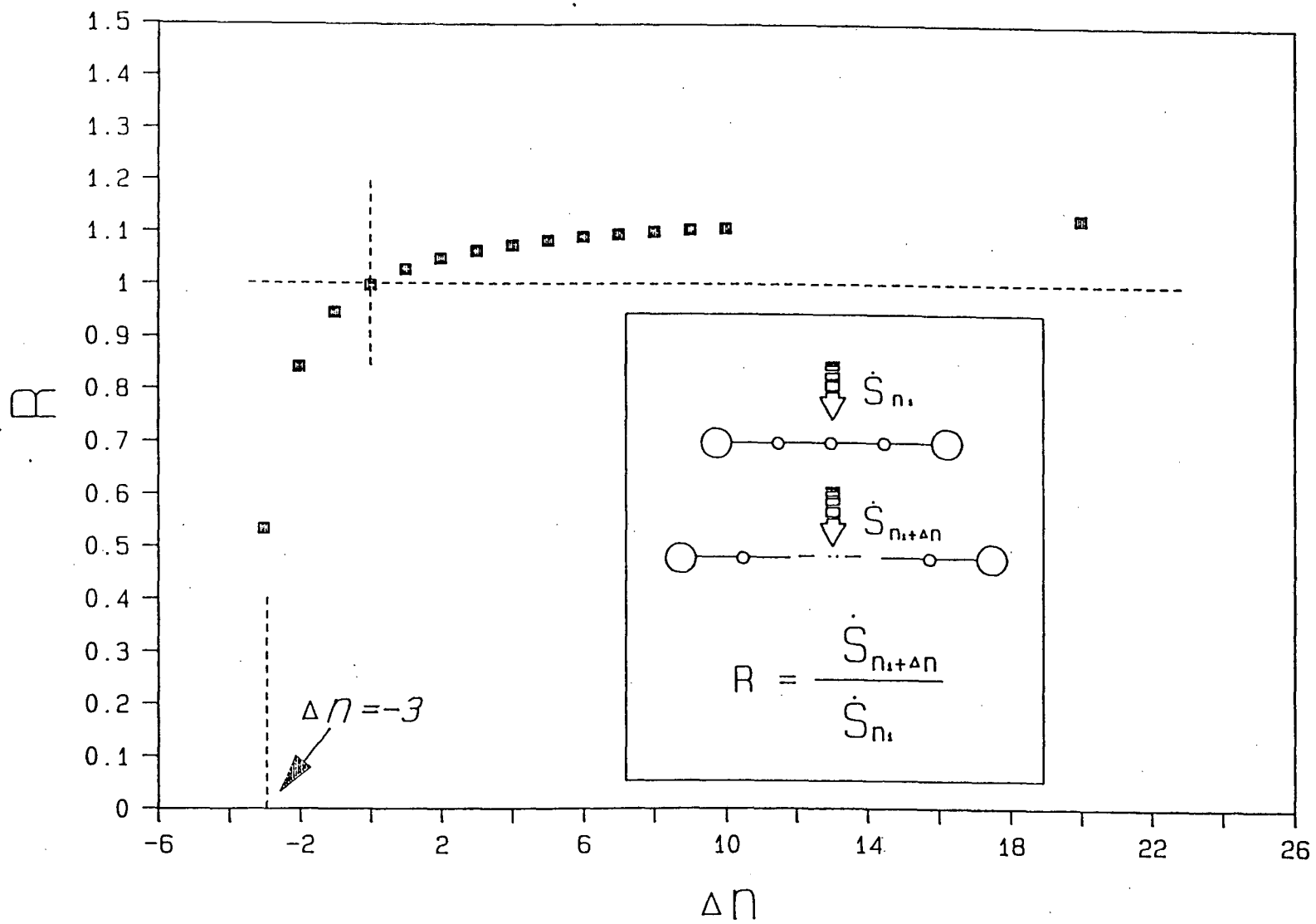


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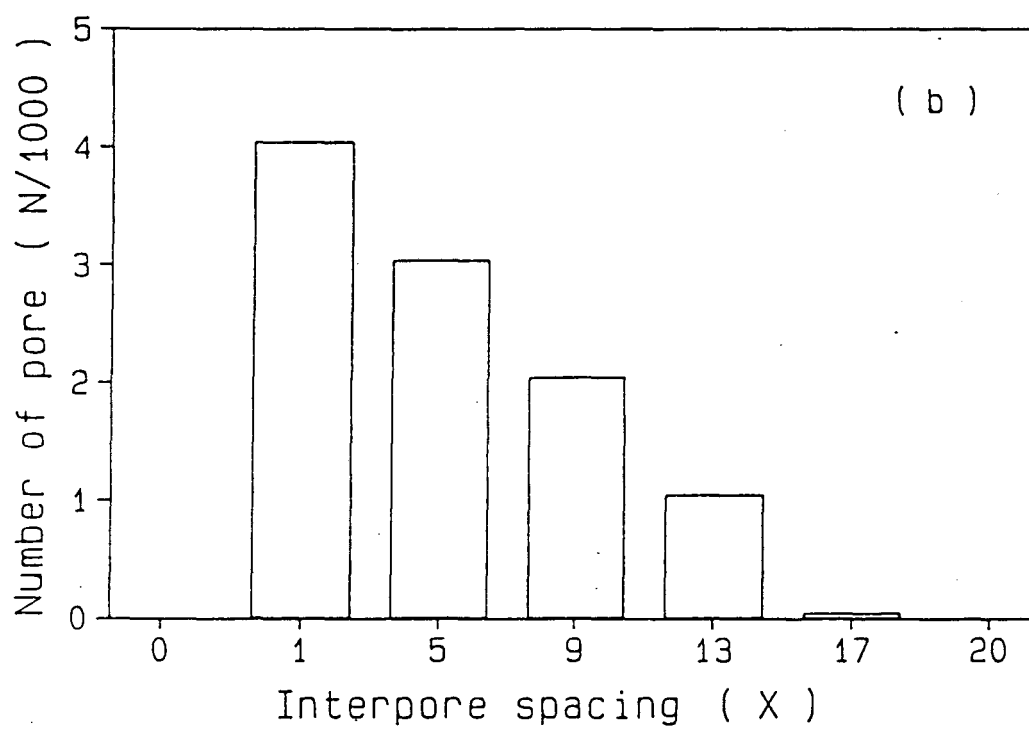
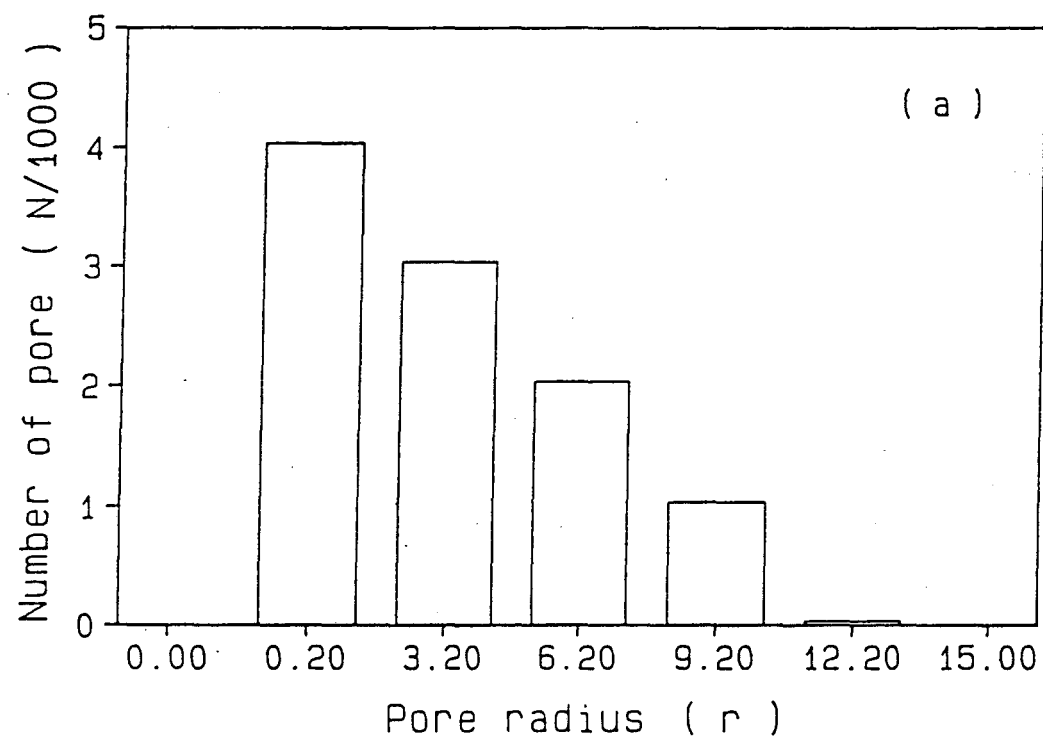


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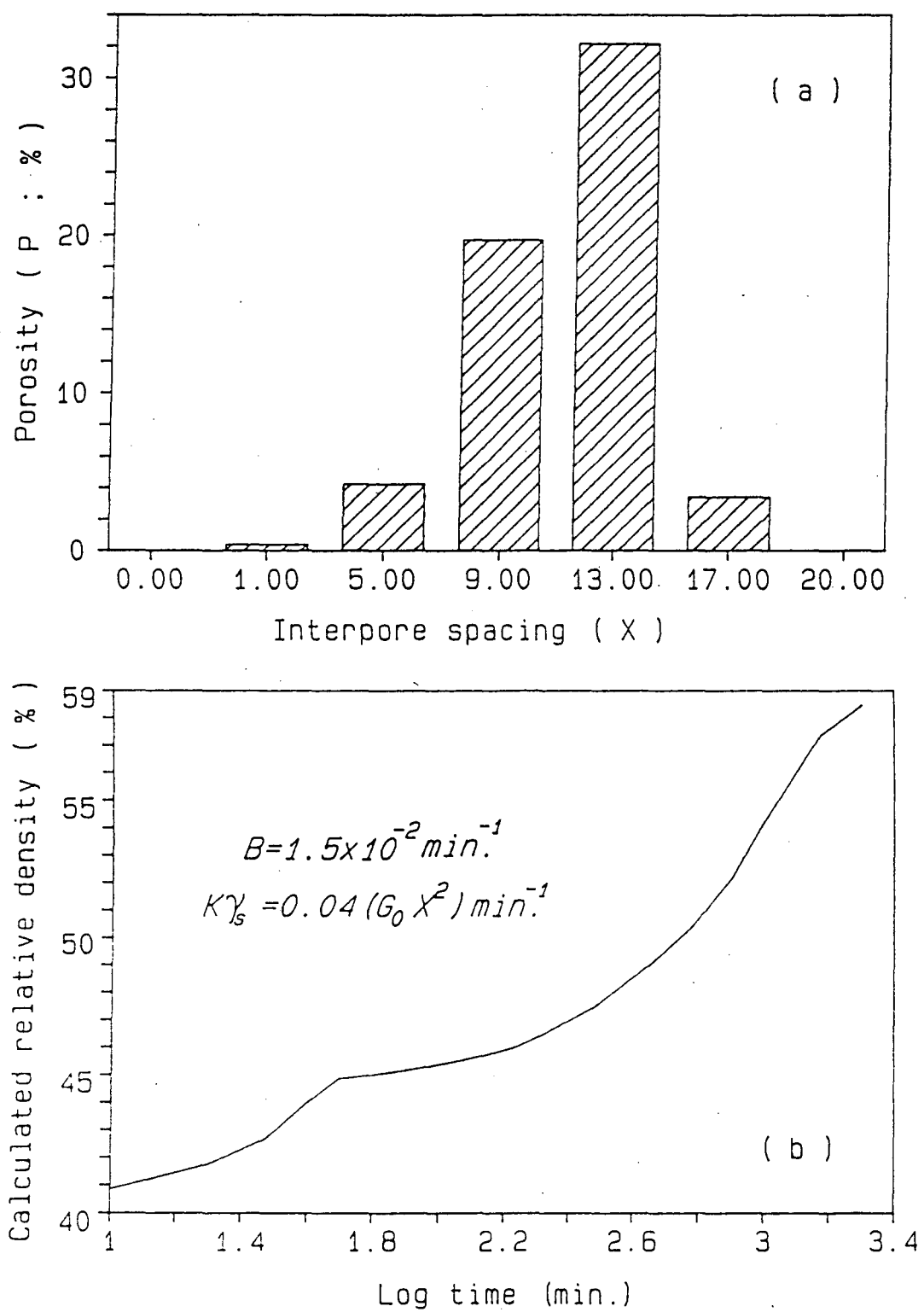


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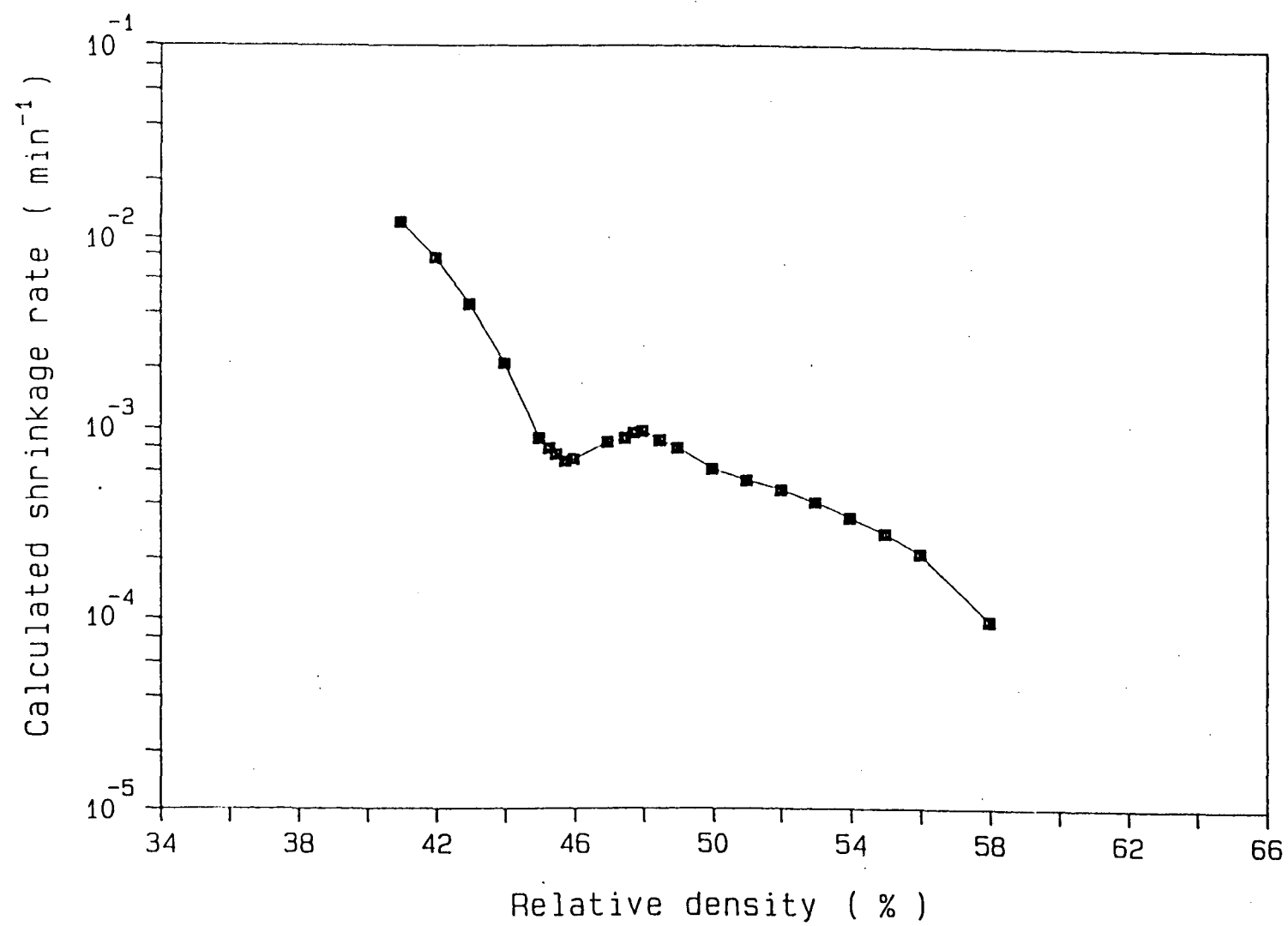
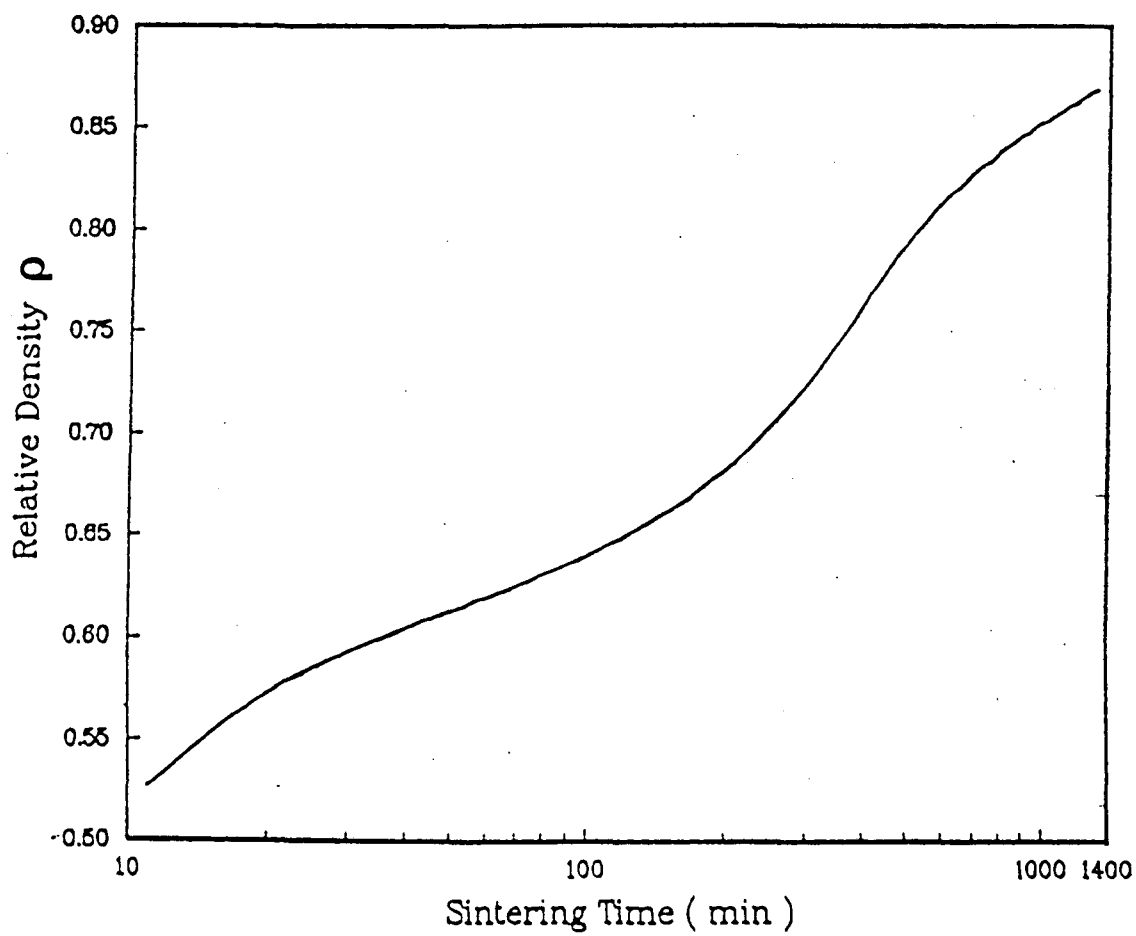
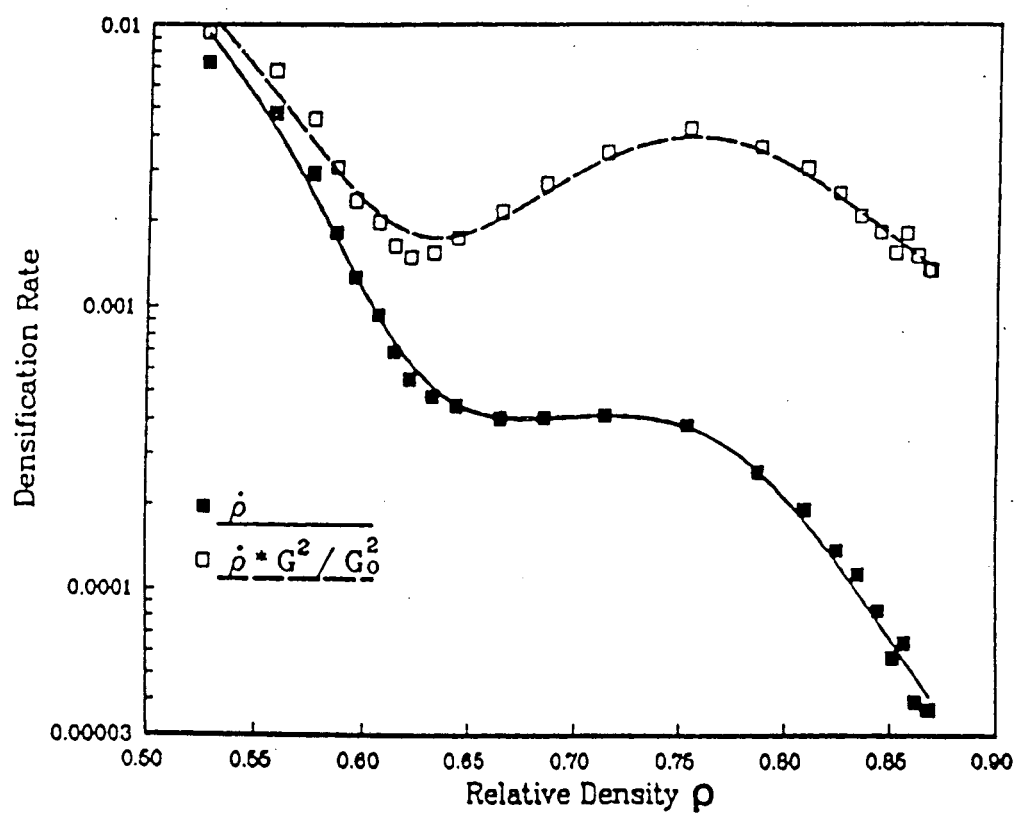


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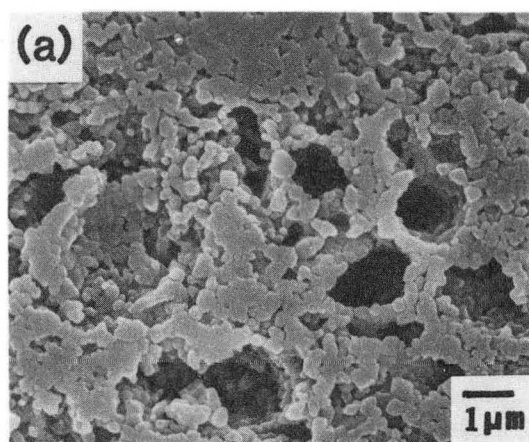
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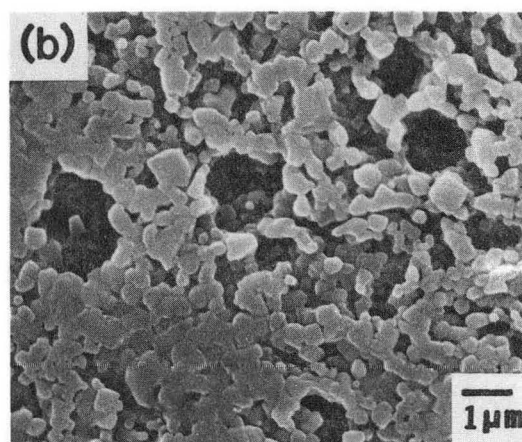


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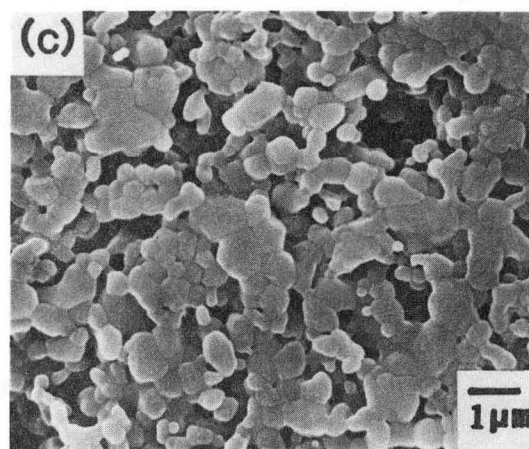
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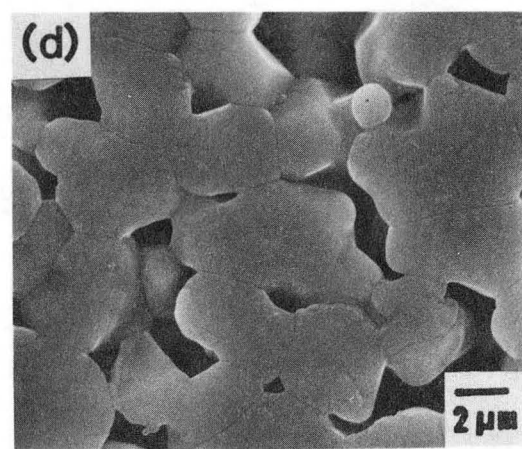
$\rho = 55\%$



$\rho = 62\%$



$\rho = 73\%$



$\rho = 80\%$

Figure 16

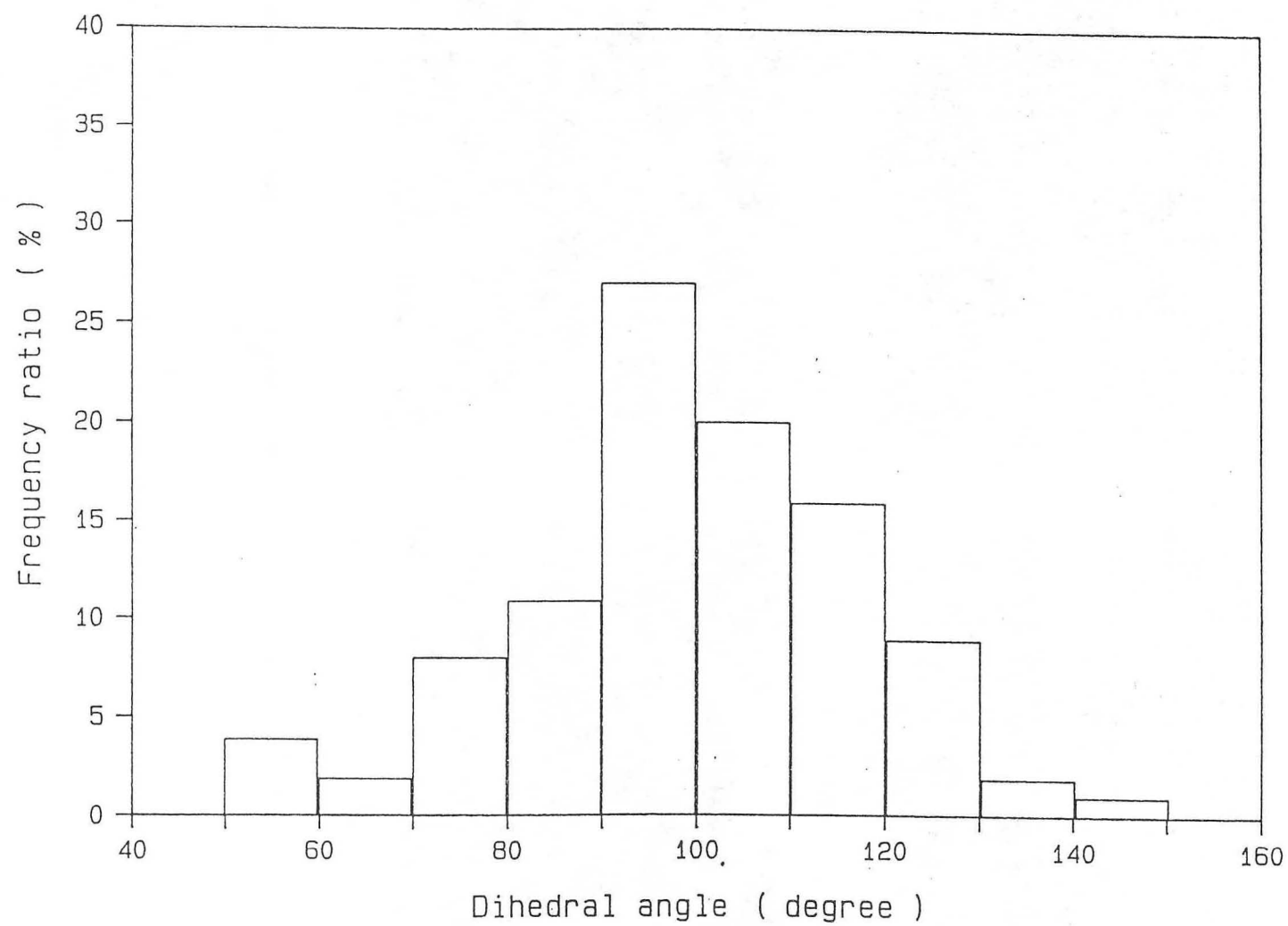


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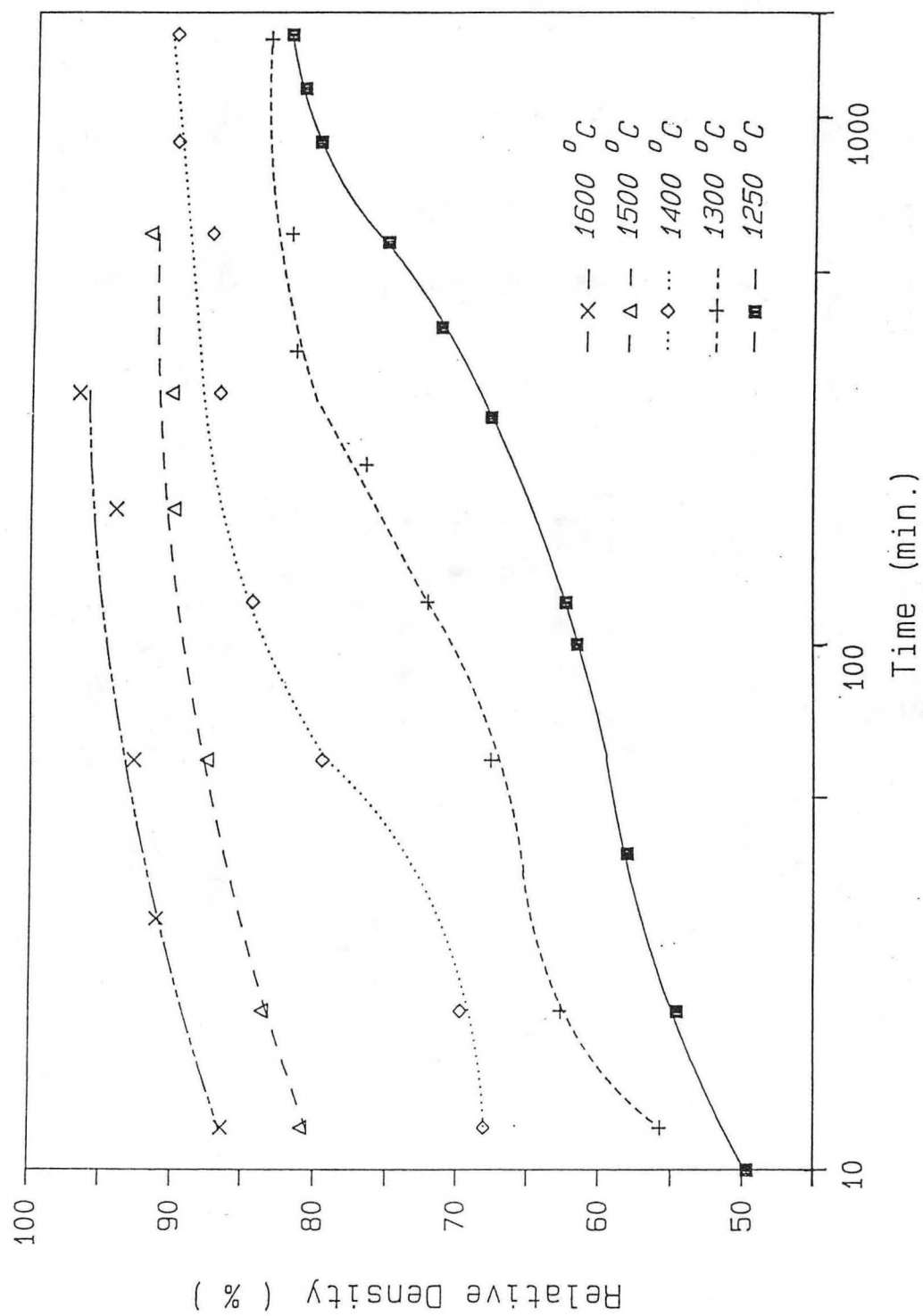


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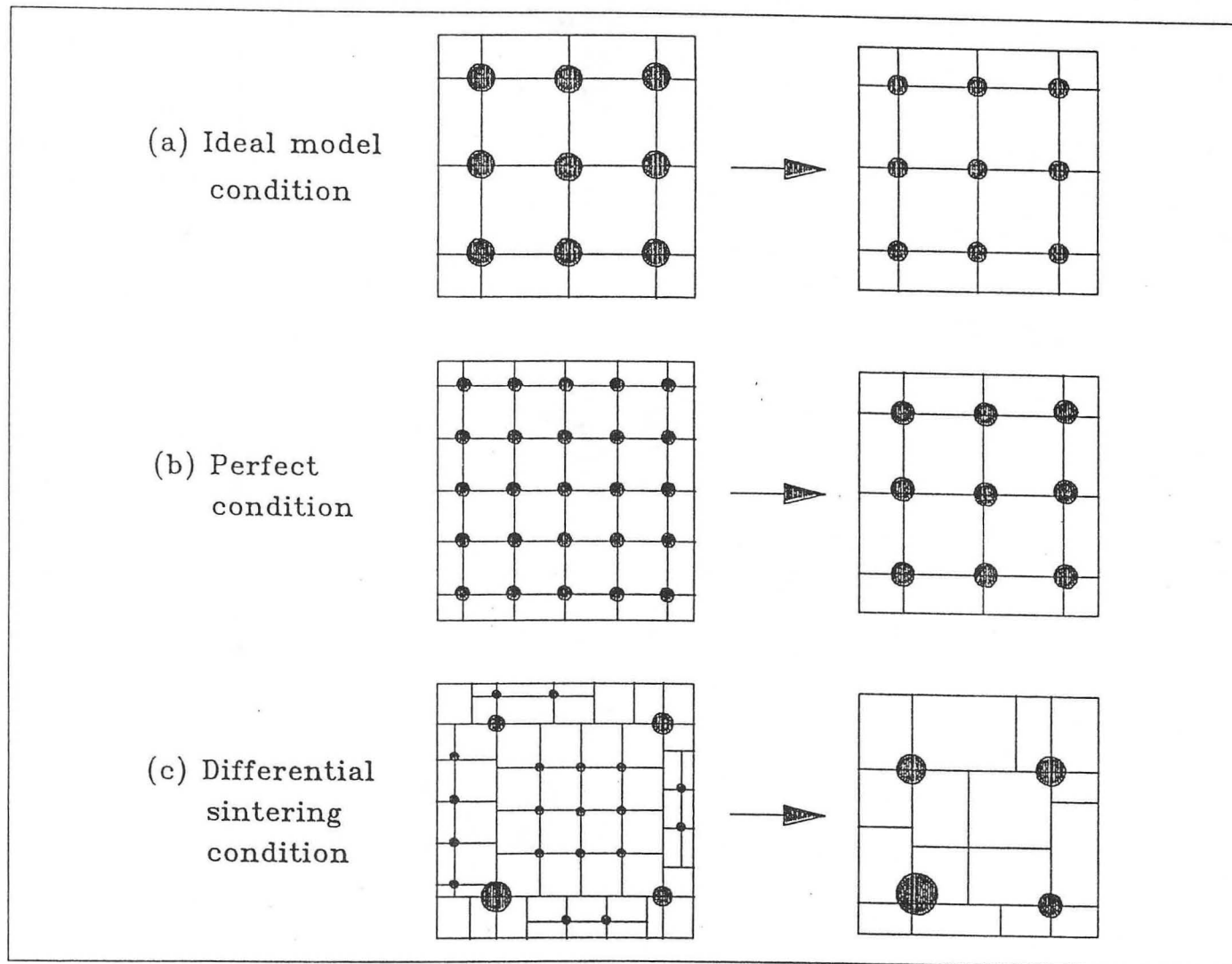


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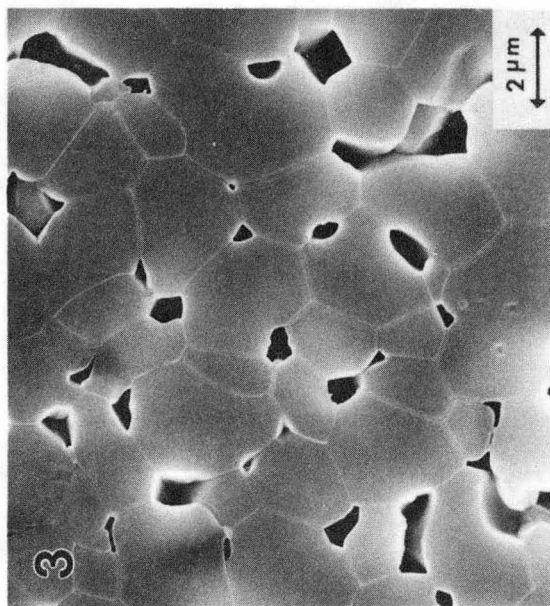
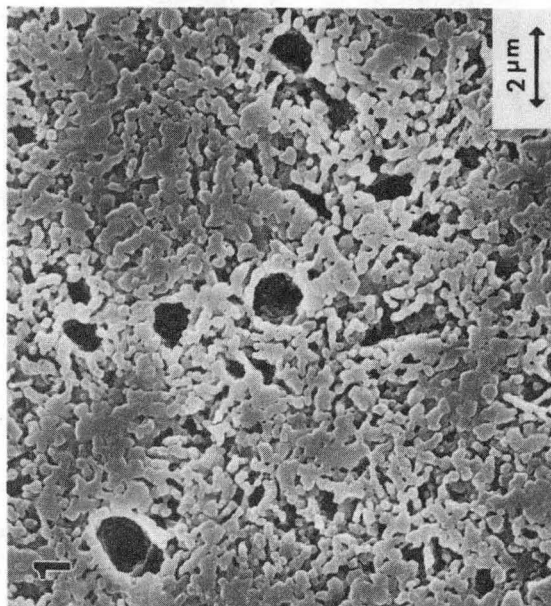
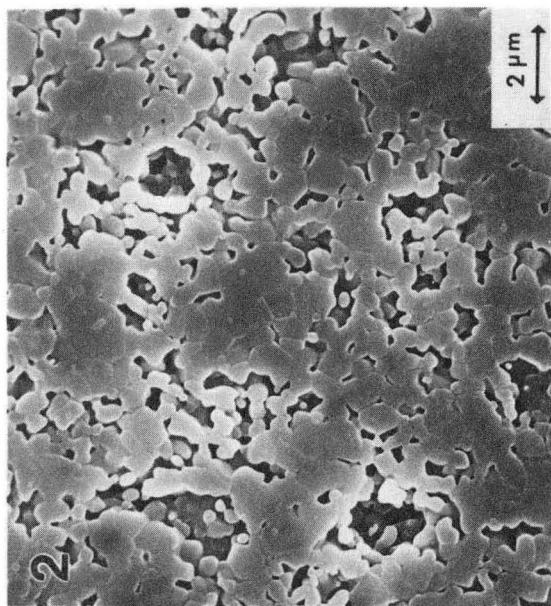


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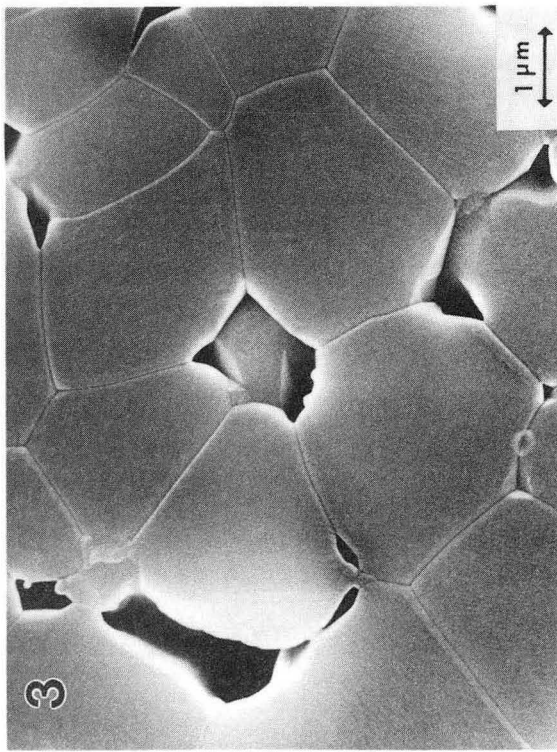
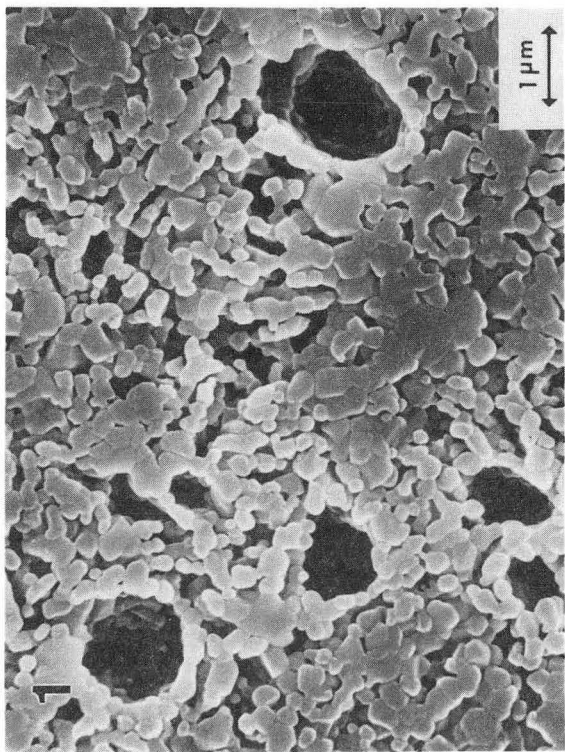
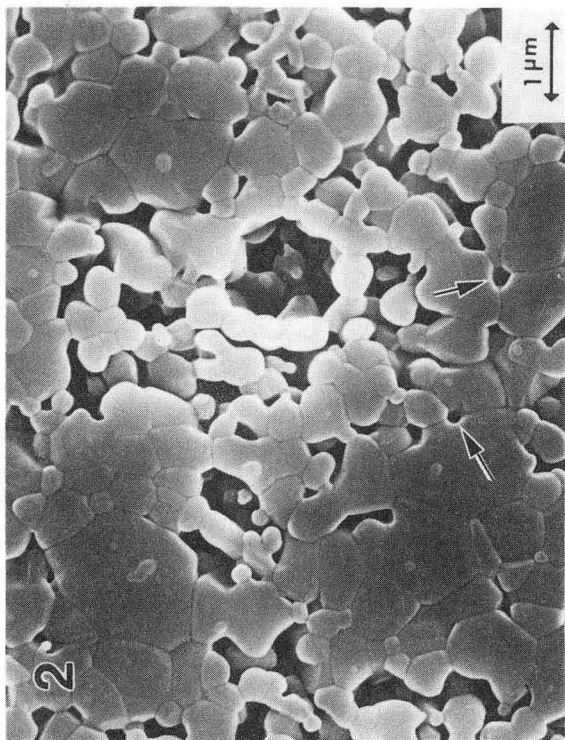


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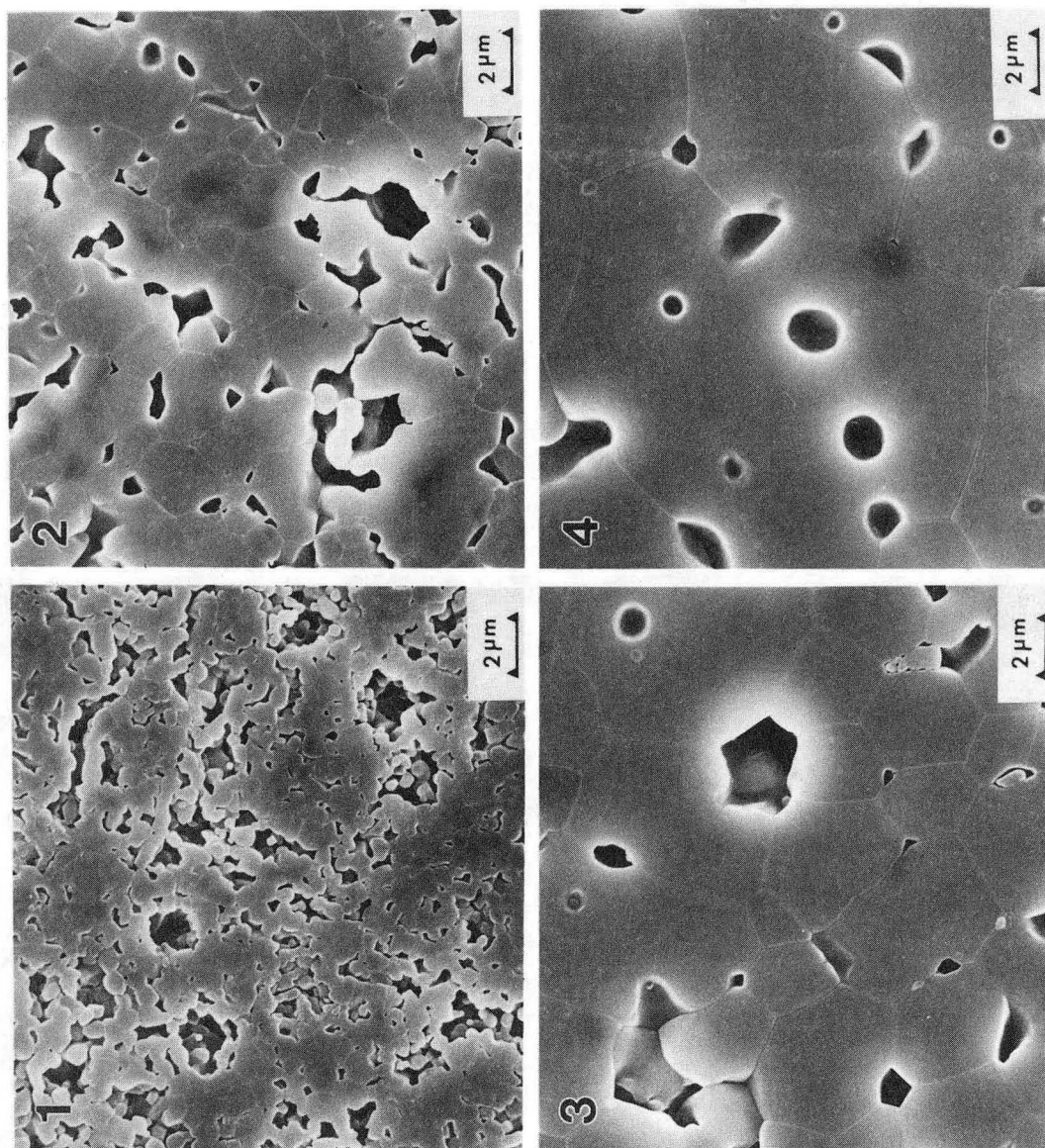


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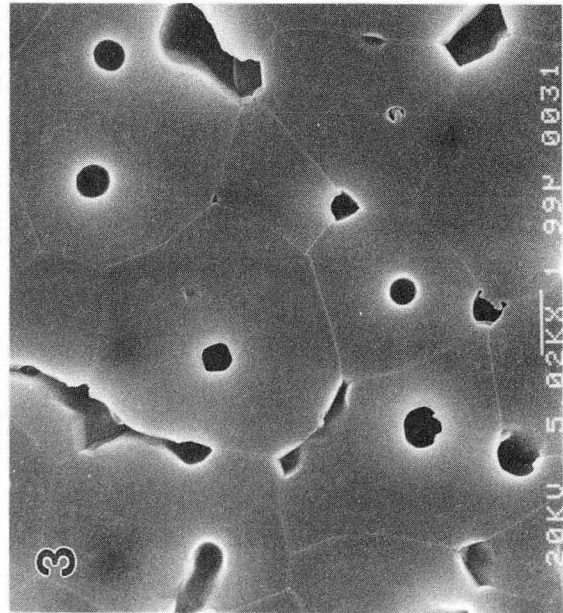
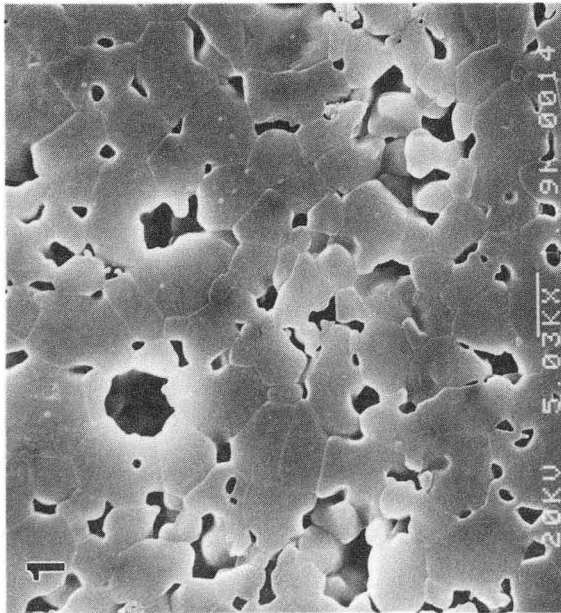
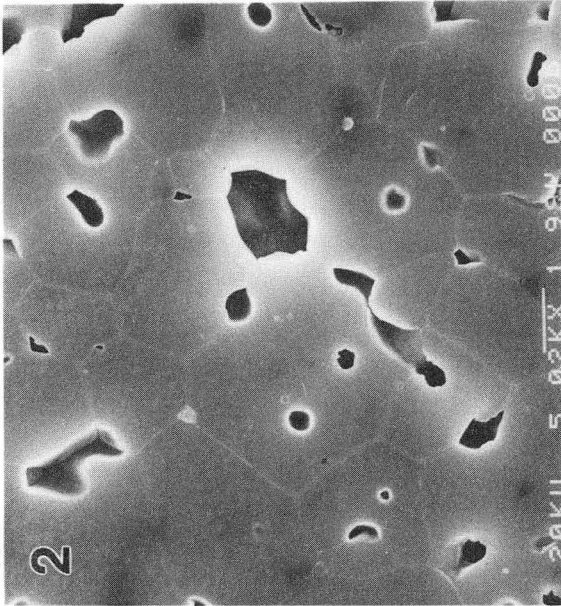


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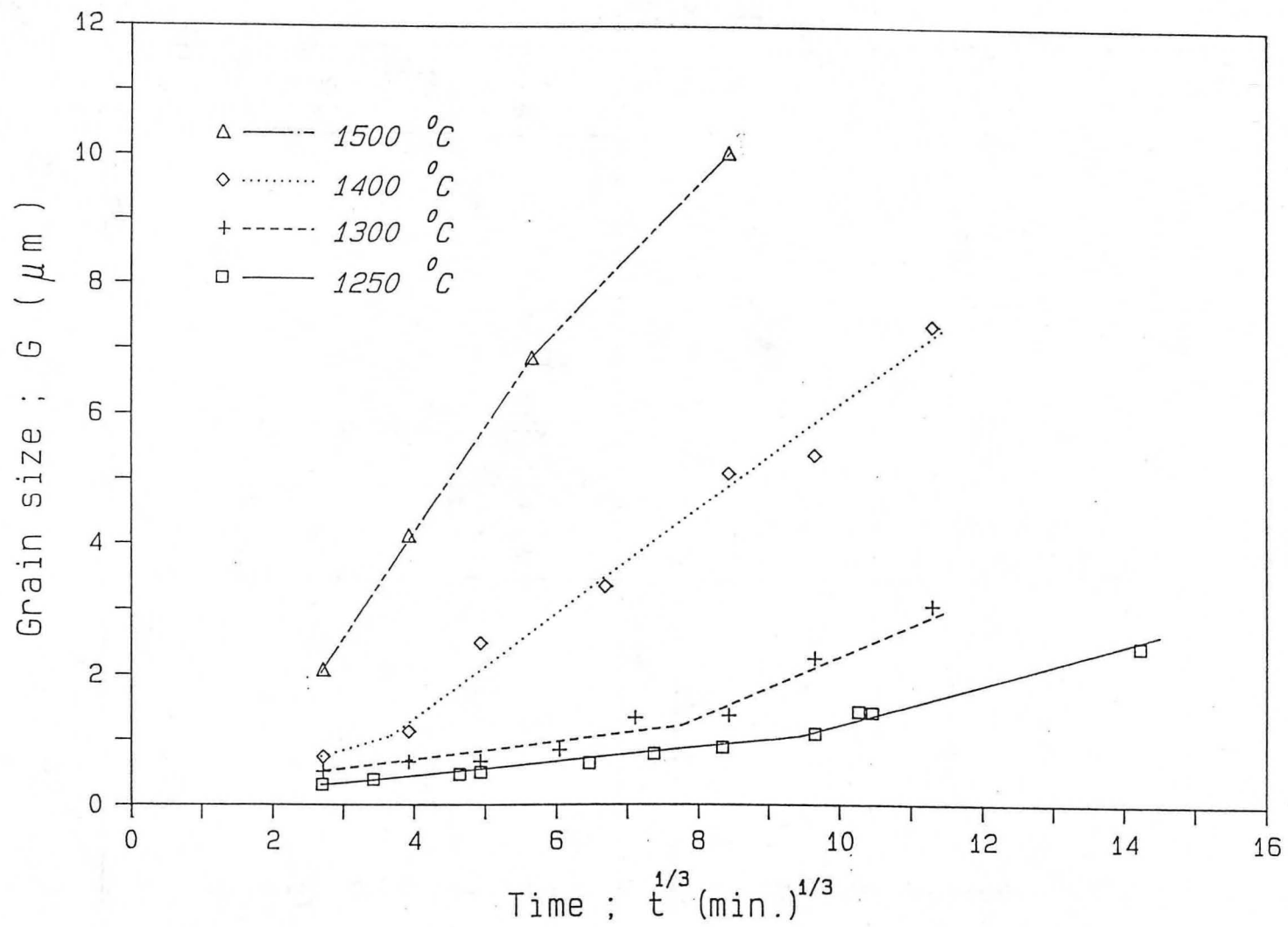


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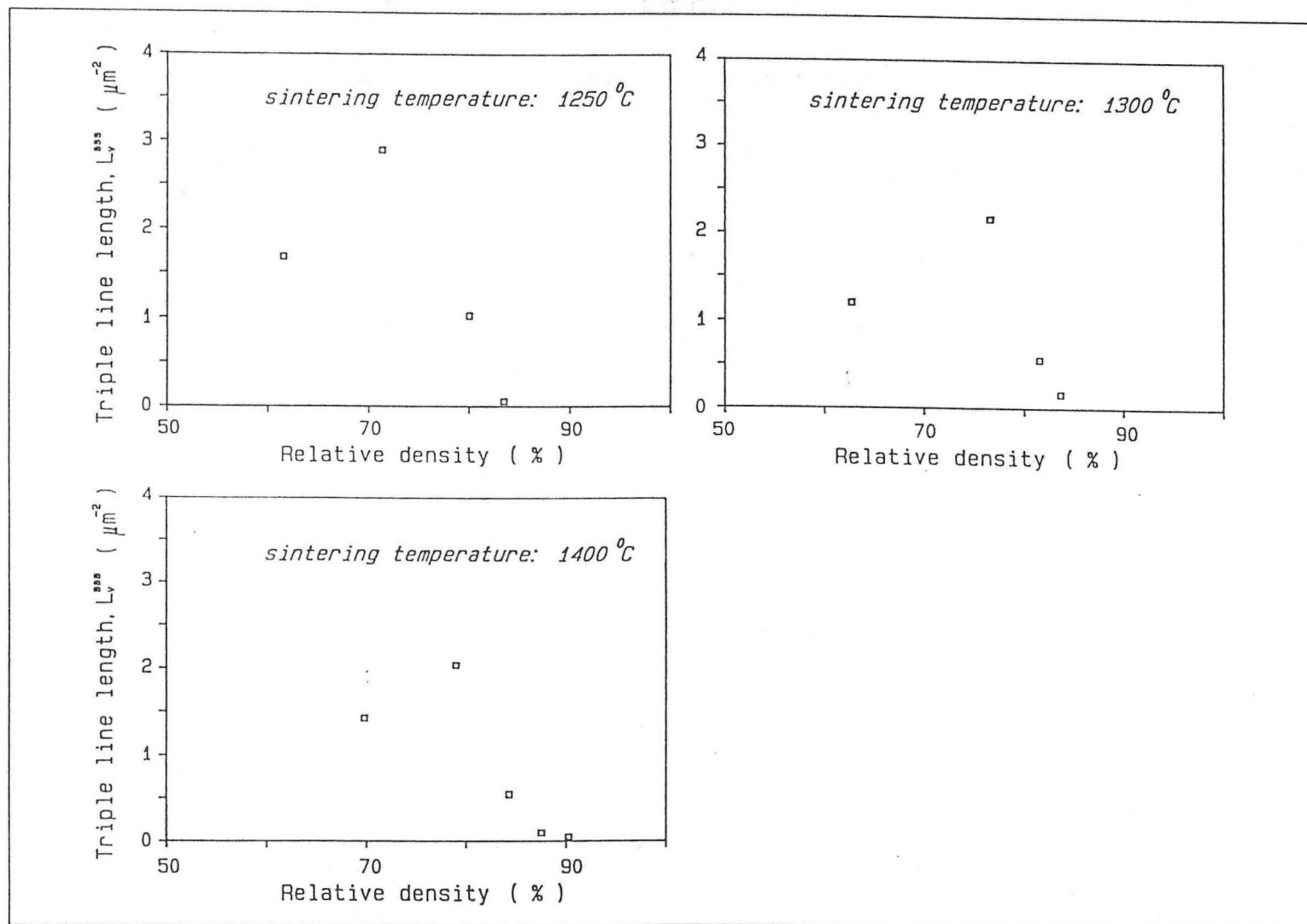


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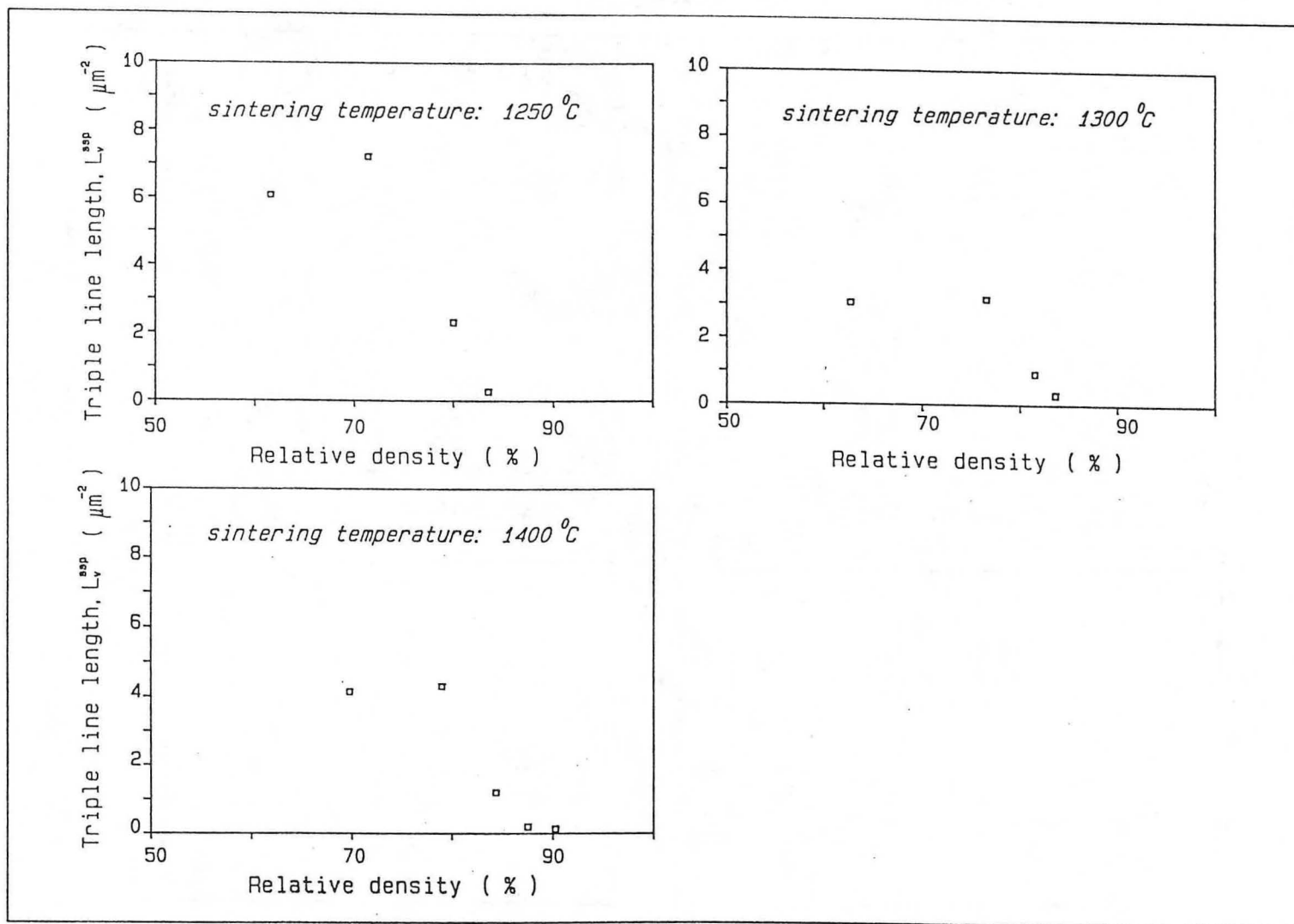


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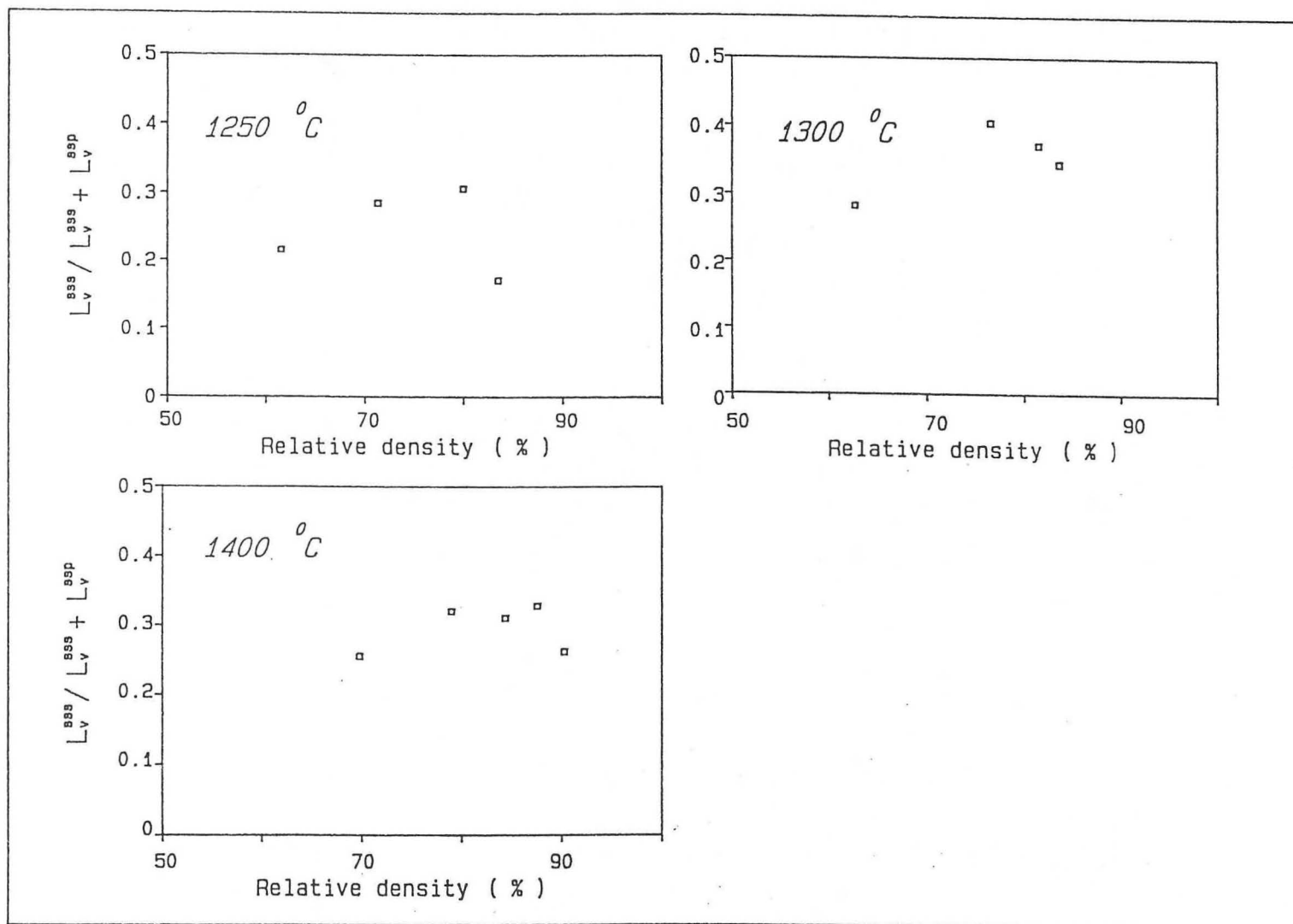


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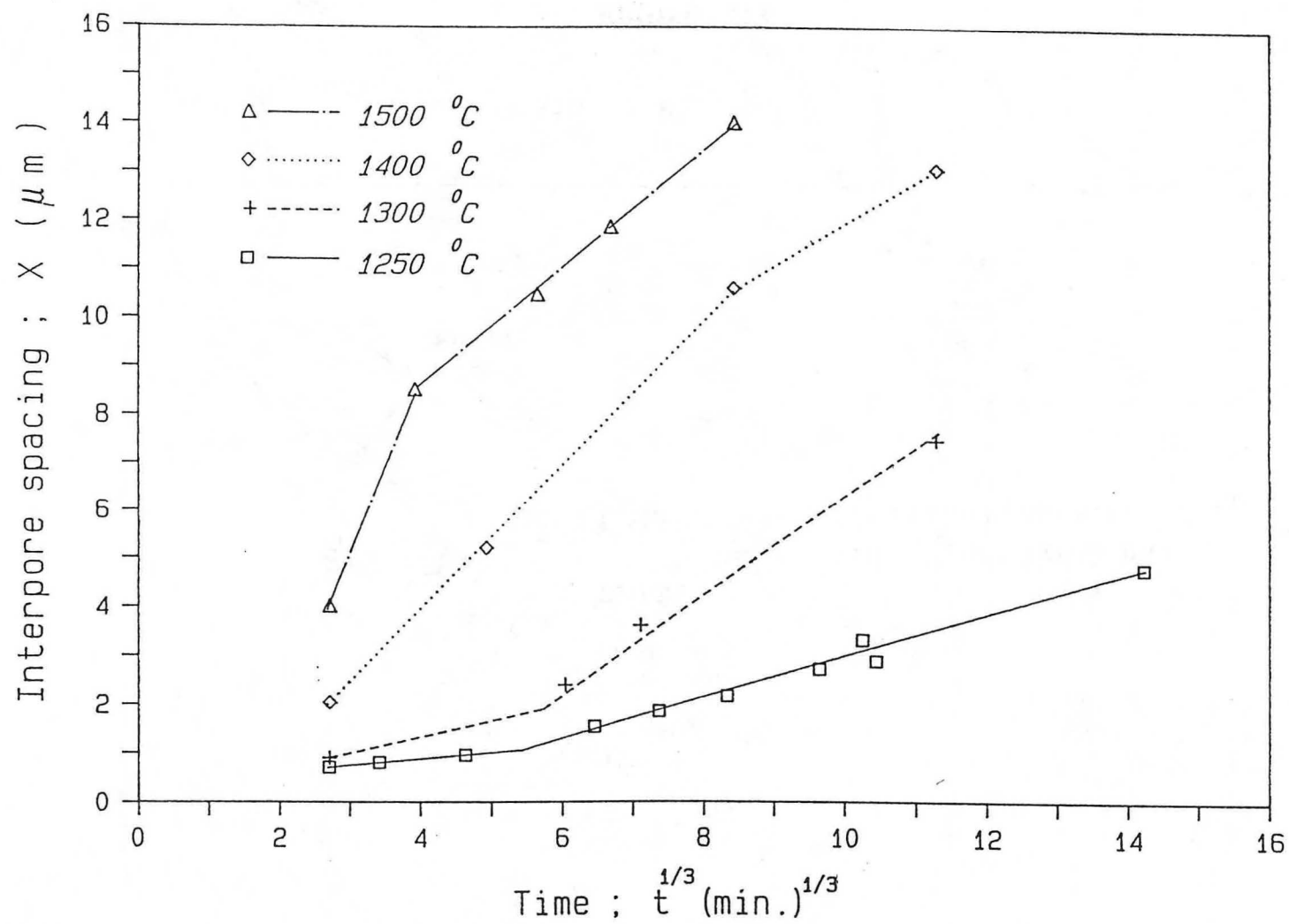


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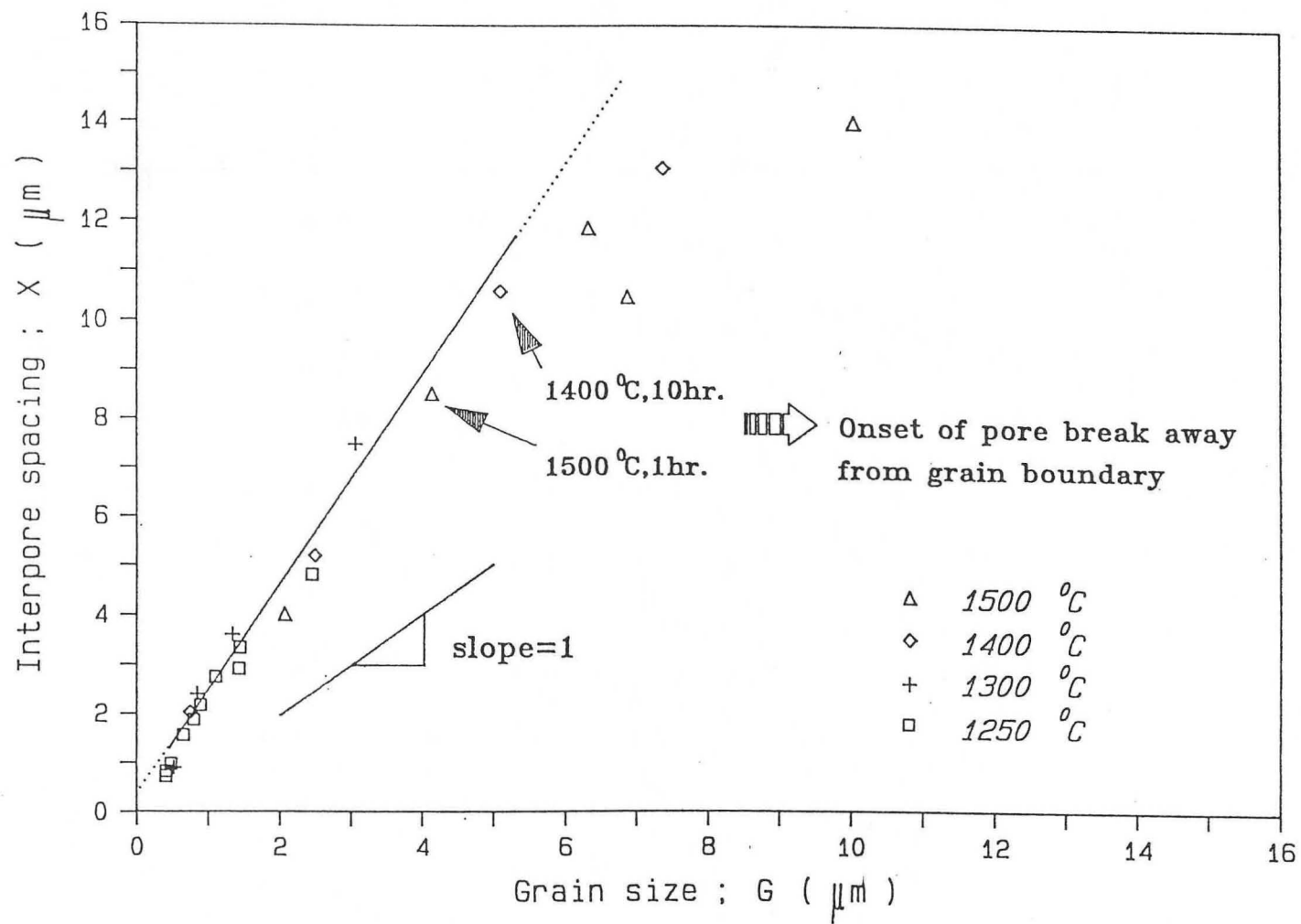


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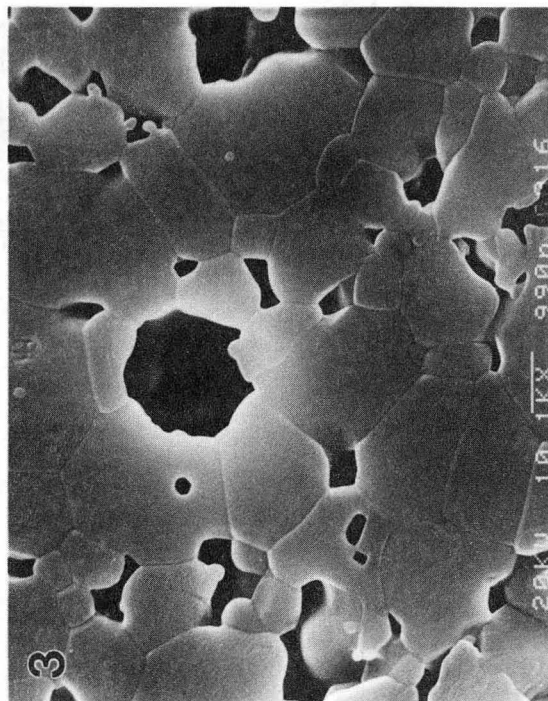
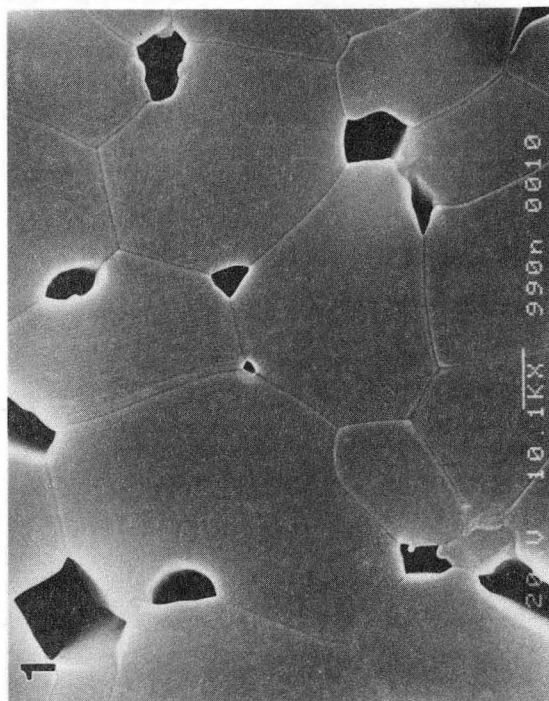
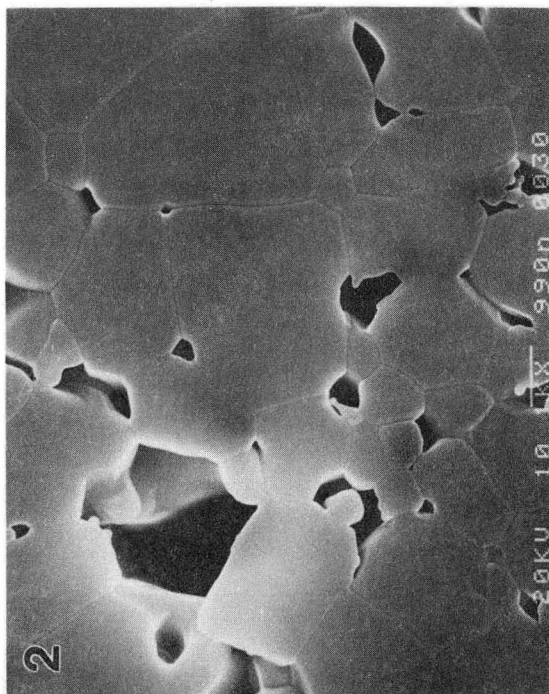


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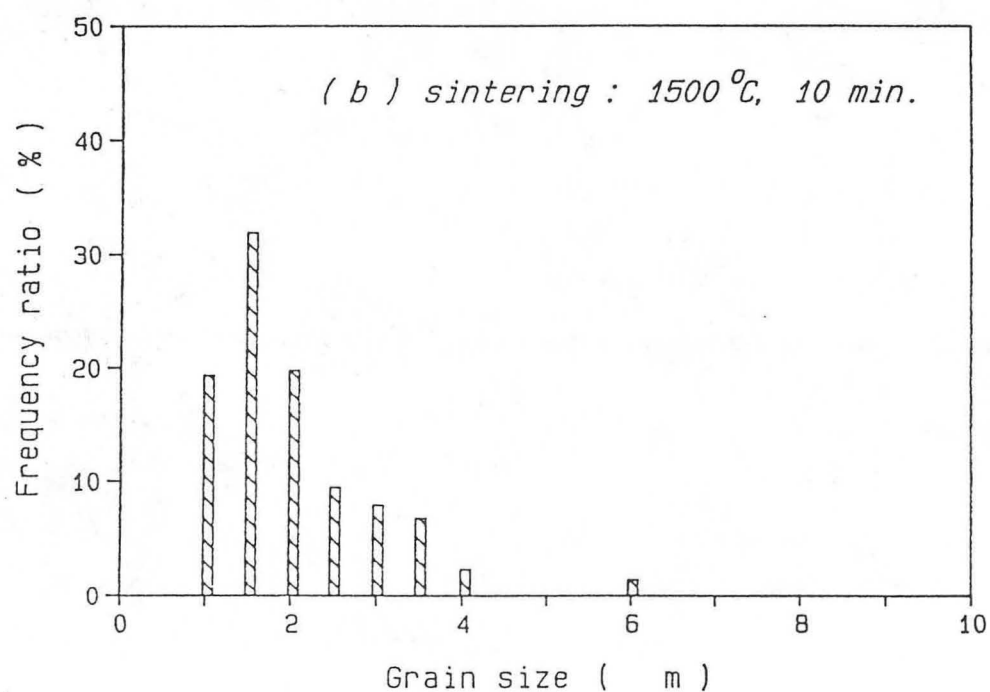
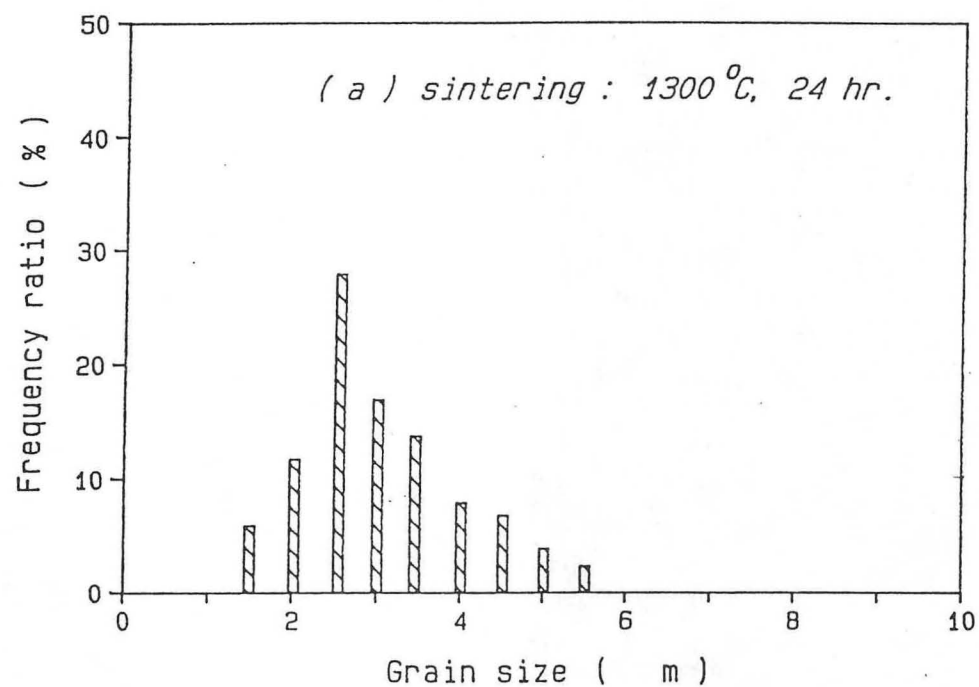


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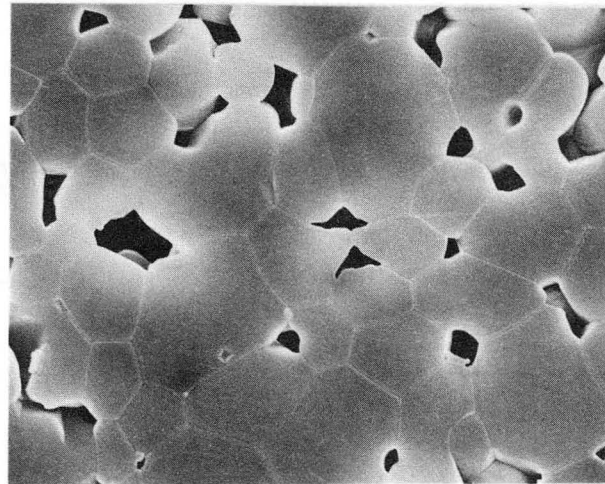
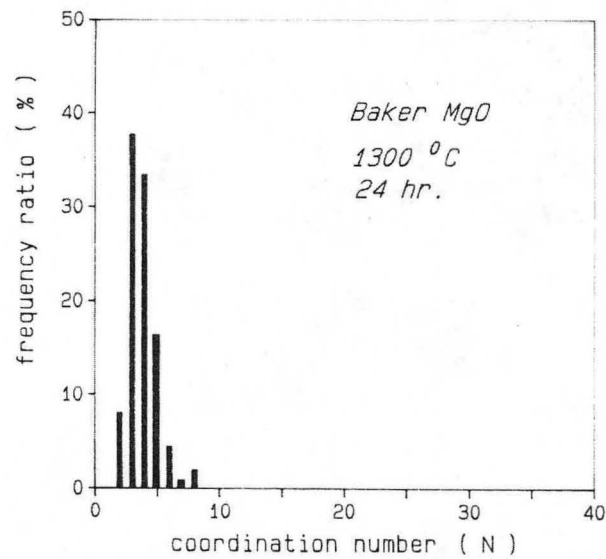
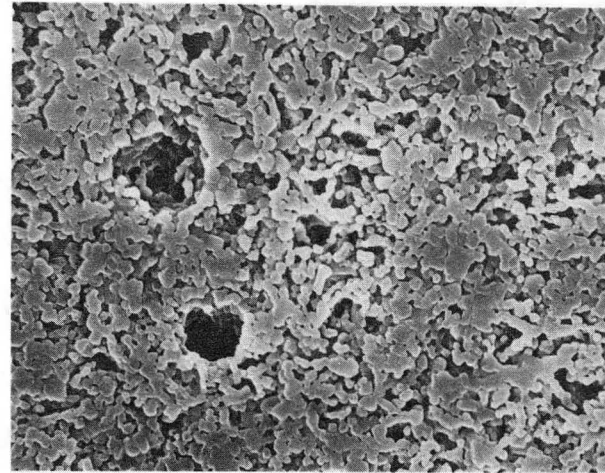
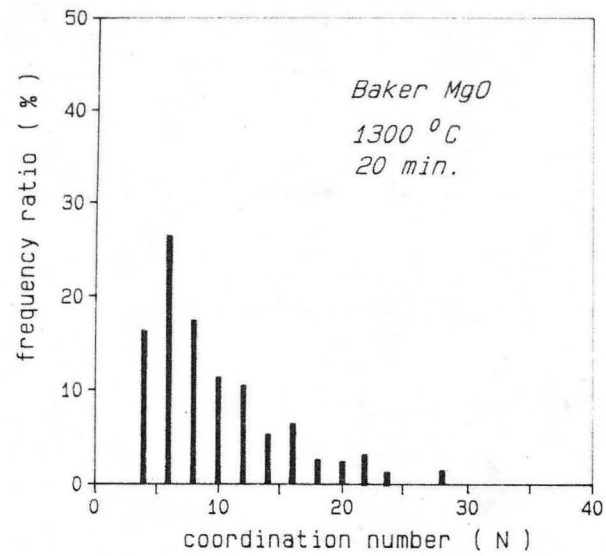


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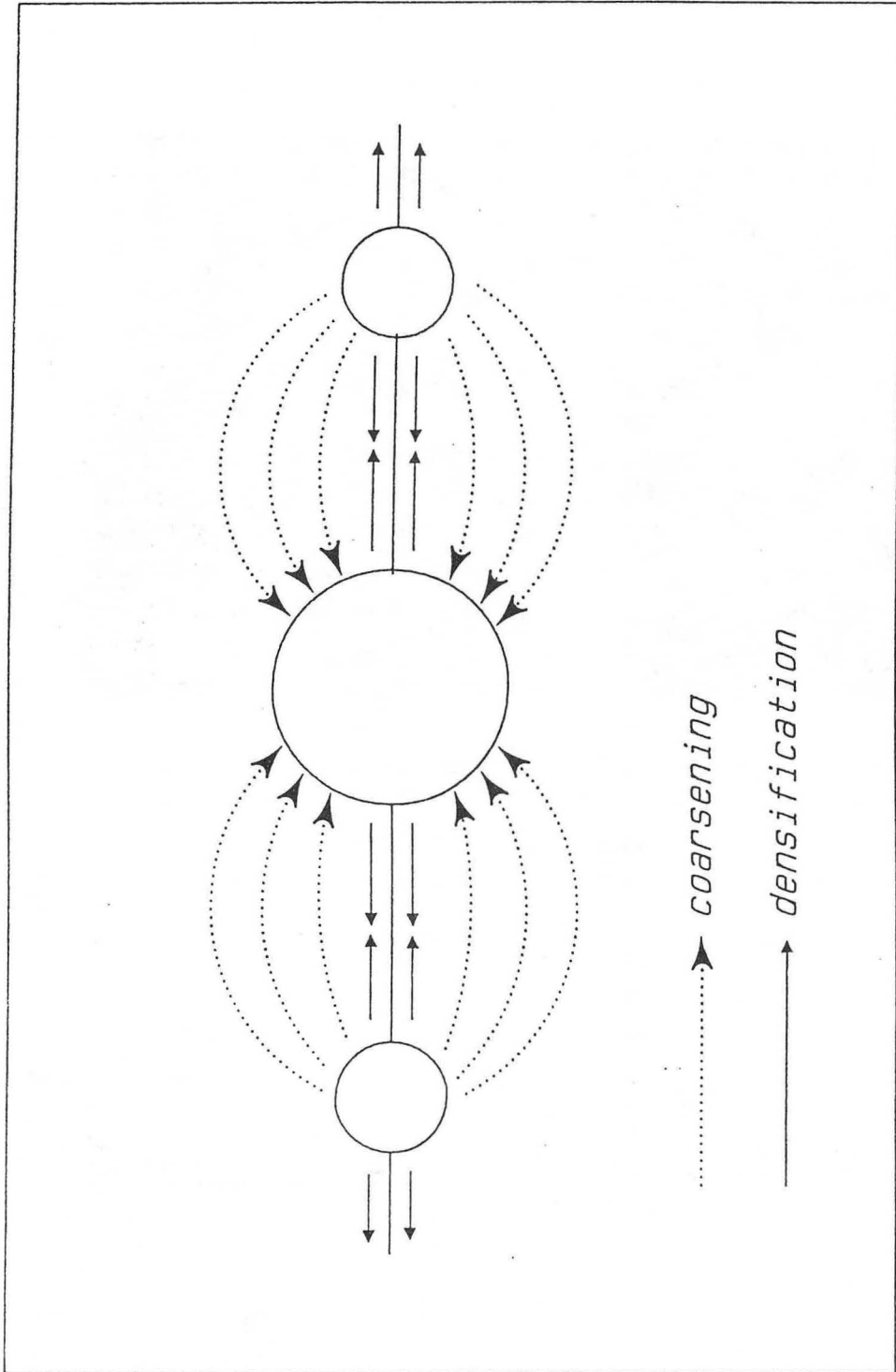


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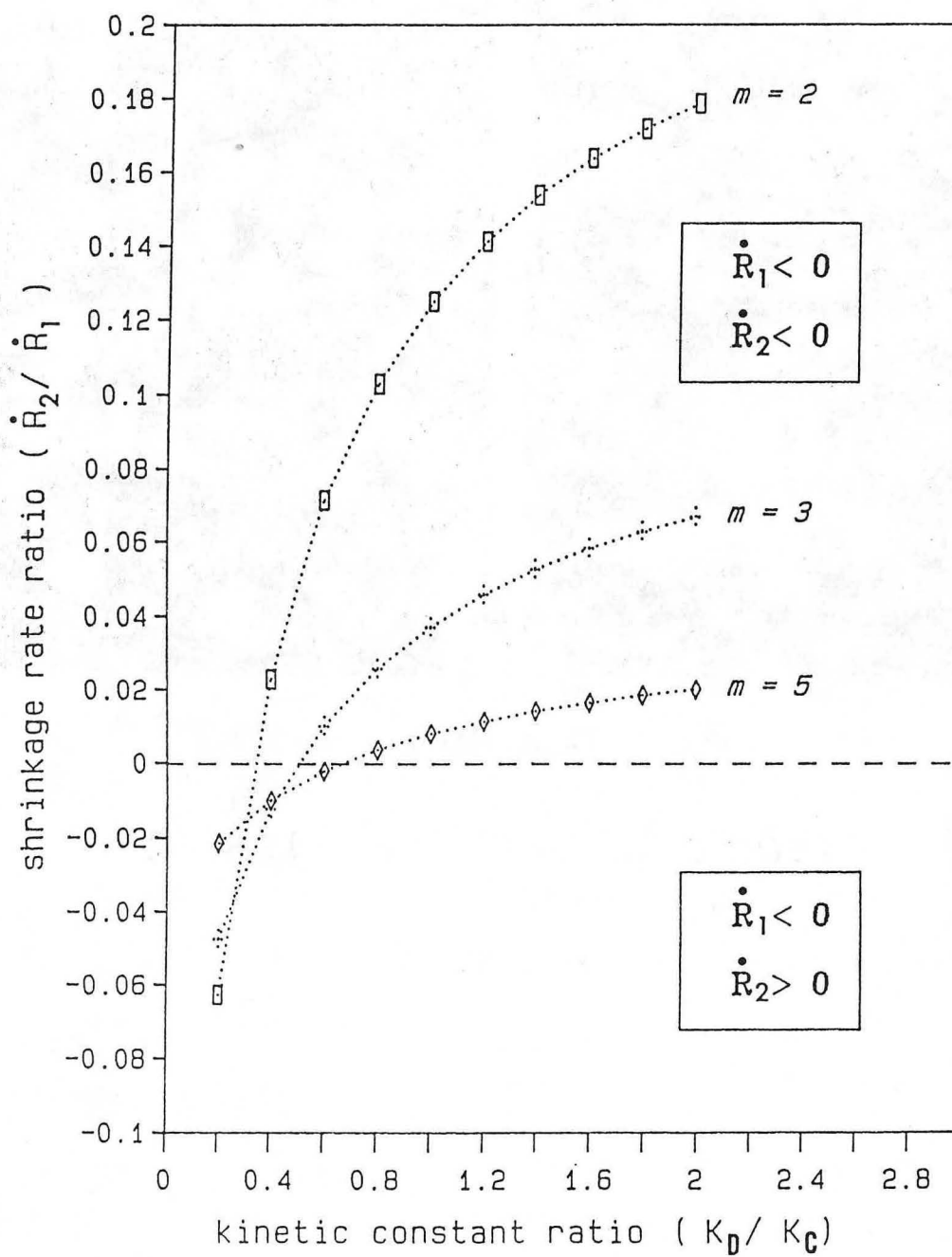
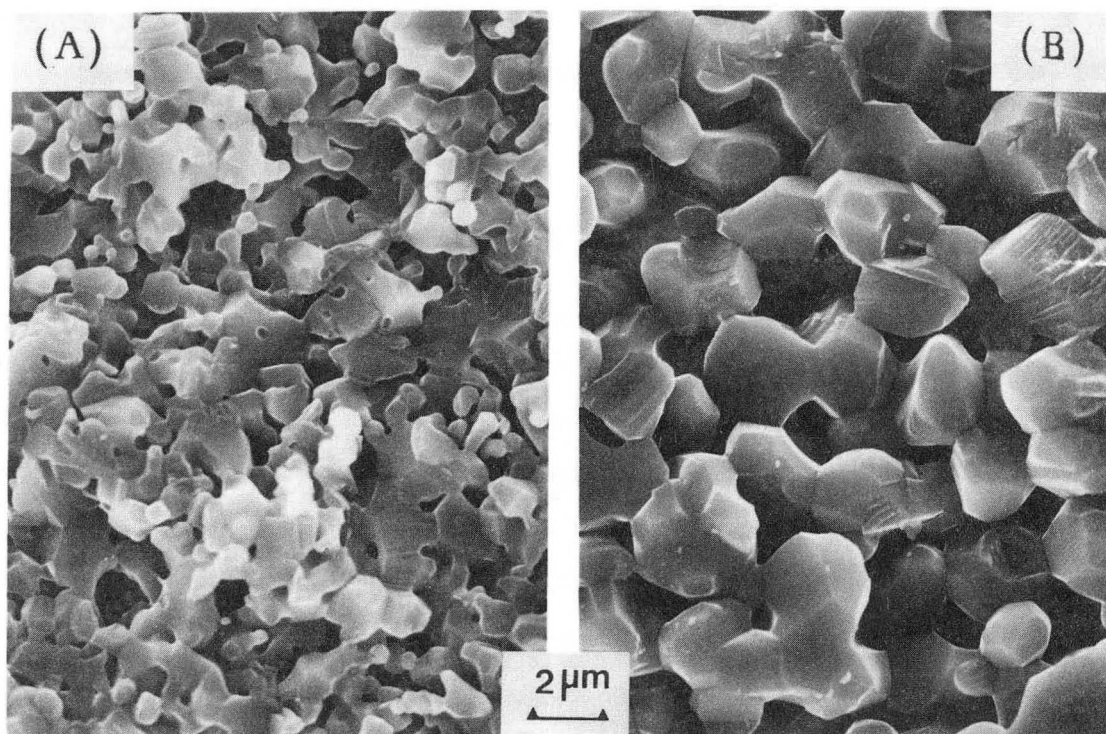


Figure 34



$\rho = 80\%$

1500°C

1250°C

Figure 35

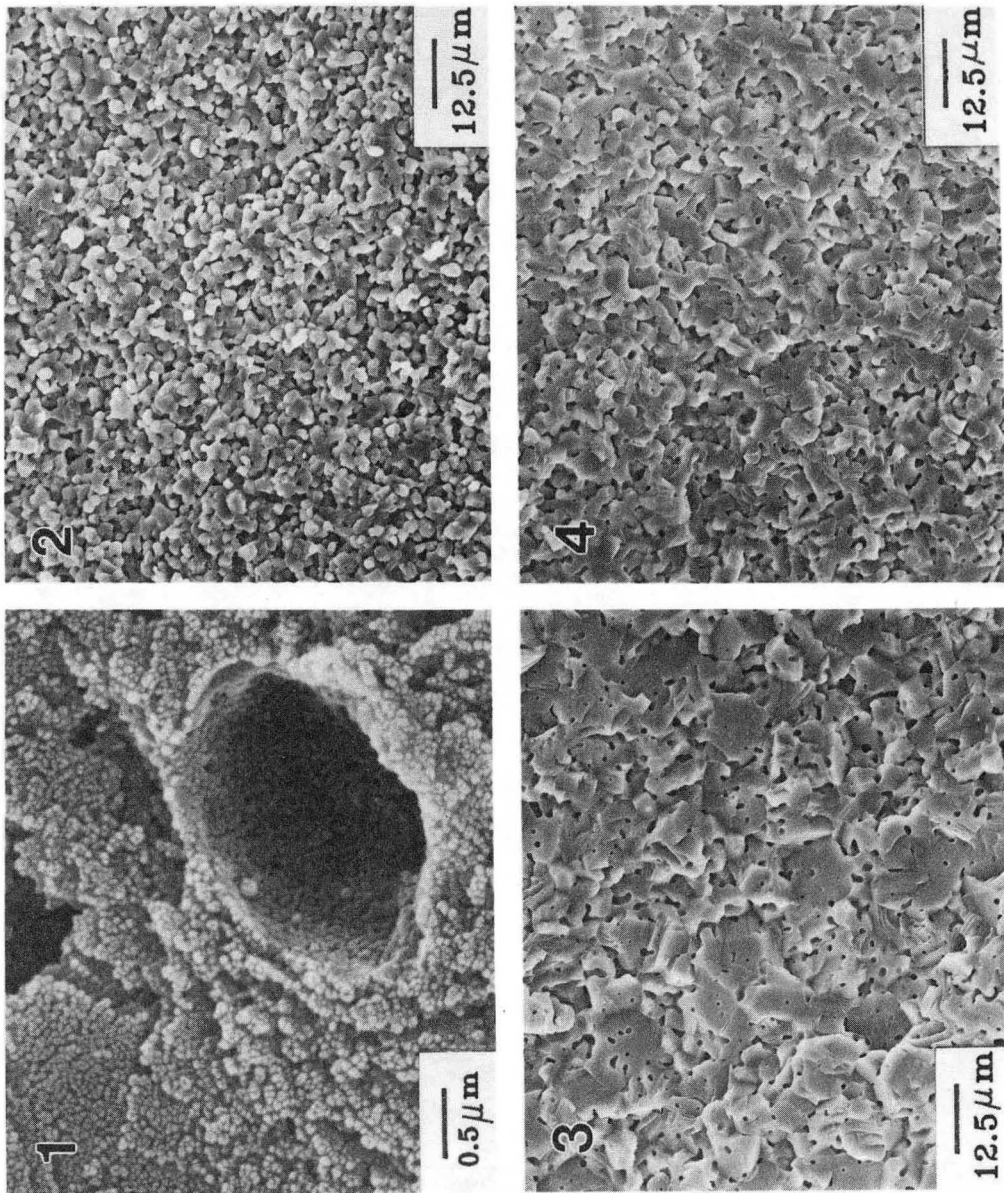


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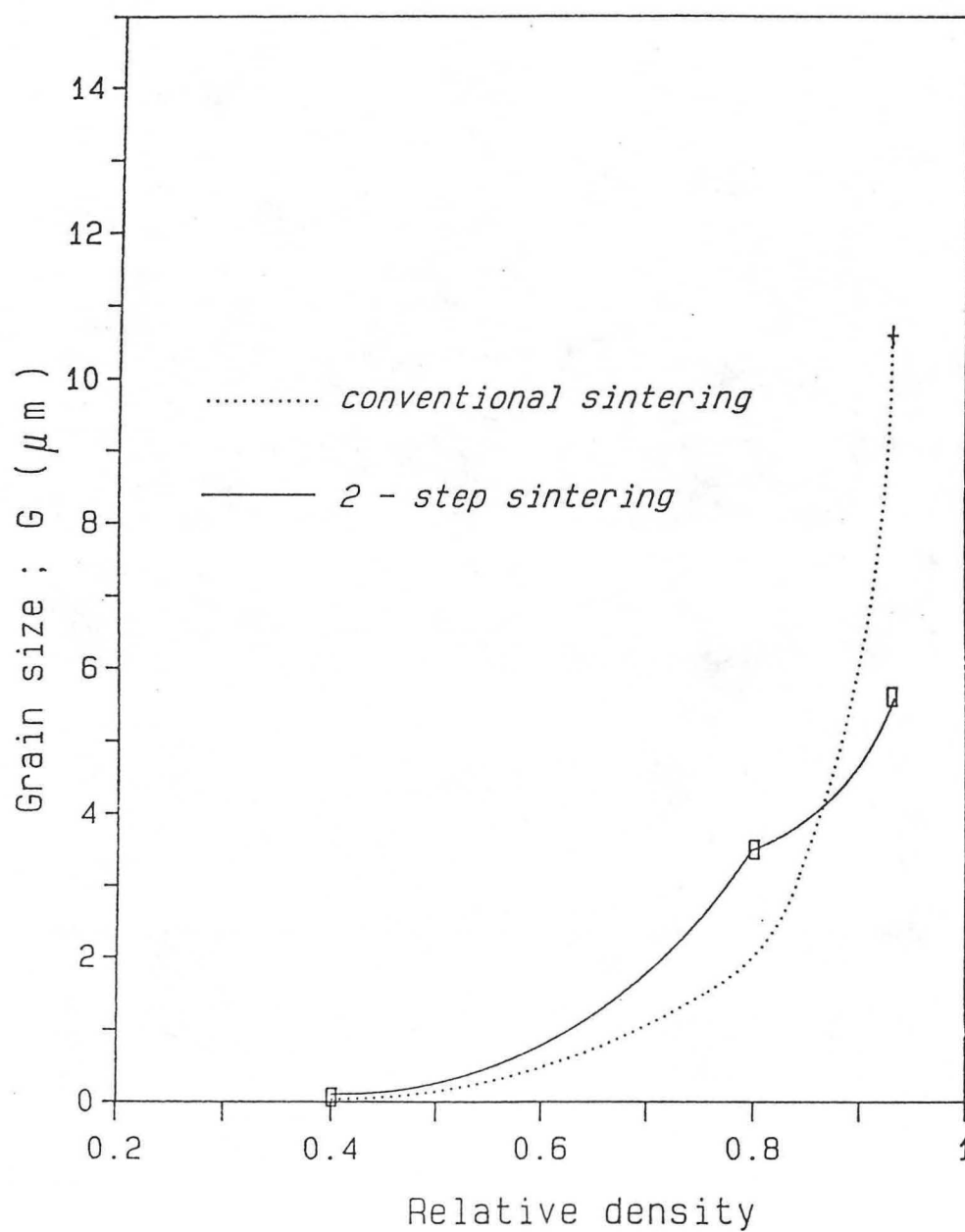


Figure 37

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