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SPRING COLLEGE IN MATERIALS SCIENCE ON 'CERAMICS AND COMPOSITE MATERIALS'

(17 April - 26 May 1989)

MICROSTRUCTURE DESIGN

(Lectures I - III)

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PRINCIPLES OF MICROSTRUCTURE DEVELOPMENT IN CERAMICS

(Lecture notes)

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Content

1. Introduction

Properties of ceramics - mechanical, electrical, magnetic and optical - are critically dependent on their microstructures. The microstructural evolution during sintering depends upon the characteristics of the starting powder (particle size and destribution, shape, agglomeration and purity), the green body microstructure (homogeniety, porosity, agglomerationa) and the sintering and coarsening processes.

Grain growth control is the major problems in preparation of contemporary high tech ceramics. Due to many variables which influence the microstructure development during the heat treatment, the understanding and control of the process is quite complex and generalizations are frequently impossible. The aim of the present series of lectures is to review the basic principles of microstructure evolution and to illustrate various phenomena by practical examples from electronic and engineering ceramics.

The introductory lecture notes are based on several review papers, notably by Smith(1), Burke(2), Brook(3), Yan, Cannon and Bowen(4) and Carpay and Stuijts (5).

2. Ceramic Microstructure: Types and evolution

Microstructures can be divided into two general categories:

1. Uniform microstructures, when the distribution of grain sizes is relatively narrow (Fig. 1) and

2. Non-uniform microstructures, when the differences in sizes between the individual grains are very pronounced. Frequently, approximately bimodal grain size distributions are observed. ("Duplex" structures, Fig. 2).

The criterion commonly taken for the existence of the "uniform" microstructure is that the largest grain should be smaller than twice the mean size (6).

Microstructures evolve during the heat treatment of ceramics. Heat treatment induces grain growth. Growth is termed "normal" or continuous, when the grain size distribution does not change during growth. On the other hand, grain growth can be "abnormal" or "discontinuous", when a small fraction of grains exhibits a pronounced growth, whereas the rest of grains grow slowly. As a result, grain size distribution become progresively wider. The resulting microstructure is non-uniform during the growth process; However, the final microstructure may be fairly uniform, when all small grains dissapear in favor of the large ones.

3. Grain growth kinetic

Grain growth evolution (normal or abnormal) and appearance of microstructure (uniform or nonuniform) are governed by the kinetic of grain growth. Growth kinetic is complicated because of wide variety of possible mechanisms.

The simplest theoretical treatment of grain growth involves rate of grain boundary movement in pure single phase system. The ideal geometry of grains in a solid is that of cells in a foam (7).

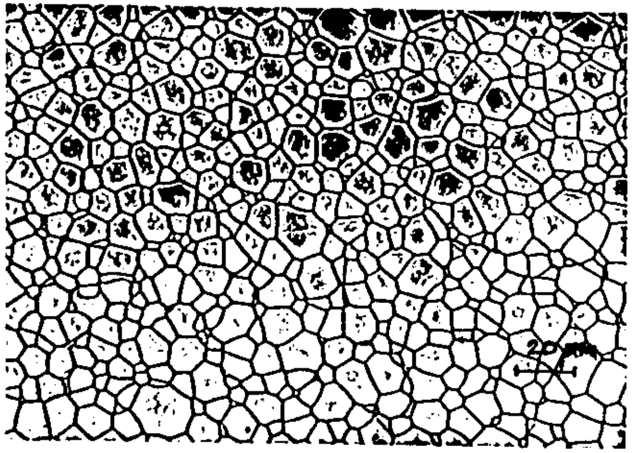

Fig. 1. Uniform microstructure of fully dense PLZT ceramic, sintered under pressure 24 hours at 1100°C

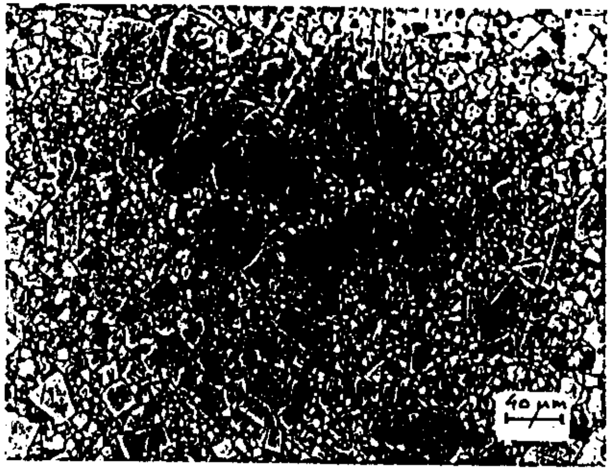

Fig. 2. Non-uniform microstructure of $BaTiO_3$-$SrTiO_3$ ceramic, sintered 3 hours at 1450°C

However, the microstructures are usually observed and described in two dimensions. Burke (2) presented well known idealized picture of microstructure, which shows some important features (Fig. 3): Grain boundaries radiate at about $120^{\circ}C$ from three-grain intersections; Six-sided grains have flat sides; all other grains have curved sides, convex if less than six, concave if more.

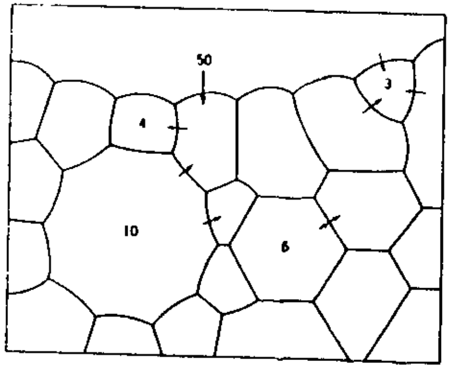

Fig. 3. Schematic drawing of polycrystalline specimen. The sign of curvature of the boundaries changes as the number of sides increases from less than six to more than six, and the radius of curvature is less, the more the number of sides differs from six. Arrows indicate the directions in which boundaries migrate. From J. E. Burke

Grain boundaries move by transfer of atoms from one grain to another across the grain boundary. The driving force F for atom migration is the chemical potential gradient caused by the difference of vacancy concentration across the boundary.

Grain grow, i.e. grain boundaries move by transfer of atoms from the decesing grain to the growing grain across the interface: The driving force for atom migration is interphase curvature. Surface tension γ causes a pressure difference across the boundary $\Delta P = \gamma (1/r_1 + 1/r_2)$, where r_1 and r_2 are the two principle radii of curvature. For spherical surface, the expression reduces to $\Delta P = 2\gamma/r$, where r is the sphere radius.

From thermodinamics we have at constant temperature

$$d\mu = V\, dP \qquad /1/$$

where V is specific volume and u chemical potential. If we take the specific volume as constant on either side of the interface we may integrate eq /1/ across the interface to obtain

$$\mu' - \mu'' = V\, 2\gamma/r$$

This equation is frequently referred to as the Gibbs-Thomson equation. Since the pressure is always higher on the concave side of the boundary, the chemical potential is always higher on the concave side and the atoms tend to diffuse across the curved surface to the convex side. This means that the curvature induced growth moves the boundary toward the concave side and grains grow toward their center of curvature.

Velocity of growth of a spherical grain is

$v = B \cdot F$

where B is mobility and F the driving force, which is in our case a difference in chemical potential over the thickness of grain boundary λ :

$F = \Delta \mu / \lambda$

since mobility is $B = D_b/KT$, the GB velocity is

$$v = \frac{D_b}{kT} \cdot \frac{V \cdot 2\gamma}{\lambda \; r}$$

At constant temperature the terms of this equation are constant so that we obtain the velocity proportional to radius of curvature as $v = c/r$, where c is the proportionality constant. If we assume that the radius of curvature of a grain is proportional to the diameter of the grain G, we may write

$v = \text{const.}\ (1/G) = dG/dt$

Integrating this equation we obtain:

$G^2 - G_o^2 = Kt$

where K is constant and G_o is the grain size at time zero. Rate constant K is exponentially dependent on temperature, since it incorporates $D_b = D \exp(-Q_b/RT)$, where Q_b is the activation energy for grain boundary diffusion.

In experimental work it is common to assume that G_o is negligible and to plot log G versus log t as obtained from a series of isothermal grain growth measurements at various temperatures. The resultant curves can usually be representable by an empirical relationship (8):

$G = K_o \exp(-Q/RT) t^n$

Simple theoretical treatment outlined above predicts the exponent $n = 1/2$ and $Q = Q_b$. However, very few grain growth studies in ceramics fit simple parabolic kinetics, or even fit $G = Kt^n$ over a significant range of G. The reasons for these discrepancies are numerous. Deduction of theoretical expression involved several assumptions, which are not necessarily correct. Those assumptions are the following (2):

1. The mobility of all grain boundaries is equal and independent of grain size.
2. The surface energy of all grain boundaries is equal and independent of grain size.
3. The shape of the grain size distribution curve is independent of grain size.
4. $(1/r_1 + 1/r_2)$ is proportional to $(1/G)$, where G is the average grain diameter.
5. The rate of disappearance of grains is proportional to grain boundary velocity.
6. Grain growth will continue indefinitely.

Even when the experimental results were in accordance with the parabolic kinetics, it was found that n is generally less than 1/2. It was reported to be equal to 1/2 for very high purity metals at high temperatures. Values less than 1/2 are in ceramics usually ascribed to impedement of grain boundary movement by impurities and inclusions.

4. Influence of impurities

Impurities can have a great effect on grain growth kinetics even if they are present in amounts below the solid solubility limit. Aust and Rutter (9) demonstrated that very small amounts of impurities can drastically reduce the grain growth rate of pure materials. Yan at all compared grain boundary mobilities, estimated from grain growth studies, with calculated intrinsic mobilities and confirmed strong impurity drag effect (4). Since ceramic materials are likely to be contaminated with impurities, experimental measurements of intrinsic grain boundary mobilities are extremely difficult to perform with accuracy.

Brook (10) applied Cahn's (11) impurity - drag effect to grain growth. He assumed $dG/dt \propto v/G$ and found that $G^3 \propto t$ should hold for large impurity levels, small grain size, and small impurity solubility. Inverse values should be in favor for $D^2 \propto t$ relationship. Exact derivation considering the effect of impurity drag on grain growth was not done.

5. Influence of inclusions

It is commonly known that a dispersion of a second phase particles will impede grain boundary movement. Pores effect grain boundary movement in a similar way as second phase particles. This may explain slow grain growth in early stage of sintering, when porosity is high. When the grain boundary moves past the inclusion, new grain boundary equal in area to the cross - sectional area of the inclusion must be formed. Because of this,

the particle might be considered to exert a restraining force per unit area P on the grain boundary proportional to the number per unit volume n and cross sectional area A of the inclusions uncountered:

$$P = n A \gamma$$

When the restraining force is balanced by the driving force, γ/G, growth will stop:

$$\gamma/G = n A \gamma$$

The cross - sectional area A of an inclusion is equal $\pi d^2/4$, where d is the inclusion diameter, and the number of the inclusions per unit volume is given by

$$n = \frac{f}{4/3\,\pi (d/2)^3} = \frac{6\,f}{\pi\, d^3}$$

where f is the volume fraction of inclusions. By substitution we obtain

$$G_{lim} = \frac{2}{3}\,\frac{d}{f} \approx \frac{d}{f} \qquad /2/$$

Where G_{lim} is the average grain size when a uniform dispersion of inclusions just prevents grain growth. Expression /2/ proposed by Zener (12), points out the important fact that a grain size can be stabilized by the presence of inclusions. Further grain growth can occur if the inclusions increase in size by coalescence i.e. the large ones grow by diffusion of atoms from the small ones along the grain boundaries or through the bulk of the host matrix. Grain growth can occur also when volume fraction of inclusions decreases with time, for example by dissolution in the host matrix.

6. Influence of pores

It was already mentioned that pores may impede the grain growth in a similar manner as particles. The pores may effectively stop the grain boundary, they may be dragged along with moving boundaries or they may remain behind the boundaries. Brook (3) analyzed the kinetics of grain boundary motion in presence of pores. If the pores are attached to the grain boundary, the boundary velocity v_b must be equal to the pore velocity, v_p, giving

$$v_p = F_p M_p = v_b = M_b(F-NF_p)$$

and $v_b = F\ M_b M_p / NM_b + M_p$

Two limiting cases can be considered:

When $NM_b >> M_p$, $v_b = F_b\ M_p/N$

Grain boundary motion is limited by pore mobility

When $NM_b << M_p$, $v_b = F_b M_b$

Grain boundary motion is limited by boundary mobility.

The maximum force which can be exerted on a spherical pore by an attached grain boundary is $\pi r \gamma$, where r is radius of GB curvature When the grain boundary moves at a velocity $v_b > v_{p\,(max)} = M_p \pi r \gamma$, it separates from the pores and isolated pores appear within the grains.

Large pores are less mobile than the smaller ones. In coarse grain size ceramics, where driving force for GB movement is low, pores will stay attached to the boundary and control the grain growth. For higher driving forces, pores may stay behind the boundaries and grain growth will depend on GB mobility.

Smaller, more mobile pores may remain attached to the boundary without exerting a significant drag on the boundary.

7. Grain growth in presence of liquid phase

Mechanism of grain growth in presence of wetting liquid is transfer of matter from small to larger particles. Driving force is reduction of the free energy associated with the particle/liquid interface area. Smaller particles have a higher free energy and thus the ions dissolve into the liquid and precipitate on the surface of larger particles which have lower free energy due to smaller curvature. Phenomenon is known as Ostwald ripening.

Difference in solubility C due to curvature is expressed by equation.

$$C = \frac{2\ \gamma\ V\ C}{R\ T\ r}$$

where r is particle radius, V molar volume and C solubility in contact with the flat surface. The rate of grain coarsening may be dependent on (a) diffusion through the liquid layer and (b) surface reaction rate.

When diffusion through the liquid layer of thickness l is rate limiting,

$$v = \frac{D_l C_l}{l} \cdot \frac{VF}{kT}$$

where D_l means diffusion coefficient through the liquid phase. On the other hand, when the grain coarsening is controlled by the surface reaction rate:

$$v'_l \quad \frac{V}{kT} \cdot F \cdot K$$

where K means the reaction constant, which is generally exponentially dependent on temperature but also depends on the particular kinetic process. It may be dependent upon orientation and driving force (4).

It is frequently observed that the liquid phase may enhance the groth rate. When some grains are surrounded by the liquid phase while others are not, non uniform structures envolve. When the amount of liquid is small, it may be hard to detect it in the final microstructure. Faceted grains may be an indication that growth from the liquid ("flux growth") has taken place. Most nonuniform microstructures showing large faceted grains are assumed to occur by growth with a liquid phase (5).

8. Discontinuous grain growth

Discontinuous growth occurs when some small fraction of the grains grow to large size, consuming the uniform grain size matrix. Usually, this results in non-uniform microstructures, although not necessarily. More detailed review of phenomena involved in discontinuous growth is given in textbooks (13). We also refer to a recent review paper, where discontinuous growth in $BaTiO_3$ - based ceramics is discussed in more detail (14).

9. Grain growth control

The basic technique employed for control of the growth process is use of additives to surpress the discontinuous growth. Additives may enter into solid solution with the host matrix or stay as a second phase (Fig. 4). In both cases they influence the GB mobility. Several other techniques has been successfully employed in particular systems, such as change in stoichiometry, usually by controlling the atmosphere, further control of the heating rate, particularly first firing. Successfull method is also hot pressing. Several examples of grain growth controll will be given in further lectures.

In conclusion we may say that the scientific understanding of microstructure evolution is quite advanced; On the other hand its effect on technological applications is mainly qualitative and the development in practical systems is still largely empirical. However with accumulation of data and availability of sophisticated characterization methods the understanding of phenomena in particular systems is constantly improving and it is to be expected that the basis for more quantitative approach will improve in the near future.

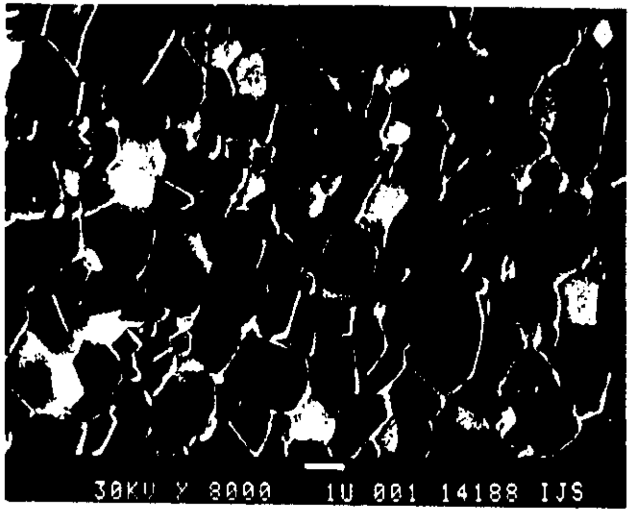

Fig. 4. ZrO_2 - inclusions in Al_2O_3 matrix, sintered 1,5 hours at 1600°C

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DISCONTINUOUS GRAIN GROWTH IN MULTIPHASE CERAMICS

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ABSTRACT

Very few grain growth studies in ceramics fit simple parabolic kinetics which theory predicts for normal grain growth. Although abnormal grain growth may be caused by several factors, it is particularly likely to occur in the presence of small unevenly distributed amounts of liquid phase. The amount of liquid phase may be so small that it may remain unnoticed.
In the present work, discontinuous grain growth in doped $BaTiO_3$ ceramics in the presence of a small amount of liquid eutectic was analysed by studying the sequence of microstructural changes with time and temperature. It is shown that various additives, i.e. Sr^{2+} and Ca^{2+}, influence microstructure evolution in opposite ways. The data are analysed in terms of nucleation and the growth process and a possible explanation is proposed.

INTRODUCTION

In 1961, Coble demonstrated that a small addition of MgO enables sintering of Al_2O_3 to near theoretical density (1). Without MgO, Al_2O_3 exhibits discontinuous grain growth which results in pore entrapment and poor densification. Although the phenomenon of discontinuous grain growth in ceramics was already recognized, the importance of Coble´s achievement triggered many studies on microstructure evolution during sintering.

The present work addresses complex phenomena of discontinuous grain growth during heat treatment of a $BaTiO_3$ ceramic containing a small amount of liquid phase. It is likely that the phenomena observed in this particular system may be governing microstructure development in many other systems which sinter in the presence of a small amount of liquid phase. It is believed that such conditions often occur unintentionally, i.e. due to unregistered impurities.

Paper presented [illegible]th meeting of The American Ceramic Soc., Cincinnati [illegible] to be published in Proceedings)

PHENOMENON OF DISCONTINUOUS GRAIN GROWTH

It is well known today that very few grain growth studies in ceramics fit simple parabolic kinetics which theory predicts for normal grain growth. Although the reasons in some cases remained unexplained (2), it has been frequently observed that the grain growth was not normal.

Abnormal or discontinuous grain growth (sometimes called secondary recrystallization or exaggerated grain growth) is characterised by rapid growth of a limited amount of grains to sizes much larger than those of the average grain population. It is particulary likely to occur when normal grain growth is inhibited by the presence of impurities and pores (3). It may originate from many possible causes, such as a wide initial particle size distribution, a small amount of liquid phase, chemical heterogeneity, heterogeneous density distribution, intrinsic boundary properties (preferential grain boundary mobility) and others.

A characteristic feature of discontinuous grain growth is a bimodal particle size spectrum, at least during the intermediate stage of the sintering process. Another characteristic is that discontinuously growing grains grow at a constant rate, frequently very rapidly, until they impinge on other rapidly growing grains and the growth rate abruptly slows down to a value encountered in normal grain growth. Thus, the resulting grain size is controlled only by the number of secondary grains that are nucleated and not by the time of heating (4). It was pointed out that a uniform microstructure can eventually evolve from a discontinuously growing duplex structure, when all the small grains disappear in favour of the large ones (5). However, in most cases such microstructures preserve a broad grain size distribution because all grains do not start to grow simultaneously. Still, many cases of discontinuous grain growth may go unnoticed because only final microstructures were examined.

Discontinuous grain growth is particularly likely to occur in the presence of a small amount of liquid phase. Generally, the grain growth mechanism in the presence of liquid phase is described as Ostwald ripening, rather than due to surface curvature induced grain boundary mobility (6,7). Ostwald ripening is caused by the difference in solubility for particles of different size,which causes matter to be transported from the smaller to the larger particles. The rate of particle coarsening may depend; (a) on diffusion through the liquid layer between the particles, or (b) on surface reaction,i.e. dissolution and precipitation.

When the amount of liquid phase is large enough to enable a uniform distribution of wetting liquid among the solid grains, analysis of "normal" grain growth predicts the cube of the grain size G to be proportional to the time: $G^3 \propto t$. This relationship has been experimentally confirmed, for example in (8,9).

However, with decreasing amount of liquid phase, normal grain growth may change to abnormal,although the chemistry of the system may not change. For example,Carpay and Stuijts presented microstructure of ZnO - 6 % Bi_2O_3 ceramics, as an example of uniform microstructure produced by continuous evolution in the presence of relatively much liquid phase (5). On the other hand, in the similar system Wong observed exaggerated grain growth, which occured in the range 0,05 - 0.5 mol % Bi_2O_3 (10).

The abnormal grain growth observed to occur in the presence of a small amount of liquid phase is believed to be caused by the combined effects of the heterogeneous distribution of the limited amount of liquid, and the presence of grains much larger than the average population. A favourable combination of wetting liquid and a large grain serves as a nucleation site for rapid growth. The growth rate of large grains dG/dt in the case where diffusion through the liquid layer of thickness δ is rate limiting may be expressed as (11):

$$\frac{dG}{dt} \simeq \frac{2\gamma VDC}{\delta RT} \cdot \frac{1}{r} \qquad /1/$$

where D is the diffusion coefficient through the liquid phase, C the saturation solubility, V the molar volume of solute, γ the surface tension and r the radius of matrix grains.

Equation /1/ shows, in accordance with experimental observations of discontinuous growth (4), that the growth rate of large grains in stationary state does not depend on time. It also shows that the growth rate is inversely proportional to matrix grain size, as already noted by Kingery at al (3). Further, the equation shows that the growth rate is enhanced by decreasing thickness of the liquid layer and increased by increased solubility of the solid matter in the liquid phase.

On the other hand, when the process is controlled by the surface reaction rate (7):

$$\frac{dG}{dt} \simeq \frac{2\gamma V}{RT\ r} \cdot K \qquad /2/$$

where K is the reaction constant, which is generally exponentially dependent on temperature, but also depends on the precise kinetic process, and may be dependent upon the orientation of growing crystal planes.

Faceted (straight sided) grains frequently result from rapid discontinuous grain growth in the presence of a liquid phase. Such grains may be anisotropic instead of equiaxed. The simultaneous occurence of large faceted grains and a wetting liquid phase has been found in many systems, e.q. relatively pure Y garnet (11), iron oxide and manganese zinc ferrite (5), Ba-doped $SrTiO_3$ (12) and others. Faceted grains, instead of cusped boundaries, may be an indication that flux growth has taken place, although the liquid layer was so thin that it may not have been detected. Therefore most non-uniform microstructures showing large faceted grains are assumed to occur by growth with a liquid phase (5,11). However, cases were reported when other causes for straight sided boundaries must be sought (2,13).

EXPERIMENTAL

The $BaTiO_3$ used in this research was electronic grade with a Ti/Ba ratio close to 1. An excess Ti (2 mole %) was added to ensure an adequate amount of liquid phase and improve its homogeneous distribution. To avoid the possible influence of chemical reaction, the excess Ti was added as prereacted $Ba_6Ti_{17}O_{40}$, although control experiments did not show any essential difference when Ti was introduced as TiO_2. Compounds used as additives ($Ba_6Ti_{17}O_{40}$, $CaTiO_3$, $(Ba_{1-x}Ca_x)_2Ti_5O_{12}$ and $Ba_2(Ti_{1-x}Zr_x)_5O_{12}$ were synthesised at 1250°C from the corresponding carbonates and oxides and confirmed by X-ray analysis. $SrTiO_3$ was commercial reagent grade.

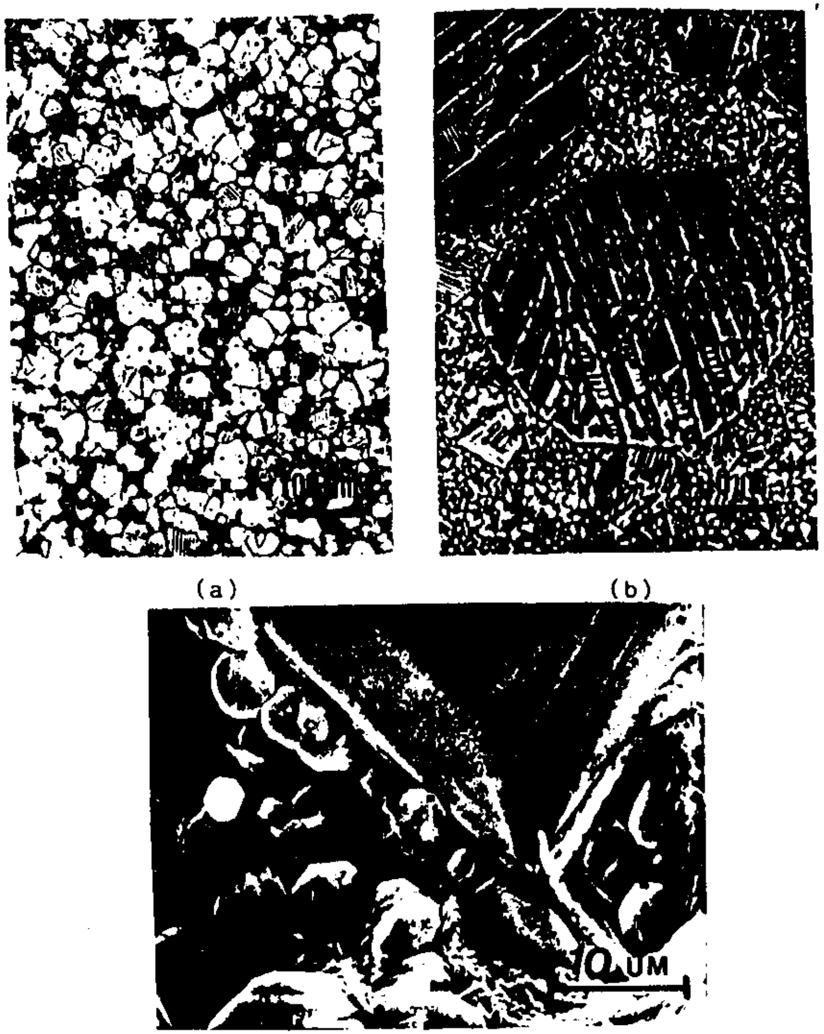
The various powders were mixed together and milled in alcohol, granulated with the addition of camphor, pressed into pellets and sintered at 1300°C for 1 hour to 92-95 % of theoretical density. At this temperature, grain growth was not significant and the average grain size, measured as the average intercept length, remained at about 1 um. Microstructure evolution was studied on samples which, after densifying for 1 hour at 1300°C, were pushed into the furnace hot zone at the desired temperature, which was kept constant to better than + 3°C. After annealing, which lasted from 5 minutes to several hours, the samples were quenched to a lower temperature. The microstructure was studied on polished and etched specimens. The grain size was determined from micrographs by the lineal intercept method. The maximum grain sizes were determined by measuring the area of the large grains and expressed as the equivalent circle diameter. The nucleation rate was estimated by counting the number of nuclei per unit area of photo micrograph. Grains were defined as "nuclei" when their diameters were a factor of 5 larger than the surrounding matrix grains. The specimens were also examined with a JEOL 2000 FX electron microscope equipped with a rotating tilting stage.

RESULTS AND DISCUSSION

$BaTiO_3$ is one of the first ceramic materials for which anomalous grain growth was recorded (14). $BaTiO_3$ based ceramics are normally sintered with a small excess of TiO_2 to promote densification. The TiO_2 excess reacts with $BaTiO_3$ to form $Ba_6Ti_{17}O_{40}$ which subsequently reacts with $BaTiO_3$ to create a eutectic melt at about 1320°C. The liquid phase triggers discontinuous grain growth which results in coarse - grained structure. With increasing amount of liquid phase, anomalous grain growth gradualy changes to normal and average grain size in sintered $BaTiO_3$ ceramic decreases (15). The largest average grain size with broad distribution was registered in $BaTiO_3$ ceramics with Ti/Ba ratio ~1 (16).

Fig. 1 a shows a typical bimodal grain size distribution in $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ ceramic after 20 minutes firing at 1350°C. Larger magnification (Fig. 1 b) shows that abnormal grains are faceted. The fracture surface (Fig. 1 c) shows large faceted growing grains and small matrix grains embedded in a solidified eutectic, thus supporting the proposed dissolution - precipitation mechanism of grain growth (17).

In flux growth, it is usually observed that nucleation of large grains and their rapid growth starts soon after the temperature of the liquid phase is exceeded. $BaTiO_3$-$Ba_6Ti_{17}O_{40}$ eutectic melts at about 1320°C and rapid nucleation and grain growth in $BaTiO_3$-$Ba_6Ti_{17}O_{40}$ ceramic has been observed at temperatures of 1330°C - 1350°C. In this temperature interval, Hennings reported an exponential increase in the number of discontinuously growing grains and a linear growth of large grains with time, at least up to 20 % of recrystallized area (18).



(a) (b)

(c)

Fig. 1. Discontinuous grain growth in $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ composition, fired at 1350°C for 20 minutes
a) magnification 110x, (b) magnification 1150x, (c) SEM Fractograph (sample fired 2 hours at 1350°C)

Discontinuous grain growth caused broadening of the grain size distribution curve and appearance of a bimodal type of distribution, as expected (Fig. 2).

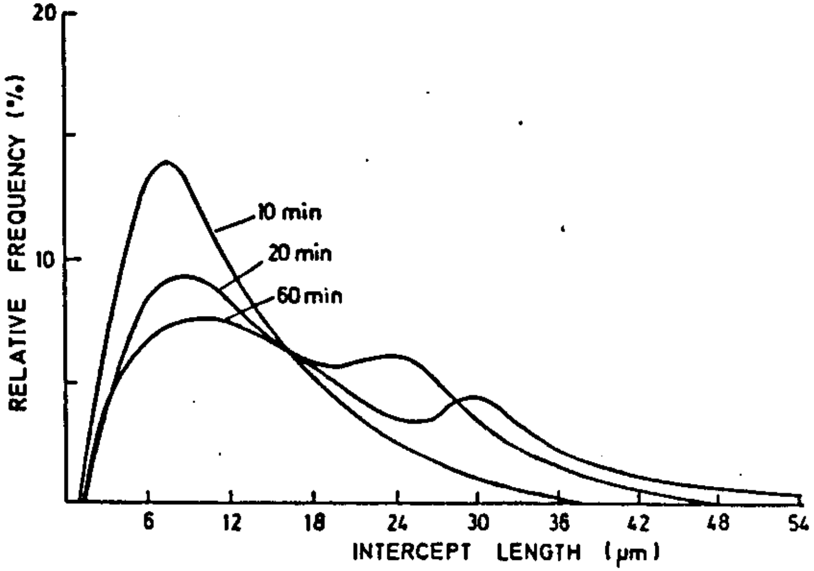
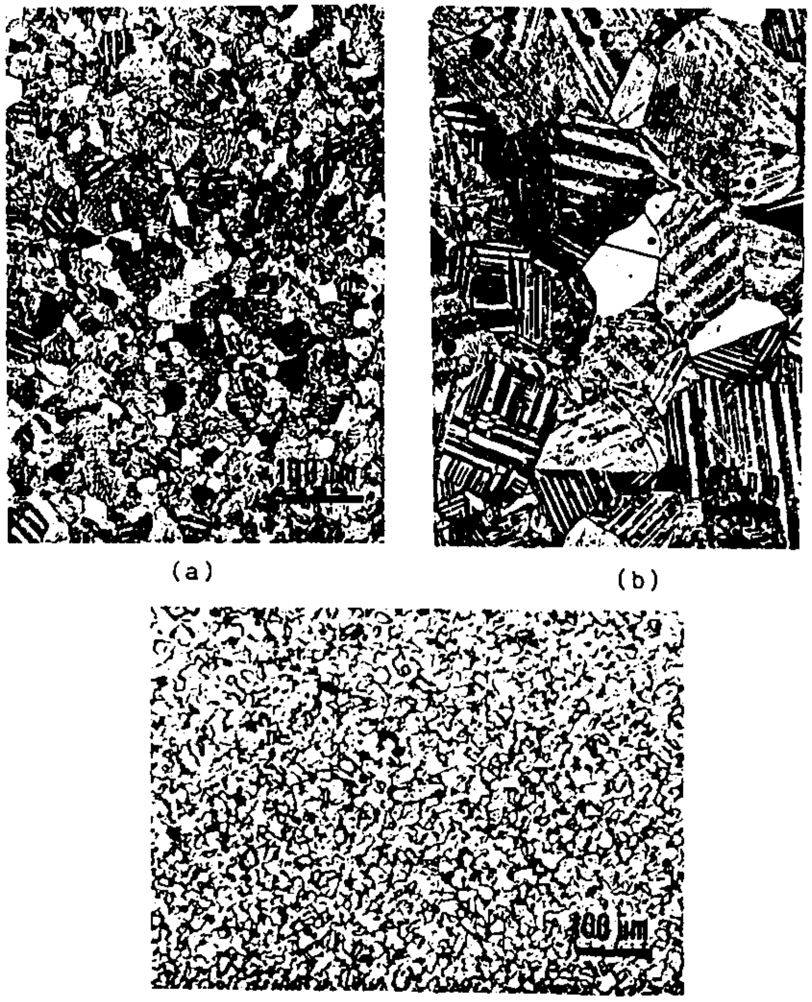


Fig. 2. Grain size distribution in sintered $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ samples after heat treatment at 1350°C

The growth rate of discontinuously growing grains was approximately 6 µm min^{-1}; however, due to impingement of grains the growth rate decreased considerably after only 10 minutes. After impingement, the grain growth rate was extremely slow. The average intercept length after 24 hours at 1350°C was 21 µm.

Figs. 3 a - 3 c show the influence of 8 mol % $CaTiO_3$ and $SrTiO_3$ additions, respectively, on the microstructure of $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ ceramic sintered 24 hours at 1350°C. The addition of $CaTiO_3$ strongly increases the final grain size, and the addition of $SrTiO_3$ reduces it (19,16). Whereas reduction of grain size due to additives is



(a) (b) (c)

Fig. 3. Microstructures of $BaTiO_3$ ceramics after heat treatment 24 hours at 1350°C
(a) $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$
(b) $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ - 8 mol % $CaTiO_3$
(c) $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ - 8 mol % $SrTiO_3$

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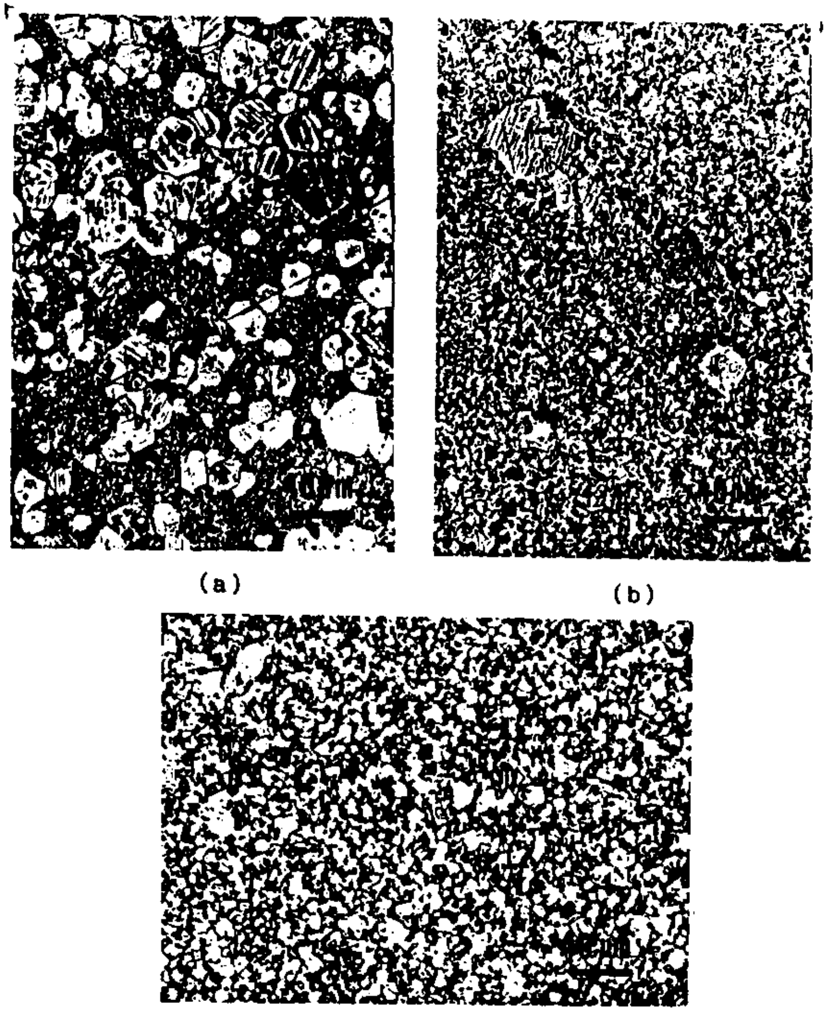

(a) (b) (c)

Fig. 4. Microstructures of $BaTiO_3$ ceramics after heat treatment 10 minutes at 1340°C
(a) $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$
(b) $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ - 8 mol % $CaTiO_3$
(c) $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ - 8 mol % $SrTiO_3$

a common phenomenon in ceramics, the coarsening influence of $CaTiO_3$ is unusual. In contrast, it was reported (20) that $CaTiO_3$ addition to PTCR ceramics based on a $BaTiO_3$-$PbTiO_3$ solid solution containing, besides Y_2O_3 dopant, 2 mol % SiO_2 and 0.5 mol % TiO_2 inhibits the grain growth. It is obvious that the influence of $CaTiO_3$ on microstructure development depends on the grain growth mechanism, firing conditions and composition.

Fig. 4 shows microstructures of undoped, Ca-doped and Sr-doped ceramics, respectively, after short heat treatment (10 minutes) at 1340°C. It is obvious that the additives influence the nucleation rate of discontinuously growing grains in opposite ways. Relevant data are given in Table 1.

Table 1: Characteristic data on microstructure development in the systems: (A) $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$; (B) $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ - 8 mol % $CaTiO_3$; and (C) $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ - 8 mol % $SrTiO_3$

	A	B	C
Average grain size after 24 hours at 1350°C (μm)	21	58	5
Average nucleation rate in the first 10 minutes at 1350°C ($N\ mm^{-2}min^{-1}$)	120	2	220

Addition of 8 mole % $CaTiO_3$ to the $BaTiO_3$-$Ba_6Ti_{17}O_{40}$ composition greatly reduced the nucleation rate of discontinuously growing grains. These grains could grow unhindered to comparatively large size, the maximum size of the grains exceeding 300 μm. On the other hand, addition of 8 mole % $SrTiO_3$ caused a high nucleation rate with consequent early impingement of discontinuously growing grains. The microstructure remained fine grained even after prolonged sintering.

The final grain size is influenced by the relative values of the rate of nucleation $\dot{N}$ and the rate of growth of nuclei $\dot{G}$. If the ratio of $\dot{N}$ to $\dot{G}$ is large, the final grain size will be small. Conversely, if the ratio of $\dot{N}$ to $\dot{G}$ is small, the final grain size will be large. Both rates strongly depend on processing parameters such as the composition, the amount of liquid phase and temperature.

Analysis of microstructure evolution in undoped and doped $BaTiO_3$ samples at various temperatures revealed that the grain growth rate was not particularly sensitive towards increase in temperature, whereas the nucleation rate strongly increased, as already noted (18). Consequently, the ratio $\dot{N}/\dot{G}$ increases with temperature resulting in finer final microstructures, as shown in Fig. 5. This curve confirms that a finer grain size may be achieved by avoiding the critical temperature region in which ratio $\dot{N}/\dot{G}$ is low. The temperature dependence presented is similar to that already reported by Matsuo and Sazaki (21), who observed exaggerated grain growth in $BaTiO_3$ doped with TiO_2, SiO_2, and Al_2O_3 in the temperature region of 1240-1250°C. In their case, the eutectic temperature was estimated to be at 1240°C. Fig. 5 may also explain different conclusions regarding the influence of $CaTiO_3$ on grain growth in doped $BaTiO_3$ ceramics, since the experiments were performed at different temperatures.

The reason for the contrasting influences of $SrTiO_3$ and $CaTiO_3$ addition, on the nucleation rate of discontinuously growing grains in TiO_2-excess $BaTiO_3$ ceramics seems to be the different chemistry in the $BaTiO_3$-TiO_2-$SrTiO_3$ and $BaTiO_3$-TiO_2-$CaTiO_3$ systems.

The systems differ from each other in several aspects. Relevant for this investigation are the facts that whereas $BaTiO_3$ and $SrTiO_3$ exhibit solid solubility at all compositions, $BaTiO_3$ and $CaTiO_3$ are soluble only to a limited extent. The second major difference is the existence of a Ca-stabilized $Ba_2Ti_5O_{12}$ phase in the BaO-CaO-TiO_2 system, which was not found in the BaO-SrO-TiO_2 system (22).

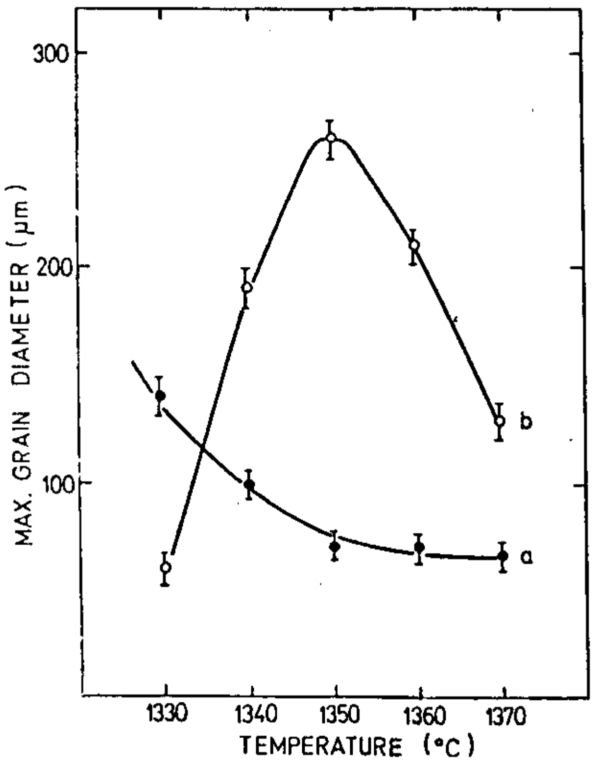

Fig. 5. Influence of firing temperature (2 hours) on diameter of the largest grain in microstructure of
(a) $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ and
(b) $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ - 8 mol % $CaTiO_3$ ceramic

TEM analysis of sintered $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ - 8 mol % $SrTiO_3$ and $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$ - 8 mol % $CaTiO_3$ revealed the presence of a Ca- stabilized $Ba_2Ti_5O_{12}$ phase in the Ca-containing ceramics. Such a phase could not be identified in Sr-containing ceramics (23).On the basis of TEM and SAED examinations the $Ba_2Ti_5O_{12}$ phase in the Ca-containing $BaTiO_3$ ceramic was found to be orthorhombic, with unit cell parameters closely related to the d_{hkl}'s of the $BaTiO_3$ phase (24).

It is proposed that the close similarity of $BaTiO_3$ and Ca-stabilised $Ba_2Ti_5O_{12}$ causes absorption of Ca-containing phase on the surface of $BaTiO_3$ grains thus diminishing the nucleation rate. In the concentration range studied, the effect is the same as that caused by the decrease in the amount of $Ba_6Ti_{17}O_{40}$-$BaTiO_3$ eutectic, which accounts for the coarse grained structure after prolonged sintering. On the other hand, addition of $SrTiO_3$ does not destabilize $Ba_6Ti_{17}O_{40}$ phase; it causes a monotonic decrease in the grain size of $(Ba,Sr)TiO_3$ ceramic by accelerating the nucleation rate.

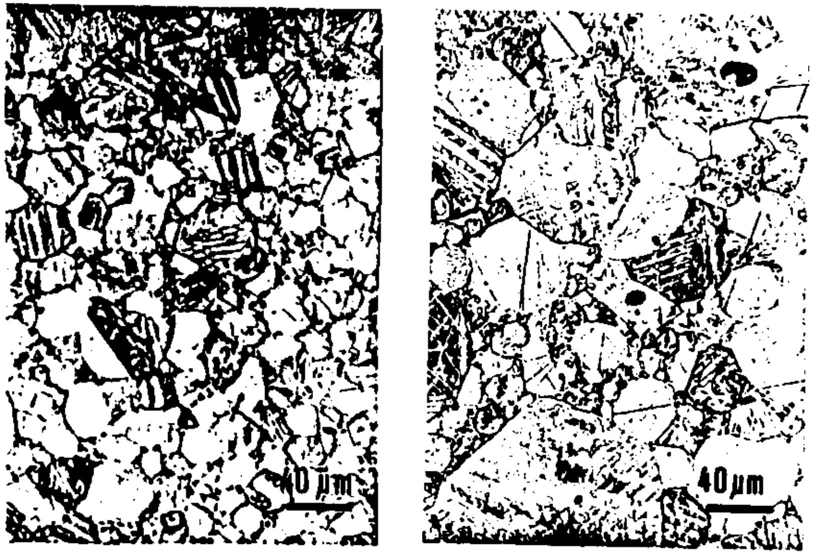

Fig. 6. Influence of Zr^{+4} on ceramic microstructure in the system $BaTiO_3$-TiO_2 (230x). Firing 1345°C, 24 hours. (a) $BaTiO_3$ - 2 mol % $Ba_6Ti_{17}O_{40}$, (b) $BaTiO_3$ - 2 mol % $Ba_2(Ti,Zr)_5O_{12}$

The existence of $Ba_2Ti_5O_{12}$ phase was also reported in the BaO-TiO_2-ZrO_2 system (25). A Zr^{4+} stabilized $Ba_2Ti_5O_{12}$ phase was recently confirmed (26). Since Ca-stabilized $Ba_2Ti_5O_{12}$ is isomorphous with ZrO_2 stabilized $Ba_2Ti_5O_{12}$ with a similar unit cell, it was speculated that ZrO_2 addition may coarsen the grain size of $BaTiO_3$ ceramic in a similar way to $CaTiO_3$. Preliminary experiments confirmed expectations, as shown in Fig. 6.

CONCLUSIONS

Abnormal grain growth is difficult to understand because of the many possible causes involved, and a general lack of detailed microstructural evidence. Discontinuous growth is particularly likely to occur in the presence of a small amount of unevenly distributed liquid phase. The present work was an attempt to illustrate phenomena of discontinuous growth in the presence of liquid phase by studying microstructure evolution in TiO_2-excess $BaTiO_3$ ceramics. It was observed that additions of $SrTiO_3$ cause microstructure refinement, whereas $CaTiO_3$ additions cause coarsening of microstructure. The mechanism of grain growth was analysed in terms of the nucleation and growth process, and it was shown that $CaTiO_3$ influences microstructure evolution by decreasing the number of nucleation sites, whereas $SrTiO_3$ causes uniform growth.

A possible reason for the decrease in the number of nuclei for discontinuous growth in the presence of $CaTiO_3$ additive is the formation of Ca-stabilised $Ba_2Ti_5O_{12}$ phase. It is proposed that $Ba_2Ti_5O_{12}$ phase hinders nucleation by absorption on the surface of $BaTiO_3$ grains. In this way, the effect is equivalent to a decrease in the amount of liquid phase. It is further shown that microstructure evolution strongly depends on temperature, because the nucleation rate increases with temperature faster than the growth rate.

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ON THE ROLE OF SINTERING RESEARCH IN CERAMIC ENGINEERING *

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1. INTRODUCTION

In September 1971, the Second International Round Table Meeting organised by the International Team for studying sintering (ITS), was held in Herceg Novi, Yugoslavia. One of the focal points was the session "Application of Sintering Theory in Practice". After an opening thesis, lively discussion followed. 13 contributions, together with the opening paper were summarized in the report issued after the Conference[1].

As is almost unavoidable on such occasions, the gap between most of the research work devoted to the sintering process (sintering theories) and the requirements of practical sintering processes in powder metallurgy and the ceramic field was discussed. Among other views, an opinion was repeatedly expressed that scientists are often unaware of the practical problems since industry keeps most of its know-how as unpublished proprietary information. In this respect, it was proposed that a catalogue of practical questions and problems should be put down and discussed.

In the meantime, many practical problems have been successfully solved, or at least, the fundamental approach to those solutions has been found and described. The importance of theoretical work has been recognized. The paper presented by Stuijts at the 3rd Notre Dame Conference may well serve as an example[2]. On the other hand, it was also confirmed that the data base and

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* Mat. Sci. Res 13, Plenum Press New York 1980

modelling are inadequate to predict quantitatively the kinetics of densification and grain growth for most systems of practical interest[3]. It seems that solution of a particular sintering problem will never be possible on a routine basis. If this is the case, continuous evaluation of new data and the practical problems solved may be an important(perhaps the only?) way to speed up considerably the solution of yet unsolved and future problems.

In this paper, we shall shortly review the limitations of the theoretical approach and confront it with some sintering problems from current industrial practice. Some problems which remain a particularly challenging area of ceramic science will be indicated.

2. LIMITATIONS OF THE FUNDAMENTAL STUDIES AND PRACTICAL REQUIREMENTS

Recent developments in the understanding of sintering and grain growth phenomena in ceramics have been reviewed on several occasions[5-6]. Much information on the sintering process of a given material may be collected from model experiments with well defined, chemically homogeneous material. In such cases, the basic sintering mechanism may be recognized and the kinetics of densification in the first sintering stage compared with equations containing the relevant parameters of the process. The extension of model experiments to practical cases represented by powder compacts usually involves several assumptions, which are rarely met in practice. In fundamental studies, we assume:

1. Pure, chemically homogeneous starting powder
2. Uniform, small, spherical grains
3. Homogeneous compact
4. Sintering at constant temperature high enough to achieve desired mass transport.

On the contrary, the main characteristics in practical sintering are:

1. Impure powders, usually chemically inhomogeneous mixtures
2. Non-uniform particle size, with size distribution dependent on the milling unit used, the shape of particles being influenced by crystal structure
3. Compacts with complicated geometry and non-uniform density distribution
4. Sintering at practically non-isothermal conditions, with limited time at maximal temperature.

And yet the practical aim is to prepare a mechanically strong, dense or intentionally porous sample with determined stoichiometry, chemically homogeneous (sometimes intentionally non-homogeneous) with controlled grain size (small or large, but always uniform) with porosity located as desired (among the grains or within the grains) and small, always reproducible firing shrinkage.

The industrial ceramist, confronted with such requirements, can not solve the problem on the basis of theoretical principles. However, he makes use of phenomenological relations which stem from theoretical analysis or from practical observations. On the other hand, although in many practical cases the models and fundamental sintering principles were a good guide in fabrication of special products, there remain several important manufacturing variables where theoretical fundamentals are almost nonexistent or at last lacking. The essentials of two such problems will be discussed in the following review, i.e. sintering in multicomponent or impure systems and nonisothermal sintering.

3. PRESENTATION OF SOME PRACTICAL SINTERING PROBLEMS

Ceramics for modern electronic applications pose particularly challenging problems for ceramists. We will briefly describe some problems which have been quite sucessfuly solved on the basis of tedious experimental work and the general applications of sintering science.

The following problems will be briefly discussed:

1. Preparation of dense, small grain size ceramics: hard ferrites
2. Preparation of dense, large grain size ceramics with residual pores located at grain corners: high permeability soft ferrites
3. High density, small grain size ceramics with some degree of chemical heterogeneity: high permitivity ferroelectric ceramics
4. Dense, heterogeneous ceramics with grain size adapted to the particular requirements: voltage dependent resistors.

The requirements described above are mostly incompatible from the standpoint of sintering knowledge as applied to simple systems. Therefore, complex formulations are developed to meet the requirements and optimize the properties. Two additional requirements must be considered: raw materials of commercial purity are to be used and the reproducibility of the ceramic properties must be high.

3.1. Dense, small grain size ceramics: hard ferrites

So-colled "hard ferrites", manufactured from Sr or Ba hexaferrites ($MeO.6Fe_2O_3$) are widely used as permanent magnetic materials[7]. To achieve high remanence (Br) and high coercive force (Hc) a ceramic with high density and small grain size is required. From the viewpoint of sintering theory, it is clear that the combination of a low porosity and small grain size is extremely difficult to realize with the normal ceramic process. The most straightforward method of achieving this goal is hot pressing, which is, however, at present expensive and too complicated for large scale production of sintered parts.

Without using extra pressure during sintering, densification of hard ferrites is usually improved by sintering compositions with excess MeO[8], or in the presence of liquid phase produced by additives, such as Bi_2O_3[9], or SiO_2 and various silicates[10].

Formation of a liquid phase during sintering results in an enhancement of sintered density, which is an easily explained phenomenon. However, liquid phase during sintering generally tends to promote exaggerated grain growth, especially when the amount of liquid is limited and its distribution among the grains is not uniform. This general rule was confirmed also in the case of hard ferrite sintering. Iron oxide defficient Sr-hexaferrite ($SrOx5.5Fe_2O_3$) when sintered at the temperature above the eutectic temperature (1210°C), showed extremely rapid exaggerated grain growth[11].

Since the exaggerated grain growth reduces coercivity, the main task in preparation of hard ferrites became to control the microstructure development during sintering.

Today, a most effective and widely used additive in manufacture of hard ferrites is silica. Its effect, when first reported, was unexpected and at first could not be reconciled with general sintering principles. It not only promoted the densification presumably by the formation of liquid phase but also strongly retarded grain growth, especially in the direction normal to the hexagonal c-axis[12]. It may be noted that in ferrites, exaggerated grain growth is strongest in the direction normal to the c-axis, as may be judged from the observation of the appearance of platelet-shaped crystals in overgrown structure.

It was further observed that the amount of silica content was critical as regards the magnetic properties and that it was dependent on the content of the excess MeO in hard ferrites.

Several experimental research projects were launched independently to clarify the special effect of SiO_2 addition. At the 3rd Int. Symposium on Electrical and Magnetic Ceramics held at Noordwijkerhout in 1977, 4 reports on this subject were discussed.[13] Although the approaches were different the general picture which seemed to emerge fits into the general frame of sintering knowledge. Investigation of ternary systems $BaO-Fe_2O_3-SiO_2$ and $SrO-Fe_2O_3-SiO_2$ proved that the ternary eutectics in these systems lay below the sintering temperature of ferrites. The presence of a liquid second phase gives rise to fast shrinkage, in accordance with the previous observations. The solid solubility data and the estimation of the eutectic composition set the basis for understanding the criticality of SiO_2 additions and its dependence on ferrite substoichiometry[14,15].

The grain growth impeding effect was explained to be a consequence of formation of solid silicate on the surface of Sr ferrite grains[15]. This silicate phase formation occurs preferably on the most reactive faces parallel to the c-axis giving rise to preferential impeding of growth of these faces. This explains the appearance of microstructure, which does not contain large hexagonal platelets, typical for liquid phase sintering of hard ferrites.

3.2. Large grain size ceramics without intragranular porosity

Another practical case concerns ceramics with large grain size. Whereas the amount of residual porosity is not of prime importance, it is essential that the large grains are free from pores and that remaining pores are located at grain boundaries. This is known to be a case with high permeability Mn-Zn ferrites, which were reviewed on several occasions[16]. The theoretically supported working principle is, that grain boundary mobility, and thereby grain growth, in pure materials is controlled by pores which impede grain growth. To achieve uniform removal of porosity, sintering at low temperatures for a long time is recommended. However, this is not enough and the greatest problem is to avoid exaggerated grain growth, which results in large porous grains.

Beside the already discussed liquid-phase induced exaggerated grain growth, abnormal grain growth may result from too large a distribution of grain sizes in the starting material or, more often, from impurities. Impurities in solid solution may alter grain boundary mobility, or, as a second phase, may obstruct grain boundary mobility to a various degree. Non-uniform distribution of impurities or simple temperature effects such as increased solid solubility or the appearance of a thin liquid phase may trigger non-uniform grain growth.

So there have been posed additional requirements for preparation of high permeability ferrites besides that of long sintering time at low temperature. These requirements are (a) chemical homogeneity of the starting powder (b) narrow grain size distribution, and (c),the highest posible purity.

Impurity-induced exaggerated grain growth in manganese zinc ferrites was recently analyzed by Yan and Johnson[17]. The authors investigated the individual effects of 20 oxide dopants on microstructure development during sintering, and found that most of the dopants which promoted exaggerated grain growth formed a liquid phase with the ferrite. Exceptions were TiO_2 and SiO_2 which sustained the growth of exaggerated grains without a liquid phase. The authors proposed two possible mechanisms for the promotion of grain growth in Mn-Zn ferrites by TiO_2: (a) preferential grain-boundary segregation of Ti^{4+} ions to repel other segregants which are more detrimental to grain growth, and (b), increased pore mobility due to the creation of excess cationic vacancies by TiO_2 addition.

3.3. Dense, small grain size ferroelectric ceramics

Modified $BaTiO_3$ is traditionally used for manufacture of ceramic capacitors because of its exceptionally high dielectric constant. For this particular purpose, the ferroelectric properties are a disadvantage[18]. The existence of dielectric hysteresis makes the permittivity highly sensitive to the applied voltage, as well as to the ambient temperature. However, the ferroelectric properties are greatly surpressed in small grain size (about 1 μm or less) $BaTiO_3$ ceramics. Moreover, the permittivity, which is about 1200 for the "normal" coarse crystalline form, is increased to 2500-3000.

Today manufacturers usually provide $BaTiO_3$ with excess of TiO_2, below 1%. This amount is above the solubility limit of TiO_2 in $BaTiO_3$ at 1400°C. During sintering higher titanates with low melting point are formed. The appearance of liquid phase above 1320°C, even in limited amounts, cause rearrangement and faster transport through the liquid phase. Therefore, sintering is promoted. The excess of TiO_2 in $BaTiO_3$ in amounts below the solubility limit is regarded as promoting sintering also in the solid state, due to the formation of defect perovskite with A position vacancies[19].

A small quantity of intergranular liquid phase at the sintering temperature creates again the problem of exaggerated grain growth, probably by a flux growth as described by Kooy in the case of ferrites[20]. Various additives were introduced to prevent exaggerated grain growth yet allowing preparation of dense ceramics. Among recent results, the addition of small amounts of Dy_2O_3 (0.8 at %) proved to be most effective in preventing grain growth[21]. Dense ceramics with 97 percent theoretical density and an average grain size of 1.5 um were prepared by comparatively high temperature sintering (1450°C), without, however, any aid from the hot-pressing technique.

3.4. Dense, heterogeneous ceramics with grain size adapted to the particular requirements: Voltage Dependent Resistors

The metal oxide varistor, marketed in last ten years by several companies, is a complex multicomponent oxide ceramic composed of about 97 mole % zinc oxide. The remaining 3 mole % consists of metal oxide additives, among which Bi_2O_3 plays an essential role. A typical composition given by Matsuoka[22] contains 97 mole % ZnO, 1 mole % Sb_2O_3 and 1/2 mole % each of Bi_2O_3, CoO, MnO and Cr_2O_3.

The sintered ZnO varistor is a semiconductor device with highly non-linear current-voltage characteristics similar to back-to-back Zener diodes but with much greater voltage, current and energy handling capabilities. They are increasingly used to protect electronic circuits from transient voltages and for limiting surges that may appear on terminals of communication systems.

The varistor microstructure consists of ZnO grains, and solidified Bi_2O_3 phase among the grains and other phases depending on composition (Fig.1). From this structure, it was proposed that the Bi_2O_3 and other additives formed a liquid phase at a sintering temperature which permeated all the grain boundaries, wetting the zinc oxide grains and isolating the grains from each other. It was later recognized that the intergranular material does not completely wet the ZnO grains and that it concentrates primarily at the three- and four grain junctions[23]. A dihedral angle of about 60° was measured in this phase where it contacts ZnO grain boundaries. On the other hand, it was shown by Auger electron spectroscopy that bismuth does segregate to the ZnO grain boundaries, but the authors do not consider it to be in sufficient amount to be actually called a separate phase. Its properties are consistent with those of an adsorbed layer. The conduction mechanism and the electrical properties of ZnO varistors are explicable in terms of the existence of barriers at the ZnO grain boundaries.

While no conclusive evidence has been found that any of the secondary phases observed in the microstructure of varistor ceramics are responsible for the non linear electrical properties[24], they do, however, affect some varistor properties through their influence on sintering and grain growth.

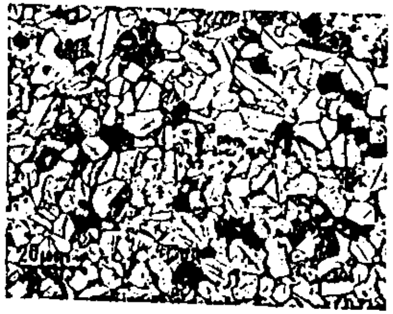

Fig. 1. Optical photomicrograph of a polished and etched section of a typical varistor.

For example, the varistor rated voltage is dependent on the ZnO grain size in the ceramic. The voltage per unit thickness is inversely related to the average grain size[24,25]. By using this relationship, the dependence of grain growth on firing conditions may be estimated and it was found that in the ZnO-Bi_2O_3-CoO varistor, the average grain size is proportional to time. On the other hand, for preparation of a desired varistor type, grain size control is necessary. This was achieved early[22] by the addition of Sb_2O_3 which was found to hamper grain growth.

Sb_2O_3 forms spinel $Zn_7Sb_2O_{12}$ dissolving Co and other possible components such as Mn and Cr[26]. These spinel particles are believed to play only a secondary role in determining device properties[27]; however, they seem to be effective in pinning the grain boundaries of ZnO grains, as shown in Fig. 2.

4. CONSEQUENCES OF CHEMICAL HETEROGENEITY

By now we are well aware that a minor dopant or impurity in a host material can drastically change the nature and concentration of defects, which can influence the kinetics of grain boundary motion, pore mobility and pore removal. Equally profound influence

Fig. 2. Varistor microstructure with spinel inclusions between the ZnO grains.

may be exerted by the second phase inclusions. Particular attention must be paid to possible interaction among various impurities. It is clear that effects of heterogeneities or "chemical sintering" are unpredictable. A few examples may be again quoted to better appreciate various influences.

An additive (impurity) may (a) stay in solid solution or (b) may remain as inclusion at the boundary or (c) initially as a second phase may dissolve at some stage during densification.

An additive in solid solution may alter the diffusion coefficient by modifying point defect concentration. On the basis of principles set forth by Ready[28] and Reynen[29], it seems possible to predict the influence of various additives provided that the type of principal defects is known. However, recently published results on the influence of Mg^{2+} and Ti^{4+} on sintering Al_2O_3 demonstrated the complexity of the problem[30]. It was shown that both ions could accelerate lattice diffusion of the Al^{3+} ion, which is considered to be the rate determining in the sintering of high purity Al_2O_3. In the case of Ti^{4+} addition, increase in cation diffusivity was early explained as a consequence of an increase in concentration of aluminum ion vacancies. On the other hand, the promoting effect of Mg^{2+} addition may be explained as a consequence of an increase in the amount of Al^{3+} interstitials.

Additives in solid solution may influence sintering by other mechanisms as well: For example, they may reduce the interfering effects of grain growth, by inhibiting boundary migration[31] or they may repel other segregates which are more detrimental to grain growth and thereby induce rapid boundary migration (TiO_2-MnZn Ferrite).[17] It was also proposed that additives in solid solution may affect the driving force for densification by altering surface energy/boundary energy ratio.[31]

As a second phase at host material grain boundaries, additives may act at the sintering temperature as solid or liquid inclusions and liquid films. As a solid second phase it may provide a high diffusivity path, as demonstrated in the system W-Ni or it may inhibit boundary migration by pinning. As a liquid second phase may decrease the rate of grain growth by decreasing the driving force for growth[32], or accelerate grain growth by a flux growth process[20].

Only a few examples were quoted, which suggest that each particular system must be treated separately and that solution of practical problems may not be expected to be achieved easily on the basis of present day sintering knowledge.

In general, heterogeneities of composition, even slight ones, oppose complete densification of the material and can lead to discontinuous grain growth. During sintering, homogenization of powder compacts occurs as a result of inter-diffusion of the components. In effect, since the diffusion coefficients of different elements are not identical, Kirkendall effect with migration of initial porosity and coalescence of pores takes place and slows down the sintering process.

As an example, we may mention the phenomena occurring during sintering in the relatively simple heterogeneous binary system, $BaTiO_3$-$SrTiO_3$[33]. Both compounds at sintering temperatures form solid solution in the whole composition range. Sinterability of the physical mixture and the prereacted solid solutions were compared and it was found that physical mixtures of $BaTiO_3$ and $SrTiO_3$ at all composition ratios sinter to lower density as compared with prereacted powders (Fig. 3). The reason was found in unequal diffusion coefficients of Ba^{2+} and Sr^{2+} ions. As a result, phases not in thermal equilibrium were created, which in turn caused mass transport from $BaTiO_3$ grains into $SrTiO_3$ grains. Excess vacancies thus formed coalesced into Kirkendall type porosity and caused deformation in neck geometry (Fig. 4) in a similar way as in metallic systems observed by Kuczynski and Stablein.[34]

Microstructures of the sintered powder mixtures of $BaTiO_3$ and $SrTiO_3$ contained large pores even after prolonged sintering. Accelerated grain growth was observed in $SrTiO_3$ regions (Fig. 5) which were in contact with the $BaTiO_3$ grains, indicating the increased grain boundary mobility.

Manganeze zinc-ferrites and the hexagonal ferrites briefly discussed above may be also mentioned as known practical examples of the harmful effect of chemical heterogeneity on sintering, porosity distribution and grain growth[36].

As a practical consequence of the awarenes of the problems associated with sintering of chemically nonhomogeneous powders, numerous methods have been

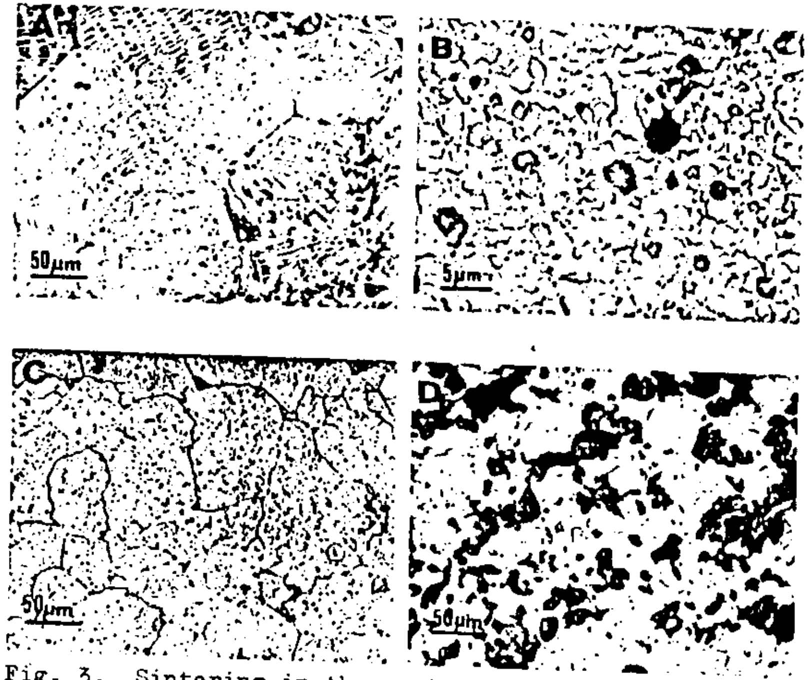

Fig. 3. Sintering in the system $BaTiO_3$-$SrTiO_3$.
A - $BaTiO_3$, 2h, 1400°C, 97.5 % TD
B - $SrTiO_3$, 2h, 1480°C, 96 % TD
C - $Ba_{0.5}Sr_{0.5}TiO_3$, 2h, 1450°C, 97.5 % TD
D - 50 % $BaTiO_3$-50 % $SrTiO_3$, 2h, 1450°C, 75% TD

developed in order to improve the homogeneity of the powders. These still unconventional methods for large scale ceramic technology such as coprecipitation, freeze drying-calcining, spray drying-calcining, spray roasting, sol-gel processes, the alkoxide process and flame spraying have been well reviewed in recent literature.35-37

The ceramic industry is reluctant to use these new methods, especially those involving liquid chemical techniques for powders under the pretext that the methods are expensive and not easily adaptable to large scale production. Yet, as it was properly pointed out,37 the same methods are common in the chemical industry, for example in the paint industry. Another objection of a traditional ceramist to new techniques is that these methods usually produce "active" powders which may need special precautions in handling and forming.

Fig. 4. $BaTiO_3$ sphere sintered to $SrTiO_3$ plate, 6h, 1300°C.

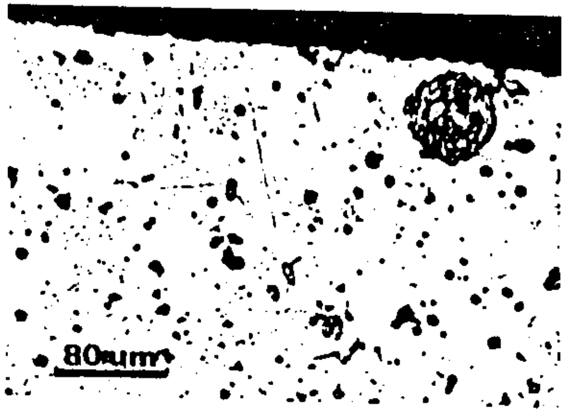

Fig. 5. $SrTiO_3$ powder sintered with $BaTiO_3$ sphere, 3h, 1450°C.

Yet fundamental research in recent years clarified several peculiarities in the sintering of active powders. We can expect that the increasing knowledge in this field, together with the awarenes of the fact that the required specially dense ceramics with uniform grain and pore size distribution cannot readily be achieved except by the use of novel methods of powder preparation, will lead in next few years toward significant changes in the classical ceramic technology.

5. NON-ISOTHERMAL SINTERING

Common sintering practice in industry is to reach the desired soaking temperature with a more-or less linear heating rate, and then to fire the bodies at constant temperature for certain period of time.

Most sintering studies are performed under isothermal conditions. Yet we are aware so-called isothermal sintering is not isothermal in the strict sense of this word. To avoid errors originating in the fact that isothermal sintering is not isothermal in the initial stage, and to simulate the industrial practice more closely a number of sintering studies under non-isothermal conditions were carried out.

Two main experimental techniques have been employed: stepwise heating or heating with a constant heating rate. For both techniques, equations have been derived for calculating of the main sintering parameters, which may allow a decision among the various sintering mechanisms and estimation of the activation energies for the sintering process[38-40].

Analysis of the data obtained uncovered an interesting phenomenon which may be of considerable practical importance. In the sintering of some powder compacts, very high rates of densification were observed in the course of the heating up period or within the first few minutes of isothermal sintering (Fig. 6). Usually this phenomenon is explained as being due to the great "activity" of the powders, caused by high concentration of crystalline imperfections and large surface areas. It was also noted that the densification rate reaches a maximum value during the initial fast heating period, while the approach to the isothermal state results in an abrupt decrease in densification rate. Ivensen pointed out[41] that such a change in porosity reduction rate (during the isothermal period dozens of times lower than that during the temperature rise period) could hardly be attributed to any changes in the concentrations of initial imperfections, since in the latter case one would have to suggest a several thousandfold drop of that concentration, which is rather improbable in so short a period of time.

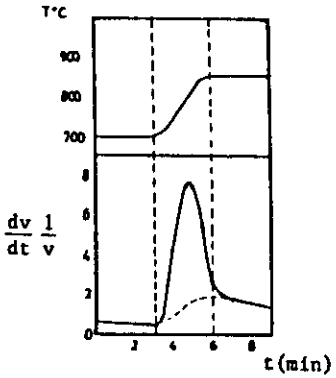

Fig. 4. Change in the rate of pore volume reduction ($\frac{dV}{dt}.\frac{1}{V}$ hour^{-1}) within the temperature jump (i.e. rapid rise in temperature) between isothermal periods. Broken line-change in rate expected from kinetic parameters of isothermal sintering[41].

Comparison of sintering results obtained under isothermal and non-isothermal conditions revealed some other anomalies which could not be accounted for by the general concept of a simple thermally activated process. Such anomalies are the extremely high values of apparent activation energy for mass transport, and the proportionality of densification rate to the temperature increase rate[42].

On the basis of these observations, supported by several experiments, the idea was put forward that the instant rate of pore volume reduction does not depend only on the corresponding temperature, capillary pressure and concentration of original imperfections retained in the compact at the sintering temperature, but must also depend on the specific state of the body being sintered, that state being directly associated with the rate of temperature increase.

In the absence of a satisfactory physical interpretation of the phenomena observed, Ivensen proposed a semiphenomenological explanation, using a hypothesis that densification was affected by short lived "active" defects resulting from thermally activated annihilation of original defects which disappear rapidly because of their interaction among themselves and with other defects[42].

Ivensen points out some very interesting phenomena that the same behaviour may be caused by impurities and additives with a temperature dependent solid solubility. Whereas Ivensen's explanation may need some further refinement and direct experimental proof, the fact remains that densification rate is strongly dependent on the rate of temperature increase. This fact is not taken into account in the sintering equations existing today. It also suggests that sintering under non-isothermal conditions deserves much more attention in future investigations. Practical interest in intentionally non-isothermal sintering in ceramic engineering is also increasing. Energy saving requirements promote the fast firing techniques, with predominant densification under non-isothermal conditions.

Common up- and hold "conventional temperature sintering" (CTS), as termed by Palmour, is hardly optimized. It stems from the tradition and is a consequence of the availability of conventional thermocouple-based control instrumentation. Yet we know of several practical examples when densification proceeds rapidly during temperature increase through the initial and intermediate stages but slows appreciably even before the soak temperature is reached. It was argued that the linear firing profile facilitates entrapment of occluded gases, entrapment of pores within grains and excessive grain growth.

In contrast with conventional sintering, Palmour and coworkers[43] proposed rate controlled sintering (RCS) as a relatively new and non-traditional method for rational control of densification dynamics during sintering. The technique is not as simple as in the case of conventional sintering, of course. It demands a feedback controlled dilatometer, which relates flow of power to the dilatometer furnace to actual specimen shrinkage. By this means, densification may be programmed to proceed at the lowest temperature which will maintain the desired density-time profile. Once determined experimentally in the laboratory dilatometer, the commonly nonlinear temperature - time profile may be used in programming periodic or tunnel kilns to achieve rate controlled sintering on a larger, repetitive scale. The authors demonstrated that microstructures obtained by RCS firing are finer and more uniform than those characteristic of CTS firing.

As far as theoretical explanations are concerned, it is interesting to note that neither the forms of the RCS density- and temperature - time curves, nor the microstructure improvements they contribute, appear to have been anticipated by the existing sintering theories.

Unusual sintering effects were also reported by the use of zone sintering[30]. In this process, powder compacts are exposed to rapid high temperature firing by being passed through a short hot-zone. Authors suggest that the use of zone sintering enables separation of the densification stage from the grain-growth stage by accelerating the former. As a possible explanation, authors point out that at very high temperature the contribution of surface diffusion to densification is relatively reduced. Consequently neck growth occurs by diffusion from the interior of the grains, which causes approach of the grain centres and thus the densification of the specimen.

Present review points out that non-isothermal sintering techniques deserve much closer study than in the past and that their optimization may lead to a better control of ceramic properties.

6. SUMMARY AND CONCLUSIONS

Main characteristics in practical sintering are impure powders or heterogeneous mixture with non-uniform particle size, compacts with non-uniform density distribution and sintering at practically non-isothermal conditions. Phenomenological explanations of the sintering process may be used as a guidance to adjust the sintering procedure to achieve the desired properties of ceramics, however, the effects of the real powder characteristics are such that separate study of each particular system is necessary.

Some contemporary technical ceramics, such as hard and soft ferrites, ferroelectrics and voltage dependent resistors, demand compromise between density, grain size and porosity distribution. Several examples show that consequences of chemical heterogeneity and impurities are generally unpredictable. Therefore, great care is to be exerted to improve the chemical homogeneity of the powder. The importance of sintering under non-isothermal conditions is increasing and more understanding of the essentials of the process is needed.

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