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CONTEMPORARY
CONCEPTIONS OF THE
SCIENCE OF SINTERING
AND ITS FUTURE;
DIALECTICS OF THE
DEVELOPMENT OF THE
SCIENCE OF SINTERING.



**SCIENCE OF SINTERING
AND
ITS FUTURE**

MOMČILO M. RISTIC

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ITS FUTURE**

by

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*This book is dedicated
to my mater Milka and
to my father Milan*

*Ova knjiga je posvećena
mojoj majci Milki i
mojem ocu Milanu*

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Preface

The vigorous swing, characterizing the science of sintering, refers, first of all, to the exceptional activities of scientists in their studies of problems relating to actual materials, or geometrically defined models. From that point of view the science of sintering is, on one hand, directly connected with solid state physics and chemistry and, on the other hand, with practice which is most often inspired with actual production. Therefore, it is not illogical that the empirical method is mostly referred to even nowadays, when one wants to describe some phenomena quantitatively.

A few books published by M. Yu. Baljshin, V. A. Ivensen, V. V. Skorohod and others are characterized by the wish to give a complete approach to the problems of sintering theory. Bearing just this in mind while writing the book "An Essay on the Generalization of Sintering Theory" (G. V. Samsonov, M. M. Ristić with the collaborators) an idea struck me: to ask the most eminent scientists in this field to present their own opinions on the theme THE SCIENCE OF SINTERING AND MODERN VIEWS ON ITS FUTURE. Then I formed 18 questions, given in the appendix, to be answered. I have presented the answers, which I received from a number of my colleagues, in 10 chapters of the second part of this book:

1. The Science of Sintering and its Place in Natural and Technical Sciences,
2. Sintering of Models,

3. Sintering Mechanisms and Roles of Defects in the Sintering Process,
4. Sintering of Real Systems,
5. Phenomenology Theories and their Place in the Science of Sintering,
6. Sintering Kinetics,
7. Sintering Thermodynamics,
8. Achievements in the Science of Sintering Important for its Development,
9. The Uniform Model of Sintering,
10. The Future of the Science of Sintering.

The initial idea, that the book should have a monograph character and in which the answers would serve as some data on the latest notions of the science of sintering, was somewhat changed since the original opinions of individual scientists are given in the book and these, are sometimes very contradictory. This, in fact, we believe, gives the book a special charm because the unsolved problems in the science of sintering are most evidently stressed in this way.

Unfortunately, a few eminent scientists from this field have not sent their answers, giving explanations that they are just writing books in which their conceptions will be presented. We are impatiently expecting these books to appear, because then our own work will certainly gain in completeness.

Detailed attention was given to the dialectics of the development of the science of sintering, presented in the fourth part of the book.

The fourth part of the book consists of papers of eminent scientists engaged in the field of sintering science (some of which were published here for the first time). This material is published in the book with the

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consent of the authors and these original contributions provide a more profound knowledge of sintering.

If this book, together with all other similar publications, could contribute to a more uniform view on many unsolved problems, and if it could be, in any way, a kind of inspiration for even more intensive research into this field, then it would justify our expectations.

The author would like to thank his colleagues for their generous help in the publication of this book.

On behalf of the author and the publisher the author wishes to acknowledge his debt to The Republic Fund for Scientific Work, SR Serbia, to The International Institute for the Science of Sintering and to The Faculty of Electronic Engineering (Nish) for the generous help which has made possible the publication of this book.

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M. M. Ristić

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"... in order to be able to understand certain facts it is necessary to have definite ideas in one's mind, so that the intellect can see what the eyes cannot see."

JUSTUS LIBIG (1865)

1.

INTRODUCTION

1. INTRODUCTION

Work on models has preoccupied scientists engaged in problems of sintering for quite a long time. However, recently in the science of sintering an ever growing wish has been felt that the sintering process should be considered, as much as possible, as a uniform complex process in which a number of elementary processes are acting, or, at least, that stages in which one elementary process has a dominant character should be determined.

Thus D. L. Johnson⁽¹⁾ has theoretically studied the matter concerning the role of particular elementary mechanisms in the initial and intermediate stages of sintering. The theoretically obtained results showed a very good agreement with the experimental ones, when sintering of spherical particles of the same sizes was concerned.

A number of investigators has tried to apply the theories of G. Kuczynski and B. Pines to sintering of real systems. However, in these attempts all that has been obtained are formal determinations of the time exponent in the already classic empirical equation of sintering ($\frac{\Delta V}{V} = kt^n$). In spite of everything, this equation is even today used in the literature, though sometimes even the very purposes of its application are not quite clear.

We consider, however, three publications, which have recently appeared, to be of exceptional signifi-

cance, as each of them in its own way contributes to the qualitative rise which has become inevitable in the sintering theory. Two of them are contributions of a further approach of models to real materials^(2,3), but in the third one⁽⁴⁾ the author has tried to generalize all knowledge about the science of sintering acquired up to now as well as to approach the fundamental knowledge of the processes at the microlevel to what is occurring at the macrolevel.

1.1. Sintering Diagrams

Starting from the fact that six distinguishable mechanisms (Table I) contribute to neck growth and densification, M. F. Ashby⁽²⁾ has considered the sintering of an aggregate of particles - even in the absence of applied stresses.

Table I

Mechanism	Transport path	Source of matter	Sink of matter	Literature
(I)	Surface diffusion	Surface	Neck	5,6
(II)	Lattice diffusion	Surface	Neck	5,6
(III)	Vapor transport	Surface	Neck	7
(IV)	Boundary diffusion	Grain boundary	Neck	8
(V)	Lattice diffusion	" "	"	6
(VI)	" "	Dislocation	"	6

Up to now it has conventionally been supposed that there are three stages of sintering. M. F. Ashby, however, has introduced a so called zero stage in which instantaneous neck-formation takes place when powder particles come into contact, so that now it can be said that there are the following sintering stages:
stage 0 - the instantaneous neck-formation,

- stage 1 - the early stage of neck growth,
 stage 2 - the intermediate stage (the necks are now quite large, and the pores are roughly cylindrical),
 stage 3 - the final stage (the pores are isolated and spherical).

In the absence of pressure (or stress), sintering is driven by surface curvature - or rather, by the difference in surface curvature between sources and sinks. This driving force differs for different diffusion paths; and, for a given diffusion path, it can depend on the configuration and geometry of the sintering particles.

If two spheres for mechanisms (I) - (III) are being sintered, the driving force is defined as the curvature differences between them which drive different fluxes:

$$K_1 = \left(\frac{1}{\rho} - \frac{1}{x} + \frac{2}{a} \right) \left(1 - \frac{x}{a} \right) \quad (1.1)$$

where $K_1 \geq 0$,

ρ - radius of curvature of the neck,

x - radius of disc of contact of two particles,

a - particle radius.

For mechanisms (IV) - (VI) the driving force is:

$$K_2 = \frac{1}{\rho} - \frac{1}{x} \quad (1.2)$$

In the case of sintering of a sphere aggregate, equation (1) is modified into:

$$K_1 = \left(\frac{1}{\rho_1} - \frac{1}{x} + \frac{2}{a} \right) \left(1 - \frac{x}{x_f - \left(\frac{f}{3} \right)^{1/3} a} \right) \quad (1.3)$$

while

$$\rho_1 = \frac{x^2}{2(a-x)}$$

$$f = \frac{\Delta_0 - \Delta_1}{\Delta_0}$$

where x_f - the final value of x when 100 per cent density has been reached,

Δ_0 - theoretical density,

Δ_1 - initial density of powder contact,

f - volume fraction of pores.

When mechanisms (III) and (V) are concerned, the driving force is also given by expressions:

$$K_2 = \frac{1}{\rho_1} - \frac{1}{x} \quad (\text{stage 1}) \quad (1.4)$$

$$K_3 = \frac{2}{\rho_2} \quad (\text{stage 3}) \quad (1.5)$$

where $\rho_2 = x_f - x$.

The sintering driving-force, defined in this way, made an approach to the general kinetic equations possible through the approximate rate of neck growth; these equations describe the process as it proceeds by different mechanisms.

Mechanism (I):

$$\dot{x}_1 = 2D_S \sigma_S F K_1^3 \quad (1.6)$$

Mechanism (II):

$$\dot{x}_2 = 2D_V F K_1^2 \quad (1.7)$$

Mechanism (III):

$$\dot{x}_3 = P_V F \left(\frac{\Omega}{2\pi\Delta_0 kT} \right)^{1/2} K_1 \quad (1.8)$$

Mechanism (IV):

$$\dot{x}_4 = \frac{4D_B \delta_B F K_2^2}{x} \quad (1.9)$$

Mechanism (V):

$$\dot{x}_5 = 4D_V F K_2^2 \quad (1.10)$$

Mechanism (VI):

$$\dot{x}_6 = \frac{4}{9} K_2 N x^2 D_V F \left(K_2 - \frac{3}{2} \frac{\mu x}{\gamma_S a} \right) \quad (1.11)$$

In equations (6)-(11)

$$F = \frac{s}{kT}$$

- D_s - surface diffusion coefficient,
- D_v - lattice diffusion coefficient,
- D_B - grain boundary diffusion coefficient,
- D_G - diffusion coefficient in the gas phase,
- δ_s - effective surface thickness,
- δ_B - effective grain boundary thickness,
- P_v - vapor pressure,
- s - surface free energy,
- B - grain boundary free energy,
- Ω - atom or molecular volume,
- k - Boltzmann's constant,
- T - absolute temperature (K),
- μ - shear modulus,
- b - Burgers vector of dislocations, or the atomic or molecular diameter,
- N - dislocation density.

Since they are all independent, the net sintering rate during stage 1 sintering is simply the sum of the six contributions listed in this section:

$$(\dot{x})_1 = \sum_{i=1}^6 \dot{x}_i \quad (1.12)$$

For the second and the third sintering stages to proceed only mechanisms (IV) and (V) are important. For the case of spherical pores, the equations which characterize the sintering kinetics are:

mechanism (IV):

$$\dot{x}_7 = \frac{1}{16} D_B \delta_B^2 F K_3 \left\{ \frac{1}{\ln\left(\frac{x_F K_3}{2}\right) - \frac{3}{4}} \right\} \quad (1.13)$$

mechanism (V):

$$\dot{x}_8 = \frac{1}{16} \times D_V F K_3^3 \left(\frac{1}{\ln\left(\frac{x_F K_3}{2}\right) - \frac{3}{4}} \right) \quad (1.14)$$

The net sintering rate during stages 2 and 3 is given by

$$(x)_{2,3} = x_7 + x_8 \quad (1.15)$$

On the basis of these kinetic equations it is possible to construct sintering diagrams namely diagrams which show for a given temperature and neck size, the dominant mechanism of sintering, and the net rate of neck-growth or densification (Fig.1). The boundaries of the fields in which a given mechanism is dominant are obtained by equating pairs of rate equations and solving for neck-size as a function of temperature. Superimposed on the fields are contours of constant neck-growth-rate (Fig. 1a), or of constant time (Fig. 1b).

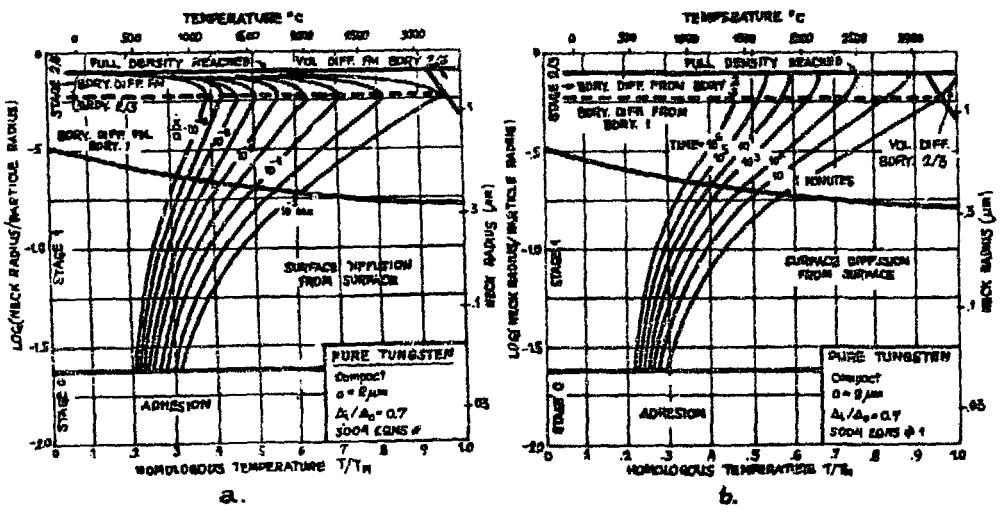


Fig. 1

As an example of the sintering of a compact, Fig. 2 shows the data of B. R. Seidel and D. L. Johnson⁽⁹⁾ for silver ($a=38\mu$). In agreement with the conclusions, of these authors the diagram suggests that volume diffusion is dominant, and that boundary diffusion is the next most important contributor.

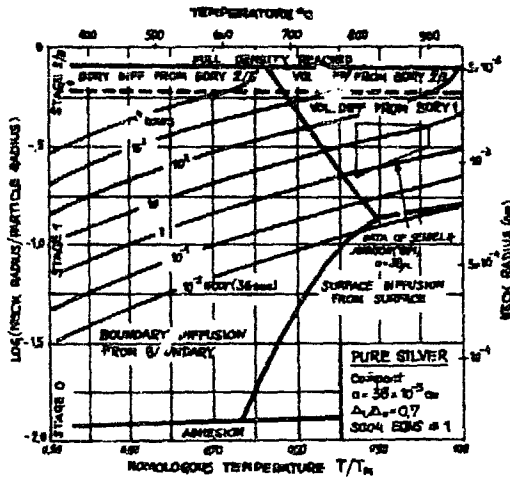


Fig. 2

It is evident that the sintering diagrams represent a further development of the theory of sintering on models, with regard to the uniform approach to the determination of the roles of particular mass transfer mechanisms, although the limited application of this method to real systems is obvious.

1.2. Effects of Particle-Size Distribution in the Initial-Stage Sintering

R. L. Coble⁽³⁾ has compared the earlier derived results for sintering of single-size particles, and on the basis of this comparison he has established a model

In the case when sintering is proceeding by grain-boundary diffusion, then

$$Y_1 + Y_2 = |B_D t (R_1 + R_2) / R_1 R_2|^{1/3} \quad (1.17)$$

where $B_D = 12 D_D W \gamma \Omega / kT$

D_D - the defect diffusion coefficient in the boundary,

W - the grain-boundary width.

For the linear random arrays of particles of variable size the relative shrinkage ($\Delta L / L_0$) can be evaluated only by separate summations in the numerator and denominator; the result for randomly located particles is:

$$\frac{\Delta L}{L_0} = \frac{N \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (Y_i + Y_j) p_i p_j}{|N(\sum_{i=1}^{\infty} 2 R_i p_i)|} \quad (1.18)$$

The size classes are for example R_i and R_j , whereas p_i and p_j are the number fractions of the total number of particles (N) of the respective sizes. To account for the number fraction of $i \cdot j$ contacts, given by the $p_i p_j$ products, use of a number distribution is required. Substitution of the values from the right side of Eq.(1.16) into Eq.(1.18) gives

$$\frac{\Delta L}{L_0} = \frac{\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} |B_D t (R_i + R_j) / R_i R_j|^{1/2} p_i p_j}{\sum_{i=1}^{\infty} 2 R_i p_i} \quad (1.19)$$

for lattice-diffusion-controlled shrinkage, and substitution of Eq.(1.17) in Eq.(1.18) gives:

$$\frac{\Delta L}{L_0} = \frac{\sum_{i=1}^{\infty} \sum_{j=1}^{\infty} |B_D t (R_i + R_j) / R_i R_j|^{1/3} p_i p_j}{\sum_{i=1}^{\infty} 2 R_i p_i} \quad (1.20)$$

for sintering of particles of different sizes. The geometry of contacts between particles of different sizes is shown schematically in Fig. 3; spherical particles of radii R_1 and R_2 are shown spaced so that they overlap by the distance $y_1 + y_2$.

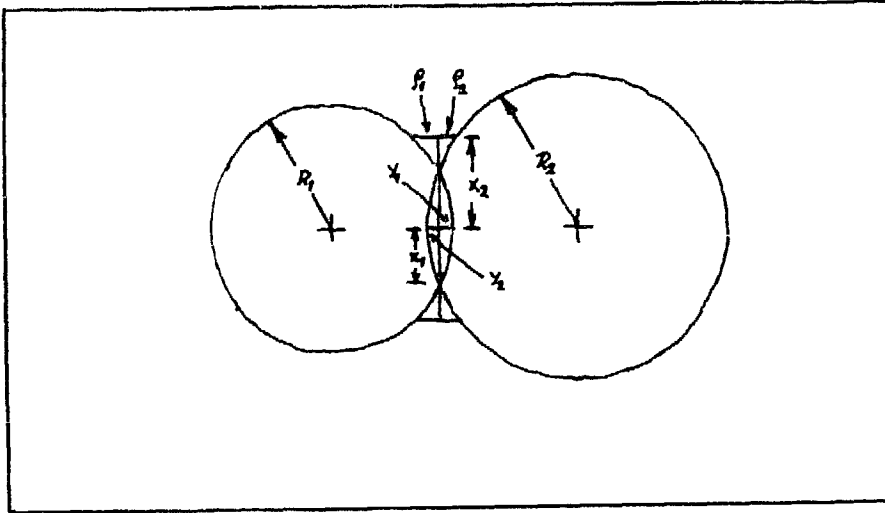


Fig. 3

By following geometrical changes on this model for diffusion mechanism it is obtained that

$$y_1 + y_2 = |Bt(R_1 + R_2)/R_1 R_2|^{1/2} \quad (1.16)$$

where $B = 8D_L \gamma \Omega / kT$

$D_L = D_V C_0 \Omega$ - the lattice diffusion coefficient,

γ - the surface energy,

Ω - the volume transported defect,

k - Boltzmann's constant,

T - the temperature,

D_V - the vacancy diffusion coefficient,

C_0 - the equilibrium vacancy concentration.

for grain-boundary-diffusion-controlled shrinkage.

A more detailed analysis, carried out by R. L. Coble, shows that by applying this model significant errors may be introduced in calculated diffusivities if particle size distribution effects are not taken into account. The calculated diffusivities would be higher than those actually required to cause the observed initial sintering rate. However, the range of shrinkage over which the models for distributed sizes are valid is smaller than that for the models which pertained to particles of single size.

In any case, even disregarding the fact that the sintering of spherical particles has been analysed, the question of the complex acting of mechanisms (1) and (6) (Tab. 1) is imposed here. From that point of view, the problem whether it is more adequate to use the mean particle diameter taking all mechanisms into account, or the reverse, to bear in mind sphere distribution and the limited number of sintering mechanisms is still unsolved. Perhaps, further improvement of models to approach real materials should provide an attempt to combine the two approaches.

1.3. The Possibility of the Generalization of Sintering Theory

Contemporary sintering theories are often an example of the theory of mathematical formalization which sometimes presses out the physical sense; the theories have begun to be distinguished not by internal contents and ideas, but by the names of authors and their collaborators. However, bearing in mind everything that has been done in this field, it is certain that the most general notions of the sintering theory might be developed on the electronic level, as mass transfer, in

in essence, depends on the solid-body electronic structure. Nevertheless, the insufficient working out of particular problems of sintering at the electronic level in detail is caused, first of all, by the lack of unequivocal notions of the electronic structure of materials in the condensed state.

Here it is of special importance to underline that by the consideration of the pressing process on the electronic level it can be shown that the processes of pressing and sintering are in essence inseparable and that they are stages of one and the same process of object formation from powder.

Formation of defect configurations (on the boundary of crystallites) and the organization of bonds between the contacting atoms on surfaces make possible electronic exchange between such atoms; while the contact area should be considered as an energetic barrier which prevents the tunnel penetration of atoms into the neighboring crystallite. The transparency of the barrier (D), according to the quantum theory, is defined by equation:

$$D = \exp\left(-\frac{4\pi\sqrt{2m}}{h}\int_a^b (U-E)^{1/2} dx\right) \quad (1.21)$$

where m - mass of electrons,

h - Planck's constant,

U - height of barrier,

E - energy of a particle,

a and b - coordinates of the beginning and the end of the barrier.

From this it follows that the intensification of the electronic exchange may be realized in three ways:

- by reducing the width of barrier $b - a$,
- by increasing the energy of tunneling electrons,
- by reducing the height of barrier U .

The first way is adequate for the approach of crystallites by increase in pressure during pressing. The second way is realized by deformations of electronic orbitals (by exciting atom configurations which are located on the surface). The barrier height depends on the degree of stability the configurations which are forming the crystallite and it increases parallel with the configuration stability. It is the high stability of $s^x p^y$ - configurations that accounts for the low pressability of boron and graphite powders. On the contrary, passing to Ae, Bi and Su, when a decrease in the stability of their configurations is concerned, the pressability is increasing intensely.

One can suppose that the statistical weight of the stable configurations in atoms located on particle surfaces is always considerably lower than that in atoms in material volumes, and at that position the weight is lower if the material is more deformed and its surface more defected. While two particles come into contact due to thermal excitement, the process of electronic exchange takes place. This is directed to the recovery of defect configurations as well as to the formation of new stable ones on the border between the particles.

An increase in temperature is needed for the real progress in the sintering process, which helps to de-range stable atom configurations as well as volume mass transfer.

Such an approach certainly contributes to the uniform view of the sintering process, although, due to the reasons given, it still does not offer sufficient possibilities for an absolute quantitative description of the process.

Perhaps the transition from the atomic theories

to the electronic theory of sintering should be examined for a uniform quantitative description of the fundamental phenomena in diffusion and creep. One of the possibilities is the use of activation volumes, especially because it allows, in a definite way, simultaneous considerations of the problem concerning both the stress and the transfer.

In any case, the science of sintering, obviously, can expect further development not only in accumulation of experimental data but, above all, in a stonger connection with solid-state physics and chemistry, which at the same time may be an inspirer for these two branches of science.

2.

CONTEMPORARY CONCEPTIONS
OF THE SCIENCE OF SINTERING
AND ITS FUTURE

2.1. THE SCIENCE OF SINTERING AND ITS PLACE IN NATURAL AND TECHNICAL SCIENCES

H. E. Evans:

The whole of modern technology is necessarily based on physical principles and the basic underlying science is of course, physics. This means that chemistry also is considered as a branch of physics. The proper description on the sintering process also requires mathematical tools. Sintering theory has progressed from early phenomenological descriptions to the present state where attempts are being made to understand the fundamental physical concepts.

I don't consider there is a science of sintering but this difference between us is largely a matter of semantics since there is most certainly a technology of sintering. This technology is in its infancy and the sintering phenomenon will, in future, prove to have a profound influence - on materials fabrication, e.g. dispersion strengthened alloys, ceramic products (e.g. nuclear fuel) and refractory alloys. There are also many fields in which the concepts developed during studies of sintering are applicable - one of the most important of these is mechanical property effects.

G. H. Gessinger:

In my mind research in sintering is very fascinating not only to the persons involved but also to the outsider. This is due to the fact that so many problems from quite different areas are touched. As a science it has taken its own place, but it has lost touch with reality in many instances. Sintering as a science I can

only see as part of the more general subjects of diffusion and surface science. On the other hand, sintering theory is only a very limited, because idealized, tool in the hands of a powder metallurgist. Powder metallurgy is the background technology for sintering, but few powder metallurgists rely heavily on sintering theory.

H. H. Hausner:

Sintering is known as a process for densification of a mass of metal powders by heat.

Although the mechanism of material transport which causes densification is still the subject of laboratory tests, the fact that material transport takes place during sintering is well established. Although this material transport does not take place during the earlier stages of sintering, it is an integral factor for the work of powder metallurgists involved in the sintering process. Most of the fundamental investigations into the sintering process do not concern the "bonding" phase of the process, but rather the material transport phase. It is somewhat strange that not a single "official" sintering definition take care of this important phase in the sintering, with the exception of the Walker definition: "Sintering is the extension of the contact area between powder particles in the solid state by the transport of materials across or around pores under appropriate conditions of time, temperature, pressure, and atmosphere". (R.F.Walker, J. Am. Cer. Soc., 38, 187 (1955)).

A well sintered material usually no longer has the structure of the compacted material, but recrystallizes during the sintering process. Grain structure determines the physical properties of the sintered product.

J. S. Hirschhorn:

The sintering of green compacts or loose powder is a very complex process. Much of the difficulty in defining and analyzing sintering is based on the many changes within the material that may take place either simultaneously or consecutively. Some of these changes may be unique to the heating of a porous material, while others are typical of the effects of elevated temperatures on any polycrystalline material. Economic use of the powder metallurgy process is critically dependent on the structural and dimensional changes produced during sintering. The subject of sintering is best approached from the viewpoint that any green compact or press of loose powder is at the very least a two phase material-porosity and solid material. Each has its own morphology; that is, size, shape, distribution and amount.

It is appropriate at this time to attempt to give a simple and straightforward definition of sintering as it pertains to powder metallurgy. *Sintering may be considered the process by which an assembly of particles, compacted under pressure or simply confined in a container, chemically bond themselves into a coherent body under the influence of an elevated temperature.* The sintered material is analogous to conventional forms of solid materials, such as castings, forgings and wrought shapes. In addition to the bonding of the particles sintering may be used to accomplish other functions; these include: alloying, heat treatment, joining and densification.

A. J. Raichenko:

In my opinion the investigation of sintering is based upon physics, chemistry and mechanics. In depen-

dence on which type of sintering one has in his mind namely - sintering of the solid phase or sintering in the presence of a liquid phase, and in what atmosphere it is carried out, either physical or chemical processes play the major part.

The science of sintering is on the border between natural and applied (technical) sciences.

F. N. Rhines:

It would be difficult to cite a basic natural science which does not have something to contribute to the knowledge of sintering. The fields from which I believe the bulk of the understanding will eventually come, however, are mathematics, physics, chemistry and the applied sciences of metallurgy, ceramics and polymers. I have listed mathematics first because it is my conviction that the central problem that must be solved is one of obtaining a mathematically exact description of the sequence of geometric events that transpires in going from the particulate to the fully massive state. The introduction of descriptive topology has seemed, of course, to go a long way toward dealing with this problem. In fact, it is now possible to provide a very good description of sintering from that moment at which the void surface approximates a minimal area for the connectivity and density of the system until separation into isolated pores begins. During both the early and late stages of sintering, however, the processes are responsive, not to average conditions, but to localized events which have not yet been sorted out. I cannot suggest what kind of mathematical approach may be necessary to deal with these early and late situations. Perhaps the statisticians will be able to help us this time.

When and if it does become possible to formulate the geometric changes that constitute all of sintering, I believe that the field of physics will provide all that we shall need in dealing with the kinetics of the process. At the present time I can visualize no major deficiencies in this area. There is no doubt in my mind that all possible kinds of transport can be and frequently are simultaneously involved in sintering. Some simple cases may involve only one or two kinds of transport and we shall probably be able first to put such cases on a firm foundation. For the most part, however, I expect that real cases of sintering will involve very complex combinations of transport processes.

The main contribution from chemistry I expect to appear in the areas of surface chemistry, surface energetics and in the areas of phase equilibria, particularly as they apply to reactions in ceramic systems. Ultimately, the surface energetics must become a very critical part of the whole subject. It seems that the major driving force must almost always be that inherent in surface energetics. There is much practical evidence that sintering processes can be greatly influenced by surface effects. I look to this area for much future practical as well as scientific advance. Insofar as the other aspects of chemistry are concerned, I feel that it is really too early to begin speculation. There is such an infinity of possibilities of systems starting from different states and proceeding by different paths toward equilibrium during the sintering operation that the combinations of events that could be expected are simply incalculatable. I have myself pointed out in a paper more than thirty years ago the fact that any sintering process which involves chemical diffusion can lead through a whole sequence of variations in physical

properties, wherein the most desirable properties may be achieved at some stage in sintering which would not from the standpoint of density alone be selected as a desirable end state. With the additional complications that occur where complex oxides can form, we can get only a glimpse of the possibilities through some of the rather remarkable properties of ceramics that have been coming to light in recent years.

The so-called sciences of metallurgy and ceramics must be relied upon, of course, for the practical contributions. Indeed, the only people who are likely to study the process will be the scientists in the areas of metallurgy and ceramics. It will be they who will have to master the chemistry, physics and mathematics that will be necessary to bring the field into some sort of order.

So far as other sciences are concerned, it is quite evident that there is much to be learned in the area of continuity of structure from the biological sciences. There is probably some to be learned about growth processes as well from the biological people. Geology will have much to tell us in retrospect about long time sintering, and so on.

Sintering is, in my opinion, one of the major processes of nature. It has the same strength of impact upon the development of events in nature that is provided by such processes as the flow of liquids and solids, by phase changes and so on. I feel that when we know enough about sintering we will greatly enhance our understanding of all of nature.

I can do no better at this time in attempting to define sintering than to say that it is that group of processes by which particulate matter merges into massive form. This is, I realize, an extremely broad defini-

tion which would include melting and perhaps other processes that are not generally thought of as belonging in the sintering area, but I do not believe that one can make the definition much narrower without curtailing the basic generality of the process.

G. V. Samsonov:

The sintering theory is based upon such interconnected sciences, as physics and chemistry of the solid state, physical-chemistry, inorganic chemistry, thermodynamics, mechanics, materials science, etc. The development of this theory has caused a re-distribution of the roles of the quoted sciences. If mechanics and thermodynamics were of great importance in the first stages when the process was mainly examined in the macro-range, lately, when the process has already been investigated at the atomic and subatomic levels, physics and chemistry of the solid state as well as the thermodynamics of irreversible processes should, most likely, take the prominent places.

The theory of sintering is based upon natural and technical sciences. It is the theoretical basis of one of the stages of technological methods namely of powder metallurgy.

Sintering is the process of change in the state of a powder system due to the thermal activation of the diffusion processes, which leads to a decrease in its free energy and consequently to changes in the mechanical, physico-chemical, physical, chemical and other properties as well. The process may be accompanied by chemical reactions and phase transformations.

2.2. SINTERING OF MODELS

E. E. Evans:

I think it most desirable that model studies are used to establish the fundamentals of a process. It is possible in this way to establish the rate controlling process - e.g. surface diffusion, grain boundary or lattice diffusion, creep flow, etc.. Extrapolation to real situations should not affect the basic controlling mechanism, but the extrapolation will require only a more realistic treatment of the aggregate. This will involve geometric consideration - particularly a variation in pore and particle size within the bulk. The influence of the sintering atmosphere and its effect on pore sintering by gas stabilisation and surface oxidation should be examined.

G. H. Gessinger:

The main value of sintering models is, in my mind, to predict certain trends rather than to give an exact description of sintering of real powders. I do not believe that a general sintering model is of too much practical use, if it could ever be found. If one wants to make a part of Fe or steel powder, then the most important thing is high density without shrinkage during sintering in order to maintain dimensional control. Most sintering theories concern themselves with the shrinkage kinetics, however, which is so undesirable.

J. S. Hirschhorn:

There is too much work on models that are completely unrelated to real cases.

A. J. Raichenko:

The investigation of sintering on models is the analysis of the process, i. e. the division of the process into its simpler components. However, the whole complex process cannot be reduced to the arithmetical sum of the components, as there is a close interaction between the components.

F. S. Rhines:

The legitimate use of models is, of course, the expression of physical relationships in a graphical form. Models have the advantage that they can be made to deal with the essence of a process shorn of unnecessary side issues. Where such a model can be constructed, it provides an excellent means for perceiving the mathematical relationships that are involved. What is essential in the process of modeling, however, and a factor that seems too often to be overlooked, is that any model to be useful must contain all of the essential parts of the process. The modeling that has been done, thus far, in the field of sintering, has in no case conformed with the latter requirement. For the most part it has not dealt with anything approaching a whole sintering process, but has dealt with peripheral matters alone. For example, the two-particle model is in fact a model of spheriodization. To be sure, some of the elements of sintering are included in spheriodization, but the essential part of the process—that which involves the assembly of a large number of particles into a single body—is not touched by this model. This is, as I have pointed out on several occasions, is because the two-particle model deals with a simply connected configuration, whereas sintering involves a multiply connected configuration. Thus,

these are fundamentally different entities and their physical behavior is not expected to be similar, i. e. the shape changes involved in spheroidization are different in kind from those occurring in sintering. At the present time I can readily present a model which follows portions of the sintering process all the way through. Such a model will, as I showed in my Plansee paper of many years ago describe the topological changes that occur. This model does not, however, take care of all of the Euclidean geometric changes that must also occur. The latter are such as changes in surface area and changes in curvature during the early and late stages of the process. No other model known to me is of assistance in this manner. Thus, I have faith that a proper model, when it is developed, can be very useful, but I feel that we still have some way to go to devise a meaningful model of sintering as a whole.

G. V. Samsonov:

Modelling is the first and one of the most important stages in the experimental investigations of any complex process, and therefore of sintering, too. Modelling, allowing a number of simplifications, makes it possible for us to determine the process by a basic mechanism and, in quite a number of cases, to express it by a simple mathematical formula. Such an example is the examination of the mass-transfer mechanism during sintering, e.g. of a model, i. e., a body of regular symmetry. Modelling must undergo several stages and at each new stage it should approach the real system more and more. For example, the transmission should be from experiments of sintering on models to investigations of the isolated pore behaviour in a homogenous isotropic medium, and then in a non-isotropic medium and finally to investigations of pore assembly in real crystal.

2.3. SINTERING MECHANISMS AND THE ROLE OF CRYSTAL LATTICE DEFECTS IN THE SINTERING PROCESS

K. Easterling:

I should like to comment on two aspects of sintering theory which you may care to consider. The first concerns the theory of cold compaction of metal powders. My comments in this respect are based essentially on work carried out by Anders Thölen and myself and published in *Acta Met.*, 20, 1001 (1972). An important result from this work is that when two clean metal surfaces come together very high stresses are set up at the contact zone, these stresses being much larger than the yield stress of the metal - in fact approaching the theoretical strength of the metal (see e.g. eq. 2 of the *Acta Met.* paper). This means that once good contact is made in cold pressing (i.e. oxide films are broken down, etc) the additional stress needed to nucleate active dislocation sources is relatively small and powder deformation and compaction is considerably aided. It also implies that the driving force for diffusion is substantially increased /as we showed in the *Phys. Sint.* special issue no. 1 (1971)/.

My other comment concerns the sintering mechanisms i.e. at temperatures where diffusion occurs. Up till now there has been no general theory of sintering, which, for a given metal or alloy, recognizes all five mechanisms of sintering (grain boundary, volume, surface, evaporation and condensation, dislocation movement) as a function of stress (i.e. powder/neck size) and temperature. However, I was recently talking to Professor Mike Ashby (Harvard University) who has attempted (successfully I think) to plot all five sintering mechanisms in the form of a map. Thus if the powder size and tempera-

ture of sintering is known, the sintering rate and mechanism can be deduced directly from the map. A unified approach to sintering has been awaited for some time and in my opinion Prof. Ashby's work is the first step towards obtaining it.

H. E. Evans:

Final stage sintering of isolated pores can be divided into two distinct regimes depending on whether or not grain boundary migration has occurred thus isolating pores within grain boundaries.

(i) In this case pores exist at the grain boundary and close by the emission of vacancies either along the boundary or through the grains. The dominant path can be easily calculated by determining the flux of vacancies into the grain and that into the boundary. Thus, consider a spherical pore of radius r situated on a grain boundary of effective thickness W whose plane coincides with the pore diameter.

The flux j_L entering the grain is

$$j_L = D_L 4\pi r^2 \quad (D_L, \text{ lattice diffusion coefficient})$$

and the corresponding quantity j_B into the boundary is

$$j_B = D_B 2\pi r W \quad (D_B, \text{ grain boundary diffusion coefficient})$$

Assuming a constant vacancy potential gradient, this means that the ratio

$$\frac{j_B}{j_L} = \frac{D_B}{D_L} \cdot \frac{W}{2r} \quad (2.1)$$

For most sizes of pores, grain boundary diffusion will predominate at intermediate temperatures; lattice diffusion will take over at high temperatures but this is a regime in which grain growth has often occurred anyway.

While diffusing along the grain boundary, vacancies have to be annihilated and the position and nature of the vacancy sinks is a matter for debate. The earlier mathematical descriptions of this process assumed that the only sink was a cylindrical surface being concentric with the pore and lying midway between pores. Such a simplified picture leads to an easy solution and a manageable final equation. This is given as equation (7) of Walker and Evans, *Metal Sci. J.*, 1970, 4, 155, viz:

$$\frac{dV}{dt} = - \frac{D_g W 2\pi}{\ln(a/2r)} \left| \exp\left(\frac{2\gamma\Omega}{r kT}\right) - 1 \right| \quad (2.2)$$

where D_g is the grain boundary self diffusion coefficient, γ the surface energy of the pore, a the interpore spacing, V the pore volume, t is time, Ω the atomic volume and kT , have their usual meanings. Making the small value expansion of the exponential further simplifies this to

$$\frac{dV}{dt} = - \frac{4\pi D_g W \gamma \Omega}{r kT \ln\left(\frac{a}{2r_0}\right)} \quad (2.3)$$

The disadvantage of this approach is that the idea of a cylindrical sink surface is, at best, an over simplification. A much more realistic model would be to consider point sinks uniformly distributed in the boundary so that vacancies are progressively annihilated as they diffuse along. This was the approach used in the second of the enclosed papers. The final equation here is somewhat more complicated and given by equation (10) of that paper.

The nature of these sinks requires clarification but the most obvious possibilities are grain boundary ledges or grain boundary dislocations.

An extra feature of the models used in the two enclosed papers is the inclusion of the effect of an entrapped insoluble gas in the voids. This imposes a limit on the amount of sintering than can occur so that the void (now a bubble) is in equilibrium when the internal gas pressure P balances the surface tension forces, i.e.

$$P = \frac{2\gamma}{r} \quad (2.4)$$

where P is the surface energy.

(ii) In this case, the pores exist within the grain having been isolated from the grain boundaries by their migration. Under these conditions vacancies leaving the pores must diffuse through the lattice and the activation energy of the process is that for lattice self diffusion.

The initial approach at a theoretical treatment again consider the only vacancy sink to be spherical and concentric with the pore. The solution is simple and gives the time t , required to close the pore as

$$t = \frac{kT V_0}{8\pi\gamma D_L \Omega} \quad (2.5)$$

where V_0 is the initial pore volume and D_L is the lattice self diffusion coefficient. This treatment presupposes an empty pore. The geometry of this model has some basis in fact since the concentric spherical sink can be identified with the grain boundary.

A more complete treatment, however, also requires some provision for vacancy sinks within the grain in an analogous way to the grain boundary diffusion case. These sinks could be jogs on edge dislocations, precipitates, etc.. I am currently working on the theoretical development of such a model.

J. S. Hirschhorn:

It seems to me that virtually every mechanism postulated can be valid for certain cases.

All are important, but not necessarily for a specific case - - the only one may be of real importance.

P. S. Nicholson and J. R. Chackelford:

It has been assumed for some time that lattice defects play a fundamentally important role in the sintering of materials by a volume diffusion mechanism. However, surprisingly little research has been done to define precisely this role. The increasing interest in non-stoichiometry and its effects on the properties of materials has produced a wealth of information on the defect structure of a wide variety of inorganic materials. This information now provides a good opportunity to make a renewed effort to define this role.

The fact that point defects must play some role in sintering by a volume diffusion mechanism seems certain. The role of point defects in volume diffusion has been an accepted part of diffusion theory for many years. However, a precise definition of their role in sintering is yet to be established. The current research program is an attempt to provide this definition.

Point defects can be introduced in two main ways: a) doping with ions of unlike charge, or b) producing non-stoichiometric material by varying the materials vapor pressure. Most work on sintering-point defect relationships has dealt with the first type of defects. This work has shown strong evidence for an effect of point defects on the sintering behavior. However, the presence of the impurity ions makes the system difficult to treat theoretically. Therefore, the current research program

deals with defects of the second type. By varying the vapor pressure of the material, the point defect structure can be systematically varied in a sample of uniformly low impurity. Various sample materials are being considered, but especially attractive are the transition metal monoxides, e.g., MnO. These materials have a wide range of non-stoichiometry as a function of oxygen pressure, and their defect structure is generally well known. The dependence of sintering on non-stoichiometry is expected in these materials by analogy to the results found for non-stoichiometric UO_2 .

Experimental results on the sintering of these materials as a function of their point defect structure (non-stoichiometry) can be analyzed in a number of ways. First, they can be interpreted in terms of traditional sintering theory relative to mechanism and rate controlling species. Second, they can be interpreted in terms of the thermodynamics of the defect structure allowing a re-evaluation of traditional theories, viz., the role of point defects in the deviation of these theories.

This analysis should provide new insight into the role point defects and sintering atmosphere on the sintering process.

A. J. Raichenko:

The diffusion processes as well as the creep processes are at the basis of sintering.

Surface and volume defects are of the greatest importance for sintering.

F. N. Phines:

Perhaps it has to do with the discussions that have flowed over the subject concerning opinion relative to transport mechanisms. About the only thing that I feel

sure of in this area is that no single transport mechanism can account for sintering in the materials that I have studied (mainly copper). It is my impression that nature makes use of just about every transport mechanism that may be available and that differences in kinetics and general behavior may, in at least some cases, be due to changes in the relative contributions of the various mechanisms of transport. As I have tried to make clear, I feel that it is much too early in the development to get involved transport discussions, since no one seems to know from whence, how far, or to where they want what transported, or, if they do make such an assertion, it is upon the basis of a fictitious model which has no obvious bearing on sintering.

The roles of crystal lattice defects must be highly individual with the material, with the stage in sintering, and with a host of undefined variables. Such a question has, to me, no meaning except as it applies to a highly specific situation.

If the point of the matter is related to the increasing complexity which is involved in going from one to two phase systems, then all I can say is that we are at present in a very early stage of dealing with matters of this sort. At present I have a student who has been trying to straighten out the topology of the three-phase situation, i.e. gas, liquid, solid. This is, as you might suppose, an order to magnitude more complex than the topology of the one metal, one vapor, sintering system. The essence of the difference is that, whereas in the simple case there is but one kind of surface involved and the sintering process can be thought of as a sequence of changes in the configuration of this single surface; wherever a second condensed phase is introduced, the number of kinds of surfaces jump suddenly to three and

immediately one must be interested in the intersections among such surfaces as well as the configurations of the surfaces themselves. There are instances, I expect, in which this situation is somewhat simplified by having, for example, a completely wetting liquid, wherein the number of surfaces is reduced to two and, in some cases at least, intersection is prohibited by the fact of wetting. We are at present engaged in trying to deal with one such case. This happens to be the sintering of a hematite ore, wherein the liquid phase is a slag which wets all of the surface of the hematite. Even though the geometry of this case may be not greatly more complicated than that of the single-solid one-gas phase system, it is immediately apparent that the difference in energetics between the two prevailing surfaces cannot help but complicate the situation. I look upon our venture into this area as merely a probing of the more distant unknown. I still feel that we need to solve the one-solid one-gas, or the oneliquid one-gas, or possibly the one-solid one-liquid case before we attack anything more complex. Item 7 mentions also sintering atmospheres. The principal point here would seem to be that the nature of the sintering atmosphere modifies the energetics of the gas to condensed phase surface, whether this be gas-liquid or gas-solid.

G. V. Samsonov:

It is appropriate to describe the sintering process from the standpoint of the mechanisms which control the process in every temperature range. It is perfectly evident that the existence of a controlling mechanism does not exclude the essential roles of secondary mechanisms for a given stage, even more so because they overlap in most cases.

a. The mechanism of mechanical formation of interparticle contacts belongs to the first (initial) sintering stage. Thus during sintering of freely poured powders, the formation of contacts occurs due to gliding and repacking of powder particles under the influence of their weights and temperature. During sintering of previously pressed powders this process already starts during pressing.

b. In the second sintering stage appears the mechanism of physical formation of interparticle contacts. This process starts proceeding by reduction of oxides and causes the formation of contacting bridges due to the appearance of active metal atoms on the surface. The increase in temperature leads to increasing diffusion mobility of active atoms, but the system tends to a decrease in surface free energy in the system makes the directed motion of these atoms along the surface possible. This results in the mechanical contact being transformed into a physical one. It is evident that surface diffusion is the controlling process of this stage.

c. In the third stage contact surfaces increase until the porosity closure occurs. The controlling mechanism is the material diffusion-viscous flow going on under the influence of capillary pressure forces. One of the possible mechanisms in this stage is also plastic flow particularly when capillary pressures reach or surpass the dislocation motion tension.

d. The fourth, final, stage of the sintering process is the coalescence of isolated pores and grain growth. The pore coalescence mechanism may be of different kinds in dependence on the medium defectiveness. While dislocation density is rather high, so that the mean distance between vacancy sources and sinks is consider-

rably less than the pore size, the diffusion-viscous-flow mechanism is dominant. With the increase in temperature and with the end of the primary re-crystallization process, dislocation density decreases so that the mean distance between vacancy sources and sinks gets longer than the mean pore size and the diffusion mechanism of pore dissolution in the vacancy becomes dominating. However vacancy volume diffusion becomes the controlling mechanism.

A scheme is given which illustrates the roles of the basic sintering mechanisms.

The joint role of crystal lattice defects is reduced to the activation of the sintering process. The activity may be determined in various temperature ranges by defects of various types.

Excessive non-equilibrium vacancies, to which the chemical potential gradient corresponds, are the basic driving-force of the sintering process. However, they are not able to activate the sintering process in essence. During the increasing temperature defects of types of vacancy disks, dislocation rings and micropores are formed from all excessive vacancies in the compact volume. These defects, serving as vacancy sources and sinks, affect the sintering kinetics. When defining the role of dislocations in the sintering process from Nabarro-Herring's theory, according to which crystal body viscosity is the function of the least linear dimension of the crystal element substructure, follows:

$$\frac{1}{\eta} = \frac{D \delta^3}{kTL^2} \quad (2.6)$$

Grain boundaries affect sintering in the same way as dislocations, although they may be also classified into lattice volume defects.

Basic Sintering Mechanisms (Scheme)

<u>Stages of the sintering process</u>	<u>Mechanism of the process</u>	<u>Changes in fine structure</u>
1. Formation of physico-mechanical contacts a/ free pouring b/ pressing	a/ mechanical engagement b/ electrostatic interaction c/ brittle fracture and plastic deformation d/ diffusion processes	Increasing number of point and linear defects during pressing.
2. Formation of physical contacts	a/ reduction of oxides b/ adsorption-desorption and surface diffusion c/ evaporation and condensation d/ volume diffusion	Point defects annihilation.
3. Increasing contact surfaces till formation of closed porosity	a/ diffusion-viscous flow b/ boundary diffusion c/ volume diffusion d/ plastic flow	Creep and gliding of dislocations and decrease in dislocation density due to the formation of polyangle boundaries.
4. Isolated pore coalescence and grain growth	a/ vacancy volume diffusion b/ diffusion-viscous flow	Decrease in dislocation density due to motion of vacancies and polyangle boundaries.

Surface defects play an important part mainly in the initial sintering stage, because with increase in temperature these defects get coalesced. The roles of surface defects and grain boundaries are evident even though the surface and boundary diffusion coefficients, at temperatures up to melting ranges, are much higher than volume diffusion coefficients in monocrystals. The role of pores, as macrodefects, depends on the ratio of pore sizes and dislocation density in the crystal. Decrease in the dislocation density and diminishing of pore sizes leads to the replacement of the diffusion-viscose mechanism by a volume diffusion mechanism during sintering.

Every compact represents a heterogenous structure consisting of two phases - particles of the pressed materials and pores containing gaseous matter which is either in a free or adsorbed state. The quantity and relative amount of these materials are determined by temperature, pressure and the atmosphere in which the powders are obtained and pressed. For this reason sintering of one-component systems should be considered as sintering of two-phase structures namely a "material-pit" with a considerable influence from the gaseous component of the pores.

The mechanism of "clean" (free of the gas component influence) densification of the two-phase system "material - pit" has thoroughly been considered in the literature. However, in real conditions such a mechanism is practically impossible: the surface of the particle sintered is always covered with a layer of chemisorbed atoms, the quantity of which may be determined if we start from the following equation:

$$n = k \exp(Q/RT) \quad (2.7)$$

where n - quantity of chemisorbed particles,
 k - coefficient, proportional to pressure,
 Q - adsorption heat,
 T - sintering temperature.

As Z. Benar has remarked, the chemisorbed layer should be considered as a particular chemical substance with a definite structure able to take part in reversible equilibria in the same way as any other chemical compound. Here the fact that the adsorbed layer does not consist only of atoms and radicals of adsorbed matter but also of metal surface atoms which materialize the bond with the adsorber, must be taken into account.

For this reason in real conditions the initial stage is the interaction of chemisorbed layers, which are formed on the surface even after the reduction of oxide films and after removing other surface compounds. These layers exist until the boiling temperature of the metal. Therefore, in the first sintering stage the controlling process is the decomposition of chemisorbed layers, regardless of everything that has been published up to now on the basis of the examination of models.

If sintering is performed in a protective atmosphere, containing impurities, then the ratio of adsorbed molecules in the adsorption layer will be described by equation:

$$\frac{n_1}{n_2} = \frac{p_1}{p_2} \exp\left(\frac{Q_1 - Q_2}{RT}\right) \quad (2.8)$$

i.e. even with a negligible difference of the adsorption heats, the metal becomes covered with a specific "film" of the matter which has a greater adsorption heat.

G. S. Tendolkar:

The cause and mode of material transport during sintering has been a subject of great interest for research

vorkers in this field. It is now universally accepted that the driving force (or the cause) for the material transport during sintering is the lowering in total surface energy of the particulate system. The mechanism (or the neede) of material transport is still a subject of great controversy.

W. A. Weyl:

One distinguishes different types of material transport which can be active in sintering, namely:

1. Viscous flow for supercooled liquids (glasses).
2. Vaporization and condensation.
3. Volume diffusion.
4. Surface diffusion.

G. C. Kuczinski studied the changes with time of a simple geometrical model, the sintering of a sphere to a plate. He calculated the isothermal change of dimensions of four mechanisms of material transport. A glass sphere of the radius a makes a point contact with a supporting plate. Sintering changes the point contact into a circle of radius x that grows with the time t through viscous flow of the glass, according to

$$x^2/a = K t \quad (2.9)$$

In this formula K is a constant that depends on the temperature and on the viscosity of the glass. For a glass the reciprocal value of the viscosity is a measure of the mobility of the material during sintering. Similar formulas describe other mechanisms of material transport. For evaporation-condensation the following formula applies:

$$x^3/a = K t \quad (2.10)$$

in which K is a temperature dependent constant that contains the vapor pressure of the material as a para-

meter.

Metallic copper was found to sinter by diffusion of atoms through the bulk of the system into the contact zone. The growth of the resulting neck between sphere and plate follows the expression

$$x^5 / a^2 = K t \quad (2.11)$$

For this type of transport the constant K includes the self-diffusion coefficient of Cu atoms that describes the mobility of the system at a given temperature.

Some systems sinter without viscous flow, evaporation-condensation or bulk diffusion because the mobility of particles within a surface layer can strongly exceed that within the bulk. Surface diffusion requires another diffusion constant K than bulk diffusion and follows a different expression:

$$x^7 / a^3 = K t \quad (2.12)$$

These expressions for the sintering of a sphere to a plate by four different mechanisms are useful approximations but rarely does one deal with one single process. For systems consisting of Al_2O_3 or MgO crystals under oxidizing conditions without the application of strong mechanical forces we may exclude all processes except diffusion. We prefer not to distinguish sharply between surface diffusion and volume diffusion.

Our concept of the "depth action of chemical binding forces" pictures surfaces and interfaces as layers which are hundreds or thousands of atoms deep. These layers are characterized by an anharmonicity of thermal vibrations which is a maximum at the geometrical surface or interface. The anharmonicity of thermal vibrations tapers off toward the interior.

Thermodynamically a surface layer has a vibrational entropy that tapers off from its maximum value at

the surface toward a minimum value in the bulk of the perfect crystal. This means that the surface contributes to the thermodynamic stability of a crystal via its entropy contribution.

With respect to the kinetics of sintering our concept of the surface structure suggests that a considerable fraction of the volume of an aggregate can participate in the so-called surface diffusion.

Our concept of an entropy gradient in a surface layer can be described also as a "free-volume" gradient. The picture that the equilibrium solubility of "space" increases gradually from a low value of the bulk of a crystal towards a high value of the surface can explain why gaseous inclusions have a tendency to migrate towards a surface or a grain boundary.

For a bubble in the interior of a large crystal there exists no driving force for escaping. The surface of the bubble contains atoms which would not change their chemical potentials if the bubble would move within the interior of a large crystal. However, a bubble located in an entropy gradient layer can increase the stability of the system by diffusing into the ambient atmosphere.

2.4. SINTERING OF REAL SYSTEMS

H. E. Evans:

The theoretical models discussed briefly in the last section are applicable to rather idealized systems in that a considerable degree of geometrical symmetry is implied. Thus, on application to a real system it must be taken that there is a very narrow distribution of pore sizes and interpore spacings so that the equations obtained for an isolated pore/sink system may be

used. In practice of course this is unlikely to be found so that there is here a clear limitation. Recently, attempts have been made (Beeré and Greenwood, *Metal Sci.J.*, 1971, 5, 107) to account for the variation in pore size (for isolated pores - i.e. the final stages of sintering) but only using the simplified equations.

H. Fischmeister:

Concerning the early stages of sintering, I still think that Kuczynski's model as modified by Wilson and Shewmon, Rockland, and above all, Johnson, is the most appropriate. I feel that grain boundary diffusion is likely to be the predominant transport mechanism in most metals under technical sintering conditions. - The early stage of sintering has technical importance only in the sintered steel industry, where one wants to avoid shrinkage above 0.5 - 1%. However, for the case of pressed iron powders, the theory must be modified to allow for the non-spherical shape of the particle contacts. A good model would be a disk-shaped contact with one actual metallic contact point which then develops into a metallic neck. The separation between the particle surfaces does not increase, in contrast to the sphere model, because sintering is stopped before the shrinkage stage is reached. Especially at low sintering temperatures, and in the presence of sintering aids such as sulphur, "undercutting" of the neck will occur and will change the shape of the neck. The relative rates of undercutting and neck growth could be calculated from the ratio of surface to grain boundary diffusivity. Such a model could quite easily be formulated in quantitative terms along the lines sketched by Johnson, and Shewmon.

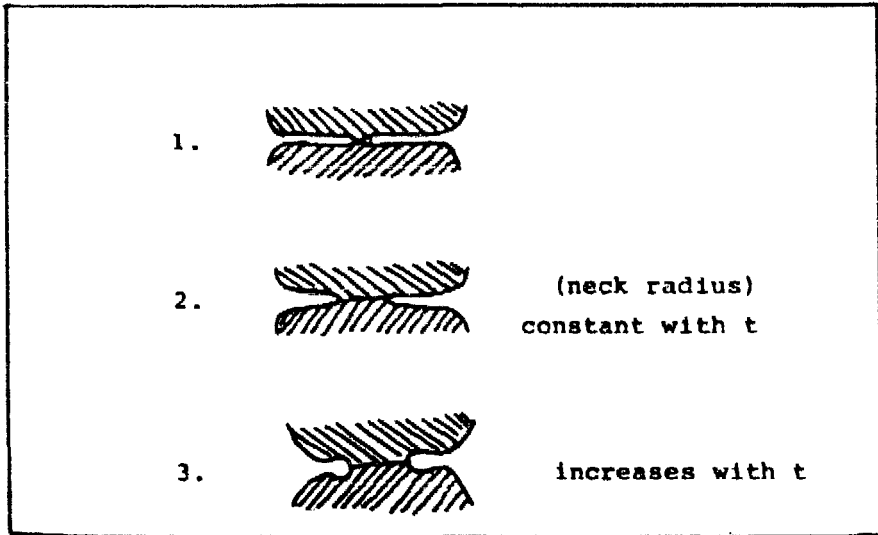


Fig.4 1) Contact after compaction, 2) after neck growth, 3) undercutting

The intermediate and final stage of sintering is of importance in the sintering of ferrite magnets and other oxide ceramics which are sintered without a liquid phase. Here, we only have the model of Coble which needs to be improved. I have discussed this at length in my chairman's discussion at II RTS, which you have in written form. The main problem is the formulation of a modified theory of Ostwald Ripening to take account of the vacancy flux between the pores. The modification required is to subtract the vacancy flux from pores to grain boundaries from that between pores. The fraction of the flux that remains between the pores must be calculated from a statistical analysis of the average distance between pores and grain boundaries. If that can be achieved, one can describe the two coupled processes of grain growth, as governed by the distribution of pores at each moment, and of pore redistribution, as governed by

Ostwald Ripening plus the loss of vacancies to grain boundaries.

Coble's original theory was quite naive in assuming constant geometry, with the pores always situated at the edges or corners of the grains. In 1964 (Paris Symposium on Powder Metallurgy) I suggested a modification where I assumed that grain growth was limited by the pores acting as Zener brakes; this gives the same mathematical formalism if a cubic grain growth law is assumed to result from a cubic growth law for the pores. However, the situation is less simple, because the pores do not ripen according to the normal Ostwald kinetics $R^3 \sim t$. Probably because of (a) the loss of vacancies to grain boundaries, and (b) the fact that most of the inter-pore vacancy transport proceeds by grain boundary rather than volume diffusion (which by itself would give $R^4 \sim t$), the pore growth is much slower. In carbonyl iron, my own measurements from 1964 and new measurements by Aigeltinger & Drolet show that pores grow according to something like $R^6 \sim t$. (I have a copy of the Aigeltinger-Drolet paper, but do not know where it was submitted. You can probably find out from the Max Planck Institute at Stuttgart, where the authors worked as guests when they did that research). At the Notre Dame Conference recently, Kuczynski tried to construct a model along the lines suggested by me, but failed to take into account the coupling of pore growth and grain growth.

J. S. Hirschhorn:

The investigation on models be applied in real systems extremely difficult because of idealistic nature of models. The possible to describe the sintering of real powder theoretically; take into account particle size and shape distributions, surface area, and internal particle porosity.

F. N. Rhines:

The question of the application of models is something that I could hardly hope to deal with, not feeling that any of the existing models are appropriate to sintering.

In all of the above discussion I have been attempting to answer this question as far as I can. From a topological point of view, loose powder consists of a defined number of individual particles which can be described by the number and form of their confining surfaces. The number of such confining surfaces is an index of the topological number of the system. When the particles come into contact and the surfaces unite at points of contact, the total number of surfaces diminishes, usually (if the particles are not porous individually) to one surface of multiply connected form. I have used the topologist's terminology in calling the property of multiple connectivity the "genus" of such a surface. During first stage sintering the genus remains constant while the surface diminishes its area toward the smallest area that will contain the existing amount of condensed phase at the prevailing density and connectivity of the system. Once having arrived at the minimal area configuration, the surface curvature must also be essentially constant over the entire system. The "average curvature" of the system goes from strongly convex at the beginning, to strongly concave by the time the minimal surface area has been achieved. The initial convex state is, of course, merely an average of highly concave curvature at the contact necks and the highly convex curvature that defines the initial shapes of the particles. The convexity is gradually swallowed up by the spreading of concavity until a uniformly concave saddle curvature is achieved. From this point onward, second stage sintering (densifi-

cation) must occur by a reduction in the connectivity of the system, that is by the closure of channels connecting pores. As the connectivity diminishes, so also does the curvature become more concave. During the course of channel closure, it may happen, from time to time, that void spaces become isolated. Whether or not such isolation takes place seems to be one of the matters which is sensitive to the mode of material transport. Atom by atom transport seems to oppose the isolation of pores, whereas dislocation transport tends to accentuate this isolation process. In most cases, however, some isolation occurs, so that presently one has a mixture of connective porosity and isolated porosity. The isolated porosity now behaves quite differently from the connective porosity. In the case of crystalline systems it seems to do nothing but conglobate, that is, while the total volume of the isolated porosity remains constant, the individual pores grow at the expense of their total number. In amorphous systems, however, the isolated pores appear to be capable of further shrinkage provided that they are not filled with a nondiffusing gas. In any case, the second stage of sintering comes to an end as the system, as a whole, approaches zero connectivity. Meanwhile an increased number of surfaces has developed, represented by the surfaces of the isolated pores. The system returns, in a sense, to the inverse of its original state, wherein the isolated surfaces were, at the beginning, the surfaces of isolated particles, but at the end, are the surfaces of isolated pores. At this point, and during the third stage sintering the average curvature tends to evolve toward a less concave state. This comes from the fact that the conglobation of the isolated pores greatly reduces their concavity and thus affects the average for the system as a whole. Even in crystalline

systems shrinkage continues to occur so long as there is any connective porosity and indeed the shrinkage force maximizes just before the last of the shrinkage porosity disappears. This is because the shrinkage porosity is becoming more and more sharply concave. The dimensional changes that are going on in the system are, however, highly localized at this stage, just as they were at the beginning of the growth of interparticle contacts. Because it affects so little of the metal, the overall volume change that takes place in the late stage is not very impressive. Once all of the connective porosity has disappeared, the system becomes essentially stable, although, with long conglobation where there is a gas content in the pores, some longtime sintering growth is possible. This has been noted particularly where the gas within the pores is of a noble character, such as argon or helium. In saying all of this, I perhaps have not really answered your question, because I notice that you ask for a "theoretical" description. What I have given you is not theoretical; it is totally factual and "documented" through careful quantitative metallography throughout the course that I have described. Surface area, curvatures, connectivities, numbers of surfaces have all been measured throughout the sintering sequences. We now have similar results for both metals and oxides.

G. V. Samsonov:

In transition from models to real systems a great number of factors, affecting the sintering process, should be taken into account. Such factors are surface geometry, material cleanliness in general but especially of surface layers, the role of the gas phase, quantity and character of structural defects, etc. In the final stage of the transition to real system, the influence of these factors, which are not taken into account in

models, may become so strong that the difference between theoretically calculated parameters and real ones is considerable. One must be aware of the fact that there is no a distinguishing border between models and the real system.

Several approaches to the theoretical description of the sintering process of real powders are possible. One of them is a thermodynamic approach by means of which it is possible to describe the complex thermodynamic process of sintering on the basis of the solution of simple equations. Another one is modelling. The third and the most adequate may be an explanation of the physical and natural process by consideration of the notions of the sintering theory at the subatomic, electronic level.

2.5. PHENOMENOLOGY SINTERING THEORIES AND THEIR PLACE IN THE SCIENCE OF SINTERING

Yu. G. Dorofeev:

Where the science of sintering is concerned, an important role is assigned to empirical theories. Thus they are considered as an indispensable stage in the creation of sintering theory. The non-existence of physical bases for sintering kinetics even more stresses the importance of the mentioned theories. Development of empirical theories must not, in any case, counteract against the creation of a physical theory of sintering kinetics. Some empirical equations comprise important hypotheses which were primarily formed for ideal models, but their applications are limited. Nevertheless some of them agree with experiments well and are used in technical studies.

H. E. Evans:

Phenomenological approaches are useful in the early stages of study of a new subject but should be gradually phased out as more mechanistic approaches become available.

V. A. Ivansson:

It is probably known, judging from the character and tendency of my papers on the field of sintering, that I give a special significance to studies of sintering phenomenology. Once in (1957) I attempted to give an explanation of the remarkable characteristics of the sintering phenomenon using notions of physics. However, I failed to do it. It was then that I began doubting whether it is possible to explain the principal characteristics of sintering by means of the contemporary conceptions of crystal lattice defections. Later on my doubts were greater and greater, and now I have no doubts at all that progress in this field will be achieved only when new notions of the crystal lattice defection state as well as of the influence of such a state on the crystal material flow have been created in physics.

Because of everything said, one should (at least should do it) restrict oneself to phenomenology generalizations which allow the phenomenology bases of numerous laws to be established in a sufficient and complete way.

A. J. Raichenko:

Today the empirical theory is the closest to a quantitative description of the sintering process.

All sintering stages may be described with one equation.

A mathematical scheme of diffusion processes during sintering of two-component compacts was developed

in my papers as well as the schemes for calculation of some physical properties of samples obtained in this way.

In addition, the correlation between the shrinkage trend and the surface state of metal powder particles has been examined, which can be observed by means of light flashed and reflected.

The experiments, carried out with the aim of investigating diffusion growth, changes in magnetic induction of saturation, electroconductivity, X-graph examination of the sintered two-component compositions, showed sufficient agreement with the proposed theoretical picture as well as with mathematical formalism for numerous calculations.

G. V. Samsonov:

There are two trends in the empirical examination of sintering.

Ya. I. Frankel laid the foundation of the first strictly phenomenology description of the sintering process, and showed that sintering may be considered as a manifestation of general-viscous flow of solid bodies. From these positions Ya. I. Frankel has given the solution of the theory of sintering on models by two approaches namely, sticking of two spherical particles and swimming of spherical pores in an infinite viscous medium.

Further development of the empirical sintering theory was concerned with a consideration of the densification process of a porous body as a whole. Y. Makkenzi has solved the task concerning a body with uniformly distributed spherical particles, but V. V. Skorohod has solved tasks concerning more general models - statistical mixtures of material and pits.

In other papers of B. Ya. Pines, Ya. E. Geguzin and V. V. Skorohod this trend has further been developed by taking into account the structural factor.

Another trend of empirical investigations of sintering, which was developed in the papers of Bal'šin, Ivensen, Ristić and others, refers to the description of the kinetics for changes in different properties during the sintering process by means of equations which are analogous to the chemical kinetics equations. In this case the most simple equation is the degree function of form: $x = kt^n$. Other equations, which are more complex, have also been suggested. Their deficiency is that the constants, which they comprise, cannot be connected with physical parameters of the material sintered, and further it is difficult to fix the boundaries between the influences of numerous factors on the sintering process.

2.6. KINETICS OF THE SINTERING PROCESS

Yu. G. Dorofeev:

The sintering process is heterogeneous and largely dependent on the kind of material which is sintered. For that reason it is impossible not only practically but in principle to describe sintering kinetics by a single universal equation. Some equations, in fact V. A. Ivensen's empirical equation

$$V = V_0 (q m \tau + 1)^{-1/m} \quad (2.13)$$

where V - pore volumen at a moment of time

V_0 - the initial pore volume

q - the rate of the relative decrease in pore volume at the start of sintering,

m - characterized the intensivity of the retarding rate of decrease in pore volume at the start of sintering; it is also the constant on the starting powder under definite sintering conditions,

offers good agreement with the experimental data and represents a real sintering law for powder bodies. However this law has not been practically documented (by his equation).

J. S. Hirschhorn:

The problem is that the physical change being considered (e.g. neck growth) may be too difficult to measure or of no practical importance.

P. N. Rhines:

Ultimately it should be possible to describe a sintering kinetics mathematically. At the present time, however, there is little chance of any real approach to it, because there are still too many variables that have not been nailed down. It is clear for example that the sintering kinetics must of necessity change in kind as we go from stage one to stage two and thence to stage three sintering. The existing kinetic curves always show this effect although many of the data that exist in the literature are too crude to make this clear. The existing kinetic equations are little more than curve fitting. I have presented some of these myself, but I have no faith in them and would not want to repeat them here.

G. V. Samsonov:

In principle, sintering kinetics may be described by one equation, as any dependence in a general case may be presented by decomposition into order, but the order, in some approach, should be approximated either to simpler or more complex functions.

As a proof of this may be taken the fact that some of the empirical equations, describing densification kinetics, agree well with a very great number of experi-

mental data. For example, Ivensen's equation (2.13), or Makipirtij's equation:

$$\frac{d}{1-\alpha} = (kt)^n \quad (2.14)$$

where $\alpha = \frac{V_0 - V}{V - V_\infty}$ - densification parameter,

V, V_0, V_∞ - volume of the body which is sintered in the given, initial and final moments of time,

k - densification rate constant

n - constant.

H. Sasaki:

I contribute a theory for sintering. I would like to tell it very shortly, as follows.

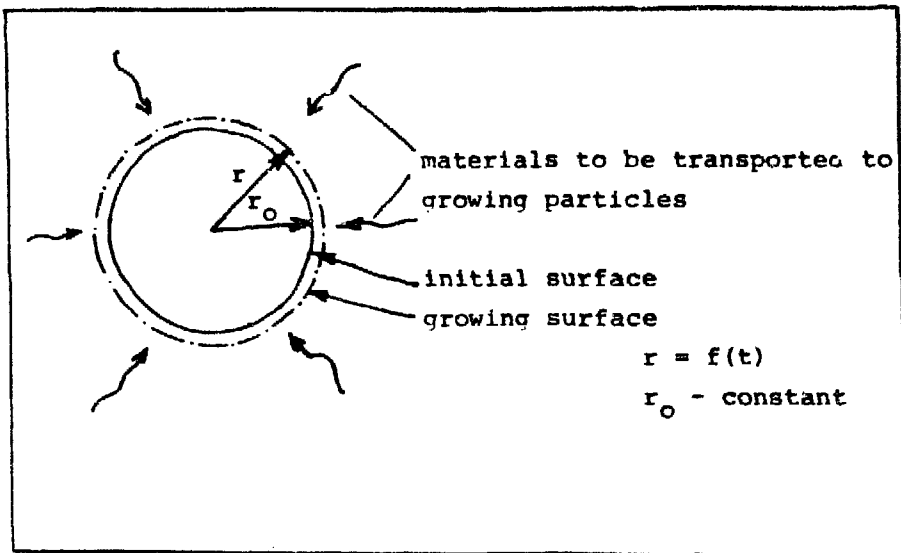


Fig. 5 Sasaki's model

Rate of material transport from the outside of the reference particle may be considered to be constant at a fixed temperature before reaching a final state. If $4\pi r^3/3$ - volume growing particles and ρ - density of

the particle materials, than:

$$\begin{aligned} \frac{dm}{dt} &= K = \frac{d(4\pi r^3/3)\rho}{dt} \\ &= 4\pi r^2 \rho \frac{dr}{dt} \end{aligned} \quad (2.15)$$

$$r^2 dr = K dt \quad (k = \text{const.})$$

After integration:

$$\frac{r^3}{3} = Kt + c \quad t=0 \quad r=r_0 - \text{initial state}$$

$$r^3 - r_0^3 = ct \quad (\bar{c}:\text{constant})$$

$$\text{or } r = r_0, \quad r = ct - \text{initial stage} \quad (2.16)$$

$$\text{if } r \gg r_0, \quad r = \bar{c} t^{1/3} - \text{final stage} \quad (2.17)$$

therefore, kinetics of sintering phenomenon must obey the rule

$$D = t^{1/3} \quad (D:\text{grain diameter})$$

Almost literatures concerning the sintering indicate $D = t^{0,3}$ experimentally. According to my theory the exponent of time will have a range from 1 for initial sintering to 0,33 for final sintering.

Although it may be true, the real sintering system must have a particle size distribution, so that experimental difficulties will occur.

W. A. Weyl:

The rate of sintering depends on the absolute temperature and on energy and concentration fluctuations. One might think that the latter can be eliminated as a factor for pure SiO_2 , MgO , Al_2O_3 or TiO_2 . In an atomistic scale, however, this is not always true. Preparing SiO_2 fumes through the pyrohydrolysis of

SiCl_4 or pure MgO from MgCO_3 or Mg(OH)_2 by calcination one obtains finely subdivided oxides which behave like a liquid. They are "fluidized" when a stream of air is passed through the material or even when shaken in a test tube. There is no "stickiness" as one might expect from unsaturated valence forces or the plus-minus force fields in the surface of each particle. The fluid character of the material is the result of the formation of Helmholtz double layers. In order to lower the energy the surface will be distorted and the cations of low polarizability are recessed and screened by a surface layer of essentially highly polarized O^{2-} ions. Such a surface structure of an oxide leads to mutual repulsive forces acting between the particles, merely by a slight shift of cations towards the interior of the crystal.

Zinc oxide is very different. Even a high purity ZnO may be chemically dissociated in order to achieve what SiO_2 or MgO achieves by the formation of an electrical double layer. It forms Zn^+ ions or Zn^0 atoms and anion vacancies in the interior of the crystal so that it can use part of the electrons to change neutral O_2 molecules in the surface layer into O_2^- or O^{2-} ions. The disproportionation lowers the surface energy of the ZnO particle without producing an electrical double layer. Such an agglomeration of ZnO particle is "sticky" and sinters at a much lower temperature than the MgO or the SiO_2 which cannot undergo a similar chemical disproportionation in air. One of the most important features that determines the beginning of sintering is the adhesion between the individual particles and conversely the prevention of their contact by Helmholtz double layers. In order to sinter and densify MgO or SiO_2 the use of polar organic lubricants is helpful.

The factors which determine the extent to which a compound forms an electrical double layer are the anion to cation ratio, the polarizability of the ions and their electron configuration. Just as "wetting" of a solid by a liquid is the prerequisite for adhesion, contact on an atomic scale is the prerequisite for sintering. The difference in the rate of sintering of pure MgO and pure ZnO is primarily the result of the ease by which the latter can establish contact between Zn and O atoms. This difference is partly the result of the 18- shell of the Zn^{2+} ions as compared with the neon configuration of the Mg^{2+} ions which enables the ZnO to form a defective structure of the formula $Zn^{2+}O_{1-x}(e^{-})_x$ (An.V.)_x that contains anion vacancies and electrons. The mobility of these electrons is an important factor in establishing atomic contact and adhesion.

The driving force for sintering includes the improvement of the screening of cations by anions in a more symmetrical surrounding. Describing the process of sintering by the increase of the average coordination number of all cations would be an oversimplification because the small MgO crystals do not have the number of cations in five fold, fourfold and threefold coordination which one might expect from their surface area. According to M. M. Nicolson the lattice parameter of a small MgO crystal (500A) prepared in vacuo is smaller than that of the macroscopic crystal or even of a small crystal prepared in oxygen.

This feature is not yet sufficiently considered because the necessary data are not yet available. In order to estimate the chemical potential of the aggregate and compare it with that of a single crystal one needs the specific heats between 0°K and the sintering temperature.

W. E. Kingston and G. F. Hüttig calculated that for a specific heat of gold powder only 5% higher than that of a single crystal the powder can be thermodynamically more stable than the single crystal. This reversal of stability would begin at $620^{\circ}\text{C}.$, which is still far below the melting point of gold ($1064^{\circ}\text{C}.$). In such a case the large surface area of the gold powder could not cause sintering above $620^{\circ}\text{C}.$

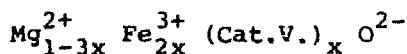
Incomplete coordination of surface atoms is not the only way to raise the free energy of a system. The screening of cations decreases also by lowering the symmetry of their environment by mechanical distortion. Mechanical stresses can greatly increase the energy of a system. In addition to the particle size, the method by which a certain particle size was prepared has a strong influence upon the rate of sintering. Stresses can be introduced by mechanical deformations or by chemical reactions. MgO prepared from $\text{Mg}(\text{OH})_2$ at relatively low temperatures is highly stressed.

During the hot pressing of oxides local stresses between adjacent particles contribute substantially to their reactivity and their rate of sintering.

The rate of sintering of solid solutions is affected by two factors. The disproportionation of binding forces in solid solutions or the vibrational entropy accelerates material transport. A combination of different cations may lower the surface energy of a crystal and with it the driving force of sintering. The oxide Cr_2O_3 contains more polarizable cations than Al_2O_3 and may therefore have a lower surface energy than Al_2O_3 . In a mixture of the two solids the Cr_2O_3 will "creep" over the Al_2O_3 if the temperature permits surface diffusion. G. F. Hüttig reports numerous observations of the creep of one oxide over another one. P. W. Clark

and J. White (1950) observed that Cr_2O_3 delays the sintering rate of Al_2O_3 . This effect may also result from the formation of CrO_4^{2-} ions in the surface of the Al_2O_3 - Cr_2O_3 solid solution.

The role of vacancies as enhancing material transport is well established. Crystals with cations of the noble gas type form only low concentrations of vacancies because of their rigid screening demands. The number of their vacancies can be increased above the thermal equilibrium concentration by introducing cations or anions with a different charge. This most effective method of increasing the rate of sintering has been utilized in the manufacture of magnesite bricks. Pure MgO requires very high temperatures for sintering but the addition of some iron ore produces a defective structure of the formula



that is stable at high temperatures.

On cooling this anomalous solid solution changes toward a mixture of MgO and MgFe_2O_4 . The defective structure sinters readily due to the vacant cation sites and the resulting high anharmonicity of its vibrations.

Oxides with non-noble gas like cations such as ZnO develop a high concentration of defects far below their melting points, hence they sinter more readily than MgO. In zinc oxide the defect concentration can be increased as well as decreased by the proper additions.

Addition of Li_2O to ZnO increases the concentration of anion vacancies and enhances sintering. Addition of Ga_2O_3 to ZnO has the opposite effect.

Systematic experiments on this phenomenon were carried out in our laboratory in order to prove that additions to an oxide may decrease as well as increase

its rate of sintering (Fig. XIV 2).

Many solid state reactions including sintering of oxides can be accelerated by the ambient atmosphere, especially by water vapor. The principle of this catalytic effect is a partial, temporary lowering of the binding forces through a decrease of the charges of anions and cations. In the presence of water an O^{2-} ion can be changed temporarily into an OH^- ion. The penetration of a proton into an $Al^{3+}O^{2-}Al^{3+}$ bond changes it into the weaker $Al^{3+}(OH)^-Al^{3+}$ bond. This process facilitates material transport and sintering. The availability of screening anions, i.e., of OH^- ions makes water a very powerful catalyst for sintering.

Reducing gases can have a similar effect upon cations. In reducing atmospheres Al^{3+} ions can be temporarily changed into $[Al^{3+}(e^-)_2]^+$ ions, thus increasing mobility and volatility of the oxide. Some materials become volatile by a temporary hydration or oxidation. Platinum metals increase their volatility by the intermediate formation of oxides. Chromium oxide is fairly volatile because it can form a higher oxide in which the cation is better screened. This process takes place also at the surface of Al_2O_3 or SiO_2 .

2.7. SINTERING THERMODYNAMICS

H. E. Evans:

The equations used in chapter 2.3 are obtained from boundary conditions governed by thermodynamic considerations.

The driving force for pore closure is the surface energy, γ , of the pore. In mechanistic terms the curved internal surface of the pore will increase the concentration of vacancies in the solid adjacent to

the pore surface. The effect is that of reducing the activation energy for vacancy formation by an amount $2\gamma\Omega/r$. The vacancy concentration at the pore, C_v , is increased over the equilibrium value, C_e by

$$\frac{C_v}{C_e} = \exp\left(\frac{2\gamma\Omega}{rkT}\right) \quad (2.18)$$

The presence of a gas in the pores at pressure, P , reduces this ratio giving

$$\frac{C_v}{C_e} = \exp\left[\left(\frac{2\gamma}{r} - P\right) \frac{\Omega}{kT}\right] \quad (2.19)$$

Clearly, when $P = 2\gamma/r$, the vacancy concentration at the pore will be at the equilibrium value and there is then no tendency for pore closure. This is the reason for the stabilization of pores by an internal pressure.

The above equation can also be used to show the effect of an applied hydrostatic pressure on the sintering body. Let P be a composite of two terms:

P_1 - the gas pressure in the pore

P_a - the applied hydrostatic pressure

and, for purposes of illustration, consider only an equilibrium bubble, i.e. a pore for which

$$P = 2\gamma/r \quad (2.20)$$

If we increase P_a then the vacancy concentration at the pore surface will increase resulting in pore closure. Such closure will increase P_1 , since we assume that the gas in the pore is insoluble in the solid, until once again

$$P = 2\gamma/r \quad (2.21)$$

and pore sintering will cease. However, if we now remove or reduce P_a , the pore will again increase in size

until an equilibrium bubble is again formed. Exactly this sort of behaviour has been found by Gittins (*Acta Met.*, 1968, 16, 517) and gives considerable support for the thermodynamic arguments used.

F. N. Rhines:

As I have pointed out previously, the role of thermodynamics in describing the sintering process should focus first upon the surface energetics and the interplay of curvature and surface tension. The basic driving force of sintering is a thermodynamic property and must be dealt with as such.

In the area of kinetics, those portions of the process which deal with diffusion will obviously be thermodynamically related. This means, of course, that nearly all of the transport processes, including plastic deformation, where it involves climb, will respond to the Arrhenius relationship. It does not mean, however, that one can draw any meaningful deductions from the so-called "activation energy", nor can one hope to get very far with predicting sintering kinetics from fundamental data. The reason for this is that there are so many interrelated processes going on in the geometric change of sintering that no one process will appear to dominate the kinetics.

G. V. Samsonov:

From the standpoint of thermodynamics, sintering is a transient irreversible process, manifested in spontaneous densification of porous defect bodies at sufficiently high temperatures. A porous disperse body is a thermodynamic system far from the equilibrium state because of the increased reserve of the surface free energy, i.e. due to the energy of uncompensated atom bonds

along disperse particle surfaces. The non-equilibrium of a disperse body is also conditioned by the fact that real powders have deranged crystal structures with various crystallograph effects, and contain certain amounts of impurities, etc. This additional non-equilibrium essentially affects the sintering kinetics. In this way thermodynamic description of sintering kinetics is reduced to the solution of the task of the kinetics for minimization of surface free energy.

In the papers of Frenkel, Makkenzi and Shatlevorts the reduction in free energy is equated with the work of deformation under the influence of forces conditioned by the capillary pressure of Laplace. Such a model requires the introduction of a definite porous body model, but the technique of the solution is completely determined by the geometry specificities of sintering and deformation mechanism. In the papers of Pines and Geguzin the change in free energy is evidently not taken into account from the very beginning, but the actual atomic-molecular process manifested in diffusion transfer of vacancies from pores to the body external surface or the internal sinks is obviously taken into consideration.

For a more thorough understanding of the nature of sintering as well as the importance of the development of sintering theory taking into account actual models and mechanisms, it is convenient to consider this process from the more general thermodynamic position. Such an approach would enable separation from specific characteristics of sintering geometry and supposed mechanisms, but taking into account factors which are general for the selection of approximately adequate models.

In order to solve the task in the most general aspect, the kinetics of the surface free energy must be linked not with the local processes of the system, which are determined by the fluctuation of thermodynamic parameters, but with the integral parameter - the total non-equilibrium of the system. Most likely, one may conclude that it is the equilibrium itself, independently of the specificities of local processes, which creates the thermodynamic force that determines the general character of the kinetics for free energy minimization. This conception is asserted by the fact that almost any transient process may be presented by equation:

$$\frac{dx}{dt} = -K X^m \quad (2.22)$$

where K - konstant,

X - free energy excess or some macroparameter which determines the free energy reserve.

On the other hand, the application of general thermodynamics methods in the analysis of the interdependent occurrences during sintering, should make the description of the densification process considerably easier when such occurrences as the degree of crystal structure imperfection, the occurrence of recrystallization, interaction with impurities, diffusion in multi-component disperse systems, etc. are taken into account.

W. A. Weyl:

Sintering of a fine powder takes place because it lowers the free energy of the system. One can use the fundamental equation

$$\Delta F' = \Delta E - T\Delta S \quad (2.23)$$

and point out that a system changes and that equilibrium is reached when the free energy has reached its mi-

nimum. This equation tells us also that the endproduct of sintering or the system that is gradually approached depends upon the temperature. The use of the Gibbs function teaches that it is unsound to expect that by waiting long enough one ends up with a single perfect crystal of a pure substance. In order to sinter a pure oxide, e.g., Al_2O_3 temperatures are required which come close to its melting point. Above 2000°K the entropy contribution TS to the value of F can no longer be ignored.

In our pictorial description we associate the value of E or of the enthalpy change with the change of the degree of screening of cations. Decreasing the number of cations which participate in surfaces and interfaces becomes a major contribution to E .

The conventional way to express this relationship is to refer to the surface free energy of the system and to the thermodynamic potential of small particles as a function of the surface curvature. This thermodynamic approach has been discussed in detail by C. Herring in his paper, "Surface Tension as a Motivation for Sintering". For a pure oxide such as Al_2O_3 there is no difference between the thermodynamic description that causes a system to lower E by lowering the surface area or decreasing porosity and our atomistic picture according to which the number of Al^{3+} ions surrounded symmetrically by six O^{2-} ions increases. Both approaches are based upon the enthalpy changes. Some scientists, in discussing the lowering of the surface free energy as the cause of sintering emphasize the enthalpy and neglect the entropy. Surfaces, interfaces, grain boundaries and vacant lattice sites lower the value of E , or as we picture it, are the seats of cations which are less screened than those in the interior of a perfect crystal. However, one should not forget that this lack of screening leads to an increase of

the value of S . Incomplete screening can contribute to the stability of a system, especially if the temperature is high. Less symmetrical polyhedra are a source of anharmonic vibrations which increase the thermal or vibrational entropy. Using the free energy change as the driving force of sintering, one has to consider the requirement for entropy and one cannot expect that a single crystal of high perfection forms even if one extrapolates to infinite sintering time. A pure oxide having no other source of entropy but the vibrational entropy that arises from surfaces and interfaces cannot be completely densified.

2.8. ACHIEVEMENTS IN THE SCIENCE OF SINTERING IMPORTANT FOR ITS DEVELOPMENT

Yu. G. Dorofeev:

My colleagues and I are engaged in questions concerning dynamic hot pressing (DHP) in which the formation process lasts $1.5 \times 10^{-4} + 4.5 \cdot 10^{-3}$ sec in dependence on the punch motion rate. The formation of materials during DHP deflexes in the occurrence of physical contacts between particles during the densification process as well as in the formation of bonds between their surface atoms. These processes are, in fact, going on simultaneously.

The welding process under pressure and the formation of metaloceramic materials taking place owing to the acting of one or more creep mechanisms. The "instantaneous creep" plays the basic part in DHP. Bonds on particle contacting surfaces are formed since they become activated during the approach of dislocations and vacancies during the "instantaneous" plastic deformation. The activation degree is determined by the quantity of energy

consumed for plastic displacement of deformed volumes, and should be such as to ensure the required density of the object. The instantaneous particle bonding proves the exclusive dependence of the obtained results on the conditions of the thermodynamic effect on the material.

The possibility of bonding during DHP is determined by the densification work (acting) value and the heating temperature of the samples.

Good quality samples of various materials are possible only when their porosity is low and when consumption of work is high. It is impossible to obtain highly-porous products of satisfactory quality by the DHP method. This limits the range of its application only to the preparation of non-porous materials or materials of low porosity.

The investigation of the coalescence process during DHP was carried out by modelling on steel straps with a little carbon /08/ and copper.

The investigation of the coalescence of monomorph metals offers a clearer model for understanding the mechanism of this phenomenon than when a polymorphic alloy is concerned, in which the phase modification changes the structure formed during DHP. The quality of the coalesced material is determined by the thermodynamic conditions in which the DHP process takes place, and whose influence in definite limits is mutually involved.

The coalescence, taking place during contact formation on the atomic level, is evidently a diffusion-free process which is possible due to the migration of grain boundaries synchronized with deformation through the physical border of the body. This can be seen in the monomorph metal when phase modifications do not affect the process under investigation.

From the above mentioned it can be seen that the process of structure formation during DHP is a short-term

one and therefore research into the sintering theory in the generally accepted sense (the long-term process) has not been carried out.

J. S. Hirsdhorn:

The topological work of Rhines and co-workers at the University of Florida have the exceptional importance in the history of sintering.

H. E. Evans:

My main interest lies in the application of sintering concepts to mechanical properties and most of the attached papers relate to this subject. During creep straining at elevated temperatures, fracture frequently originates in the formation and growth of small cavities at grain boundaries. Final failure will occur when these have grown to such an extent that they link up to form a rapidly propagating crack. Frequently in real service conditions there are periods when the component is subjected to negligibly small values of stress and strain rate but still remains at temperature. The cavities are now thermodynamically unstable and begin to sinter in a manner exactly analogous to the final stage sintering of compacts. The complete or partial removal of cavities during these periods of low strain rate results in a corresponding increase in the total strain experienced by the component at subsequent failure. In the extreme case, of course, complete and regular removal of cavitation damage will postpone indefinitely, failure by this mechanism and an apparent infinite ductility will result. Clearly such a phenomenon has profound implications.

The process has been described quantitatively in the papers by use of a recovery parameter ϕ defined again as in the papers. Figure 2 of Evans and Walker (Metal

Sci.J., 1970, 4 210) shows the agreement obtained using the general grain boundary sintering model (with gas stabilization of the cavities) with the parameter ϕ which measures the improvement in ductility obtained by giving intermediate anneals to a stainless steel. The agreement is encouraging and quite satisfactory at the two highest annealing temperatures but less so at the lowest temperature. I believe the explanation for this lies in the kinetics of the stabilization process.

When the cavities are first formed they are true voids and contain no gas. There is gas in solution, however and this must diffuse and gradually collect in the cavities reaching some sort of quantity which is in equilibrium with the surrounding solid solution. With decreasing temperature, the quantity in solution tends to decrease so that the quantity in the cavities increases resulting in the stabilization of cavities of larger diameters - i.e. lower values of ϕ . At 750° and 725°C , one can postulate that the rate of approach to equilibrium between gas in solution and in the cavities is sufficiently fast to be considered as existing from the onset of the tests; at 700°C the gas diffusion rate is less fast and equilibrium is reached gradually during the annealing period. This effect will help explain the discrepancy between theory and experiment observed for anneals at 700°C and also the good agreement at the higher temperatures.

F. N. Rhines:

I do not feel that we are far enough along at this time to speak of the existence of "the science of sintering". When we do arrive at this point, I think that the first real achievement will be a complete description of the geometric changes involved in the process, from beginning to end, couched in sufficiently

exact terms so it will then be possible to deal with them mathematically. Until this is accomplished, there can hardly be any significant contributions to the kinetics of sintering.

Again I feel that the word "achievement" is premature. If I have been able to introduce anything into the field, I think that it will be the matter of drawing attention to the importance of recognizing that the sintering process is a topological one.

G. V. Samsonov:

The bases of the physical sintering theory were first laid by Ya. I. Frenkel in 1946. He gave the basic methods for the solution of the two main tasks: the kinetics for the interparticle contact growth and the kinetics for decrease in porosity during sintering in the case of individual contact and individual pores. Frenkel gave the methods for solution of these problems basing them on two different assumptions of the sintering mechanism: either as a result of the volume viscous flow under the influence of surface tension forces or as a result of the migration of more mobile surface atoms. The laws which Frenkel derived on the basis, of the assumption of the existence of the viscous-flow mechanism. Were experimentally confirmed later these were the constancy of the rate of pore radius decrease, and the proportional dependence between the two-particle surface contacts and the time of sintering.

Ya. I. Frenkel's ideas were further developed by B. Ya. Pines who elaborated the sintering diffusion theory. The application of this theory has given possibilities for the solution of the sintering theory basic tasks when crystal bodies are concerned. Pines's theory starts from the assumption that there is a self-diffusion mechanism of solid crystal body atoms due to different

vacancy concentrations in different points of the sintered body.

Then the ideas of Ya. I. Frenkel and B. Ya. Pines have been examined in the papers of Herring, Nabarro and others. These papers dealt only with investigations of the sintering process in real crystal bodies, taking into account not only the existence of point defects (vacancies) but also dislocations, grain boundaries, etc., which together with free surfaces may be vacancy sinks.

Important experiments on models for the establishment of the quantitative laws of sintering kinetics have been carried out by Kuczynski. They are especially useful for descriptions of the initial sintering stage.

The most general conceptions of the sintering theory should evidently be developed on a uniform principle, in fact at the subatomic (electronic) level. The bases of such a theoretical approach have been given in a number of G. V. Samsonov's papers, especially in the report "The Electronic Sintering Mechanism" presented at II International Round Table Meeting on Sintering in Yugoslavia, 1971. Now the development of theoretical conceptions of sintering on the electronic level is in progress, and the following series of questions will be evaluated completely: the role of the interelectronic interaction in formation of mechanical contacts during pressing, physico-mechanical and physical contacts in the first sintering stages; adsorption occurrences, evaporation and condensation processes, recrystallization processes as well as the processes of surface, boundary and volume diffusions, diffusion-viscous and plastic flows will also be considered.

The monograph "An Essay on the Generalization of the Sintering Theory", written by a number of scientists from U.S.S.R and Yugoslavia is the first result of this work.

Development of the conception of the sintering theory from the standpoint of electronics is based on a great number of experimental results and theoretical achievements in this field.

2.9. UNIFORM MODEL OF SINTERING

Ya. G. Dorofeev:

Today much research into the influence of dislocations as well as of surface and volume diffusions on the sintering process has been carried on. It has been shown that diffusion is of primary importance for the sintering mechanism. New investigations are necessary, connected with the advancement of the theory of crystal material defects and with the influence of their physical nature. The questions of sintering should also be studied from the standpoint of the electronic theory, because the laws of all the processes taking place during sintering are defined, first of all, by the material electronic structure. Then also, as G. V. Samsonov and M. M. Ristić and his collaborators have shown, the processes of pressing and sintering during hot pressing are considered as a uniform process of the formation of material structure and properties.

H. E. Evans:

It is not yet possible to write a comprehensive sintering theory mainly because the major rate controlling processes have to be unambiguously identified under the various imposed conditions. It is particularly important to understand the role of plastic flow in the early stages of sintering, the nature of vacancy sinks and the manner in which surfaces can act as vacancy sources. These are fundamental physical questions.

A. J. Raichenko:

It is evident that it is impossible to set a uniform model for all different cases. No uniform way of formulation of the general sintering theory is possible, either.

F. N. Rhines:

Yes, it is possible to develop a model, but this will involve somewhat deeper geometric understanding than is yet available to us.

G. V. Samsonov:

A uniform sintering model is possible in principle. While constructing it, one must start from the fact that conceptions on which it is to be built, should correspond to a number of indispensable requirements. They should:

- a. be built up on a uniform basis and by uniform principles;
- b. follow from the need for solution of actual practical tasks;
- c. be sufficiently general;
- d. offer possibilities for obtaining results which would make solutions of actual production tasks possible;
- e. be sufficiently simple and accessible;
- f. ensure possibilities of prognostications.

Today there are few sintering theories, but the principles on which these theories were built up are not uniform. They give advantage to diffusion processes, surface forces, etc. Evidently, developments of the sintering theory in each of these and many other trends are useful and necessary; however, soon will come the time when the need for their unification on a uniform principle will arise; the need is dialectic, connected with the transition of quantity into a new quality. As

generally in the material science here, too, it is possible to point out three stages of conceptions of natural phenomena:

1. Establishment of correlation bonds between different measured material properties.
2. Establishment of bonds between material properties, on the one hand, and crystal structure and its defects, on the other hand.
3. Establishment of bonds between material properties and its electronic structure.

It is evident that the same also refers to sintering theory, which has mainly passed through the first stage of the comparison of parameters of the "original accumulation" of information and is today being developed in the second stage of conceptions. This is much easier due to the well developed apparatuses of the theory of dislocations and diffusion processes. Possibilities for the development in the third stage have not been used yet, though it is just this stage that should give the most general and, at the same time, the most correct and concrete possibilities for interpretations and, consequently, for prognostications, development of materials of required properties and processes with optimum parameters. In this way, the most general conceptions of sintering theory should be, most likely, developed at a sub-atomic, electronic level, as any conceptions of mass and energy transfer have electronic structure in their fundamental base as a final result.

2.10. THE FUTURE OF THE SCIENCE OF SINTERING

H. E. Evans:

Sintering is one of the increasingly found areas of study in which the understanding of the fundamental

processes has an immediated outlet in technology and obviously the sintering phenomenon has obvious applications to fabrication methods. Perhaps of more importance, however, the understanding of the behaviour of surfaces and point and line defect interactions which will emerge will have implications for the whole of physical metallurgy.

H. Fischmeister:

I do see some worth-while areas for further theoretical refinement:

- (1) a statistical treatment of the influence of mixing particles of varying size such as started by COBLE at II RTS.
- (2) the development of a theoretical understanding of inhomogeneous shrinkage (the occurrence of "centres of densification") in powder beds and compacts. Exner at Notre Dame presented a very interesting experimental paper on this, and I suppose that his paper submitted to III RTS will be ancontinuation of that work.
- (3) A theoretical study of some typical cases of contact geometries developed in compacting various types of powder. This could be based on scanning electron microscope studies of compacts, analyzing the distribution of the radii of curvature in the mating particle surfaces. Once the radii of curvature are known, the Kuczynski-Johnson model offers a ready framework for the calculation of sintering rates for each contact. The problem arising next is the development of stresses due to differences in sintering and shrinkage rate at neighbouring contacts.
- (4) Further research into activated sintering. This, however, should be done on cerafully specified geometries, in order to get a grip on the quantitative side of the process. Experiments with powders of varying calcination

temperature or varying BET surfaces only add to the already considerable body of unexplained experimental knowledge, not to the understanding of "activity".

(5) Careful quantitative studies on grain growth and grain boundary motion as influenced by pores and impurities should be very rewarding. I was greatly impressed with the paper by Stefanović at II RTS on that subject, and I hope that the Yugoslav school of Sintering will continue their fine work.

Let me add a few words about approaches in which I do not believe. With all due respect for Samsonov, whom I admire greatly, I think that his picture of electron states is too much a semi-quantitative approach to be capable of exact application to sintering. I have been unable to see more than conclusions by analogy in his sintering theory, and cannot see how these could be quantified and made predictive, which, after all, is the basic requirement of a theory.

Plastic flow in the process of sintering is the subject of an age-old controversy, which strikes me as rather academic. I believe that it is now fairle weel agreed that plastic flow will play a role only in the very early stages of sintering, and only in the case of very fine particles. For any theory which attempts to explain technical behaviour, plastic flow can, in my opinion, safely be left out of consideration. The situation becomes quite different, of course, as soon as pressure is applied during sintering. The development of a good theory of hot pressing in the intermediate and final stage of densification is a task which still is open.

J. S. Hirschhorn:

Not very good unless there are radical developments.

F. N. Rhines:

As I think must be clear at this point, my belief is that the direction that must be followed in order to establish a science of sintering is to conquer the mathematics of the geometric changes involved. Once this is accomplished, there should be available many satellite issues that could, in the course of time form a substantial body of science of sintering.

G. V. Samsonov:

Probably, the future of the science of sintering, as the transition to electronic views is the only way to the formation of uniform conceptions of sintering, because it is the demand of the contemporary scientific-technical revolution for the transformation of sciences into direct production force, of strong unification of natural and technical sciences.

3.

DIALECTICS OF THE
DEVELOPMENT OF THE
SCIENCE OF SINTERING

Today the history of science is not, according to De Broglie's standpoint, considered to be only the source of necessary information on when and what has been solved in science but also a science which points to methods of solving unsolved tasks. From that point of view the history of science is becoming an active factor in the development of science as a whole.

When the development of the science of sintering and the historical analysis of this development are concerned, then one can state that the development of this science, although it is very young, cannot be analysed independently of developments in physics and in chemistry. These are basic sciences, on the border of which the science of sintering has in fact developed. Bearing this in mind, S. Plotkin gave, in his paper⁽¹⁰⁾, a chronological survey of achievements in the field of theoretical and experimental researches into the sintering process, which may serve as a basis for consideration of the dialectic development of the science of sintering.

The contemporary science of sintering is characterized by a great number of different theories which often mutually differ both in the systems of generalization and in the insights into the very nature of this phenomenon. Besides the important contributions to the science of sintering given by T. Sauerwald⁽¹¹⁾, W. Yu. Balshin⁽¹²⁾ and W. Trzebiatowsky⁽¹³⁾ in the thirties of this century, and especially (after Second World War) those given by Ya. I. Frenkel, B. Ya. Pines, V. A. Ivensen, G. Kuczynski, Rhines, G. Kongery, R. Coble, D. L. Jonson and others the one should certainly underline that the books "Physics of Sintering"⁽¹⁴⁾, "The Reological Bases of the Sintering Theory"⁽¹⁵⁾, "Densifikation Kinetics of Metal Powders during Sintering"⁽¹⁶⁾, "Scientific Bases of

Powder Metallurgy and Fibre Metallurgy" (17), "an Essay on the Generalization of the Sintering Theory" (18), and others represent considerable contributions to the all-comprising insight into sintering theory. However analysis of the published papers, dealing with problems of sintering theory, indicates that, disregarding different approaches to solutions of these problems, among different sintering theories, especially when a comparative analysis is concerned, still there is something in them which in a definite way also determines some uniformity of a thorough grasp of the problems.

In connection with this our analysis (19) of the science of sintering development (1946 - 1973), produced quite a number of interesting data. On the basis of the analysis of results from over 2000 papers and using electronic computers, important information on the way how the science of sintering has developed were obtained. It is of interest to notice here that up to 1971 the development of sintering theory had proceeded within the frames of the fundamental bases of the model sintering theory and phenomenology theories of the sintering kinetics. Within this, regardless of the fact that in some definite cases a definite advantage was given to one or other sintering mechanism, all theoretical conceptions have moved within the frame of atomistic notions of solid body structure and the processes occurring in them. It has, however been the basis for derivations of kinetics laws of the sintering phenomenon.

Developments in solid-state physics and especially in solid-state electronic theory conditioned the analysis of the possibilities for the creation of a generalized sintering theory. Here, it seems, a configuration model of material structure (20) offers an important basis for the interpretation for the sintering mechanism in a

more generalized sense of the word. It is quite logical that according to this, one should expect further contributions from electronic theory to the creation of a uniform kinetics of sintering theory, which would represent a basis for the transition to a stage in which projection of new materials would be possible. Here one should certainly point out the possibilities offered by the Savić-Kashanin theory⁽²¹⁾ of materials behaviour under high pressures while considering the pressing process as one stage of the whole process of consolidation of materials.

All these analyses of the science of sintering point to the fact that its development may be schematically presented as a function dependence of the information mass on the time of development (Fig. 6), according to the method worked out by V. I. Kuznecov⁽²²⁾. Dialectic jumps in the development of the science of sintering, evidently, were made at the time when the mass of information was such that the jumps were inevitable.

After the experimental researches of P. G. Sobolevski into sintering as a technological procedure, which lasted many years, the papers of F. Sauerwald, W. Trzebiatowsky and M. Ya. Balshin in the 1930s conditioned contributions to the comprehension of the sintering process at the microstructure level, which conditioned a quantitative jump in the development of sintering science.

The development in solid-state physics, which has already been stated, has also conditioned two exceptional jumps in the development of the science of sintering:

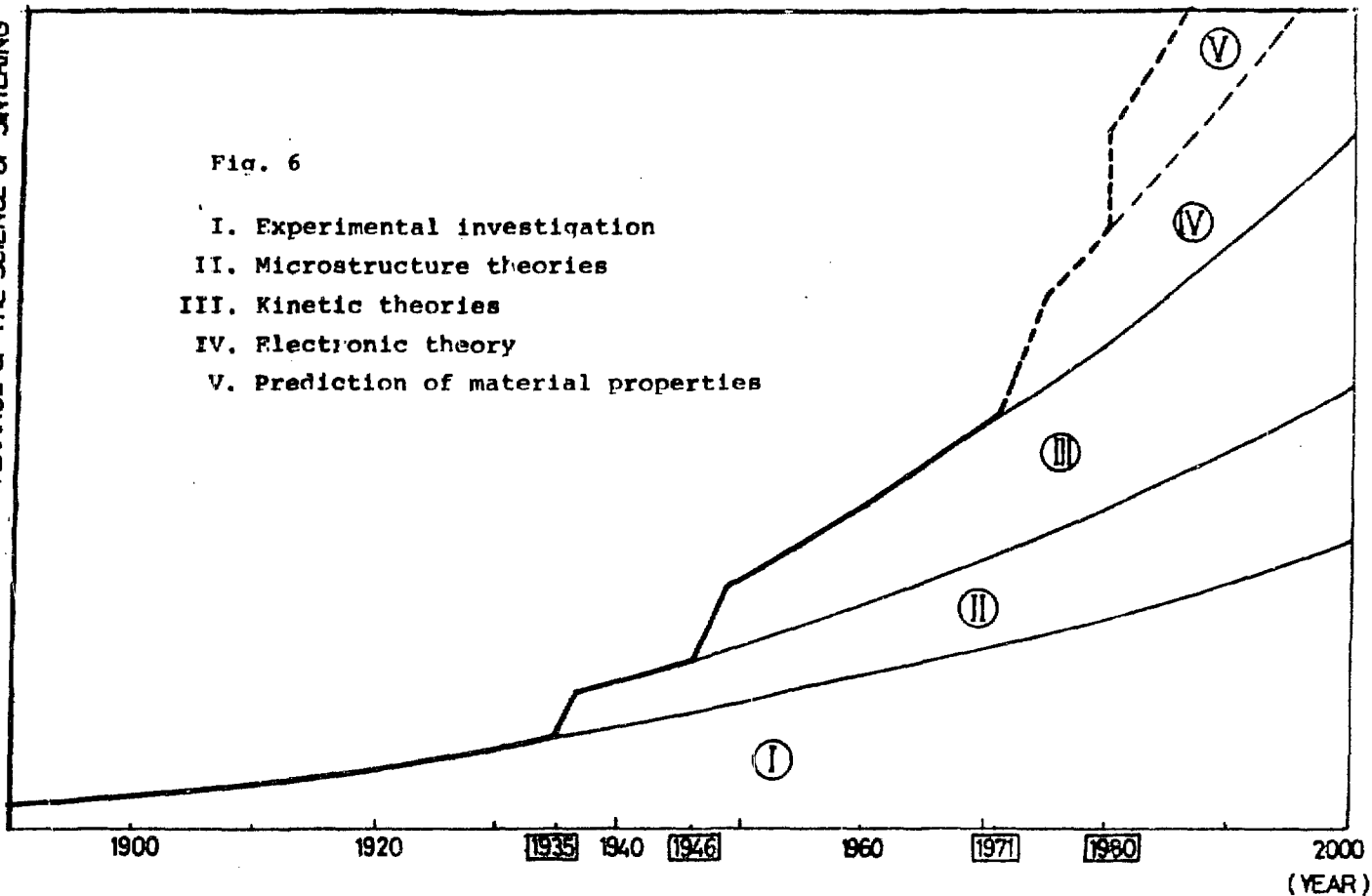
- development of sintering theory at the atomic level and

- application of solid-state electronic theory with the aim of establishing a generalized sintering theory.

ADVANCE OF THE SCIENCE OF SINTERING

Fig. 6

- I. Experimental investigation
- II. Microstructure theories
- III. Kinetic theories
- IV. Electronic theory
- V. Prediction of material properties



Generally considered, all this, on the other hand, points to the dialectic uniformity reflected in the unification of relative opposites (Fig. 6). This unification of opposites does not lead to some formal-logical opposites⁽²³⁾. On the contrary, just from this, evidently, even in the case of the science of sintering are born more profound theories, theories with corresponding new basic conceptions and principles.

During the further progress of time and in connection with the appearance of new methods and especially the new possibilities using computer techniques, when correct calculation of wave functions becomes possible, the solution of an ever greater number of problems concerning the science of sintering will be possible. Thus in the period 1980-1990 it is expected⁽²⁴⁾ that the establishment of a uniform theory of solid state, matter and material, will take place which will condition and enable us to calculate and obtain materials with properties planned in advance in the years from 1990-2000.

On the basis of everything stated above it follows that further development of the science of sintering stresses that in solving fundamental problems the dialectic approach to developments of new notions and theories is needed.

4.

FOUNDERS OF THE
SCIENCE OF SINTERING

P. G. SOBOLEVSKY

P.G.Sobolevsky (1782-1841) - Corresponding Member of Peterburg Academy of Sciences, member of numerous foreign scientific associations, is one of the pre-eminent Russian metallurgists and chemist of the first half of the last century. He was the first in Russia to work out gas-light fittings, he constructed steam-ships to be navigated on the Volga, improved methods of obtaining cast iron, participated in investigations concerning the use of electric energy in various fields and so on.

Sobolevsky acquired a world reputation by his fundamental works on obtaining and use of platinum, which are the basis of the contemporary powder metallurgy methods.

Sobolevsky, in 1826 in Peterburg, invented the method of processing platinum and obtaining various objects of it. Here he applied two main operations: he had pressed a sponge-like platinum powder and then sintered it. A year later (1827) in the "Miners Journal" he published his scientific paper in which he described his new, original method of processing platinum which essentially differed from up-to-then known methods of platinum processing. Sobolevsky became very popular and for years his name could constantly be found on pages of Russian and other foreign periodicals. So N.P.Shchegalov (1827) wrote:

"Almost all European eminent chemists had been trying during last 75 years to find out a simple and easy method of obtaining pure platinum, but up to the appearance of P.G.Sobolevsky their endeavours were unsuccessful."

A.Humbolt, 1829, wrote:

"In Peterburg more successfully than in any other place technical difficulties in refining and processing platinum were overcome. Sobolevski is - one of the leading engineers in Europe.

By applying Sobolevsky's method platinum coins (more than 4000 rubles) were made for 18 years and medals, decorations, crucibles, retorts, etc. were produced.

M. Yu. BALJSHIN

M. Yu. Baljshin devoted his first publications, 1935, to the study of specific problems of powder metallurgy. But already in 1936 Baljshin began thoroughly working out general scientific bases of powder metallurgy in the cycle of articles "On the Theory of Metallo-ceramics Processes". In 1938 he published the book "Metallo-ceramics".

The principle of autonomous deformation of structure elements during powder consolidation was stated (only qualitatively) for the first time in those papers.

In the papers published from 1936 - 1938 Baljshin established, for the first time, different states important for further development of powder metallurgy. It was then that the role of elastic deformations during the sintering and pressing processes was attested for the first time. It was also demonstrated for the first time, without regards to the non-existence of the crystallographic anisotropy, that there are the anisotropy quality and orientations of particles in compacts of powder. The degree of anisotropy was determined quantitatively. The shrinkage anisotropy during the sintering process was also established. The dependence sinterability on the powder apparent density was established. The linear dependence of density decrease with the spacing from the end of the compact was found out. It was stated that the optimum density (during constant pressure) agree with the clearly defined ratio of the given height to the diameter.

In regard to sintering and sintering under pressure, Baljshin is one of the first that proved that, in the courses of these processes, the deformation rate is submitted to the laws of quasi-viscous flow. He also took

the rapid plastic deformation into consideration.

Baljshin has published a series of papers and monographs in which he has stated (established) agreement and disagreement among the consolidation processes of powder and fibres, and among their properties as well.

Ya. I. FRENKEL

The scientific field Yakov Ilich Frenkel has been interested in is unbelievably wide. It stretches from mathematics through all parts of physics up to nuclear physics, geophysics, physiology and technics. Quite a number of his ideas are to be found in modern science. Regarding nuclear physics such ideas, for example are: the notion of temperature and thermodynamics of atom nuclei, the notion of nucleon evaporation, the notion of energetic level width, etc. In the physics of solids those are the conceptions of vacancy formation and transfer, their role in the diffusion and adsorption mechanism, the dislocation formation mechanism in the solid body, etc.

The role of Ya. I. Frenkel in the creation of the modern sintering theory should particularly be stressed. It was Ya. I. Frenkel who gave the proper emphasis to the idea of the viscose flow of crystal bodies for description of the material flow mechanism during the sintering. Assuming that sintering could take place by means of diffusion flow, he has solved the problems of the spherical pore closure and the sintering of two particles. These were among the first papers that quantitatively described the shrinkage process during the sintering.

B. Ya. PINES

Name of B. Ya. Pines is closely connected with a series of very important and fruitful courses in the development of the fundamentals of modern physics of metals - the molecular theory of solid dissolutions, particularly surface phenomena, diffusion in the metal systems, the theory of sintering in the solid phase, the creep diffusion theory, etc.

Developing Yakov Ilich Frenkel's vacancy diffusion theory in a logical way, B. Ya. Pines has described the sintering diffusion mechanism in the solid phase, based on the oversaturation of crystals with vacancies in the vicinity of the convex surface. This is the base of a whole course which is making a successful progress today.

A significant scientific activity of B. Ya. Pines is connected with a detailed study of self-diffusion in real polycrystals and metalocrystals bodies during the simultaneous influence of temperature and stress.

G. C. KUCZYNSKI

Georges C. Kuczynski's activities have been connected with the sintering process. His theoretical and experimental works in this scientific field are an exceptional contribution to the quantitative description of this very important process.

G. C. Kuczynski has given his own sintering models for all the basic mechanisms by means of which the process can proceed, basing them on his mathematical and physical considerations. His theory has been used, in a whole series of papers, for the explanation of the experimentally obtained results.

It should also be stressed that G. C. Kuczynski has created an original method of the establishment of diffusion coefficient in crystalline materials, the application of which is of particular importance.

5. APENDIX

THE LIST OF THE SCIENTISTS
WHO PARTICIPATED IN THE INQUIRE OF THE PROBLEM
"THE SCIENCE OF SINTERING AND ITS FUTURE"

1. Prof.dr Yu. G. Dorofeev,
Novocherkasskii politechnicheskii institut,
Novocherkassk, USSR
2. Prof.dr K. Easterling,
Department of Materials Technology, The University
of Technology, Lulea, Sweden
3. Dr H. E. Evans,
Berkeley Nuclear Laboratories, Berkeley, USA
4. Prof.dr H. Fischmeister,
Chalmers Tekniska Högskola, Göteborg, Sweden
5. Dr G. H. Gessinger
6. Prof.dr H. H. Hausner
7. Prof.dr J. S. Hirschhorn,
University of Wisconsin, Madison, USA
8. Dr V. A. Ivensen,
VNIITS, Moskva, USSR
9. Prof.dr P. S. Nicholson,
Mc Master University, Hamilton, Ontario, Canada
10. Dr A. J. Raichenko,
Institut problem materialovedeniya AN USSR, Kiev, USSR
11. Prof.dr F. N. Rhines,
University of Florida, Gainesville, USA

12. Prof.dr G. V. Samsonov
Institut problem materialovedeniya AN USSR, Kiev, USSR
13. Dr H. Sasaki
14. Dr J. F. Shackelford,
Mc Master University, Hamilton, Ontario, Canada
15. Prof.dr G. S. Tendolkar,
Indian Institute of Technology, Bombay, India
16. Prof.dr W. A. Weyl,
Pennsylvania State University, University Park,
Penn., USA

THE INQUIRY QUESTIONS

1. *THE SCIENCE OF SINTERING AND ITS PLACE IN NATURAL AND TECHNICAL SCIENCES*

Which basis sciences mutually connected ensure the interdisciplinary of the science of sintering? The role of each of them in the crucial development of the sintering theory.

The place of the science of sintering in the natural and technical sciences.

How can the sintering process be, in your own opinion, defined in a most proper way?

2. *SINTERING OF MODELS*

In what degree can the study of sintering on models make it possible to comprehend the very nature of the process?

3. *SINTERING MECHANISMS AND ROLES OF DEFECTS IN THE SINTERING PROCESS*

Which are, in your own opinion, the basic mechanisms responsible for the sintering? (Explain in detail with mathematical and physical proofs, if possible).

The role of particular crystal-lattice defects (point, linear, surface, volume) in the sintering process.

The sintering of one-components systems, as the sintering of two-phase systems and the role of the gas phase (sintering atmospheres).

4. SINTERING OF REAL SYSTEMS

In which way can the results obtained by the investigations on models be applied in real systems? (Give mathematical and physical considerations, if possible).

In which way is it possible to describe the sintering of real powders theoretically?

5. PHENOMENOLOGY THEORIES OF SINTERING

Phenomenology sintering theories and their place in the science of sintering.

6. SINTERING KINETICS

Is it possible to describe the sintering kinetics mathematically? (Give the equations and conditions they stand for).

7. SINTERING THERMODYNAMICS

In which way can the sintering be described, in your own opinion, from the thermodynamics point of view?

8. ACHIEVEMENTS IN THE SCIENCE OF SINTERING IMPORTANT FOR ITS DEVELOPMENT

Which achievements in the science of sintering do you consider to be of the exceptional importance in the history of sintering?

Give an account of your theoretical achievements in this field.

The most important experimental assertions of your theoretical works.

9. THE UNIFORM MODEL OF SINTERING

Is it possible, in your own opinion, to set a uniform sintering model which would be, eventually, the basis of some general sintering theory?

What direction would be of advantage for the science of sintering to follow, regarding its place in the solid body physics and chemistry?

10. THE FUTURE OF THE SCIENCE OF SINTERING

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