Scientific Approaches to Problems of Mixtures Sintering*

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Abstract:
Existing theories cannot convincingly explain relationships observed during sintering of mixtures and do not always help solve practical problems of sintering metal materials and ceramics. The main weakness of the known theories is insufficient attention to the phenomenon of alloy formation and its effect on volume changes of compacts, faulty ideas regarding driving forces for the sintering process, the mistaken mechanism of dissolution of solid phase in liquid, and the inaccurate mechanisms of growth and densification during the sintering of mixtures. Besides, obsolete theories are developed, as a rule, on the basis of a two-partial model that does not permit taking into account the skeleton structure of a powder body and the presence of interparticle pores in it. Essentially fresh concepts in the theory of mixture sintering are formulated and defined in this paper. The new approaches eliminate the drawbacks and discrepancies in the existing theories and provide the scientific basis for solid state and liquid phase sintering of mixtures.

Keywords: Sintering mixtures, Solid state sintering, Liquid phase sintering, Structure

Introduction

Experimental and theoretical work performed by us has initiated a new scientific trend in the science of sintering systems with interacting components [1]. Two-component interacting systems are those, whose components have noticeable mutual or one-sided solubility in each other or which form intermediate compounds.

Although the monograph [1] is available for everybody, researchers prefer to use elementary ideas and conceptions, which are very old now, in their studies. As a matter of fact, experts ignore the new approach to the problem of sintering mixtures of interacting components, including systems forming intermetallics. At the same time no experts have criticized the fresh ideas put forward in our work.

The purpose of this presentation is to introduce scientists and experts to these basic conceptions of the sintering theory of interacting systems. It is time now for specialists to accept and adopt the new scientific trend in sintering, develop it further and apply in practice or reject it as false in press.

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Driving forces for sintering of mixtures

The problem of the driving forces for sintering binary and multiple-component powder mixtures is of great importance in the science of sintering. Correct understanding of the nature of the driving forces is the key to objective explanation of basic sintering effects and to the effective control of the sintering process.

The driving force for sintering of a single-component or one-phase powder compact accompanied by its densification is a decrease in the free surface energy of the system due to reduction of the total surface area of interparticle pores.

A porous body compacted from a powder mixture of two or more components, capable of interacting with each other possesses, besides excess free surface energy, excess free energy connected with the potential of the system to form an alloy. Hence, sintering of a binary powder mixture involves two processes: volume shrinkage of the compact under the action of capillary forces and volume changes due to homogenization.

To determine which of the two processes – the action of capillary forces or alloy formation – dominates during sintering, it is necessary to compare their driving forces, that is to compare their contributions to the reduction of the system’s free energy.

Quantitative estimation demonstrates that the energy released by systems due to alloy formation is from two to three orders of magnitude higher than the energy that can be liberated as a result of the complete elimination of interparticle pores [1,2-5].

Because of intense heat evolution, sintering of some systems can take place at ambient room temperatures. This phenomenon constitutes the basis of the self-propagating high-temperature synthesis (SHS) of intermetallic compounds [6,7].

Huppmann [2] comments on this quantitative ratio between energies as follows:

"The driving force for densification of a liquid phase sintering system – as of any sintering system – is the reduction of interface energy which for a particle size of 10 \(\mu\)m is of the order of 1 to 10 J/mole. The chemical reaction on the other hand is driven by the decrease of the free enthalpy of the system which is typically 100 to 1000 J/mole, two orders of magnitude larger than the driving force for densification. Therefore it must be expected that the course of the chemical reaction has a profound effect on densification".

Petzow and Kaysser [3] add:

"In spite of the magnitude of the free energy decrease caused by chemical reactions, it must be noted that only decrease in interfacial energy results in the driving force necessary for densification phenomena".

Thus, though all researchers admit that alloy formation has a drastic effect on the volume changes of compacts during sintering, none of them consider alloy formation as an organic part of the sintering process, inherent to multiple-component powder systems.

What is the specific influence of alloy formation on compact densification during sintering? Various researchers give opposing answers to this question. Some researchers consider that inequality of partial diffusion coefficients can lead to the appearance of diffusion porosity, thereby lessening the value of shrinkage during sintering or even causing growth of the compact [8-11].

Other investigators believe that the homogenization process accelerates sintering and promotes densification. These scientists assume that alloy formation during sintering decreases the material viscosity and, hence, stimulates material flow under the action of capillary forces. The point is that a high concentration of defects is formed during heterodiffusion, resulting in an increase in the diffusion mobility of atoms and, consequently, in a decrease of the material viscosity [8,12].

The reason for such an ambiguity in predictions of the behaviour of mixed powder compacts during sintering is the non-scientific approach to this problem. The much more powerful chemical process of alloy formation is assumed by researchers to play the role of an
additional rather than the main driving force for the sintering of mixtures. From the thermodynamic point of view, this is a serious mistake.

The correct scientific conclusion resulting from the comparison of chemical and surface energies is that the basic driving force for the process of sintering mixtures is the reduction of the system’s free energy owing to diffusion alloy formation, while the tendency of a system to decrease its surface free energy is an additional driving force. The surface energy becomes dominant only when the system has reached a chemical equilibrium.

The action of the surface tension always results in compact densification, while the homogenization process can be accompanied by both compact shrinkage and compact growth. An advantage of the new approach to the problem of the driving forces for sintering multi-component systems is that it takes into account the direct contribution of the mass transfer caused by alloy formation to volume changes of powder compacts, including to their densification. In fact, the way in which a system attains its chemical equilibrium during sintering, determines whether the sintering process will be activated or deactivated.

**Definition of the term “sintering”**

In 1977 Hausner [13] in his presentation at the Fourth International Round Table Conference on Sintering claimed: “A careful study of the literature revealed that the term ‘sintering’ is frequently used in a wrong and often misleading way”. A quarter of a century has past since this claim was made, but the situation regarding this term remains the same. Though a special Committee was formed during the said Conference with the aim of formulating a correct definition of the term “sintering”, various formulations of the term still occur in the literature today.

All these definitions reflect different aspects of sintering: technological, property, mass transport and driving forces. Scientists are usually concerned with the mechanism of material transportation during sintering and its driving force, while the interest of the technologists is concentrated on the changes of the compact properties.

From the standpoint of the driving forces for sintering mixtures of interacting components, the definition of the term "sintering" could be formulated as follows:

*Sintering is a thermal treatment of powder bodies which change their dimensions and physical-mechanical properties as a result of the diffusion flow (redistribution) of the material under the action of alloy formation and capillary forces.*

This definition does not contain secondary details and can satisfy both technologists and scientists, because it covers all the major aspects of the sintering phenomenon. Besides, it describes sintering in just one brief sentence. The definition of the term “sintering” for single-component powder compacts follows from this generalized definition as a particular case, when there is no alloy formation.

New understanding of the driving force for sintering of mixtures also enables definition of the terms "activated" and "deactivated" sintering. If the directions of mass transport caused by the alloy formation and capillary forces coincides, then the sintering process is "activated". If these directions are opposite, then the sintering process is "deactivated" [1].

**Two-component powder compact model**

Sintering of binary systems is often analyzed on the basis of the elementary volume of a mixed powder body containing only two dissimilar particles [8]. In particular, the concept of "contact shrinkage" is introduced when densification is considered as the sum of shrinkage at homogenous and heterogeneous particle junctions [11,12]. However, such a model does not take into account a few very important features of the compact made from a mixture of two
interacting components: the "arch" effect caused by the skeleton structure of the compact; the presence of interparticle pores; which component particles form the base of the compact and which are the additive; the direction of the predominant inter-diffusion flow of atoms; the main sinks for excess vacancies in the base component – dislocations and surfaces of particles or micropores within particles.

In a real binary powder compact, particles of one component are mostly surrounded by particles of the other component over a sufficiently wide range of mixing ratios. All particles are in more or less tight contact with each other. Hence, a group of particles of an arbitrary shape and size, where the central particle is the additive component while those surrounding it form a monoparticle layer of the base component can be considered as an elementary volume, i.e., a model of a two-component particulate solid. The empty spaces between the particles in the model represent interparticle pores in a compact (Fig. 1).

**Fig. 1** Scheme of volume changes of compacts being sintered in solid state [1,14]: a) mutual location of base and additive component particles; b) swelling of the base particles without pore formation in the additive; c) densification as a result of the predominant diffusion of base component atoms; d) absolute densification of elementary cell due to the complete dissolution of the base component; e) formation of vacancy pores in the additive component; f) formation of vacancy pores in the base component particles.

Such a multiple-particle model of the mixed powder compact can take into account all its main features enumerated above, which cannot be taken into consideration by the two-particle model.

**Volume changes of compacts during solid state sintering**

Analyzing experimental data on solid state sintering of interacting systems, we discovered two ways in which the shrinkage value of two-component compacts depends upon concentration [1,14]. In the first case, if one of the components being added to another enhances densification, the other reduces it when introduced into a compact based on the
former component (Fig. 2a). In the other case, either component decreases densification when added to a compact based on the other (Fig. 2b).

Only by applying the multi-particle model, is it possible qualitatively to explain these experimental results [1,14,15]. Indeed, due to the very nature of metals, in a diffusion couple, as a rule, preferential mass transfer from one component into the other occurs owing to the inequality of partial diffusivities. Let us assume first that the predominant flux of atoms is directed from the additive component into the base one, i.e., $A \rightarrow B$ (Fig. 1a).

What will happen, if at least most of the vacancies accumulated in the particles of the component with the greater partial diffusion coefficient do not produce pores inside these particles but are absorbed by edge dislocations or annihilated at the external surface of the particles? Actually, it means that the particles $A$ which lose more atoms than accept decrease in size (Fig. 1b,c). On the contrary, the volume of particles of component $B$, towards which the resulting diffusion flow of atoms is directed, increases owing to the origination of new crystal lattice sites occupied by excess atoms of the other component.

![Fig. 2](image)

**Fig. 2** Two sorts of the dependence of densification of two-component compacts on the mixture concentration with preferential diffusion flow of an additive component $A$ into the base $B$: a) S shape (extra vacancies are annihilated at dislocations), b) V shape (extra vacancies form pores inside particles) [1].

At first glance, it is not clear why in the absence of pore formation within the particles, the preferential mass transfer causing a volume decrease in one sort of particles and nearly the same volume increase in the other sort of particles should result in considerable volume changes of the entire compact. However, these volume changes will become obvious if we take into account the so called an arch effect (Fig. 1).

Since the base particles $B$ constituting a rigid skeleton of the compact are rather closely packed, their volume increase causes the arch effect, owing to which the initial space occupied by the alloying additive particle $A$ and the interparticle pores grow in the same ratio as does the volume of particles $B$ surrounding this space (Fig. 1b).

The swelling of the base component particles $B$ adjacent to the additive ones $A$ because of the arch effect results in an increase of the entire compact. Thus, the increase of the elementary volume occurs not due to vacancy pore formation in the central particle $A$ but because the surrounding particles $B$ move apart as their sizes increase (Fig. 1b,c).

The swelling phenomenon is impossible during solid state sintering of a binary system, when the predominant atomic flux is directed from the base particles toward the additive component (Fig. 1c). In this case, the diffusion process within the elementary volume leads to material redistribution from the periphery to the center. In the extreme case, when the surrounding base particles $A$ are completely dissolved in the additive particle $B$, the volume of the central particle $B$ will increase but be less than the total starting volume of the
elementary cell containing interparticle pores (Fig. 1d). Since the volume of each elementary cell is reduced, such mass transfer will promote densification of the compact as a whole (the right-hand part of Fig. 2a).

As the direction of the preferential diffusion flow of atoms is to be quite definite and constant in any given binary system and determined by the very nature of the heterodiffusion phenomenon, the two components may act as an "activator" and a "deactivator" relative to each other during sintering (Fig. 2a). This means that in a two-component system, if diffusion micropores do not form, the sign of the volume change will be determined by which component is the base and which one serves as an additive.

As a rule, one can readily determine from the phase diagram the possible role of one or the other component in sintering of a binary system. The unipolar solubility in solid state of one of the components in the other indicates the existence of a pronounced unipolarity of the atomic diffusion flux directed to the solvent component. Therefore, solvent-based compacts exhibit a reduced densification during sintering as compared to a pure component or, moreover, tend to swell, whereas compacts with a base soluble in the additive are, on the contrary, subjected to an enhanced densification (Fig. 1a). When sintering components have an infinite mutual solubility, the predominant atomic diffusion flux is determined by the difference in the evaporation heats and, consequently, by the difference in melting points of the components [16].

Assume now that the major fraction of vacancies accumulated in the particles of the component with the greater partial diffusivity produces micropores inside these particles, and the pores serve as main sinks for excessive vacancies. When the predominant atomic flow is directed from the additive component $A$ towards the base particles $B$, growth of the entire compact is not due to pore formation inside particles $A$, but because of the arch effect, as in the previous case (Fig. 1e).

When the predominant atomic flow is directed from the base component $A$ towards the additive $B$, the increase in volume of the elementary cell is brought about by the growth of the central particle $B$ causing the outlying particles $A$ to move apart, the sizes of the base particles $A$ in the cell being virtually the same due to the vacancy pore formation within them (Fig. 1f).

It can be easily seen that if pores inside particles are the main vacancy sinks owing to, for example, low stacking fault energy of the metal with an excess vacancy concentration, the mixed powder compacts must exhibit either decreased densification or swelling for any mixing ratio of the components (Fig. 2b). In other words, the $V$-shaped concentration dependence of densification must be observed when the vacancy porosity forms in any component of a compact.

**Interaction of solid and liquid phases**

An essential shortcoming of the widely used three-stage theory of liquid phase sintering is incorrect understanding of the diffusion interaction between solid and liquid phases, and of the succession and direction of predominant diffusion fluxes of atoms through the interface. There is a generally accepted assumption [17] that the dissolution process occurs by transition of atoms from the surface of the solid into the liquid and diffusion of these atoms from the solid-liquid interface into the liquid bulk (Fig. 3b).

The alternative insight into the dissolution mechanism consists in our new conception that transition of the solid into the liquid phase is realized by means of diffusion of atoms from the liquid into the solid phase (Fig. 3c). As a result, an alloyed layer of some thickness is formed on the solid surface, so that the concentration of the layer enables it to transform into the liquid state by melting. Such an event is the consequence of the phase transition caused by lowering the melting temperature of the layer when its chemical composition has changed [18].
It is important to emphasize that the diffusion flux of atoms from the liquid into the solid phase occurs not only in the first stage of their interaction, but also during the complete period of dissolution until the chemical equilibrium between phases is established or only one phase remains. Such a fresh view of the mechanism of diffusion interaction between the solid and liquid phases affords the possibility of not only explaining the nature of the phenomena taking place at the solid-liquid interface, but also of controlling them.

**Volume changes of compacts during liquid phase sintering**

The undoubted merit of the multi-particle model is that it automatically transitions into the model of powder compact sintering in the presence of liquid phase after imagined melting of the second component (Fig. 4). It is such a transition from solid state sintering to liquid phase sintering which occurs during sintering of real two-component compacts.

The problem of sintering compacts in the presence of liquid phase occupies a special place in the science of sintering, as over 90% of sintered materials including hard alloys and ceramics are produced using this method. However, the existing theory that assumes three stages of the liquid phase sintering can be primarily applied to "non-interacting" systems, whose components dissolve in each other in the solid and liquid phase in minor or limited amounts.

The main disadvantage of existing concepts of liquid phase sintering is that, as in the case of solid state sintering, insufficient attention has been paid to the phenomenon of alloy
formation. This is connected to the fact that the scientific theory of diffusion interaction of the solid and liquid phases has not been developed so far.

Fig. 4 Scheme of volume changes of compacts being sintered in the presence of liquid phase: a) mutual location of base and additive particles before sintering; b) the volume growth of the base particles due to the diffusion of atoms from the melt; c) all melted additive is absorbed by the base particles; d) a decrease in volume of the base component particles as a result of dissolution in the liquid phase.

The observed growth of compacts during liquid phase sintering (Fig. 5) is opposite to the ordinary concept of inevitable densification due to rearrangement of solid phase particles after the melt formation. The theory of three stages of sintering in the presence of liquid phase does not take into account important events such as: the deformability of particles during pressing, the solubility of components in the solid and liquid phases and the sequence of these processes, formation of intermetallic compounds, Kirkendall and the "arch" effects. The substantial disadvantage of the old approach is that the nature of the compact growth during liquid phase sintering is usually connected only with processes of wetting and penetration of the melt into contacts between solid phase particles, under an oxide film and along grain boundaries. This approach exists because its authors adhere only to the concept of the reduction of the surface energy of the solid phase as a result of its wetting with the melt. The narrowness and shortcomings of this "mechanical" approach are in the fact that it does not take into consideration the presence of diffusion processes on the interface caused by the interaction of the solid and liquid phases, which might be called "chemical".

In this connection, the main difference between liquid phase sintering and solid state sintering is not in change of capillary forces with the appearance of a liquid phase, as it is usually assumed, but that the surface area of the interaction of the components sharply increases due to wetting of particles. As a result, an acceleration of the alloy formation process takes place, and due to this event, the heat and volume effects arise immediately [1].

The diffusion of atoms from the liquid into the solid phase in the first stage of their interaction leads to a volume increase of particles forming the skeleton of the powder body, to distancing of their geometrical centers and, therefore, to an increase in the dimensions of the whole compact (Fig. 4b). The further gradual transition of the solid phase on its surface into the liquid state is accompanied by a volume decrease of particles, by reducing the distance between their centers due to action of the capillary forces and, as a consequence, by densification of the whole compact (Fig. 4d). Thus, the direction of the dominant mass transport at the interface changes its sign during sintering time. As a result, the powder body grows at first and then shrinks [1]. This is the second peculiarity of liquid phase sintering of interacting systems.

If the solubility in the solid phase is significant or if intermetallic compounds form, but the amount of the melt is limited, then the liquid phase, due to absorption by the solid, can be exhausted before the concentration in the surface layer of the solid has reached the value
enabling its melting. In this case, the powder body should demonstrate growth only (Fig. 4c). Besides, pores must remain in places of the melted additive, keeping the approximate shape and dimensions of the former particles. The multi-particle model predicts the formation of such pores, due to the existence of a relatively rigid skeleton from the particles of the base component. Skeleton formation is caused by the comparatively close packing of the particles which were deformed during pressing of the compact. When the volume of particles increases, this tight packing provides the possibility of arising of the arch effect at the pore periphery due to friction forces between particles and interparticle adhesion.

![Graph](image)

**Fig. 5** The influence of copper concentration on the volume changes in Al-Cu powder compacts during sintering at 580 °C. The copper concentration: 1) 3; 2) 4; 3) 5; 4) 6 mass %. 5) the compact temperature; 6) the temperature in the dilatometer tube [1].

Thus, the described multiple particle model of two-component powder body sintering in the presence of liquid phase predicts an inevitable growth in the first stage of sintering, if any amount of melt exists, and shrinkage in the second stage, if a sufficient amount of liquid phase is available.

**Growth and shrinkage due to alloy formation as independent stages**

Though the phenomenon of compact growth during liquid-phase sintering has already been studied in many studies, it was not recognized as an independent stage. Since the nature of diffusion interaction of solid and liquid phases is common for all systems, volume changes of compacts during liquid-phase sintering are qualitatively of the same character. Owing to diffusion into the solid phase, the first stage of sintering in all the interacting systems is growth in volume of the compact. The amount and duration of the swelling stage depend on the solubility limit in solid, additive quantity, green porosity, particle size, and the ability of the system to form intermediate compounds.

The reliable proof of the diffusive nature of compact growth during liquid phase sintering was obtained as a result of X-ray measurements of the parameter of the aluminum lattice and the angle width of an X-ray reflection profile during liquid phase sintering of Al-Mg and Al-Cu systems [1].

Sintering of Al-Mg compacts containing 21.7 at. % Mg was performed in a vacuum dilatometer at 500 °C and interrupted after different durations of the process by means of blasting a sample with a jet of an inert gas. Studying the influence of interrupting the sintering process by means of quick cooling of the samples on their volume changes during subsequent sintering under the same temperature showed that the repeated process of sintering began
practically with that compact state in which it had been interrupted and did not depend on the fact at what stage it had taken place. Thus, quenching of compacts with an inert gas jet and removal of samples together with the dilatometer tube from the furnace reliably fixed and preserved the specimen state at a given sintering instant.

To measure an averaged parameter of the lattice, the angle positions of edges of the (422) line and its middle on their basis were determined. As a result of compact sintering, the width of the X-ray (422) line profile by the angle position of which the parameter of the aluminum crystal lattice was determined is considerably broadened. This fact indicates formation of solid solutions with a wide range of concentrations.

The dilatogram and the results of X-ray studies of sintering of Al-Mg compacts are depicted in Fig. 6. The points on the dilatogram curve designated by the numbers mark the time instants when the sintering process was interrupted to carry out X-ray studies. Comparing curves I and II one can see a clear correlation between a relative change of sample dimensions at the stage of compact growth and the formation of solid solutions. The main increase in the aluminum lattice parameter occurs during the period of time when intensive compact growth takes place. Such a connection of volume growth with the change of the lattice parameter is direct confirmation of the fact that the main cause for the growth of Al-Mg compacts during liquid phase sintering is formation of solid solutions. They form because of the diffusion of magnesium atoms from the melt into aluminum particles.

There is an opinion that part of the growth of Fe-Cu compacts during liquid phase sintering is directly caused by enlargement of the crystal lattice parameter of iron owing to the diffusion of copper atoms into solid phase particles [19]. In order to show that the compact swelling during liquid phase sintering has no direct connection with the increase of the crystal lattice parameter of the base component in a compact, particularly, of aluminum in the case of the Al-Mg system, similar experiments were conducted on the Al-Cu system. The point is that dissolution of copper in aluminum leads to contraction of the aluminum crystal lattice parameter.

Fig. 6 The changes in dimensions (I), in the parameter of aluminum lattice (II), and in the temperature (III) of aluminum compacts with 21.7 at. % Mg during sintering at 500 °C [1].

Fig. 6 The changes in dimensions (I), in the parameter of aluminum lattice (II), and in the temperature (III) of aluminum compacts with 21.7 at. % Mg during sintering at 500 °C [1].
Al-Cu compacts with 1.3 and 2.6 at. % Cu were sintered in a dilatometer at 580 and 620 °C, respectively. After various durations of sintering the process was interrupted. This enabled correlation of X-ray data with specific points on the dilatometric sintering curves. The formation of copper solid solutions in aluminum was checked by measuring the aluminum crystal lattice parameter and the width of the X-ray (422) diffraction profile.

Figure 7 shows dilatometric curves describing the relative variation of the linear dimensions of compacts during sintering. The numbered points on the dilatograms represent the instants at which sintering was interrupted. The specimens with 1.3 % Cu during sintering undergo only growth. When the amount of copper is insufficient, all copper from the melt is absorbed by aluminum. As a result, the sintering process comes to an end in the first stage, and growth alone is recorded (Fig. 7, curve a).

![Fig. 7](image.png)

**Fig. 7** The dilatograms of sintering Al-1.3 at. % Cu compacts at 580 °C (a) and Al-2.6 at. % Cu compacts at 620 °C (b) with the points marking the moments of interruption of sintering. 12, 13 – the curves of heating the compacts [1].

It can be seen that the process of liquid phase sintering of Al-2.6 at.% Cu compacts is realized two stages (Fig. 7, curve b). The distinguishing feature of the first one is compact growth, whilst the second stage is characterized by their densification. If the composition of a mixture at the sintering temperature in an equilibrium state falls, according to the phase diagram, in the region of the solid-liquid state, after growth densification takes place.

The fact that growth is brought about by the formation of solid solutions due to the diffusion of copper atoms from the liquid phase into aluminum is witnessed by a change its lattice parameter (Fig. 8). However, in contrast to increasing of the aluminum lattice parameter in the Al-Mg system, in this case there is a decrease of the parameter.

Besides, within the same sintering time interval when the main change of the lattice parameter proceeds, one can observe an increase in width of the X-ray diffraction profile which disappears as soon as the lattice parameter attains its minimum value. This line widening also supports the conclusion that formation of the solid solution with a variable concentration is a result of diffusion of copper into aluminum.

The increase in the concentration of copper in the mixture to 2.6 % and the rise of the sintering temperature to 620 °C do not qualitatively change the growth effect observed by X-ray measurements at the first stage (Fig. 8b, curve 1). It rises only quantitatively.
These experiments clearly show that the increase in value of the crystal lattice parameter of the base component during liquid phase sintering does not produce a noticeable effect on growth in volume of compacts.

In a similar manner as growth, the phenomenon of dissolution of particles in the melt is usually treated only as an indirect factor ensuring densification during the rearrangement process as a result of the liberation of interlocking particles. In the presence of a liquid phase, particles can slide due to smoothing and lubrication of their surfaces [20]. The old three-stage theory by Kingery in no way takes into account compact densification, which is directly determined by dissolution of particles in liquid.

Our experimental studies conducted for more than 30 years have finally convinced us that the processes of both growth and shrinkage caused by mutual dissolution of solid and liquid, which do not coincide in time, should be considered as independent, separate stages.

Thus, the theory of liquid-phase sintering of interacting systems should include the analysis of two stages of the process, which do not take place during sintering of non-interacting systems: volume growth caused by dissolution of liquid in solid, and densification determined by dissolution of the solid phase in liquid.

After saturation of the liquid phase with a solid component, a chemical equilibrium is reached in the system being sintered, and then densification can go on through the ordinary mechanism of solution-reprecipitation as in non-interacting systems or during supersolidus sintering of alloy powder compacts.

**Peculiarities of rearrangement processes**

Some features of the rearrangement process during liquid phase sintering should be specified for the interacting systems. Historically, the first detailed investigations on liquid-phase sintering were carried out with technically relevant non-interacting systems of cemented carbides and heavy alloys. The base particles of these systems possess a limited solubility in liquid, whereas the components forming the liquid phase are practically insoluble in the base.

A peculiar feature of the base particles of such systems is that they can not practically be deformed during compacting. The absolute rigidity or weak deformability of the particles...
results in the absence of tight and extended contacts and cold-welded bridges between particles in compacts. In such highly porous compacts with particles not bonded with each other, rearrangement can easily take place after liquid formation. Thus, it is rearrangement that makes the main contribution to the densification process in non-interacting systems.

Unfortunately, later on this mechanism of shrinkage by means of particle rearrangement was automatically transferred by researchers to all interacting systems in which the base particles are ductile. In reality, the rearrangement process is impossible in compacts with a base of plastic metals immediately after liquid formation [21]. As a result of pressing, deformed particles become closely fitted with each other and cold-welded contacts form between them, due to which their mutual motion is blocked at the moment when the liquid phase has formed. Thus, the rearrangement process leading to densification in the interacting systems with ductile metals becomes possible only after particles are freed from interlocking due to dissolution in liquid.

At the first stage of sintering, before the dissolution of particles, compacts grow in volume due to diffusion from liquid phase into solid. But the amount of growth often exceeds the value which could be reached due to the Kirkendall flow alone. The additional increase in volume of compacts is caused by, the so called negative rearrangement of particles which is associated with the uneven diffusion from liquid into solid over particle peripheries. The magnitude of the contribution of negative rearrangement to the value of compact growth depends on the average size of the particles. The larger the particles, the more the compacts swell.

Thus, it is important to distinguish rearrangement during growth of compacts from that accompanying densification. It should be noted that, on the whole, the rearrangement phenomenon is in need of further investigations, deeper analysis and quantitative description.

Quantitative description of compact changes in volume during liquid phase sintering

These new conceptions also enable quantitative description of volume changes of compacts during sintering in the presence of a liquid phase, taking into account particle rearrangement [1]. Analytical deriving of equations describing these changes is based on the assumption that the geometrical shape of the particles and their mutual positions do not change during sintering. Only the particle size changes. Densification due to rearrangement of solid phase particles is described by a special coefficient which indicates what amount of the starting porosity remains in the powder body after shrinkage owing to the rearrangement process only. The analytical equation for final porosity of the sintered body has the following form:

\[ P = R P_0 + \frac{C_S (1-C) - C C_L}{1-C - C_L} (1 - R P_0), \]

where \( P_0 \) is the starting porosity of the green compact, \( C \) is the atomic concentration of the additive in the mixture, \( C_S \) is the atomic concentration of the additive in the solid phase by the end of sintering, \( C_L \) is the atomic concentration of the base phase in the liquid, and \( R \) is the rearrangement coefficient. Porosity and atomic concentration are taken in parts of the unit.

If a system possesses one-sided solubility of the additive component in the solid phase, the equation for final porosity has the following form:

\[ P = R P_0 + C_S (1 - R P_0) \]

In the case of one-sided solubility of the solid phase in the liquid, the equation for final porosity is as follows:
Thus, the new conceptions enable formulation of practically important criteria of choosing additives, their concentrations and sintering regimes which provide the needed dimensions of sintered parts during liquid phase sintering [1].

References


Резюме: Уже существующие теории не могут убедительно описать соотношения в процессе спекания смесей и не всегда помогают в разрешении практических проблем спекания металлических материалов и керамики. Основная слабость таких теорий – недостаточное обращение внимания на явление образования сплавов и на его влияние на объемные изменения прессовки, ошибочные идеи в связи с движущими силами процесса спекания, ошибочный механизм растворения твердой фазы в жидкой и неточные механизмы роста и уплотнения в ходе спекания смесей. Кроме того, развиваются неценные теории, которые, как правило, базированы на двухкомпонентной модели, недопускающей учесть основную структуру порошка и присутствие пор между частицами. В данной работе сформулированы и заложены
фундаменты новых представлений в теории спекания смесей. Новые подходы исключают недостатки и противоречивости в существующих уже теориях и дают научное обоснование спекания смесей в присутствии жидкой и твердой фаз.

Ключевые слова: Спекание смесей, твердофазное спекание, жидкофазное спекание, структура.

Содержание: Постоянные теории не могут убедительно описать особенности процесса спекания смесей и не помогут в решении практических проблем спекания металлических материалов и керамики. Основная слабость известных теорий — недостаточное внимание феномену формирования лёгких и его влияния на размерные изменения и исчерпывающие идеи в отношении сил, управляемых процессом спекания, неправильные механизмы растворения и засыхания смесей и спекания. Кроме того, развиваются ненужные теории, основанные на двухкомпонентном моделировании, которые не допускают учета основных структурных особенностей пор и присутствия пор между частицами. В этом смысле формулированы и уточнены новые концепции в теории спекания смесей. Новые подходы исключают недостатки и противоречивости в существующих теориях и дают научную основу для спекания смесей в присутствии твердых и фаз.

Ключевые слова: Спекание смесей, спекание в присутствии твердых фаз, спекание в присутствии жидких фаз, структура.