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Address: Univerzitetski trg 2, 18000 Niš, YU, Tel: (018) 547-095, Fax: (018)-24-488

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MODELING AND COMPUTER SIMULATION OF DIFFUSION PROCESS DURING LIQUID PHASE SINTERING*

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INVITED PAPER

Zoran S. Nikolić¹, Momčilo M. Ristić²

¹Faculty of Electronic Engineering, Department of Microelectronics
University of Niš, PO Box 73, 18000 Niš, Yugoslavia

²Serbian Academy of Sciences and Arts, Joint Laboratory for Advanced Materials
Knez Mihailova 35, 11000 Belgrade, Yugoslavia

Abstract. *Liquid phase sintering is widely used for consolidation of materials. Low sintering temperatures, relatively fast densification and homogenization, and high final densities are the main advantages of this production method. A very interesting approach to better understanding of its extreme complexity due to the simultaneous and successive action of numerous elemental mechanisms would be the determination of the qualitative and quantitative effects from the stand-point of the process modeling and simulation. In that sense, this paper outlines a computer-based method for simulation of diffusion process and boundary migration on liquid/solid interfaces during liquid phase sintering. This results could be especially of interest in an building a computer aided design system, which introduces a new way of investigation: developing a new engineering design on the basis of theoretical knowledge, experimental experience, process modeling and process simulation.*

1. INTRODUCTION

Progress in the synthesis of new materials is retarded due to the lack of efficient methods which can define new technologies by a minimal number of experiments. Computer-aided design (CAD) methodology introduces a new way of investigation: developing a new engineering design on the basis of theoretical knowledge, experimental experience, process modeling and process simulation. The main task of CAD or computer simulation is to provide a good theoretical basis from which one could obtain a better understanding of the functional connection between microstructure and properties. It is

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especially important for those materials for which experimental access to these properties is impossible or limited.

The application of the computer in scientific research has become essential especially in recent years and a very powerful tool in design and manufacturing of new materials and new electronic components. CAD involves any type of design activity which makes use of the computer technique to develop new engineering design, or to analyze, or modify current engineering design. A modern CAD system should be a user-oriented system in which the computer is employed to create, transform, and display data in the form of pictures or symbols. The designer performs the portion of the design process such as conceptualization, and uses the CAD tools to solve a design problem using the computer capabilities such as very high speed of calculations, visual display possibilities, storage of large amounts of data, etc. There are many benefits of computer-aided design: this interactive process is much faster than the traditional design by experimental investigations; the design analysis helps to consolidate the entire design process into a more logical work pattern; CAD analysis saves the time of investigation (designer time and elapsed time); CAD analysis saves the people's and material's resources; CAD results in most cases are/or could be closer to optimum.

The new materials design process can be characterized in general as an iterative procedure, which consists of some very important steps: Definition of the main characteristics (physical, functional, electrical, etc.) and specifications (cost, quality, operating performance) of the new material, and possible composition which could be of interest in the design process; Synthesis, which involves both theoretical (mathematical process modeling and simulation) and experimental investigations - synthesis results are improved through the analysis procedure, and redesigned; Analysis and optimization; Evaluation as the last step which can involve the fabrication and testing of a prototype model to access operating performance, quality, reliability, etc. This step can also include documentation of the design. Synthesis and analysis are very closely related and highly iterative in the designing process. This process must be repeated until the design has been optimized. In order to build such a complex system, we need to undertake a detailed study of liquid phase sintering.

Liquid phase sintering has been studied by numerous researchers during the past few decades, beginning with Lenel [1]. It is an important process for the production of many metallic and ceramic materials. Its application is especially important from the aspect that it enhances densification and affects microstructural development. The main characteristic of this process is that the composition of the powder and the firing temperature must be chosen such that a small amount of liquid forms between the grains. Accordingly, the powder compact must satisfy three general requirements: that there is a liquid phase at the sintering temperature, that the solid phase is soluble in the liquid and that the liquid wets the solid. This process is especially important for systems that are difficult to densify by solid state sintering or when the use of solid state sintering requires high sintering temperatures. Unfortunately, the liquid phase used to promote sintering in most case remains as a glassy grain boundary phase that may lead to a deterioration of materials' properties.

The main feature of the liquid phase sintering is its extreme complexity due to the simultaneous and successive action of numerous elemental mechanisms. From many experiments with mixtures of small and large single particles annealed in the presence of liquid phase, it can be concluded that shrinkage is directly linked to grain growth. During

liquid phase sintering, small particles partially dissolved and the solid phase precipitated on the large solid particles. Because of that, large particles change towards polyhedral shapes by reprecipitating materials. At the same time, the number of small particles decreases due to coarsening in the set of small particles. The small dissolving particles give way to further densification by rearrangement of small and large particles. The starting system geometry change may occur either by large particles growing during the Ostwald ripening process or by shape accommodation.

This process can be simulated on the model system [2-5]. Small particles in between larger particles dissolve during the sintering process and the larger ones grow. Because of a high concentration gradient in this area, dissolution and reprecipitation processes are very fast. After that, the growing process of the larger particles continues with a precipitation process of dissolved material from the smaller particles. After further liquid phase sintering, the larger particles grow but the distance between the particle centers remains essentially constant.

A particularly interesting approach to understand better liquid phase sintering phenomena would be the application of numerical procedures, because they have great flexibility and can be used to obtain solutions for any model system configuration. Computer modeling and simulation of this process offer better possibilities for comparing theoretical and experimental results. Optimization of the liquid phase composition and concentration could be a compromise between achieving high density and microstructure control. However, the efficiency of the method depends on the accuracy of physical and mathematical considerations of basic processes and phenomena.

2. CHEMICAL POTENTIAL DISTRIBUTION

The explanation of phenomena that particles of different size in a liquid phase show a tendency to grow into neighbors is largely based on empirically established laws [6,7]. For a study of diffusion during the liquid phase sintering process, particularly interesting are the investigations of Yoon and Huppmann [8,9]. Studying grain growth, they concluded that the driving force of the process is not, as in usually assumed, equivalent to the difference in the particle size of the solid phase, but the difference of the chemical potential between solid phase particles which solve in the liquid phase and solid phase obtained by precipitation. If it is assumed that the liquid phase is in equilibrium with the solid phase, with which it is in contact, the concentration gradient between solid phase particles which dissolve and the solid phase formed as a reprecipitation product will carry the material through the thin layer of the liquid.

A particularly interesting approach to this problem would be the application of a simulation method which enables the introduction of a model-system with a regular or a completely arbitrary geometry, and its observation during the simulation of the real time of the process development. It also offers a model-experiment interaction, and so its introduction is fully justified.

To realize the computer simulation of diffusion during liquid phase sintering, we must first define the initial state of the liquid-solid system. It is also necessary to define the model-system, keeping in mind the convenience for the application of the simulation method and the possibility of the simulation of all characteristic phenomena during the sintering process. The difference in chemical potential, which exists in solid-liquid

systems, causes atoms to be dissolved from the solid phase, to diffuse through the liquid phase, and to be reprecipitated onto the grain, resulting in the sintering process. Since the chemical gradients must be continuous, it is implied that corresponding gradients in the concentration of the solid phase are dissolved in the liquid.

Let there is a solid particle in a liquid phase. Then a chemical potential of atoms on the grain surface is

$$\mu_s = \mu_0 - \sigma \Omega_s + \gamma_{s\ell} \kappa \Omega_s$$

where μ_0 is the reference chemical potential, σ is the stress normal to the surface, Ω_s is the atomic volume in the solid, $\gamma_{s\ell}$ is the specific energy on the solid/liquid interface, and κ is the curvature of the grain surface. If C is the concentration of atoms dissolved in the liquid phase, and C_0 is the equilibrium concentration, then a chemical potential of atoms of solid phase dissolved in the liquid phase is

$$\mu_\ell = \mu_0 - \sigma \Omega + \gamma_{s\ell} \kappa \Omega + kT \ln(C/C_0)$$

where Ω is the atomic volume in the liquid phase and kT has its usually meaning. The difference in the chemical potential $\Delta\mu = \mu_s - \mu_\ell$ causes a dissolution process at the grain surface, diffusion of the dissolved solid phase through the liquid, and a reprecipitation process onto the grain surfaces. The diffusion through the liquid is governed by the chemical gradient in the liquid. In a one-dimensional case, the flux (mass transfer) is determined by

$$J \equiv -\frac{D_L C}{kT} \frac{d\mu}{dx} = D_L \left(\frac{C \Omega}{kT} \frac{d\sigma}{dx} - \frac{dC}{dx} \right)$$

where conservation of matter dictates that the solid phase volume entering a liquid element, by both dissolution and diffusion processes, must be equal to the volume leaving that element.

For ideal solution and small differences in the activities $\Delta C \equiv C_0 (\Delta\mu/kT)$.

3. PROCES MODELING

Investigations of liquid phase sintering process on model systems suppose sintering of solid particles with liquid phase as diffusion medium. From the standpoint of geometry of particles any consideration of this process should be made in three-dimensional $Oxyz$ system. However, it can be shown that the 3D computation of system state is connected with many difficulties of mathematical type (extreme complex mathematical functions, linearization of mathematical problems, stability of convergence, real initial and boundary conditions, topological relationships, long computation, rapidity of convergence, etc.) and physical type (there are no corresponding analytical and/or empirical functions of all characteristic phenomena and parameters). Even more, when problem statements can be solved by approximation theory the quality difference between 3D and 2D simulation result is very low. Therefore, not diminishing the generality of this consideration, it will be just enough to use Oxy system as first approximation of 3D real system.

Let there be a general model system of N contours (solid phase), M pores and a liquid

phase. In Oxy system the contour as a closed boundary of regular or irregular shape is a two-dimensional particle representation. Its boundary is approximated by a series of line segments and the two-variable data formed by the (x, y) coordinates denoted as (x_i, y_j) .

The model system contours can be represented using the boundary points of contours. Let there be the sets of points

$$D_c^s = \{\mathbf{R}^s; \mathbf{r}_1^s, \mathbf{r}_2^s, \dots, \mathbf{r}_{n_s}^s\} (s = 1, 2, \dots, N),$$

where \mathbf{R}^s is the position vector of the center of the s -th contour, and \mathbf{r}_j^s is the position vector of the j -th point on the interface of this contour with its origin at the center of the contour, and n_s is the number of its boundary points. Similarly, let there be the sets of points

$$D_p^s = \{\mathbf{R}^s; \mathbf{r}_1^s, \mathbf{r}_2^s, \dots, \mathbf{r}_{n_p}^s\} (s = 1, 2, \dots, M),$$

where \mathbf{R}^s is the position vector of the center of the s -th pore, and \mathbf{r}_j^s is the position vector of the j -th point on the interface of this pore with its origin at the center of the pore, and n_p is the number of its boundary points. If

$$S_0 = \{\{\mathbf{R}^s, \mathbf{r}^s\} | (\mathbf{R}^s, \mathbf{r}^s) \in D_{c0}^s, s = 1, 2, \dots, N\}$$

is the initial structure of the model system with no pores, and if

$$S_c = \{\{\mathbf{R}^s, \mathbf{r}^s\} | (\mathbf{R}^s, \mathbf{r}^s) \in D_{ct}^s, s = 1, 2, \dots, N\}$$

and

$$S_p = \{\{\mathbf{R}^s, \mathbf{r}^s\} | (\mathbf{R}^s, \mathbf{r}^s) \in D_{pt}^s, s = 1, 2, \dots, M\}$$

is the structure of contours and pores after sintering (simulation) time t , respectively, then the transformation $S_0 \rightarrow S_c + S_p$ describes the liquid phase sintering of the model system.

4. NUMERICAL SOLUTION OF DIFFUSION EQUATION

We shall discuss here some of the problems occurring in the numerical solution of the diffusion equation and the analysis of the numerical method. For the sake of simplicity in nomenclature, we shall consider only the two-dimensional case. However, all results given in the following can be generalized to 3D in a straightforward manner.

Mass diffusion outside the particles is assumed to be the only mass transfer process. If D_L is the concentration independent diffusivity of the solid in the liquid diffusion through the liquid phase is defined by the partial differential equation of the parabolic type

$$\frac{\partial C}{\partial t} = D_L \nabla^2 C. \quad (1)$$

If $C = C(x, y, t)$ we replace Eq. (1) by

$$\frac{\partial C}{\partial t} = D_L \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right). \quad (2)$$

For the computation of time dependent concentration of liquid phase (the numerical solution of Eq. (2)) we will use a finite-difference technique [10].

Let there be an experimental domain of a rectangular shape that is partitioned into subregions by a mesh. Let there be the two distance coordinates x and y , and time t as independent variables, and that the respective grid spacings are Δx , Δy , and Δt . Subscripts i , j , and k may then be used to denote that space point having coordinates $i\Delta x$, $j\Delta y$, and $k\Delta t$, so called the grid-point (i, j, k) . For an approximate solution of the Eq. (2), the classical five points approximation can be used

$$C_{i,j,k+1} = (1 - 2\lambda_1 - 2\lambda_2)C_{i,j,k} + \lambda_1(C_{i+1,j,k} + C_{i-1,j,k}) + \lambda_2(C_{i,j+1,k} + C_{i,j-1,k}), \quad (3)$$

$(i = \overline{2, n-1}; j = \overline{2, m-1}; k = 0, 1, \dots)$

where $\lambda_1 = D_L \Delta t / (\Delta x)^2$, and $\lambda_2 = D_L \Delta t / (\Delta y)^2$. If all the $C_{i,j,k}$ at the time level t_k are known, $C_{i,j,k+1}$ at the time level t_{k+1} can be calculated for all i and j directly using Eq. (3). For reasons of computational stability, care values of distance and time interval (Δx , Δy , and Δt) must also be taken so that $\lambda_1 + \lambda_2$ does not exceed 0.5.

In the general case the first and the last meshline coincide with the boundaries. Then we can defined the following initial conditions

$$C_{i,j,0} = g_{i,j} \quad (i = \overline{2, n-1}; j = \overline{2, m-1}), \quad (4)$$

and boundary conditions

$$\begin{aligned} C_{i,1,k} &= f_{1;i,k} \\ C_{i,m,k} &= f_{2;i,k} \\ C_{1,j,k} &= f_{3;j,k} \\ C_{n,j,k} &= f_{4;j,k} \quad (i = \overline{1, n}; j = \overline{1, m}; k = 0, 1, 2, \dots) \end{aligned} \quad (5)$$

5. PROCESS SIMULATION

Let there be N contours in the liquid and that model system geometry is defined by

$$\begin{aligned} G & \text{ Rectangular domain} \\ \bigcup_{s=1}^N D_c^s & \text{ Solid phase} \\ G \setminus \bigcup_{s=1}^N D_c^s & \text{ Liquid phase} \end{aligned}$$

For defining the probable state of the system at which the precipitation process starts, it can begin with assumption that the dissolution of solid phase takes place in liquid phase. The growth of a liquid phase concentration continues up to the saturation and then the random liquid phase fluctuation at certain boundary points between liquid and solid phase causes the formation of the precipitated region.

In that sense, the initial state of a liquid phase can be defined by three different states:

C_a - no dissolved solid phase in a liquid phase, C_b - equilibrium concentration of liquid phase, and C_c - saturated liquid phase. From the point of process simulation after short simulation time there is no difference in the state of system with C_b or C_c as the initial state. If $C_{s,L}$ is the concentration of a solid in contact with the liquid and C_L is the equilibrium concentration of liquid, then the initial conditions (4) are defined by

$$C_{i,j,0} = \begin{cases} C_{s,L} & (x_i, y_j) \in D_c^s \\ C_a, C_b \text{ or } C_c & (x_i, y_j) \in (R \setminus (\bigcup_{s=1}^N D_c^s)) \\ (i = \overline{2, n-1}; j = \overline{2, m-1}; s = \overline{1, N}) \end{cases}$$

The boundary conditions (5) can be defined

$$\begin{aligned} C_{i,1,0} &= C_{i,m,0} = C_{1,j,0} = C_{n,j,0} = C_L, \\ C_{i,1,k} &= C_{i,2,k}, \\ C_{i,m,k} &= C_{i,m-1,k}, \\ C_{1,j,k} &= C_{2,j,k}, \\ C_{n,j,k} &= C_{n-1,j,k} \quad (i = \overline{1, n}; j = \overline{1, m}; k = \overline{0, 1, 2, \dots}) \end{aligned}$$

because this form provides time depended liquid phase concentration profile. These conditions are very well from the point of view of the numerical solution of the diffusion equation, because the initial and, particularly, boundary conditions are relatively simple: the boundaries of the domain are then straight lines parallel to the coordinate axes. However, it is a fact that the amount of liquid is very small and very often is located only in the contact region between the solid particles. From that point, we must define new initial and boundary conditions for the time $t = 0$, as well as changeable boundary conditions for time $t > 0$.

If G_1 is the domain of contact region in which liquid phase is present, and G_2 is the set of boundary points of liquid phase, the model system geometry is defined by

$$\begin{aligned} G & \text{ Rectangular domain} \\ \bigcup_{s=1}^N D_c^s & \text{ Solid phase} \\ \overline{G_1} \cup G_2 & \text{ Liquid phase} \end{aligned}$$

with new initial conditions

$$C_{i,j,0} = \begin{cases} C_{s,L} & (x_i, y_j) \in D_c^s \\ C_a, C_b \text{ or } C_c & (x_i, y_j) \in (G_1 \cup G_2) \\ 0 & (x_i, y_j) \in (G \setminus (G_1 \cup G_2 \cup (\bigcup_{s=1}^N D_c^s))) \\ (i = \overline{2, n-1}; j = \overline{2, m-1}; s = \overline{1, N}) \end{cases}$$

and new boundary condition

$$C_{i,j,k} = \min_{\substack{(x_i, y_{j-1}) \in G_1 \\ (x_{i+1}, y_j) \in G_1}} (C_{i,j-1,k}, C_{i+1,j,k}) \quad ((x_i, y_j) \in G_2; k = \overline{1, 2, \dots})$$

When taking the above mentioned fact as the starting assumption a general algorithm will be as follows:

P R E P R O C E S S O R

Materials Data	Specific Interface Energy Solid - Liquid, Molar Volume, Composition of Liquid and Solid, Diffusion Coefficient in Liquid, Sintering Temperature, etc.
Analysis Conditions	System State, Initial and Boundary Conditions.
Model	Configuration: Regular or Irregular Shape.
Discretization	Designing a Mesh, Simulation Parameters.

S I M U L A T O R

◆	Concentration of Liquid Phase (vs. Simulation Time)
◆	Flux
◆	Mass Flow
◆	New Sets of Boundary Points of Solid Phase

P O S T P R O C E S S O R

◆	Time Depended Morphological Change of Model System
◆	Concentration Profile of Solid and/or Liquid Phase
◆	Process Characterization (Grain Growth, Kinetics, etc.)

6. MODEL EXPERIMENT

The experimental fact that the contours of different sizes being in the liquid show a tendency for growth into their neighbors, so that the smaller ones dissolve in liquid and the larger ones grow can be demonstrated and simulated on the model system with seven contours of different radii (Fig. 1). The smaller ones dissolve in the liquid matrix and dissolved atoms flow from the matrix to the larger contours.

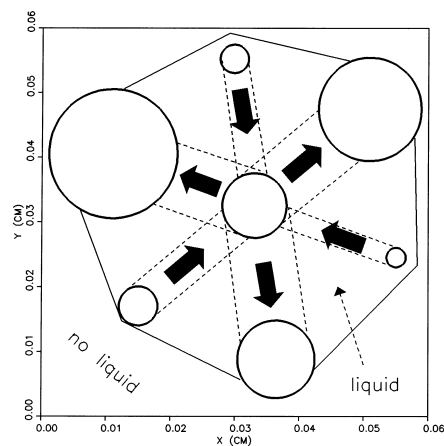


Fig. 1. Model system of seven contours and equivalent diagram depicting mass transfer flow

We will use the present algorithm for the study a sintering of the W-Ni system, although it should be noted that the theoretical basis of this analysis is general and applicable to any multi component system in which there is a liquid phase at sintering temperature. The accuracy of the calculated simulation results depends primarily on how well the compositions of liquid phase and precipitated alloy and the diffusion coefficient in the liquid are known. Since a contour boundary is approximated by a polygon of many sides that depend of mesh size, the smoothed contour's line needs large enough mesh size.

For the W-Ni system the next data were used: the composition of the precipitated alloy: 99.55 at.% W [11]; the composition of the liquid in contact with this alloy: 35 at.% W; the composition of liquid in contact with pure W: 35.16 at.% W; the diffusion coefficient in the liquid, $D_L = 10^{-5} \text{ cm}^2/\text{s}$ [12]. All calculations were performed on 60×60 mesh points.

The sintering of the W-Ni can be simulated on the idealized model system of six contours of regular shape of radii $r_{i+1} = r_i / 2$ ($i=1,2,\dots,5$; $r_1=240\mu\text{m}$) with liquid phase that is localized in contact region only (Fig. 2a). Shown in Fig. 2b is the starting concentration profile of liquid phase in contact with the solid phase. The assumption was that the concentration is proportional to $1/r$. The characteristic of such system is that a contour is surrounded by two contours of different size. Therefore the dissolution and the precipitation processes take place simultaneously on the same contour but on in different boundary points. Because of a high concentration gradient in these areas, dissolution and reprecipitation processes are very fast. Therefore, two smallest contours disappear after a few minutes only (Fig. 3). The other contours dissolve toward the larger contours and grow toward the smaller ones. Pure tungsten dissolved into the liquid and transported through the liquid precipitate as W(Ni) solid solution on the larger contours. After further liquid phase sintering, the contours dissolve and grow but the distance between the contours' centers remains essentially constant. These phenomena were previously described by Yoon and Huppmann [9].

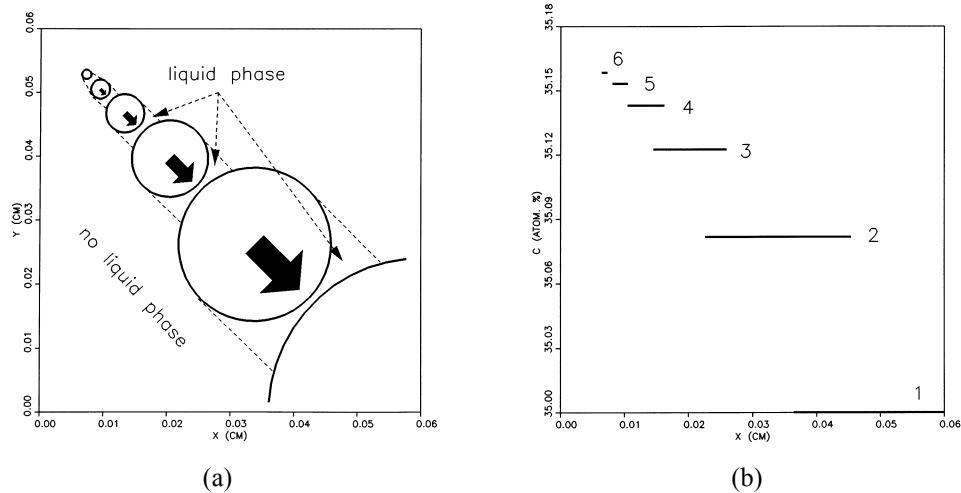


Fig. 2. The investigated model system of six contours.
 (a) Initial geometry. (b) Initial concentration profiles.

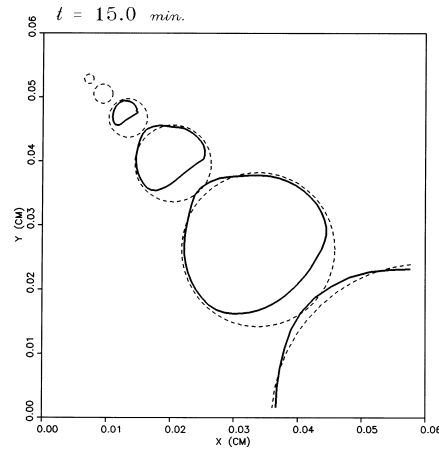


Fig. 3. Simulation results of microstructural changes for model system of six contours after 15 min.

The present model system was based on the assumption that there were two phases (solid, liquid) and no pores during liquid phase sintering. The morphological change of model system with pore distribution and their elimination is more complicated.

7. PROCESS KINETICS MODELING

As a consequence of the diffusion process in the liquid-solid system, as well as the solution-precipitation process, there is a change of the boundary contour's point place during sintering time. If

$$T = \{t | t = k\Delta t, k = 0, 1, \dots, K\}$$

is set of sintering (simulation) time, where Δt is finite time increment, and

$$(x_s(t), y_s(t)) \quad (s = 1, 2, \dots, N)$$

then the one direction grain growth is defined by

$$\Delta\rho(t) = \rho(t) - \rho(0),$$

where

$$\rho(t) \equiv \rho(x(t), y(t)) = \sqrt{[x(t) - x_c]^2 + [y(t) - y_c]^2}$$

is the distance between the contour's center (x_c, y_c) and the contour's boundary point (x, y) , so that the average grain growth for the s -th contour is now

$$\langle \rho_s(t) \rangle = \frac{1}{n_s} \sum_{i=1}^{n_s} [\rho_i(t) - \rho(0)].$$

Let us know sets of values $\langle \rho_s(t) \rangle$ ($s = 1, 2, \dots, N$) for all contours of model system. The average grain growth rate value for the s -th contour after simulation time t is now

$$V_s = \frac{\langle \rho_s(t) \rangle}{t}.$$

If the values of $\langle \rho_s(t) \rangle$ in each simulation time points $t \in T$ are determined, the time dependence of the grain growth for the s -th contour can be defined when it adds a set of simulation times (t_0, t_1, t_2, \dots) to the set of $(\langle \rho_{s,0} \rangle, \langle \rho_{s,1} \rangle, \langle \rho_{s,2} \rangle, \dots)$, i.e. $(\langle \rho_{s,k} \rangle, t_k)$ ($k=0, 1, 2, \dots, K$). Similarly, the time dependence of the grain growth rate can be defined by adding the time set to the set $(V_{s,0}, V_{s,1}, V_{s,2}, \dots)$, i.e. $(V_{s,k}, t_k)$ ($k=0, 1, 2, \dots, K$).

8. SIMULATION PROCEDURE

The main characteristic of the solution-precipitation process is that the smaller solid particles dissolve at solid/liquid interface (thermodynamically unstable), diffuse through the liquid and precipitate on the larger particles.

Let there be a system consisting of a dispersion of spherical particles with different radii in a liquid in which the solid phase has some solubility. Thus, the concentration of the dissolved solid, C , around a particle of radius r is given by

$$\ln\left(\frac{C}{C_0}\right) = \frac{2\gamma_{sl}\Omega}{kTr}. \quad (6)$$

If $\Delta C = C - C_0$ is small, then Eq. (6) becomes

$$\Delta C = C_0 \frac{2\gamma_{sl}\Omega}{kTr}. \quad (7)$$

This Eq. is not valid for a very small particle since ΔC becomes infinite as its radius goes to zero. However, the number of the small particles at any simulation time is sufficiently small so that Eq. (7) can be assumed to be valid for all particles.

After simulation time $t > 0$, the most of the particles are no longer circular. It is expected because the diffusion field around and between particles is highly asymmetric. Therefore we define the radius of a noncircular particle as $r_s = \sqrt{a_s/\pi}$ ($s=1, 2, \dots, N$), where a_s is the area of the s -th particle.

It can be seen from Eq. (7) that a higher concentration around a smaller particle gives rise to a net flux of matter from the smaller to the larger one. Then the flux vector is

$$\mathbf{J} = -D_L \nabla C. \quad (8)$$

Applying Eq. (8) at boundary points of solid interface, the effects of the dissolution ($dM/dt < 0$) and precipitation ($dM/dt > 0$) processes can be computed.

8.1. Definition of initial model system

If (x_c^s, y_c^s) and r_s are the center position and the radius of the s -th circular contour respectively, then the solid phase of the model system is

$$\bigcup_{s=1}^N \{(x_i, y_j) | (x_i - x_c^s)^2 + (y_j - y_c^s)^2 \leq r_s^2\}$$

with the contours' boundary points

$$D_c^s = \left\{ (x_i, y_j) \mid (x_i - x_c^s)^2 + (y_j - y_c^s)^2 = r_s^2 \right\} (s = 1, 2, \dots, N).$$

The initial model system is characterized by a contour size distribution that is generated by random generation for discrete contour size region $[r_{\min}, r_{\max}]$. The center positions of the contours are randomly distributed ("gravity free" and "drop-freeze" methodology) without contour intersection (Fig. 4(a)).

The rearrangement process assumes that if there is good wetting between liquid and solid phase, solid particles will rearrange themselves under the action of surface tension forces producing more stable packing. This stage may be dominant only over a few minutes of the liquid phase sintering process.

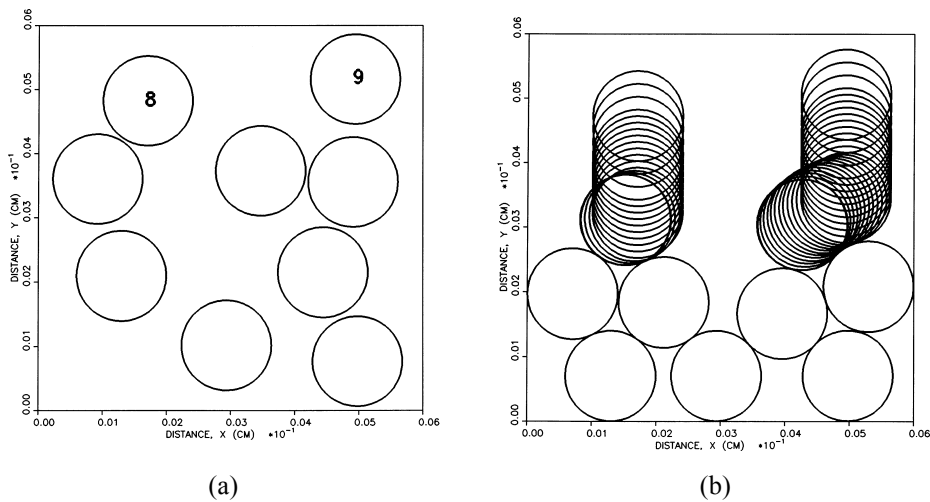


Fig. 4. Simulation of rearrangement process. (a) Initial monosized contour distribution generated by random generator. (b) Packed model system with displayed steps of packing contours numbered with **8** and **9**.

The method applied for the simulation of the initial rearrangement process is the settling procedure in which contours are subjected to a simulated gravity field: the contour falls under gravity and slides down over the already settled contours. This procedure will be applied to each contour starting with the contour having the lowest position in the vertical direction of experimental region (Fig. 4(b)). Let us assume that the bottom wall and walls on both sides of the experimental region are stationary and the upper wall is the moving wall. Now we can define a new (final) experimental region in which the upper wall position is defined by the highest contour position.

The key parameters such as contact and dihedral angle, packing of the solid particles, amount of liquid phase, the thickness of the liquid bridge, δ , distribution of the liquid phase between the solid grains are all directly defined by the model system.

We will use the present simulation method for a study of diffusion and boundary migration during liquid phase sintering of an Al_2O_3 -glass system. Such a system is

relatively well characterized. The observation that the alumina-glass system has a continuous glassy boundary indicates good wetting. Hence, it can be used as a model system.

An initial model system (Fig. 5(a)) was obtained assuming that for the polycrystalline Al_2O_3 the particle size range was 5-10 μm ($\langle\rho_s(t)\rangle = 7.05\mu\text{m}$) inside experimental region 120 $\mu\text{m}\times 150\mu\text{m}$. The next model shown in Fig. 5(b) was obtained during the rearrangement process ($\delta=0.1\mu\text{m}$, exp. region 120 $\mu\text{m}\times 100\mu\text{m}$). The initial surface area fraction of the solid phase after the rearrangement process is rather difficult to estimate and is lower than expected (66%) because of the wall effect during packing. Therefore, we will consider the narrower experimental region (dashed box on Fig. 5(b)) in which the surface area fraction of solid is 75%.

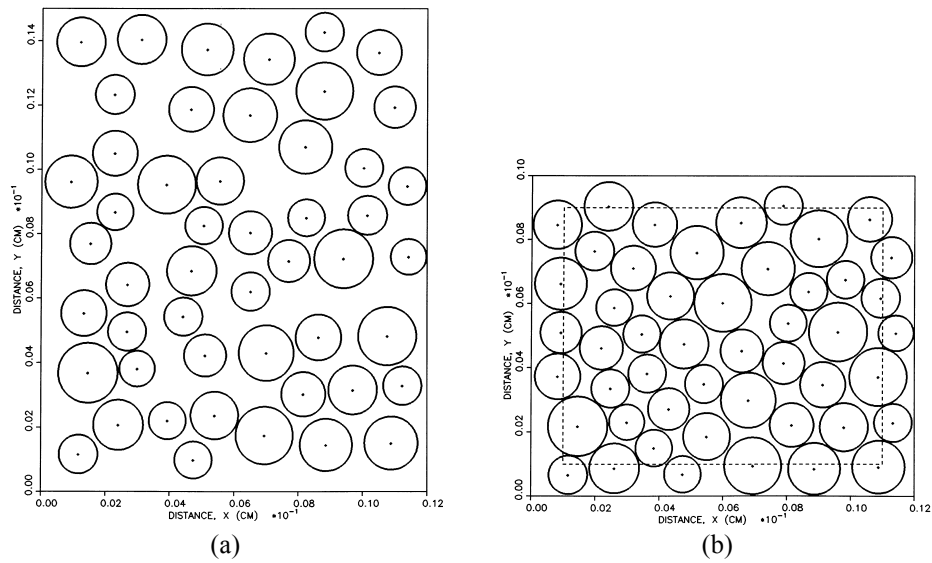


Fig. 5. Geometry of investigated model system for Al_2O_3 - glass system. (a) Before rearrangement. (b) After rearrangement.

Since the solution-precipitation model makes no assumption about the starting model system, the defined simulation method can be applied to any model system. In that sense, the obtained packed system has been used as the starting model system.

For the Al_2O_3 -magnesium aluminosilicate glass system with an equilibrium composition of liquid 14.6 MgO, 44.1 Al_2O_3 , and 41.3 SiO_2 , in wt% [13], the following data were used:

$$C_o = 29.00\text{mol\%} \quad [14], \quad D_L = 1 \times 10^{-10} \text{m}^2/\text{s} \quad [15], \quad \Omega = 4.25 \times 10^{-29} \text{m}^3 \quad (\text{Al}_2\text{O}_3), \quad T = 1873 \text{K},$$

$$\gamma_{s\ell} = 0.5 \text{J/m}^2 \quad [16].$$

All calculations were performed on 128 \times 128 mesh points.

8.2. Simulation of densification without rearrangement

In this section a selection of computed results is presented to illustrate the application

of the defined simulation model for the solution-precipitation processes. The initial boundary concentration was as it defined by Eq (7). After a few minutes, solution-diffusion-precipitation processes are just beginning to occur along the solid/liquid boundary interfaces. The driving force of those processes is not the difference in the size of contours, but the concentration gradient between solid and liquid phases. Smaller contours have the highest concentration levels and they dissolve in the liquid matrix. Dissolved atoms diffuse through the liquid bridge or through the liquid matrix and precipitate on the larger contours. During this stage liquid thickness remains nearly constant because dissolution and precipitation simultaneously take place over short distances. The smaller dissolving contours give way to densification by second rearrangement of small and large contours. From simulation results at time 80 min, shown in Fig. 6, it can be seen that morphological evolution depends on the contour's location: the large contours with small contours as neighbors have extensive grain boundary change because they have the fastest growth. This means that small contours, which are very close to the bigger ones dissolve very quickly and will disappear.

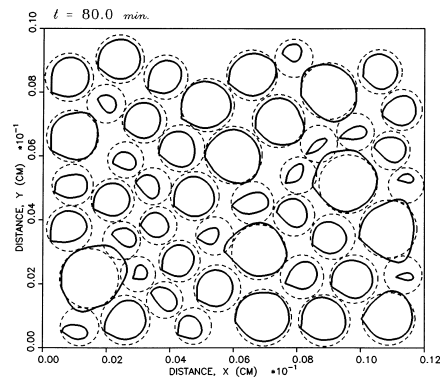


Fig. 6. Simulation results of microstructural changes after 80 min.

8.3. Simulation of densification with rearrangement

The influence of particle shape on packing efficiency has been recognized for a long time. However, most of the studies deal with the packing of spherical or nearly spherical particles, whereas the studies of packing of nonspherical particle mixture appear to be limited.

The densification is accompanied by considerable coarsening and by changes in the shape of particles. The sizes of the particles and their locations change as simulation time increases and the particles can pack more efficiently because of a non-spherical-symmetric diffusion field.

The initial liquid concentration can be taken as the concentration of pure liquid with no dissolved solid (C_a). However, because the dissolution process starts very quickly after additive melts the same results can be obtained with equilibrium liquid concentration or with minimal liquid/solid interface concentration as the initial concentration. This model assumes that the liquid phase is uniformly distributed into a model system, although the experiment by Shaw [17] has shown that the liquid phase

distribution can not be uniform even when a large volume of liquid is present.

The boundary composition is not constant during simulation. It changes with time as a function of diffusion in the liquid and of amount of dissolved solid phase: boundary concentration can increase or decrease but the material's flow outside the experimental region is not allowed. Time dependent boundary concentration is especially important for a particle that is located near the edge of the experimental region to avoid the effects of finite model system size.

Figure 7 show the shape and location of the center of the model system contours. From simulation result at time 70 min it can be seen that morphological evolution and migration depend on the contour's location. In the present simulation the small contours tend to be located near the large contours during densification by rearrangement. The large contours with small contours as neighbors have extensive grain boundary movement because they have the fastest growth. This means that small contours, which are very close to the bigger ones dissolve very quickly and will disappear. The growth of larger contours (the precipitated areas) does not occur uniformly around the contours. The largest shape distortion in center-to-center direction is a result of interparticle diffusion interactions at relatively small interparticle distances (large concentration gradient). It can be seen also that a diffusion field surrounding some contours has no influence on the precipitation process because of relatively large distances between contours. Such contours dissolve very slowly. After long time, most of the smallest contours have disappeared, some of the smaller contours are still dissolving and the bigger ones are growing only. Evident is the decrease in the number of contours and an increase in the average contour's size with simulation time. By such model system evolution it can be concluded that although the liquid bridge thickness slowly increases with time, which will certainly alter the flux of dissolving material, the average liquid thickness remains approximately constant as a result of a moving grain boundary. As a result of the solution-precipitation process some of the contours with starting radius close to the average radius show a tendency of dissolution and precipitation at the same time: such contours grow on one side and dissolve on the other. All of these processes will be ended by completely reaching a uniform concentration distribution.

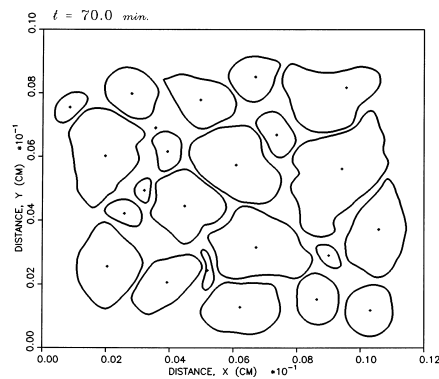


Fig. 7. Simulation results of microstructural changes after 70 min.

A general conclusion can be drawn that the largest contours grow at the expense

of the surrounding smaller contours. Because of that, the distances between the interfaces of the large contours that are located near one another decrease with simulation time. However, when small contours have disappeared some large contours can grow at the expense of the others. This process probably depends of the size difference between these large contours. As Akaiwa and Voorhees have been concluded [18], this process must be fairly rare, for it depends on two large contours of nearly the same size being located near each other.

It can be seen also that during coarsening the sizes of contours and their centers' locations change with simulation time. The migration of the contours is a result of the nonuniform concentration gradient over their surfaces. For some contours this migration can be significant inside the experimental region. Even small changes in the locations of the contours relative to one another can have large effects on the resultant morphological evolution of model system.

9. CONCLUSIONS

This paper outlines a computer-based method for simulation of diffusion process and boundary migration on liquid/solid interfaces during liquid phase sintering. The theoretical basis of such analysis is general and applicable to any multicomponent two phase system. The simulation method developed is based on the defined submodels for rearrangement and solution-precipitation with and without densification. With the initial model system based on randomly distributed particles, the rearrangement process was simulated by a settling procedure. The solution-precipitation was modeled based on the corresponding model system that restructures itself so that the larger particles can grow by transfer of dissolved atoms through the liquid phase. Such a model system can be used to assist in analysis of experimental data and in the optimization of sintering of ceramics in the presence of a liquid phase.

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MODELOVANJE I SIMULACIJA PROCESA DIFUZIJE TOKOM SINTEROVANJA U PRISUSTVU TEČNE FAZE

Zoran S. Nikolić, Momčilo M. Ristić

Sinterovanje u prisustvu tečne faze predstavlja tipičan proces za konsolidaciju materijala. Glavne karakteristike ovog procesa su niža temperatura sinterovanja, relativno brzo skupljanje i homogenizacija i velika gustina dobijenog materijala. Posebno interesantan pristup boljem razumevanju izuzetne složenosti ovog procesa, koja je posledica simultanog i sukcesivnog delovanja niza elementarnih mehanizama, predstavlja određivanje kvalitativnih i kvantitativnih efekata procesa primenom metoda modelovanja i simulacije. U tom smislu, u ovom radu je razvijen fizički i numerički model simulacije procesa difuzije i pomeranja granice medjupovršine tečno/čvrsto tokom sinterovanja u prisustvu tečne faze. Ovi modeli mogu biti deo složenog sistema za planiranje i projektovanje procesa, s obzirom da uvode nov način projektovanja procesa na osnovu postojećih teorijskih znanja, eksperimentalnih rezultata i rezultata modelovanja i simulacije procesa.