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# On the mathematical theory of microstructure evolution during final stage of liquid phase sintering

*A new mathematical theory of the microstructure evolution during the final isothermal stage of liquid phase sintering has been developed. The basis of this theory has been formed by materials science and continuum mechanics. The microstructure evolution has been described by the system of non-linear differential equations, which contain more than ten parameters. Finite difference analysis has been performed for a heavy alloy cylindrical specimen. The results of the calculations have been compared with experimental data.*

*Keywords*: *mathematical theory, microstructure evolution, liquid-phase sintering, finite difference method, heavy alloys.*

## INTRODUCTION

At present there are only a few investigations related to the problem of the equilibrium distribution of the liquid phase in a sintered pore-free sample during heat treatment [1–2]. Different models of the microstructure were used in these works. In addition, the driving force for liquid migration is assumed to be equal to the derivative of the excess free energy, associated with interfaces, with respect to liquid volume. Such energy was defined in [1] from a planar multi-grain array of hexagonal grains. The excess free energy was determined from the model, in which each particle in an aggregate is enclosed into a Voronoi cell [2]. To determine the minimum interface energy configurations of a uniformly intermixed grain-matrix system in [3], a microstructural model was used, which consisted of a rhombic dodecahedron grain in contact with the matrix at its curved surfaces along truncated edges and corners.

The sintering of cemented carbides with graded metal binder content is modeled in [4]. The equations of linear viscous creep are laid in the base of finite element method. It is shown that during liquid phase sintering solid–liquid interfaces contribute substantially to the kinetics of the refractory skeleton distortion and binder migration. In gradient materials the evolution of a solid skeleton takes place even in pore-free components.

The migration of liquid is accompanied by shape distortion of a powder sample. In particular, papers [5–6] reported the investigation of this problem.

In the present paper, a new mathematical theory of the microstructure evolution during the final isothermal stage of liquid phase sintering of a pore-free compact is presented. The materials science and continuum mechanics form the basis of the theory. In contrast to [1–3], we do not introduce any kind of the microstructure model. It is assumed that the microstructure is defined by the linear intercept method. The appropriate full system of differential equations contains the following quantities: the mean grain size, contiguity of solid skeleton, volume

fraction of liquid, solid–solid grain boundary energy, liquid–solid surface energy, densities of the solid and liquid phases, solid–solid grain boundary viscosity, viscous analogy of the Poisson's ratio, grain growth rate constant, and holding time. The comparison of calculated and experimental data on a cylindrical sample indicates that the theory can reflect the microstructural changes during the final stage of liquid phase sintering of heavy alloys.

## CONSTITUTIVE EQUATIONS

The constitutive equations fill a highly important place in the mathematical theory of microstructural changes during the final stage of liquid phase sintering, which is developed. We choose such equations in the form

$$\sigma_{mn} = -p\,\delta_{mn} + \lambda\,e_{kk}\delta_{mn} + 2\mu e_{mn}, \quad p = \rho^2 \frac{\partial F}{\partial \rho}, \tag{1}$$

where

$$\rho = \rho_L V_L + \rho_S V_S. \tag{2}$$

Specific free energy $F$ (per unit weight of the solid–liquid media) is assumed to be a function of density $\rho$, temperature $T$, and microstructural parameters.

In the capacity of thermodynamic potential $F$ we choose free energies of solid–solid and solid–liquid interfacial surfaces. The areas of these surfaces per unit weight of the considered system are defined by the following relations

$$A_{SS} = \frac{2}{\rho d_S} V_S C, \quad A_{LS} = \frac{4}{\rho d_S} V_S (1-C), \tag{3}$$

where $C$ is the contiguity of the solid skeleton and $d_S$ is the mean grain size of the solid phase. Denoting $\gamma_{SS}$ and $\gamma_{LS}$ as the excess free energies per unit area of interfaces, we have the following expression of potential $F$

$$F = \frac{4\gamma_{LS}}{\rho d_S} \left[ \left( \cos\frac{\Phi}{2} - 1 \right) C + 1 \right] V_S. \tag{4}$$

Here $\Phi$ is the dihedral angle, which is defined by the formula $\cos(\Phi/2) = \gamma_{SS}/(2\gamma_{LS})$.

The dependence of the contiguity and grain diameter on $\rho$ is taken into account by us at differentiation of $F$ with respect to $\rho$. As the final result we get

$$p = p_1 + p_3;$$
$$p_1 = \frac{\alpha}{d_S} \left\{ 1 + \gamma \left[ C + \frac{\rho}{\rho_L} (\rho - \rho_L) \frac{dC}{d\rho} \right] \right\}; \tag{5}$$
$$p_3 = -\frac{4\gamma_{LS}}{d_S^2} \rho\, V_S (1 + \gamma C) \frac{\partial d_S}{\partial \rho}$$

with

$$\alpha = \frac{4\gamma_{LS}}{\Delta\rho} \rho_L, \quad \gamma = \cos\frac{\Phi}{2} - 1, \quad \Delta\rho = \rho_S - \rho_L. \tag{6}$$

Note that the dependence of dihedral angle on $\rho$ is also taken into account [7].

Thus, for final definition of the thermodynamic pressure, $p$, it is necessary to have the specific expressions of functions $C(\rho)$ and $d_S(\rho)$. In what follows we shall use the relations [8]

$$C = V_S^2 \left(0.43 \sin\Phi + 0.35 \sin^2\Phi\right), \quad V_S = \frac{\rho - \rho_L}{\Delta\rho};$$

$$d_S^3 = d_{S0}^3 + K\,t\,V_L^{-\frac{2}{3}}, \quad V_L = 1 - V_S. \tag{7}$$

Transform expressions (5) with the use of (7) to the form

$$p_1 = \alpha\left[1 + \gamma\,C\left(1 + 2\frac{\rho}{\rho_L}\right)\right], \quad p_3 = -\frac{2}{9}\alpha\frac{k\,t\,\rho}{\left(V_L^{\frac{5}{3}} + k\,t\,V_L\right)\rho_L}V_S\left(1 + \gamma C\right). \tag{8}$$

Here $k = \dfrac{K}{d_{S0}^3}$.

Accordingly, the thermodynamic pressure depends on the microstructure parameters, $d_S$, $C$ and $V_L$, energy quantities $\gamma_{SS}$ and $\gamma_{LS}$, and densities of solid $\rho_S$ and liquid $\rho_L$ phases. In addition, all these quantities depend on the temperature. Note that in the theory of classical viscous compressible homogeneous fluid the thermodynamic pressure depends on the density and temperature only.

Let us now return to constitutive equations (1). The macroscopic coefficients of viscosity $\lambda$ and $\mu$ depend first of all on the viscosity of the solid and liquid phases. We shall use expressions

$$\mu = \mu_S\frac{1.5\,V_S^2}{V_L + 1.5\,V_S}, \quad K = \frac{1}{V_S}\left(K_S + \frac{4}{3}V_L V_S\mu_S\right);$$

$$\lambda = K - \frac{2}{3}\mu, \quad K_S = \mu_S\frac{2\left(1 + \nu_S\right)}{3\left(1 - 2\,\nu_S\right)}. \tag{9}$$

Here $\nu_S$ is the viscous analogy of the Poisson's ratio. The first two formulae correspond to the appropriate relations for shear and bulk moduli of two-phase elastic composite provided that $\mu_1 \ll \mu_2$ and $K_1 \gg K_2$ [9]. Thus, it is assumed that shear viscosity of the liquid phase is much smaller and its bulk viscosity is much larger than such viscosities of the solid phase.

As the final result, constitutive equations (1) contain eleven independent variables: $d_S$, $C$, $V_L$, $\gamma_{SS}$, $\gamma_{LS}$, $\rho_S$, $\rho_L$, $K$, $\mu_S$, $b$, and $\nu_S$.

### FULL SYSTEM OF THE DIFFERENTIAL EQUATIONS

The full system of differential equations consists of constitutive equations, geometrical equations defining the strain rates, equations of motion, equation of mass conservation, and kinematic equation. The dependency among strain rates $e_{mn}$ and velocity $u_n$ is the linear relation

$$e_{mn} = 1/2(u_{m,n} + u_{n,m}). \tag{10}$$

Using the balance of momentum, the equation of slow (acceleration is neglected) motion in the reference configuration is

$$\operatorname{div}\mathbf{P} = \vec{k}, \tag{11}$$

where $\vec{k}$ denotes the body force.

The conservation of mass gives the relation between the material density in the reference configuration, $\rho_0$, and material density in the present configuration, $\rho$,

$$\rho_0 = J\rho. \tag{12}$$

The kinematic equation is

$$\vec{u} = \frac{d\vec{R}}{dt}. \tag{13}$$

In (11) **P** is the first Piola-Kirchhoff stress tensor. The relation between **P** and Cauchy stress tensor $\boldsymbol{\sigma}$ is given by

$$\mathbf{P} = J\boldsymbol{\sigma} \cdot (\mathbf{F}^{-1})^T, \tag{14}$$

where $F$ is the deformation gradient and $J$ is its determinant.

The relations (10–14) are taken from [10]. In examination of a boundary value problem some boundary conditions in the reference configuration and some initial conditions must be stated.

### AXIALLY SYMMETRIC BOUNDARY VALUE PROBLEM

Let us introduce the cylindrical coordinate system ($r$, $\varphi$, $z$). In the case of symmetry with respect to the $z$-axis $R(r, z, t)$ and $Z(r, z, t)$ are the coordinates of a material point in the present configuration. The position of this point in the reference configuration (at $t = 0$) is defined by the coordinates $r$ and $z$. The Cauche stresses are

$$\sigma_R = -p + \lambda\theta + 2\mu\frac{\partial u}{\partial R}, \quad \sigma_\varphi = -p + \lambda\theta + 2\mu\frac{u}{R},$$

$$\sigma_Z = -p + \lambda\theta + 2\mu\frac{\partial w}{\partial Z}, \quad \tau = \mu\left(\frac{\partial u}{\partial Z} + \frac{\partial w}{\partial R}\right); \tag{15}$$

$$\theta = \frac{\partial u}{\partial R} + \frac{u}{R} + \frac{\partial w}{\partial Z}.$$

Here ($u$, $w$) are the velocity components of the material point expressed in the present configuration.

The Piola-Kirchhoff stresses are defined by

$$rP_r = R\,I\left(\sigma_R\frac{\partial R}{\partial r} + \tau\frac{\partial R}{\partial z}\right), \quad P_\varphi = I\sigma_\varphi, \quad rP_z = R\,I\left(\tau\frac{\partial Z}{\partial r} + \sigma_Z\frac{\partial Z}{\partial z}\right),$$

$$rP_{rz} = R\,I\left(\sigma_R\frac{\partial Z}{\partial r} + \tau\frac{\partial Z}{\partial z}\right), \quad rP_{zr} = R\,I\left(\tau\frac{\partial R}{\partial r} + \sigma_Z\frac{\partial R}{\partial z}\right); \tag{16}$$

$$I = \frac{\partial R}{\partial r}\frac{\partial Z}{\partial z} - \frac{\partial R}{\partial z}\frac{\partial Z}{\partial r}.$$

The equations of quasi-static motion [10] are

$$\frac{\partial}{\partial r}(rP_r) - P_\varphi + r\frac{\partial}{\partial z}P_{zr} = 0;$$

$$\frac{\partial}{\partial r}(rP_{rz}) + r\frac{\partial}{\partial z}P_z - r\rho_0 g = 0, \tag{17}$$

where $g$ is the acceleration of gravity.

The substitution of (16) with allowance made for (15) reduces (17) to the system of the differential equations. This system is linear concerning u and w, and nonlinear concerning $R$ and $Z$. These variables are connected by the kinematic relations

$$u = \frac{dR}{dt}, \quad w = \frac{dZ}{dt}.$$

(18)

The given system is also nonlinear relative to material density ρ. Equation (12) takes the form

$$\rho = \rho_0 \frac{r}{RI}.$$

(19)

## NUMERICAL RESULTS

Let us consider a cylindrical sample of radius $r_c$ and $h_c$ in height. The sample has initial homogeneous microstructure and density $\rho_0$. We introduce the dimensionless quantities. Relate coordinates $r$, $z$, $R$, $Z$ to $r_c$, time $t$ to holding time $t_h$, and the velocity to $V$. The quantity, $V$, is a velocity of the order of 1.0 μm/s. The dimensionless velocities, strain rates, and density are

$$u' = \frac{u}{V}, \quad w' = \frac{w}{V}, \quad e'_{mn} = e_{mn} \frac{r_c}{V}, \quad \rho' = \frac{\rho}{\Delta\rho}.$$

The dimensionless stresses are chosen in the form

$$\sigma'_{mn} = \frac{\sigma_{mn}}{\Delta\rho \, g \, r_c}.$$

As the result we get such dimensionless numbers

$$\Gamma = \frac{4\gamma_{LS}\rho_L}{\Delta\rho\Delta\rho g r_c d_S}, \quad G = \frac{\mu_B V}{r_c \Delta\rho g r_c}.$$

(20)

These numbers contain five parameters, which define the properties of liquid–solid media considered, the sample radius, the holding time and the acceleration of gravity.

The initial boundary value problem for the given sample was solved under the boundary conditions

$$
\begin{aligned}
&P_{rz} = 0, \; u = 0, \; r = 0; \\
&P_{zr} = 0, \; w = 0, z = 0; \\
&P_{zr} = -p_{cap}\frac{R}{r}\frac{\partial Z}{\partial r}, \; P_z = p_{cap}\frac{R}{r}\frac{\partial R}{\partial r}, \; z = h; \\
&P_{rz} = -p_{cap}\frac{R}{r}\frac{\partial R}{\partial z}, \; P_r = p_{cap}\frac{R}{r}\frac{\partial Z}{\partial z}, \; r = 1.0
\end{aligned}
$$

(21)

and the initial conditions

$$\rho = \rho_0, \; R = r, \; Z = z, \; t = 0.$$

(22)

In (21), $p_{cap}$ is the capillary pressure [3] and the primes over letters are omitted. We assume that friction at the sample bottom is absent.

The problem was solved by finite difference method. In the domain ($0 < r < 1.0$, $0 < z < h$), a regular rectangular mesh was introduced. At each interior node, we

employ the centered difference formulae to approximate the relevant first and second order derivatives. At the boundary nodes, the normal first derivatives were approximated by forward or backward differences. The Crank–Nicolson scheme and the method of simple iteration were used. As a result, the node values of velocities, density, and coordinates were defined solving the algebraic system of nonlinear equations. In addition, the changes of mass $m(t)$, gravitational potential energy $E(t)$, and free energy $F(t)$ of the sample were computed using the expressions

$$m(t) = \int_V \rho \frac{R}{r} I \, d\tau, \quad E(t) = g \int_V \rho Z \frac{R}{r} I \, d\tau, \quad F(t) = \frac{4\gamma_{LS}}{d_S} \int_V V_S (1 + \gamma C) \frac{R}{r} I \, d\tau. \quad (23)$$

These integrals are taken along the initial volume of the sample.

Unfortunately, we have no necessary experimental data at sintering temperature. Therefore, we restrict ourselves to the comparison of the theoretical results with experimental ones at room temperature [11]. In this paper, W–Ni–Fe alloys with compositions ranging from 78 to 93 wt% tungsten, which were liquid-phase sintered at 1500 °C for 30 min, were investigated. Cylindrical samples were approximately 12.8 mm in diameter and 7 mm in height. For the calculations we took the parameters values:

$$\rho_L = 8.4 \text{ g/cm}^3, \ \rho_S = 18.9 \text{ g/cm}^3, \ t_h = 1800 \text{ s}, \ r_c = 7 \text{ mm},$$

$$h_c = 7 \text{ mm}, \ d_{S,0} = 20 \ \mu\text{m}, \ kt_h = 0.19, \ v_S = 0.45, \ b = 0.5, \Gamma = 2.5, \quad (24)$$

$$G = 1.0, \ h_1 = 0.1, \ h_2 = 0.1, \Delta t = 0.01, \ V = 1.0 \ \mu\text{m/s}, \ \Phi = 30 \text{ deg}.$$

The results are presented in Table 1.

**Table 1. Calculated (above a line) and experimental (under a line) values of liquid volume fraction and contiguity**

| Initial liquid volume fraction | Final liquid volume fraction | | Contiguity | | Alloy [11] |
|---|---|---|---|---|---|
| | top | bottom | top | bottom | |
| 0.20 | 0.22/0.20 | 0.17/0.17 | 0.18/0.48 | 0.21/0.52 | 93W |
| 0.30 | 0.32/0.31 | 0.28/0.27 | 0.14/0.29 | 0.16/0.32 | 88W |
| 0.40 | 0.43/0.46 | 0.37/0.23 | 0.10/0.25 | 0.12/0.26 | 83W |

The analysis of the table data allows the conclusion that there is a quite good agreement between calculated and experimental results, except for values of the contiguity and final liquid volume fraction at the bottom for the 83W alloy. The $V_L$ calculated is the mean value. The necessary agreement between the experimental values of $V_L$ and C does not exist. Possibly, it is a misprint. In general, the contiguity at room temperature must be much greater than the contiguity at sintering temperature for alloys with an enlarged liquid content. Note that the initial liquid volume fractions and the dihedral angles chosen by us can differ from those for alloys at the sintering temperature. The microstructure evolution is accompanied by the changes of other sample quantities.

In Table 2 $\Delta E$ and $\Delta F$ denote the change of gravitational potential energy and free energy of the sample, respectively. The decrease of the free energy of the sample diminishes with increasing $V_L$. The grain coarsening at the bottom differs from that at the top, which is in accord with the experiments [11]. The sample size

changes are listed in last two columns of Table 2. Here $h$ and $r_B$ denote the sample height and radius of its bottom. The sample distortion is small.

**Table 2. Changes of the other quantities**

| $V_L$ | $\Delta E$, % | $\Delta F$, % | min $d_S/d_{S0}$ | max $d_S/d_{S0}$ | $h/h_c$ | $r_B/r_c$ |
|---|---|---|---|---|---|---|
| 0.2 | −4.7 | −22.3 | 1.27 | 1.35 | 0.96 | 1.03 |
| 0.3 | −4.18 | −19.0 | 1.22 | 1.25 | 0.97 | 1.03 |
| 0.4 | −7.17 | −16.48 | 1.19 | 1.21 | 0.95 | 1.04 |

Let us compare the theoretical and experimental results from [6]. The cylindrical samples 12.7 mm in diameter and 10.0 mm in height with green densities 60 % of theoretical were liquid phase sintered. The 88W sample height is equal near 8.5 mm at 30 min holding time and near 7.9 mm at 60 min holding time [6]. The sintering temperature was 1500 °C. We took for computations $r_c = 5.4$ mm, $h_c = 8.4$ mm. The other parameters were the same as in (24). The calculated values of $h$ are 8.2 mm for 30 min holding time and 7.5 mm for 60 min holding time. So, the calculated values are close to the experimental ones.

For the parameters of (24) the liquid–solid surface energy $\gamma_{LS} \approx 0.012$ kg/s$^2$ and the grain boundary viscosity $\mu_S = 5.2$ MPa·s. Such small values may be to some extent attributable to the high sintering temperature $T = 1500$ °C, the multi-component liquid, and the thin liquid films between the grains. Note that liquid–solid surface energy at $T = 1700$ K was taken equal 0.1 kg/s$^2$ in [12].

## CONCLUSIONS

The developed mathematical theory is essentially macroscopic in that the two-phase liquid–solid system has been replaced by the one-phase continuum media with non-homogeneous microstructure. Its advantages consist in the total accounting of the microstructure measured by the linear intercept method. The theory contains such independent variables as mean grain size, contiguity of solid skeleton, liquid volume fraction, solid–solid grain boundary and liquid–solid surface energies, liquid and solid densities, grain boundary viscosity, and viscous analogy of the Poisson's ratio. The coarsening of the microstructure and the capillary pressure at free boundaries of the compact have also been taken into account. As a mechanism of deformation, the grain boundary sliding has been assumed. In general, the given theory is very complicated and further experimental investigations are necessary for its verification.

*Розвинено нову математичну теорію зміни мікроструктури на заключній ізотермічній стадії рідкофазного спікання після зникнення пористості, використано основні положення механіки суцільного середовища і теорії спікання композитних матеріалів на основі тугоплавких карбідів та металів. Еволюцію мікроструктури описано нелінійною системою диференціальних рівнянь, в якій присутні більше десяти параметрів. Розрахунки виконано для циліндричного зразку із важкого сплаву на вольфрамовій основі методом скінчених різниць. Виявлено хорошу відповідність між теоретичними та експериментальними результатами, що отримано для спечених важких сплавів.*

*Ключові слова: математична теорія, еволюція мікроструктури, рідкофазне спікання, метод скінчених різниць, важкі сплави.*

*Развита новая математическая теория изменения микроструктуры на заключительной изотермической стадии жидкофазного спекания после исчезновения пористости, использованы основные положения механики сплошных сред и теории спекания композитных материалов на основе тугоплавких карбидов и металлов. Эволюция микроструктуры описана нелинейной системой дифференциальных уравнений, содержа-*

*щей более десяти параметров. Численные результаты получены для цилиндрического образца из тяжелого сплава на вольфрамовой основе методом конечных разностей. Обнаружено хорошее соответствие между теоретическими и экспериментальными результатами, полученными для спеченных тяжелых сплавов.*

***Ключевые слова**: математическая теория, эволюция микроструктуры, жидкофазное спекание, метод конечных разностей, тяжелые сплавы.*

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