Abstract: In this paper we will investigate gravity induced skeletal settling during liquid phase sintering. In this approach skeletal settling will be combined with extrication of some solid-phase domains. The main goal will be the need to relate dissolution, diffusion and precipitation phenomena to essential geometric and topological changes of the tungsten-nickel porous microstructure influenced by differential skeletal settling due to large density difference between tungsten domains and the matrix. This study will be based on domain topology (no shape restriction) and control-volume methodology. The microstructural evolution will be simulated by computation of displacement of the center of mass (combined gravity induced settling and random motion) and mass transport due to dissolution and precipitation at the interfaces between solid-phase and liquid matrix.

Keywords: Liquid phase sintering, Skeletal settling, Solid phase extrication, Gravity.

Introduction

Settling of solid grains in a two-phase liquid-solid is a phenomenon common to several metallurgical processes including liquid-phase sintering (LPS). Gravity induced solid-liquid segregation leads to non-uniform sintered properties due to grain size, grain shape, and solid-volume fraction dependence on vertical position [1]. Niemi and Courtney [2] were the first to document quantitatively this phenomenon. As proposed by Courtney [3], the formation of solid skeleton is the result of interparticle collisions caused by Brownian motion and/or density difference between solid and liquid. Heaney et al. [4] investigated possible relation between the segregated solid-volume fraction and the density difference. They concluded that if the density difference is sufficiently large, then solid grains pack to a volume fraction similar to that of maximum loose packing of monosized spheres. However, if the density difference is small, grains settle with lower velocity, which allows time to form a solid skeleton at a lower packing density.

In this paper we will be concerned with definition of a two-dimensional (2-D) numerical method for simulation of microstructural evolution due to gravity induced skeletal settling during LPS. The method will be based on domain topology (no shape restriction) and on a model for skeletal settling and solid-phase extrication. Common to this study is the need to relate some diffusional phenomena to essential geometric and topological attributes of the W-Ni porous microstructure influenced by skeletal settling combined with extrication of some solid-phase domains during LPS.

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Model definition

Let us assume the rectangular experimental region that is replaced by a finite difference mesh containing a finite number \( n \times m \) of grid points and defined by grid spacings \( \Delta x \) and \( \Delta y \) for Cartesian coordinates \( x \) and \( y \), respectively. Using control-volume (CV) methodology [5], the domain will be a region that is equitably divided into boundary and internal CVs halfway between adjacent grid points \((x_i, y_j)\). These internal grid points will be at the center of the corresponding control volumes if the mesh is defined by constant grid spacings, i.e. \( \Delta x = \Delta y = h \). Now the \( \ell \)-th domain is fully defined by its \( n_{\ell} \) boundary control volumes, i.e.

\[
D_{\ell} = \{ CV_{k_{\ell}} \}_{k=1,2,...,n_{\ell}} = \{ CV_{\ell}(x_k, y_k) \}_{k=1,2,...,n_{\ell}}. \tag{1}
\]

Such arbitrary domain definition will be used as 2-D particle/pore representation for simulation of LPS.

A porous microstructure consisting of \( S \) solid-phase and \( P \) pore-phase domains can be now completely mapped by on integer matrix \( m_{ij} \times n_{ij} \), where the value of the element \( e_{ij} \) indicates the phase (solid, liquid or pore) present at \( CV_{i,j} \)

\[
e_{ij} = \begin{cases} 
> 0 & \text{when } CV_{i,j} \text{ belongs to the solid phase} \\
0 & \text{when } CV_{i,j} \text{ belongs to the liquid phase} \\
< 0 & \text{when } CV_{i,j} \text{ belongs to the pore phase} 
\end{cases} \tag{2}
\]

so that zero, positive \((1,2,...,S)\) and negative \((-1,-2,...,-P)\) values of the element \( e_{ij} \) indicate \( CV_{i,j} \) that belong to liquid, solid and pore phase, respectively. Further, contiguous CVs of the same \( e_{ij} \) form solid-phase or pore-phase domains, solid-phase domain boundaries exist between neighboring CVs of different \( e_{ij} \), solid-phase interfaces exist between neighboring CVs with \( e_{ij} > 0 \) and liquid phase, and pore-phase interfaces between neighboring CVs with \( e_{ij} < 0 \) and liquid phase.

Settling procedure

During LPS differential settling of the solid phase occurs due to a density difference between the liquid and solid phases. This problem is especially true when the solid and liquid phase densities are very different. When the density difference is small, the falling grain's terminal velocity is lower which allows time for sinter bonds to form a skeleton at a lower packing density. The grains settle to the bottom of the specimen when the density of the solid phase is greater than that of the liquid phase. Floating occurs when the solid-phase density is less than that of the liquid phase.

Therefore we will assume that during LPS solid-phase domains will be settled due to gravity. As the domains arrive over the already settled domains they make point contacts with each other and necks between them form. Neck growth will be ended when the equilibrium dihedral angle between the domain boundaries and the liquid is established. Thus a solid skeleton forms.

Under Earth-based experimental conditions Stokes’s law settling usually dominates
microstructure formation [3]. The settling time for solid domains to travel time dependent average separation distance $\langle \lambda(t) \rangle$ between domains [6] in liquid matrix can be calculated as

$$
\tau(t) = \frac{9\eta \langle \lambda(t) \rangle}{2g \langle r(t) \rangle^2 (\rho_s - \rho_L)},
$$

where $\eta$ is the liquid viscosity, $g$ is the gravitational acceleration, $\langle r(t) \rangle$ is the time dependent average domain radius and $\rho_s - \rho_L$ is the density difference between the solid and liquid.

The settling procedure will be applied to simulate the gravity force. The solid-phase domains will be subjected to a simulated gravity field [7]: they fall under gravity (Fig. 1a) and slide down over the already settled solid-phase domains. Such a procedure will be applied to each solid-phase domain starting with this one having the lowest position in the vertical direction of the experimental region. This procedure will be modeled by domain translation (described in details elsewhere [8]) along the gravitational direction, i.e.

$$
D^f(x^f_c, y^f_c) \rightarrow D^f(x^f_c, y^f_c - h),
$$

where $(x^f_c, y^f_c)$ is its center of mass. However, the packing of solid-phase domains will be the result of translation in the gravity direction or combined translation in horizontal (sliding over already settled domains) and in vertical (gravity) directions (Fig. 1b and Fig. 1c). Such a procedure will be applied to all CVs of the settling domain (Fig. 2). In that sense, the domain translation (4) must be generalized as follows

$$
D^f(x^f_c, y^f_c) \rightarrow D^f(x^f_c \pm h, y^f_c - h),
$$

where the sign $\pm$ in (5) means that the signs + and - will be taken at random or both ones in sequence. Horizontal and vertical translations combined in a sequence or parallel give way to reach local equilibrium system state.

Fig. 1 Schematic representation of the settling procedure. (a) Domain falls under gravity, (b) domain slides to the left and falls under gravity, and (c) domain slides to the right and falls under gravity.

Fig. 2 Schematic representation of domain settling. The settling procedure will be applied to all control volumes of settling domain.

Fig. 3 Two contacting domains.
Solid skeleton definition

Let \( D^a \) and \( D^b \) be two contacting solid-phase domains, as shown in Fig. 3. Let \( CV_a \) and \( CV_b \) be said to be 4-adjacent if \( d(CV_a, CV_b) = h \) and diagonally adjacent if \( d(CV_a, CV_b) = h\sqrt{2} \), where \( d(CV_a, CV_b) \) is the Euclidean distance function between the centers of two distinct control volumes \( CV_a \) and \( CV_b \) defined in a 2-D discrete space as

\[
d(CV_a, CV_b) = \sqrt{(x_b - x_a)^2 + (y_b - y_a)^2}.
\]  

(6)

If the length of discrete neck line between them \( (L_{N}) \), defined as the sum of contacting faces \( (L_{CF}) \) of 4-adjacent and/or diagonally adjacent boundary CVs, fulfills the inequality

\[
L_N = \sum L_{CF} \geq L,
\]

(7)

where \( L \) is the minimal (or critical) length of neck line, then these domains will form a solid skeleton unit consisting of two solid-phase domains with a neck between them. One or more connected skeleton units arranged in a long chain of connected domains form a solid skeleton. The critical length \( L \) is an empirical parameter. It is reasonable to assume that it is less than smaller of two average effective domain radii.

During LPS s-th skeleton structure (SS) of length \( K_s \) (arranged as a long chain of \( K_s \) connected domains) will be represented by topology

\[
SS^{s, K_s, v_i} = \bigcup_{k=1}^{K_s} D^{v_i, k} = \bigcup_{k=1}^{K_s} \{CV^{v_i, k}(x_m, y_m)\}_{m=1,2,\ldots,n_{v_i, k}}
\]

(8)

where \( v_i, k \) is the ordinal number of \( k \)-th domain included in \( s \)-th skeleton. Such skeleton structure, given as a system of functions of some topological parameters, changes monotonically with time by adding new solid-phase domains or by losing some smaller domains during skeleton settling.

Domain extrication definition

As proposed by Niemi and Courtney [2] settling of the skeletal structure during LPS will be controlled by extrication of domains from the skeleton and their subsequent settling within the liquid phase, where domains will be extricated presumably by capillarity driven mass transfer processes and the similarity driven processes of Ostwald ripening. The rate of skeletal settling will be reduced in comparison to free settling because domain extrication is a relatively slow process.

Fig. 4 Domain \( D^s \) and its contacting neighbors.
The extrication itself will be modeled as a procedure in which $s$-th solid-phase domain, $D^s$, taken at random and characterized by neck lines $L_{N1}, L_{N2}, \ldots$ (Fig. 4) between its contacting neighbors inside the skeleton network (connected straight lines) can be extricated from the skeleton if the condition
\[
\max\{L_{N1}, L_{N2}, \ldots\} < L^s
\] (9)
is fulfilled. The critical length $L^s$ is also an empirical parameter that can be equal to or different from the previously defined length $L$.

**Solution-precipitation**

We will assume that liquid penetrates domain boundaries of the solid phase. Therefore, domains of the solid phase are entirely surrounded by liquid, a thin film of which is present between neighboring solid-phase domains. For such a system in which the solid phase has some solubility, concentration of the dissolved solid, $c_{i,j} = c(x_i, y_j)$, around domain of radius $r$ is given by the Gibbs-Thomson equation [7]
\[
\ln \left( \frac{c}{c_o} \right) = \frac{2\gamma_{dl}\Omega}{kT} \frac{1}{r},
\] (10)
where $c_o$ is the equilibrium concentration of liquid in contact with the flat solid, $\gamma_{dl}$ is the solid/liquid interfacial energy, $\Omega$ is the molecular volume of the solid, $k$ is the Boltzmann constant, and $T$ is the sintering temperature. If $\Delta c = c - c_o$ is small, the governing equation (10) becomes
\[
\Delta c = c_o \frac{2\gamma_{dl}\Omega}{kT} \frac{1}{r}.
\] (11)
The concentration at an interface solid/liquid with high curvature will be above that at an interface with low curvature, thus higher concentrations around smaller solid-phase domains give rise to a net flux of matter from the smaller to the larger ones.

If $D_L$ is the diffusivity of the solid in the liquid, 2-D flux for the control volume $CV_{i,j}$ from the solid-phase toward the liquid phase (due to dissolution of solid phase domains) and/or vice versa (due to precipitation of dissolved materials) is now
\[
J_{i,j} = J_{i,j}^x + J_{i,j}^y.
\] (12)
The flux components along $x$ and $y$ directions, $J_{i,j}^x$ and $J_{i,j}^y$, are given by
\[
J_{i,j}^x = -D_L \left( \frac{c_{i,j} - c_{i+1,j}}{\Delta x} \delta_{i+1} + \frac{c_{i,j} - c_{i-1,j}}{\Delta x} \delta_{i-1} \right)
\] (13)
\[
J_{i,j}^y = -D_L \left( \frac{c_{i,j} - c_{i,j+1}}{\Delta y} \delta_{j+1} + \frac{c_{i,j} - c_{i,j-1}}{\Delta y} \delta_{j-1} \right)
\] (14)
where $\delta_{i\pm 1}$ and $\delta_{j\pm 1}$ provide that the flux will be computed between solid and liquid phases and not between solid-phase domains inside neck region (for $e_{ij} > 0$ and $e_{i\pm 1} = 0$ or $e_{j\pm 1} = 0$ they are equal 1, for $e_{ij} = 0$ and $e_{i\pm 1} > 0$ or $e_{j\pm 1} > 0$ they are equal 0).
Simulator

During sintering solid-phase and pore-phase domains co-evolve: grow and/or shrink. The solid-phase domains evolution due to combined gravity induced settling combined with random motion (as displacement of the center of mass), as well as mass transport due to dissolution and precipitation at the interfaces between solid-phase domains and the liquid matrix (as change in average effective domain radius), will be now modeled by two corresponding transformations explained below. In our approach domain movement will be modeled very similar to the scenario assumed by Courtney [3] in which he proposed solid skeleton formation as a result of interparticle contacts due to random motion and/or settling due to a solid-liquid density difference. The settling procedure will be applied to simulate the gravity force.

Thus for simulation time interval \( \Delta t \) each solid-phase domain should travel an average separation distance \( \lambda(t) \)

\[
q(t) = \frac{\Delta t}{\tau(t)} \lambda(t) = \frac{2g \langle r \rangle^2 (\rho_s - \rho_L) \Delta t}{9\eta},
\]

where \( \tau(t) \) is the settling time defined by equation (3). Complex movement of domain \( D^s \) induced by settling and random motion can be modeled by combined translations in horizontal (sliding over settled domains) and in vertical (gravity) directions, i.e.

\[
D^s(x^s_c, y^s_c) \rightarrow A_D^s(x^s_c \pm q(t + \Delta t), y^s_c - q(t + \Delta t)),
\]

where \( A_D^s \) is the translated domain, and the signs "+" or "-" can be taken at random. The transformation by the translation (16) will be successful if the new position of domain after its translation is not already occupied by other domains. During this procedure already settled domains hit by the settling domain can also move horizontally due to accommodation with the arrived domain.

The solid-phase domain evolution due to mass transport (dissolution and precipitation at the interfaces between solid-phase domains) and liquid matrix as change in average effective domain radius, will be now modeled by a second transformation

\[
D^s(\langle r_s(t) \rangle) \rightarrow D^s(\langle r_s(t + \Delta t) \rangle).
\]

For the pore-phase evolution we will apply the model described elsewhere [9].

Movement of a skeleton can be realized in a similar way by simultaneous translation of type (16) for all domains included in this skeleton. At the same time, geometry change of existing skeletons due to solution-precipitation will be realized by the transformation (17) for all belonging domains.

Results and discussion

We will apply the above defined numerical method combined with the previous by defined simulation method for grain growth by grain boundary migration during LPS [7] for simulation of gravity induced skeletal settling with extrication during LPS of W-Ni. The large density difference between tungsten domains and the matrix induces settling of tungsten domains along the gravitational direction. This density difference (over 10 g cm\(^{-3}\)) enhances distortion and slumping by inducing severe solid settling and solid/liquid segregation [10]. In this calculation the same data as in [11] will be used. An initial randomly generated model containing non-uniformly distributed solid-phase domains of different radii (white colored regions in Fig. 5a) will be applied. This system was filled by liquid at the contacts between
the solid-phase domains generating \( (P) \) three- and four-fold coordinated pores shown in Fig. 5b (black colored regions).

**Fig. 5** Randomly generated model (a) with solid phase (tungsten) domains, and (b) after filling by liquid nickel and generating three- and four-fold coordinated pores. White, black and gray colored regions are solid phase, pores and liquid.

**Fig. 6** Microstructural and skeleton network evolution at different times (a) 10 min. and (b) 20 min. Black lines are skeleton networks.

Figure 6 shows consecutive microstructural and skeleton network evolution snapshots of liquid phase sintered W-Ni after 10 and 20 min. In the early stages of liquid formation, the solid-phase domains settle in the liquid matrix in a similar fashion to spheres settling in a liquid media. It is believed that higher solid-liquid density differences will result in more domains settling with higher packing. However, due to settling strong solid bonding occurs. Thus stable skeletons will also be formed during settling.
Quantitative prediction of pore filling [9] clearly indicated sequential filling of pores in order of increasing coordination number or size. Our computed microstructures obtained by the model containing both small and large pores showed similar behavior where the smaller pores were filled first and the largest ones last.

![Fig. 7](image)

**Fig. 7** Microstructural and skeleton network evolution at different times (a) 30 min and (b) 60 min.

![Fig. 8](image)

**Fig. 8** Fully densified microstructure of W-Ni after 120 min. Black lines indicate initial domain geometry.

Fig. 7 shows consecutive microstructural and skeleton network evolution of liquid phase sintered W-Ni after 30 and 60 min. It can be seen that compared to 30 min after 60 min almost all pores are already filled by liquid producing a very long chain of connected domains. However, since the pores are separated from the solid-phase domains, the porosity effect on solid-phase domain growth was negligible because isolated pores have no obvious effect on the controlling diffusion path. Decreasing of pore domains by pore filling provides a
way for migration of the isolated solid-phase domain or even solid skeletons and their coarsening, where smaller domains near to larger ones dissolve, dissolved material diffuses through the liquid and precipitates on the larger domains. Because of that noncircular morphologies do develop from initially circular domains (Fig. 7b).

Fig. 8 shows microstructural evolution of liquid phase sintered W-Ni after 120 min. It can be seen that the matrix is fully densified. It was observed that free settling of isolated solid-phase domains was finished after a very short time. Due to combined domain displacement some domains have formed bonds with neighboring domains prior finishing complete settling and producing chain-like clusters. Therefore densification inside these regions was stopped, although further densification through skeletal settling was observed too. It can be seen that smaller separation distances between solid-phase domains inside solid skeletons or between isolated domains enhance the mass flux between domains and thus increases the coarsening rate.

**Conclusion**

In this paper we have investigated numerically gravity induced skeletal settling during LPS of a tungsten heavy alloy. Solid skeleton formation due to domain settling was modeled as formation of skeleton units and their evolution to long skeletons by domains or skeletons connections. Microstructural evolution was simulated by computation of displacement of the center of mass (combined gravity induced settling and random motion) and computation of mass transport due to dissolution and precipitation at the interfaces between solid-phase domains and the liquid matrix. Computed microstructures substantiate previous observations proposed by Niemi and Courtney [2] that the settled solid-volume fraction can be directly related to the solid-liquid density difference but dictated by the formation of a solid skeleton. Liquid-solid separation was not so distinct because of formation of long skeletons with very few isolated solid-phase domains inside or outside them. Such skeletons were not able to settle due to geometric hindrance of adjacent domains.

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**References**

Садржај: У овом раду истраживан је утицај гравитације на таложење скелетона током течно-фазног синтеровања, при чему је таложење скелетона комбиновано са екстракцијом појединих домена чврсте фазе. Да би се то реализовало потребно је феномене растварања, дифузије и таложења повезати са суштинским променама геометрије и топологије волфрам-никл порозне структуре која је резултат таложења скелетона услед велике разлике густина домена волфрама и течне фазе. Ово истраживање биће базирано на топологији домена (без рестрикције облика домена) и тзв. методологији контролних запремина. Еволуција микроструктура биће симулирана израчунавањем померања центара масе (комбинацијом таложења услед гравитације и рандом кретања) и транспорта масе услед процеса растварања и таложења на граничама чврсте и течне фазе.

Кључне речи: Течно-фазно синтеровање, Таложење скелетона, Екстракција чврсте фазе, Гравитација.