

UDK 662.785:66.063.6

**Liquid Phase Sintering – II. Computer Study of Skeletal Settling and Solid Phase Extrication in a Microgravity Environment****Z. S. Nikolic**University of Nis, Faculty of Electronic Engineering, Department of Microelectronics  
18000 Nis, PO Box 73, Serbia**Abstract:**

*A two-dimensional numerical method based on the Brownian motion model and on the Densification model for simulation of liquid phase sintering in microgravity environment will be developed. Both models will be based on domain topology (two-dimensional particle representation) and control volume methodology and on three submodels for domain translation, solid skeleton formation and domain extrication. This method will be tested in order to conduct a study of diffusion phenomena and microgravitational effects on microstructural evolution influenced by skeletal settling combined with solid-phase extrication during liquid phase sintering of porous W-Ni system.*

**Keywords:** *Liquid phase sintering, Skeletal settling, Solid-phase extrication, Microgravity.*

**1. Introduction**

Controlling microstructural evolution during liquid phase sintering (LPS) is sometimes a difficult problem because of the large number of parameters that must be understood and controlled. In recent years, a range of computer simulation models has been developed with the aim of simulating the detailed evolution of microstructure during grain growth. Coarsening models are the most numerous and most mature of the microstructural evolution models. Many investigators have used a number of different numerical techniques to simulate coarsening by processes such as grain growth and Ostwald ripening. Recently the results of a computer simulation of boundary migration during LPS have been reported [1]. This approach was further applied for computer study of LPS under gravity and microgravity conditions [2,3]. However, all these studies ignored the effects of pores on grain growth and on grain coarsening assuming zero porosity.

During LPS particles have a rigid body motion due to the nonuniform concentration gradient over their surfaces, make point contacts with each other and necks between them form. When the equilibrium dihedral angle between particles and liquid is established neck growth will be ended and solid skeletons form. Therefore for computer simulation of a skeletal structure three submodels for domain translation, solid skeleton formation and domain extrication must be developed. These submodels were successfully applied for two-dimensional (2-D) simulation of microstructural evolution due to gravity induced skeletal settling combined with extrication of some solid-phase domains during LPS [4]. In this paper we will develop 2-D method based on Brownian motion model and on Densification model

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for simulation of microgravity induced microstructural evolution due to skeletal settling combined with solid-phase extrication during LPS.

### Model definition

For 2-D computer simulation of LPS we will use a model of 2-D domains, instead of the very often used model of particles of a regular - circular shape. Even more, after simulation time  $t$  ( $t > 0$ ) most of the initially circular particles will no longer be circular due to the highly asymmetric diffusion field around and between them. In that sense, let us assume a 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  $CV$ s 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

$$D^\ell = \{ CV_k^\ell \}_{k=1,2,\dots,n_\ell} = \{ CV^\ell(x_k, y_k) \}_{k=1,2,\dots,n_\ell}. \quad 1)$$

Such arbitrary domain definition will be used as 2-D particle/pore representation for simulation of LPS. Thus a porous microstructure consisting of  $S$  solid-phase and  $P$  pore-phase domains, i.e.

$$\{ \{ CV_k^S \}_{k=1,2,\dots,n_S} \}_{S=1,2,\dots,S} \cup \{ \{ CV_k^P \}_{k=1,2,\dots,n_P} \}_{P=1,2,\dots,P} \cup \{ \text{Liquid phase} \}, \quad 2)$$

can be now completely mapped on an integer matrix  $\| e_{ij} \|_{n \times m}$ , where the value of the element  $e_{ij}$  indicates the phase (solid, liquid or pore) present at  $CV_{i,j}$

$$e_{ij} = \begin{cases} > 0 & \text{when } CV_{i,j} \text{ belongs to the solid phase} \\ 0 & \text{when } CV_{i,j} \text{ belongs to the liquid phase} \\ < 0 & \text{when } CV_{i,j} \text{ belongs to the pore phase} \end{cases} \quad 3)$$

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

### Random displacement

Unbalanced random molecular forces induce Brownian motion. Using Einstein's treatment [6] for the mean displacement of a grain, the average time between domain contacts can be calculated as

$$\tau(t) = \frac{3\pi \langle r(t) \rangle \eta \langle \lambda(t) \rangle^2}{kT}, \quad (4)$$

where  $\langle r(t) \rangle$  is the time dependent average domain radius,  $\eta$  is the liquid viscosity,  $\langle \lambda(t) \rangle$  is the time dependent average separation distance between domains,  $k$  is the Boltzmann constant, and  $T$  is the sintering temperature.

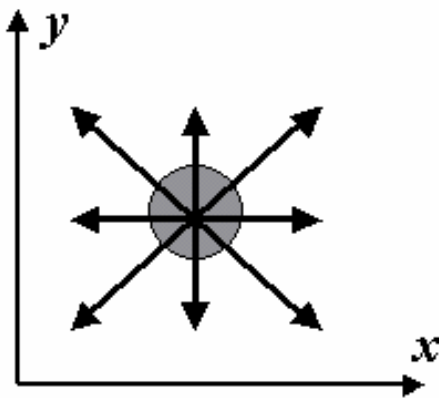
Unbalanced random motion can be modeled by domain translation along positive or negative  $Ox$  axis or  $Oy$  axis directions (in 8-near points directions, so called 8-directional model [7]) as it shown in Fig. 1. Thus Brownian motion can be modeled by domain translation along one of eight possible random directions, i.e.

$$D^\ell(x_c^\ell, y_c^\ell) \mapsto D^\ell(x_c^\ell \pm h, y_c^\ell \pm h), \quad (5)$$

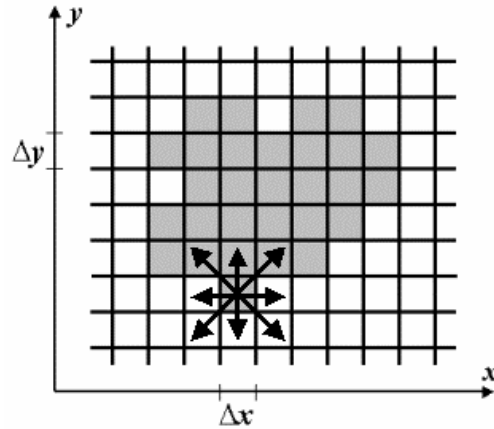
where  $(x_c^\ell, y_c^\ell)$  is its center of mass. The sign  $\pm$  in (5) will be taken at random for each separate domain. Such a procedure will be applied to all  $CV$ s of the moving domain (Fig. 2).

### Densification model

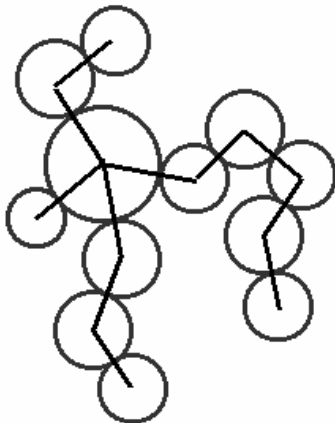
Densification via LPS generally requires transportation of dissolved solid through the liquid. The characteristic process is solution-reprecipitation in which smaller solid domains dissolve at the solid/liquid interface, diffuse through the liquid and precipitate on the larger



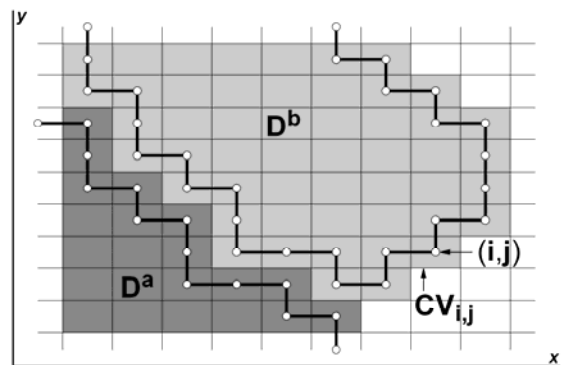
**Fig. 1.** Schematic representation of possible displacement directions (8-directional model).



**Fig. 2.** Schematic representation of domain displacement. All  $CV$ s that represent domains will be translated in the direction determined at random.



**Fig. 3.** Schematic representation of a solid skeleton and solid skeleton network.



**Fig. 4.** Two contacting domains.

domains. As a result larger domains grow at the expense of the surrounding smaller ones. This process will be followed by a center-to-center approach. Rearrangement only involves repositioning of solid-phase domains, leading to limited densification.

### Solid skeleton definition

During LPS solid-phase domains will be moved inside an experimental region. As the domains move 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 (Fig. 3).

Let  $D^a$  and  $D^b$  be two contacting solid-phase domains, as shown in Fig. 4. If the length of the discrete neck line between them ( $L_N$ ), defined as the sum of contacting faces ( $L_{CF}$ ) of 4-adjacent [4] and/or diagonally adjacent boundary CVs, fulfills the inequality

$$L_N = \sum L_{CF} \geq L, \quad (6)$$

where  $L$  is the minimal (or critical) length of the 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 the smaller of the two average effective domain radii.

If there is a set of  $K$  solid-phase domains in which each domain has contact with one or several neighboring solid-phase domains, then the  $s$ -th solid skeleton (SS) will be defined as an union of these contacting domains, i.e.

$$SS^s = \bigcup_{k=1}^K D^{h_s(k)}, \quad (7)$$

where  $h_s(k)$  is the vector of the ordinal number of the  $k$ -th domain included in the  $s$ -th skeleton. Such a 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.

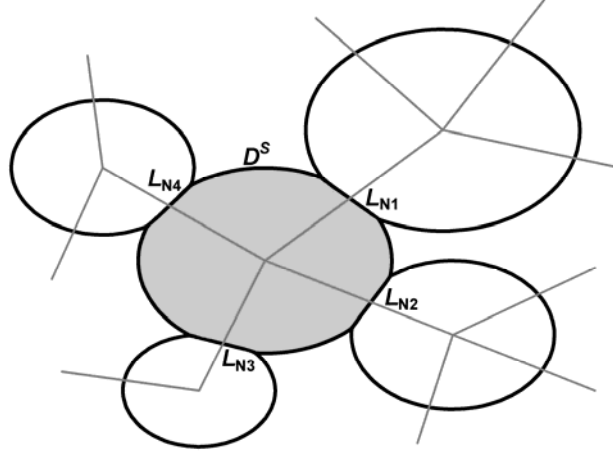
### Domain extrication definition

As proposed by Courtney [8], the formation of a solid skeleton is the result of interparticle collisions caused by Brownian motion and/or density difference between the solid and liquid. They reported that 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 extrication itself will be modeled as a procedure in which the  $s$ -th solid-phase domain,  $D^s$ , taken at random and characterized by neck lines  $L_{N1}, L_{N2}, \dots$  (Fig. 5) between its contacting neighbors inside a skeleton network (connected straight lines) can be extricated from the skeleton if the condition

$$\max\{L_{N1}, L_{N2}, \dots\} < L^* \quad (8)$$

is fulfilled. The critical length  $L^*$  is also an empirical parameter that can be equal to or different from the previously defined length  $L$ .



**Fig. 5.** Domain  $D^s$  and its contacting neighbors.

## Simulator

During sintering solid-phase and pore-phase domains co-evolve: pore domains shrink, solid-phase domains (grains) grow or shrink. One can see that the main topology of the model system given by (2) is time dependent, so that

$$D^s = D^s(t) \quad (s = 1, 2, \dots, S) \quad (9)$$

$$D^p = D^p(t) \quad (p = 1, 2, \dots, P) \quad (10)$$

During the simulation process the simulator continuously checks for possible new solid- and pore-domain positions, where the domains (9) and (10), as a function of time, will be updated by

$$D^s(t + \Delta t) = D^s(t) + \Delta D^s(\Delta t) \quad (s = 1, 2, \dots, S) \quad (11)$$

$$D^p(t + \Delta t) = D^p(t) + \Delta D^p(\Delta t) \quad (p = 1, 2, \dots, P) \quad (12)$$

New subdomains (domains' increments)  $\Delta D^s(\Delta t)$  will be the result of current dissolution and precipitation processes, and  $\Delta D^p(\Delta t)$  the result of pore growth and pore filling processes.

The solid-phase domains evolution due to Brownian 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 bellow. For the pore-phase evolution we will apply the model described elsewhere [9].

For the simulation time interval  $\Delta t$  each solid-phase domain should travel the average separation distance  $\lambda(t)$

$$q(t) = \frac{\Delta t}{\tau(t)} \langle \lambda(t) \rangle = \frac{kT \Delta t}{3\pi \langle r(t) \rangle \eta \langle \lambda(t) \rangle}, \quad (13)$$

where  $\tau(t)$  is the average time defined by equation (4). Complex movement of domain  $D^s$  induced by Brownian motion can be modeled by combined translations in horizontal and in vertical directions by modification of transformation (5), i.e.

$$D^s(x_c^s, y_c^s) \mapsto D_T^s(x_c^s \pm q(t + \Delta t), y_c^s \pm q(t + \Delta t)), \quad (14)$$

where  $D_T^s$  is the translated domain, and the signs "+" or "-" can be taken at random. The transformation by the translation (14) will be successful if the new position of the domain after its translation is not already occupied by other domains.

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

$$D^s(\langle r_s(t) \rangle) \mapsto D_T^s(\langle r_s(t + \Delta t) \rangle). \quad (15)$$

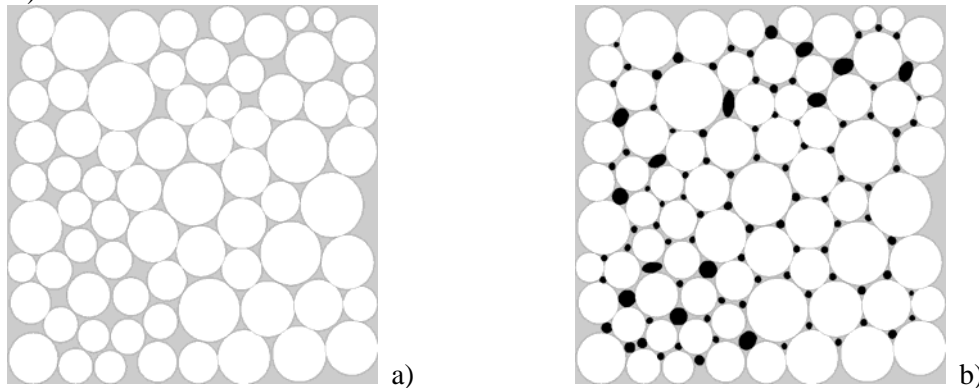
All updated topological information will be recorded and saved for each time interval for the next analysis and computation.

Skeleton movement can be realized in a similar way by simultaneous translation of type (14) for all domains included in this skeleton. At the same time, geometry changes of existing skeletons due to solution-precipitation [4] will be realized by transformation (15) for all belonging domains.

## Results and discussion

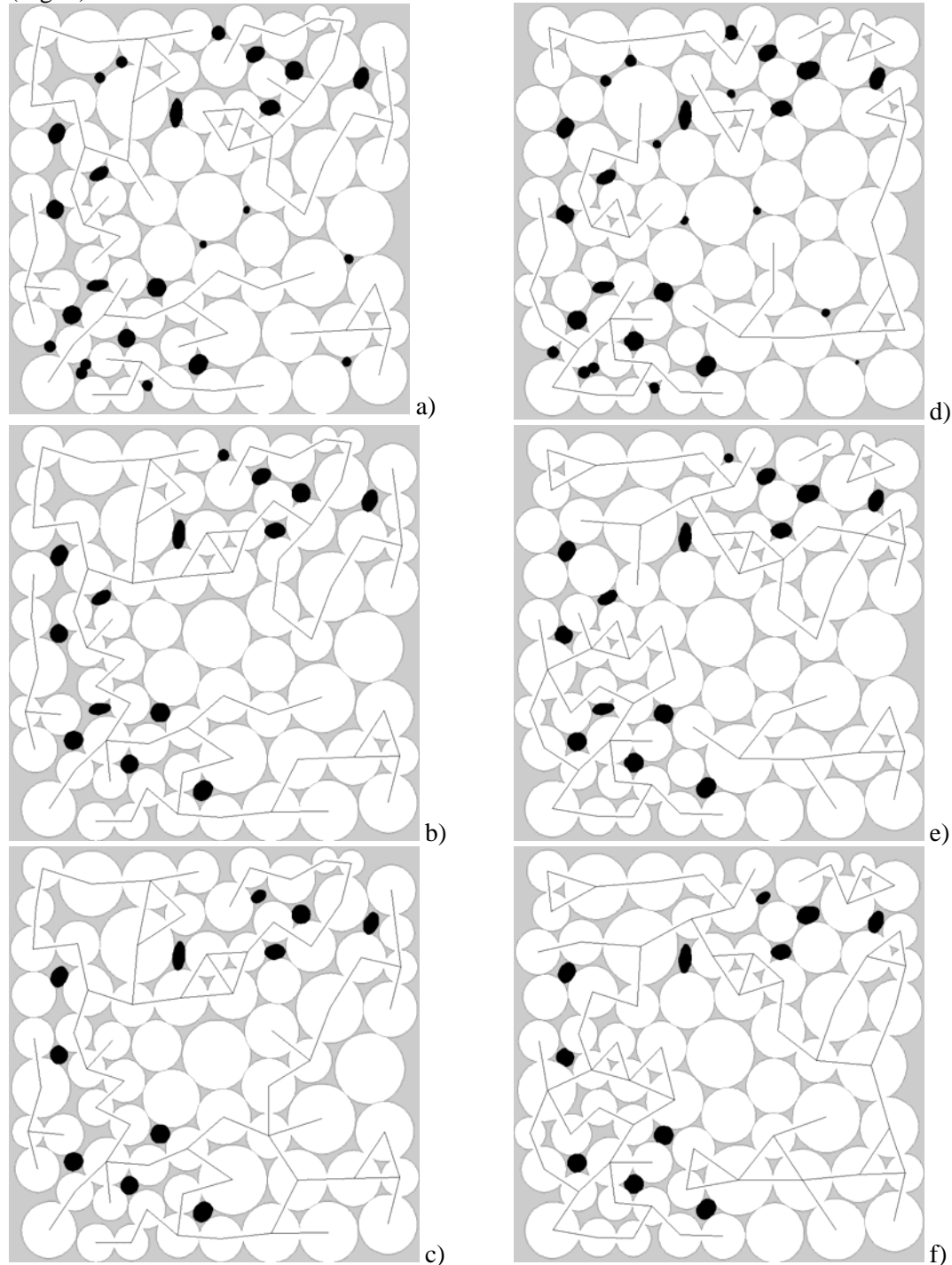
For computation of the liquid phase concentration (numerical solution of the diffusion equation) inside the experimental region and all solution-reprecipitation effects [4] the finite-difference technique (all details were described elsewhere [1]) will be used and it will be included in the previously defined simulator.

For simulation of LPS under microgravity conditions we will use the two previous defined models: (A) Random model (Brownian motion model) and (B) Densification model. These models will be tested in order to conduct a study of diffusion and microgravitational effects on microstructural development of the W-Ni system. In this calculation the same data as in [10] will be used. An initial randomly generated model containing non-uniformly distributed solid-phase domains of different radii (white colored regions in Fig. 6a) will be applied. This system will be filled by liquid at the contacts between the solid-phase domains generating (P) three- and four-fold coordinated pores shown in Fig. 6b (black colored regions).



**Fig. 6.** 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.

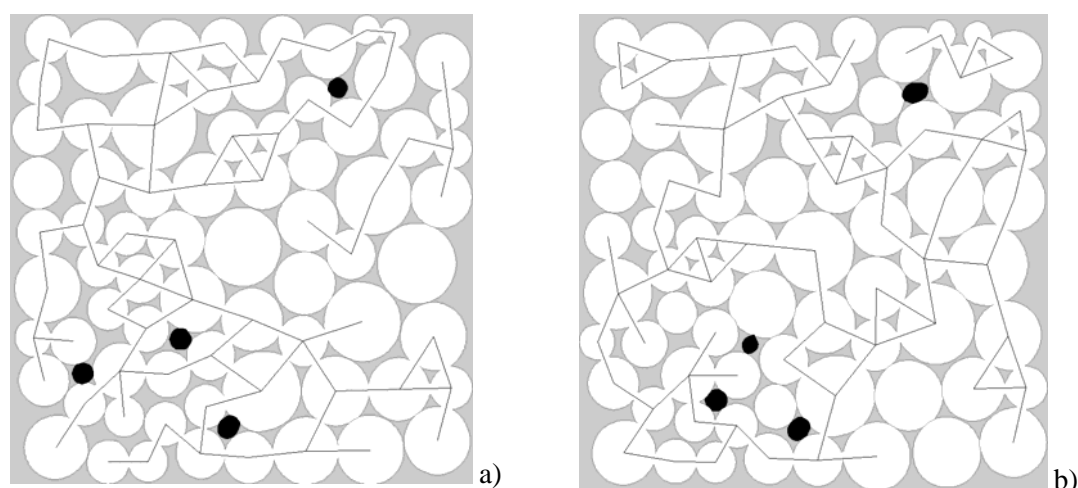
Figures 7a, 7b and 7c show the computed microstructure obtained by model A (Brownian motion, random directed translation), which implies that the domains have moved more dynamically, including linear displacement along one of the eight possible directions (Fig. 1).



**Fig. 7.** Three typical snapshots of the computed microstructure (white colored regions are solid phase and gray colored region is liquid phase; connected gray straight line segments represent skeletal networks.) evolving by Model A under different sintering time (a) 10, (b) 20, (c) 30 min, and by Model B under different sintering time (d) 10, (e) 20, (f) 30 min.

The average time between domain contacts or the domain to travel the average separation distance in the liquid matrix was calculated by (4). It can be noted that even for a short sintering time (10 min, Fig. 7a) many solid-phase domains are connected forming six solid skeletons. However, movement of isolated domains was almost not possible besides through neighboring pore-phase domains during their decreasing in size by the pore filling process. Therefore, dissolution of smaller domains and growing of larger domains due to precipitation are only processes occurring for longer sintering times and responding to domain coarsening. As a result of the asymmetrical diffusional field around domains which form a solid skeleton the boundary solid-liquid of smaller domains continue to dissolve and of larger domains to grow due to precipitation. Figures 7b and 7c show skeleton network evolutions with an equal number of skeletons (=2) but of different lengths.

Applying model B (Densification model, center-to-center approach), the domains will be more closely packed inside domain clusters (Figs. 7d, 7e and 7f). Compared to the previous model the number of solid skeletons vary with sintering time, so that after different sintering times 10, 20 and 30 min the number of skeletons was 7, 5 and 2, respectively. It can be seen that only shorter skeletons (domain clusters) can move according to the Densification model inside the experimental region. Even more, there are also a few still isolated domains that can move between skeletons and/or isolated domains. It can be seen that some smaller domains inside the corresponding skeletons dissolve and disappear during LPS. Larger domains only grow due to precipitation of the dissolved material.



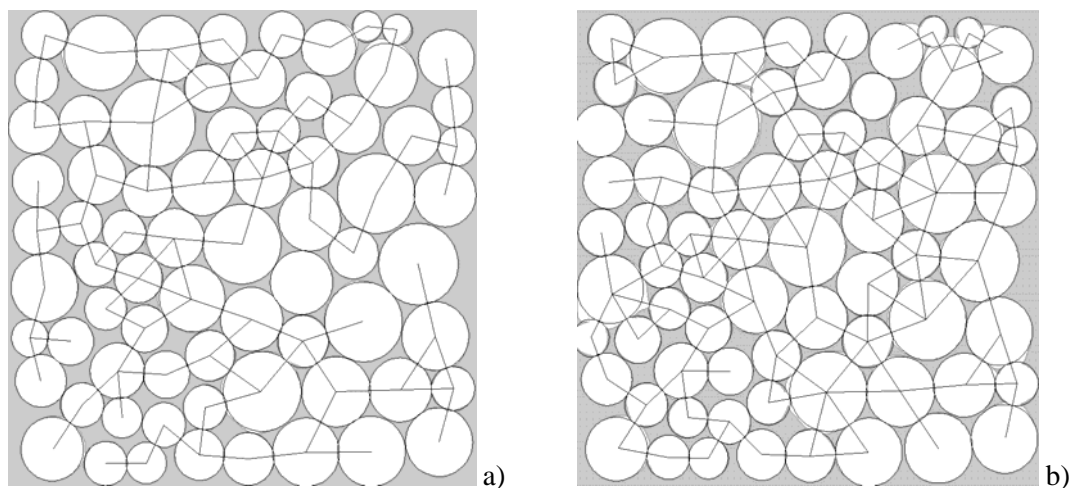
**Fig. 8.** Two typical snapshots of the computed microstructure correspond to sintering time 60 min that obtained by (a) Brownian motion model, and (b) Densification model.

Fig. 8 shows the microstructural and skeleton network evolution of the liquid phase of sintered W-Ni obtained by model A and B after 60 min. It can be seen that for both models almost all pores are already filled by liquid producing two very long chains of connected domains. Decreasing of pore domains by pore filling provides a way for migration of isolated solid-phase domains or even solid skeletons and their coarsening, where smaller domains near to larger ones dissolve, the dissolved material diffuses through the liquid and precipitates on the larger domains.

Fig. 9 shows the microstructural evolution of liquid phase sintered W-Ni obtained by both models after 120 min. It can be seen that both matrices are fully densified. It was observed that free movement of isolated solid-phase domains was already finished. Due to combined domain displacement some domains have formed bonds with neighboring domains prior to finishing complete displacement and producing (very long) chain-like clusters. Therefore densification inside these regions was stopped. 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.



**Fig. 9.** Two typical snapshots of the computed microstructure correspond to sintering time 120 min that obtained by (a) Brownian motion model, and (b) Densification model.

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 a model containing both small and large pores showed similar behavior where the smaller pores were filled first and the largest ones last.

## Conclusion

In this paper we have investigated numerically microgravity induced skeletal settling combined with solid-phase extrication during LPS of a tungsten heavy alloy. Microstructural evolution was simulated by computation of displacement of the center of mass (Brownian motion or center-to-center approach) 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 Courtney [8] that the solid-volume fraction can be directly related to the solid-liquid density difference but dictated by the formation of long skeletons with very few isolated solid-phase domains inside or outside them. Such skeletons were not able to move due to geometric hindrance of adjacent domains.

## Acknowledgements

The present work was performed under the project (No. 142011) supported financially by the Ministry of Science of the Republic of Serbia.

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**Садржај:** У овом раду биће развијен дводимензионални модел за симулацију течно-фазног синтеровања у условима микрогравитације коришћењем модела Брауновог кретања и модела скупљања. Оба ова модела ће користити топологију домена (дводимензионална репрезентација честице) и методологију контролних запремина, као и три подмодела за транслацију домена, формирање скелетона и одвајање (екстрикацију) домена. Симулациони метод биће тестиран у циљу проучавања дифузионих феномена и утицаја микрогравитације на еволуцију микроструктура услед таложења скелетона комбинованог са одвајањем чврсте фазе током течно-фазног синтеровања система W-Ni.

**Кључне речи:** Течно-фазно синтеровање, таложење скелетона, екстракција чврсте фазе, микрогравитација.

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