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Gradualism in sintered porous materials obtained by powders sedimentation

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Gravitational sedimentation of metallic and ceramic powders is a way of obtaining porous sintered materials with porosity gradient, materials with high functional performance especially in microfiltration. For this studies spherical nickel powders (size range 1-65 μm) was used. The sedimented and dried samples were sintered in vacuum at 950°C and 1000°C, for 10 and 20 min. The porous structures were investigated by scanning electron microscopy and mercury porosimetry. The sintering should be conducted in such a way that particles in the top layers (small particles) and the bottom layers (coarser particles) shouldn't be under or over sintered.

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1. Introduction

Porous materials with porosity gradient have certain advantages over symmetric porous structures, in terms of permeability, filtration, surface area and the capillary potential. Powder metallurgy provides multiple possibilities for obtaining such materials. By powder spreading, multilayer porous materials were prepared by co-sintering of layers with different porosities. Madaeni and collaborators proposed a method for obtaining asymmetric porous structures by thermal spraying [1]. Mesoporous and nanoporous membranes are obtained by dip coating [8, 9], electrophoretic deposition [2, 3], slip and centrifugal casting [4-6] and generally require a porous support. By wet powder spraying [7, 8] and screen printing [7] composite membranes were prepared by depositing titania (TiO2) on a stainless steel porous support. The deposited layer's quality is influenced by the porous support's surface quality (roughness, pore size). To avoid the formation of defects in the active layer the deposition of intermediate layers is required and thus the techniques become more complicated [8, 9].

The researches of Darcovich show the possibility of overcoming these drawbacks, by obtaining the gradual porous structures by sedimentation [10]. Centrifugal and gravitational sedimentation provide the formation of gradual porous layers from suspensions based on the sedimentation rate which depends on the particle size [10-12]. Pore size and porosity gradient is provided by the successive sedimentation of particles starting from the largest to the smallest in size.

In the literature there are a large number of studies on the kinetics of sedimentation of ceramic particles from suspension and the interactions that occurs between powder particles and between particles and the sedimentation environment [12-16]. There are relatively few published data referring to the formation of gradual porous structures by gravitational sedimentation. In general, gravitational sedimentation studies aims at obtaining stable (for sol-gel processes) or unstable (for rapid sedimentation of particles by flocculation/agglomeration in liquid-solid separation processes) suspension.

Several authors have developed mathematical models to establish optimal sedimentation conditions [17-20]. In [18] a study on the influence of particle size, the adhesion forces between particles and the thickness of the deposited layer on the sedimented layer's porosity is presented. To obtain gradual porous structures by gravitational sedimentation the following conditions must be met: a wide size distribution of the used powders and a viscosity of the suspension which prevent the agglomeration / flocculation of the particles [9]. It is known that for small particles the sintering temperature and time is lower [21-23] than for coarser particles. Fine particles in the upper layers will be sintered faster than the bigger ones in the lower layers.

This work fit among the concerns mentioned above, the use of gravitational sedimentation for the development of gradual porous structures. The work includes a study of the sedimentation process and the sedimented structure's sintering. Based on SEM images a new method of assessment of the porous structures was developed by mapping the isogranulation bands.

2. Materials and experimental method

A spherical nickel powder (size range 1-65 μm with a mean particle size (d_{50}) of 23 μm) was used during this study. The starting powders were investigated by scanning electron microscopy (SEM) and laser scattering particle

size analyzes. For each experiment 2 g of powders were used with different amounts of dispersant. The dispersant used is a commercial detergent based on sodium pyrophosphate ($Na_4P_2O_7$). The powders were sedimented in a glass tube having the diameter of 30 mm and the height of 1,000 mm, in which the sintering dies were placed [24]. The samples were dried in a stove under vacuum. The sedimented and dried samples were sintered in vacuum ($1.3 \cdot 10^{-3}$ Pa) at 950 and 1000 °C for 10 and 20 min. The obtained structures were analyzed using scanning electron microscopy and mercury porosimetry

3. Results and discussion

3.1. Sintering studies of the gradual porous Structures

In Fig. 1, cross-section images of the obtained samples after sintering are presented. All samples have a particle size gradient due to the gradual sedimentation of particles with different diameters and, in consequence, a pore size gradient too. Due to the small particles, the sintering time needed for the formation of the sintering necks is short [25]. The effect of particle size on sintering can be explained by Herring's scaling law [21].

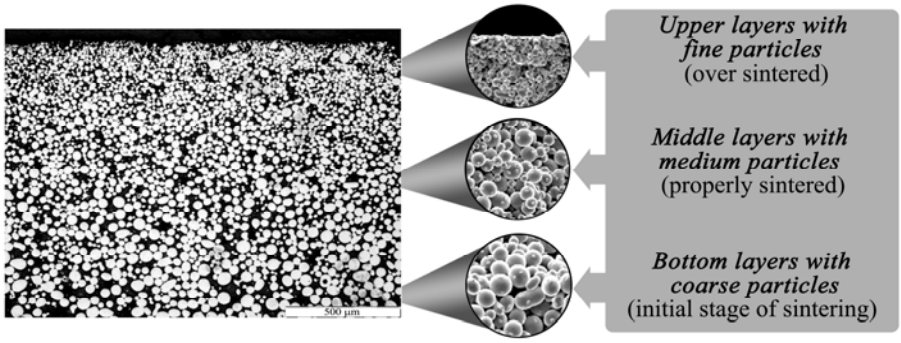
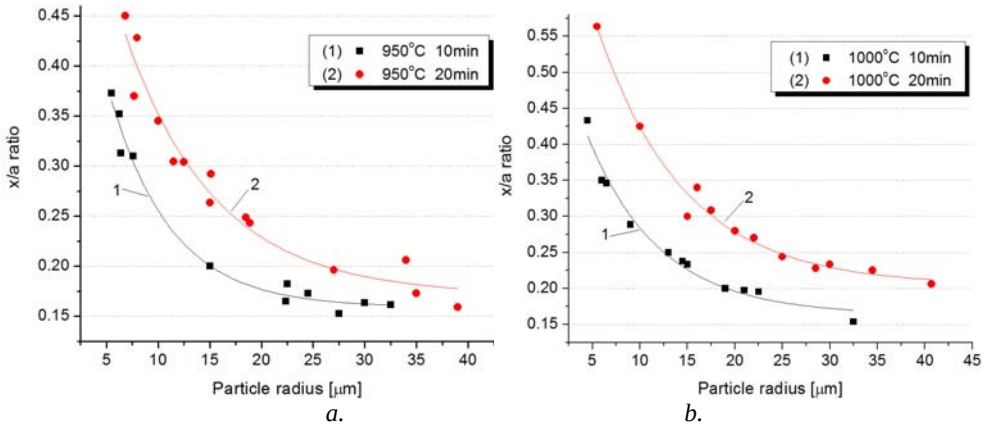


Fig. 1. Cross-section of the obtained gradual porous sample.

In the present case, if the top layer is made up of particles of d_1=10 μm and the bottom layer of particles with d_2=60 μm. The time needed for the same degree of sintering differs significantly for the two powder sizes (τ_2=216 τ_1). At the used sintering regime the top layer is over sintered, while at the bottom of the sample, the coarser grains are in the initial stage of sintering.

Samples were sintered under the same conditions using different particle size fractions and analyzed by SEM. An image analysis software (ImageJ) was used to measure the particles diameter and the sintering necks on the SEM images. The ratio of particle diameter and of the sintering necks was calculated for samples of different particles size ranges.

The dependence of the sintering degree (defined as the ratio between the sintering necks "x" and particle radius "a") on the particle diameter "d_g" is presented in fig. 2.



a. *b.*

Fig. 2. Dependence of the x/r ratio with the particle diameter for different sintering regimes.

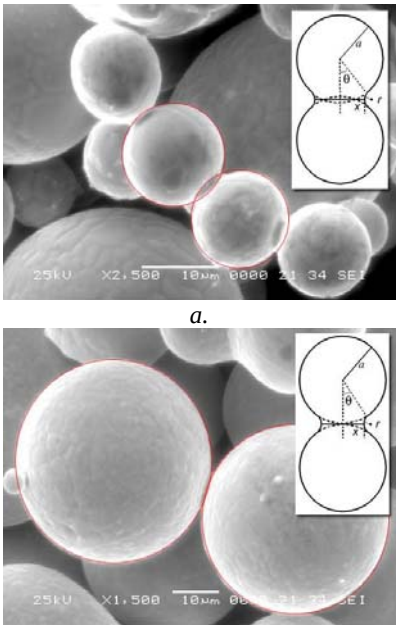


Fig. 3. The sintering mechanism of particles of different sizes (a. with shrinkage b. without shrinkage).

It is noted that the x/a ratio is decreasing with increasing particle diameter. As also described in reference [26] the sintering shrinkage is greater for small particles than in the case of the large particles. The particles centre approach for small particles figure 3.a), while for large particles the distance between centres remains constant (the particles are in the initial stage of sintering figure 3.b).

Sintering powder layers of different sizes in the same conditions, leads to over sintering in the small-particle layers and insufficiently sintered in the large particles layers. Thus requires finding an optimal sintering regime (temperature and time) to ensure a good bonding in the gradual porous structure regardless of particle size. After the optimization of the sintering process, the sintering temperature of 1000°C for 10 minutes was chosen. A more intense sintering regime led to over sintering and even to the coalescence of the small particles in the top layer. A less intense regimen does not produce adequate sintering of the large particles.

3.2. Gradualness of the porous sintered structures

In figure 4.b cross section SEM image of the sintered structure is presented. The powders are successively disposed as the coarser particles had higher sedimentation speeds than the smaller ones. The bottom layer is made up from the biggest particles; the top layer contains the smallest particles of the powder. Each band includes particle in a narrow sizes range. It can be seen that particle size is statistically ordered in descending sequence from the bottom up, respectively in succession according to the sequence of the order of sedimentation determined by the particles size (figure 4.c). A close match is observed between the particles size distribution (figure 4.a) and the obtained values. In figure 4.d the calculated porosity bands are presented based on the theoretical relationship considering the cubic arrangement of particles (D_p = $0.414d_g$).

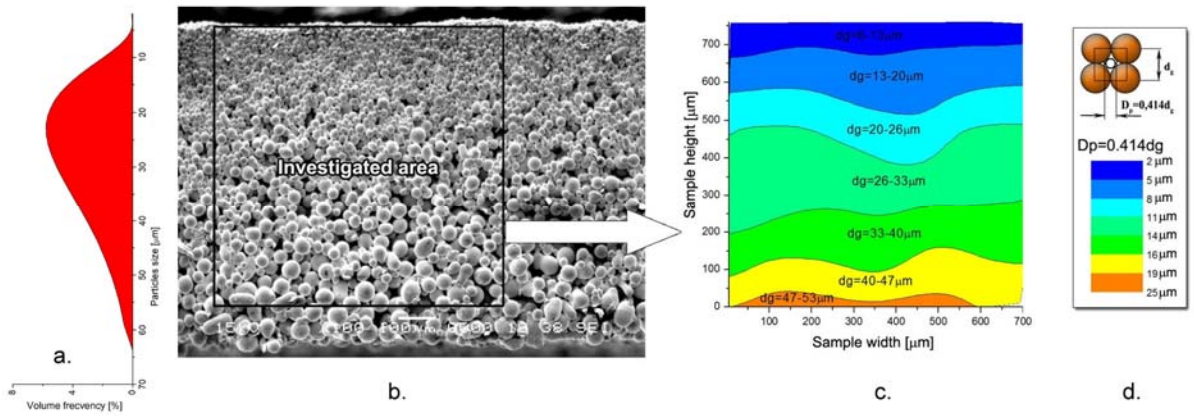


Fig. 4. Gradualness of the porous sintered structures:
a. - particles size distribution; b. - investigated area; c. - isogranulation bands; d. – calculated isoporosity.

The width of granulation bands is uneven, and it was caused by the existence of particles with different sizes in the same band. This observation can be explained by the existence of structural defects due to the influence of disturbing factors in the sedimentation process previously presented.

The existence of pores size gradualism is shown in Fig. 4, but it is difficult or impossible to accurately measure pore size in the presented image. In figure 5 the pore size distribution obtained by mercury porosimetry is given. Comparing this distribution with the calculated values (figure 4.d) one can find that the diameters exceed those calculated (over 25 µm). The percentage of those

over 25 μm pore size is relatively small and is caused by structural defects appeared during the sedimentation.

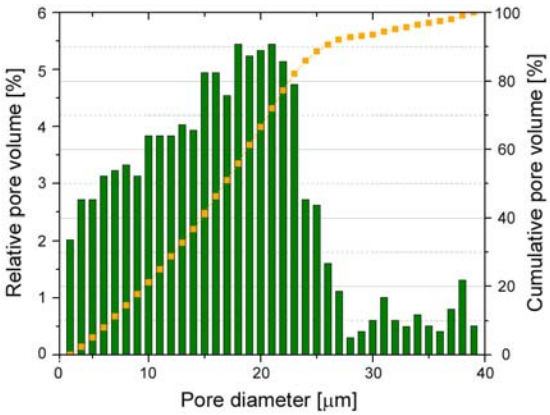


Fig. 5. Pore volume distribution function of pore diameter on the sample obtained using spherical particles.

4. Conclusions

Powder sedimentation offers the possibility of obtaining graded porosity membranes with good functional performance. During sedimentation a limitation of the clogging defects is necessary in order to be able to obtain high quality graded structures.

During the sintering of the gradual structure an optimal sintering regime is required in order to avoid over or incomplete sintering of certain layers in the structure.

The gradual porous structure obtained by sedimentation can be considered as an arrangement of isogranulation or isoporosity bands in descending order from the upper to lower layers, according to the sedimentation order of the particles.

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