Bulletin of the *Transilvania* University of Braşov
Series I: Engineering Sciences • Vol. 4 (53) No. 1 - 2011

STUDY OF SINTERING OF GRADUAL POROUS STRUCTURES OBTAINED BY GRAVITATIONAL SEDIMENTATION

V. MOLDOVAN[1] I. VIDA-SIMITI[1] N. JUMATE[1]
Gy. THALMAIER[1] D. NEMES[1] E. BRUJ[1]

Abstract: *In our studies we used spherical nickel powder. When powders with similar shapes but different sizes are sintered under the same conditions, the sintering time required to get the same degree of sintering varies. Due to the small particles, the sintering time needed for the formation of the sintering necks is short. The top layer of sedimented samples is over sintered while at the bottom of the sample are in the initial stage of sintering. This phenomenon was studied by sintering of nickel powder with different particle size ranges. The analysis of the sintered layers has been done using scanning electron microscopy. The influence of the sintering regime on the formation of the sintering necks were investigated.*

Key words: *sedimentation, sintering, metallic membrane, porosity gradient.*

1. Introduction

The sedimentation technique of powders from suspension is a relatively simple method for obtaining gradual porous structures based on different sedimentation rates depending on the size and shape of powder particles [7]. Asymmetric gradual structures ensure more efficient separation and exploitation characteristics compared to symmetrical porous structures. The variable porous structure of a filter is characterized by changes of the structural parameters with thickness: porosity, pore size, specific surface. The bottom layer will contain larger particles while the upper layer will have the particles with the lowest sedimentation rate (the smallest particles). Thus, porous thin layer with small pores ensures proper filtration fineness, while the bottom layers (occupied by larger particles) provides a good permeability to fluid flow with low pressure loss and a good mechanical resistance (durability) to the gradual porous structure [1], [5], [6].

In a gradual porous structure obtained from a large powder particle size range the difference between particles contained in upper and lower layers may be tens of micrometers. This difference will influence the sintering behavior of particles; the ratio between particle size and the size of intergranular sintering necks would be different at various particle sizes.

2. Materials and Experimental Method

We used spherical nickel powder. Within research samples were obtained both by free spreading the powders (obtained by

[1] Dept. of Materials Science and Technology, Technical University of Cluj-Napoca.

sieving) and by sediment the integral powder into dies. The starting powders were characterized by electron microscopy and laser particle size analysis. The powder ranges used was between 2 to 90 μm. Particle shape factor (F) was determined by the ratio between the minimum particle diameter (d_{min}) and the maximum particle diameter (d_{max}). The shape factor of particle shows the deviation from spherical shape (F = 1 for sphere). The form factors resulted from SEM images (Figure 1) Fs = 0.91.

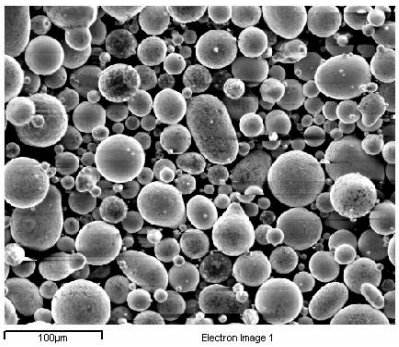


Fig. 1. *Morphology of the used nickel powder*

Figure 2 shows the particle size distribution curves obtained by laser diffraction analysis. The average particle size of the cumulative curve d_{50} = 26 μm. The powders were sedimented in a glass tube having the diameter of 30 mm and the height of 1000 mm, in which the sintering dies were placed.

The sedimentation liquid was distilled water. As a dispersant a commercial detergent based on sodium pyrophosphate ($Na_4P_2O_7$) was used.

The sedimentation liquid was distilled water. As a dispersant a commercial detergent based on sodium pyrophosphate ($Na_4P_2O_7$) was used. The dispersant agent's concentrations were calculated according to the volume of the sedimentation column. The quantities of the dispersant agent in the sedimentation media were 0.86 mL/L. The samples were dried in an oven under vacuum.

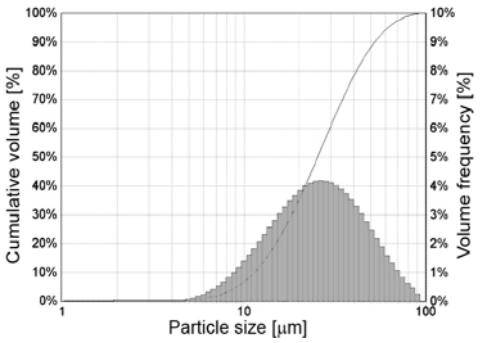


Fig. 2. *Particle size distribution of the used nickel powders*

The samples were than sintered in vacuum ($1.3 \cdot 10^{-3}$ Pa) at the temperature of 1000 °C for 10 minutes. The obtained porous materials were than analyzed by scanning electron microscopy (SEM).

3. Results and Discussions

In Figure 3 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.

After the optimization of the sintering process, the sintering temperature of 1000 ˚C for 10 min was chosen.

The sintering time needed for the formation of the sintering necks is short due to the small particles [2]. The effect of particle size on sintering can be explained by Herring's scaling law [3]. When powders with similar shapes but different sizes are sintered under the same conditions and by the same sintering mechanism, the scaling law predicts the relative periods of sintering time required to get the same degree of sintering. For the sintering of two kinds of powders with radii d_1 and d_2, where:

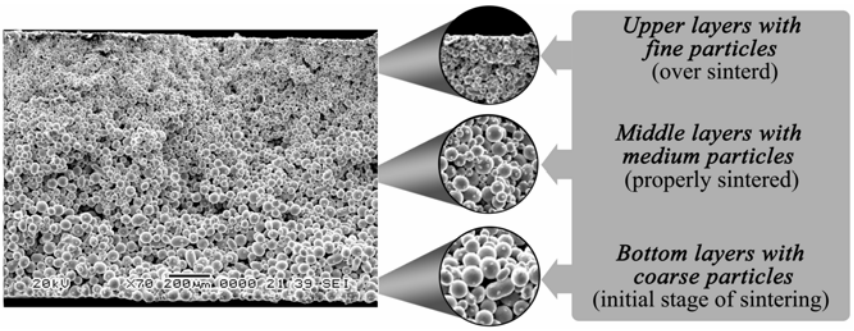


Fig. 3. *Cross-sections of the obtained gradual porous samples*

$$d_2 = \lambda d_1, \quad (1)$$

the required sintering times τ_2 and τ_1 are interrelated as:

$$\tau_2 = \lambda^{\alpha}\tau_1, \quad (2)$$

where α is an exponent. In the case of sintering, which occurs by lattice diffusion (α = 3), the period of time required to get the same degree of sintering for powders of different sizes is proportional to λ^3.

For the particle size ranges used in sedimentation (2 to 90 μm) the upper layers contain particles ranging from 2 μm to approximately 10 μm. The bottom layer is composed of the larger particles (~90 μm) who settle in the mold at higher speed.

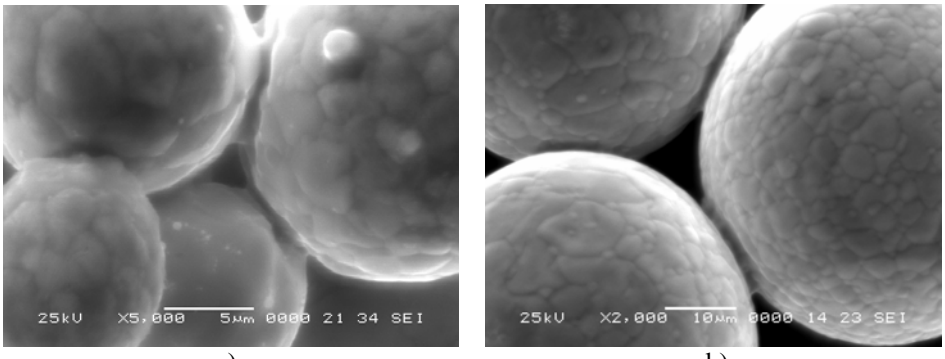
The time needed for the same degree of sintering differs significantly for the two powder sizes. For this particle size ranges the Herring (2) relation is:

$$\tau_2 = 729\tau_1, \quad (3)$$

where τ_2 is the sintering time for particles with d_2 = 90 μm, and τ_1 is the sintering time of the smaller particles in the particle size ranges with d_1 =10 μm.

The smaller size particles require a much less sintering time compared to larger ones (3).

In both cases the sintering degree was measured by the size of sintering necks, and was emphasized by scanning electron microscopy (Figure 4). At the used sintering regime the top layer is over sintered (Figure 4a), while at the bottom of the



a) b)

Fig. 4. *Different sintering degrees for powders of different diameters: a) top layer - over sintered small particles; b) bottom layer - larger particles in the initial stage of sintering*

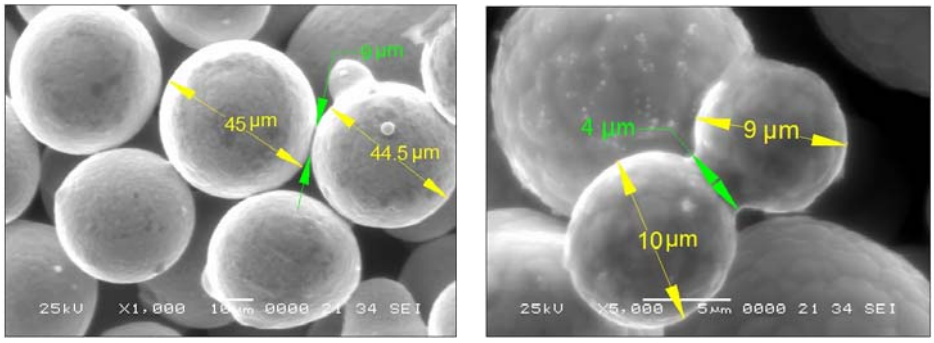


Fig. 5. *Different sintering degrees for powders of different diameters*

sample the coarser grains are in the initial stage of sintering (Figure 4b).

Sintered samples from different particle size ranges were obtained using the same sintering regime. Subsequently these samples were subjected to scanning electron microscopy.

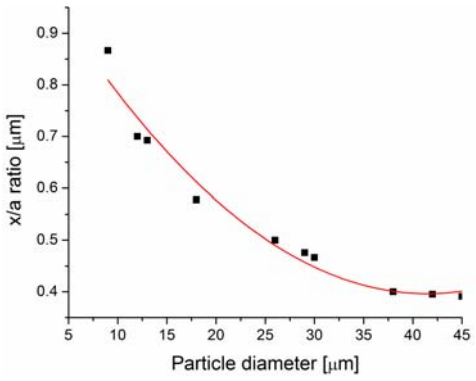


Fig. 6. *x/a ratio function of dg*

The obtained images were analyzed and processed to measure the particle diameter and the diameter of the sintering necks.

The graph in Figure 6 represents the dependence of *x*/*a* ratio function of particles diameter *dg*. From the image analysis performed for different particles sizes the *x*/*a* ratio was determined. *x* is the radius of the sintering necks and a is the radius of the particle.

It was found that *x*/*a* ratio decreases with the increment of the particles diameter, thus the sintering necks become smaller with the augmentation of the particle size.

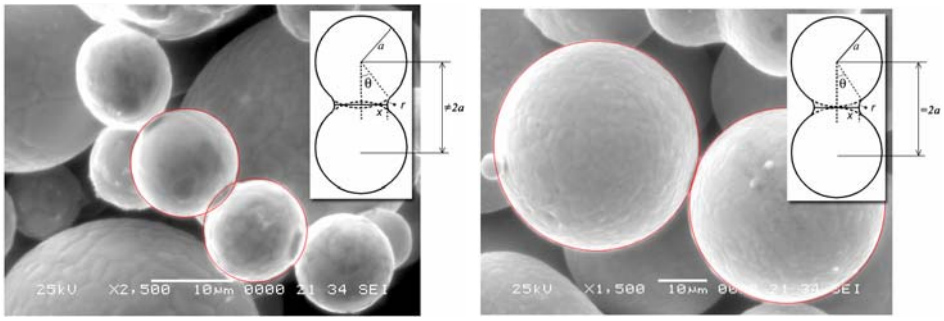
According to the model described by Suk-Joong L. Kang [4] the small particles shrink during sintering (distance between particle centers decreases) (Figure 7a). Larger particles do not shrink (the sintering necks do not develop) therefore the sintering is reduced (Figure 7b).

The relation for the curvature of the sintering neck *r* and the neck area *A* differ depending on the sintering mechanism [4].

Changing the sintering mechanism will modify the dependence between the *curvature of the neck, the particle radius and the neck radius,* and also between the *neck area*, *the particle radius and the neck radius* (Table 1).

Equations for radius of neck curvature and neck area Table 1

Sintering mechanism	**Radius of neck curvature**	**Neck area**
Without shrinkage	$r = \frac{x^2}{2a}$	$A \approx 2\pi x 2r = \frac{2\pi x^3}{a}$
With shrinkage	$r = \frac{x^2}{4a}$	$A \approx \frac{\pi x^3}{a}$



a) b)

Fig. 7. *The sintering mechanism of different particle sizes*
a) *with shrinkage; b*) *without shrinkage*

These phenomena lead to an insufficient sintering of the layers consisting of large particles and a decrease of their mechanical resistance. Thus the layers containing larger particles cannot fulfill their support role.

On the other hand, the layers consisting of smaller particles in the used particle size range can be over sintered in the same sintering conditions. By forming too big sintering necks, pores can shrink too much and be partially or completely clog. Thus, the membrane loses its permeability and filtration capacity.

4. Conclusions

Powder sedimentation method offers the possibility of obtaining gradual sintered porous structures provided that the choice of sintering parameters and particle size ranges to be adequate in order to achieve superior flow properties and satisfactory mechanical resistance.

This requires strict control of the sintering process and sintering parameters because the time needed for the same degree of sintering differs significantly for the two powder sizes. The sintering temperature has been chosen to ensure an appropriate degree of sintering for each sedimented layer on the samples height. It was shown that particles with diameter of 90 µm require a sintering time of 729 times higher than 10 µm particles to achieve the same degree of sintering. From this we can deduce that the choice of a large particle size range to obtain gradual porous structures involves sintering complications.

The correct choice of particle size ranges for the powder used is a good way to optimize the process. Choosing a narrow particle size range mitigates the effects of differential sintering of different size powders.

More intense sintering of powder layers with small particle size (larger shrinkage) compared with those of large particles (less shrinkage), is an argument for cracks and exfoliation on the superficial layers containing fine powders.

Further research is needed to optimize the technological parameters of the sintering process that ensure appropriate degrees of sintering across the gradual porous structure with the entire thickness of the samples.

Acknowledgements

This work was supported by CNCSIS - UEFISCSU, project number PNII - IDEI 749/2009.

Valentin Moldovan, Emil Bruj, Dorel Nemeş would like to thank Project development of doctoral studies in advanced technology – "PRODOC", contract no. POSDRU 6/1.5/S/5, project co-funded from European Social Fund through Sectorial Operational Program Human Resources 2007-2013 for the financial support.

References

1. Baker, R.W.: *Membrane Technology and Applications*. California. John Wiley & Sons Ltd., 2nd ed., 2006.
2. Ch'ng, H.N., Pan, J.: *Sintering of Particles of Different Sizes*. In: Acta Materialia **5** (2007) Issue 3, p. 813-824.
3. Herring, C.: *Effect of Change of Scale on Sintering Phenomena*. In: Journal of Applied Physics **21** (1950), p.301-303.
4. Kang, S-J.L.: *Sintering, Densification, Grain Growth and Microstructure.* Oxford. Elsevier, 2005.
5. Kieback, B., Neubrand, A., et al.: *Processing Techniques for Functionally Graded Materials*. In: Materials Science and Engineering **A 362** (2003), p. 81.
6. Vida-Simiti, I., Jumate, N., et al.: *Study of Gradual Porous Metallic Membranes Obtained by Powder Sedimentation.* In: Journal of Porous Materials, (2010) DOI 10.1007/s10934-010-9442-9.
7. Vida-Simiti, I., Jumate, N., et al.: *Preliminary Studies and Researches on the Elaboration of Gradual Porous Sintered Structures by Powder Sedimentation.* In: Materials Science Forum, Researches in Powder Metallurgy **672** (2010), p. 137-140.