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Gradual porous membranes obtained by powder sedimentation

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Abstract. The aim of this work is to review our group's studies and results on sintered porous membranes with graded structure for microfiltration by sedimentation and sintering of metallic and ceramic powders. The powders were sedimented into a sintering die in a sedimentation medium consisting of water and dispersant agent. After drying, the samples were sintered. The structures obtained were characterized by scanning electron microscopy and mercury porosimetry. The flow rate – pressure drop curves were experimentally determined and the viscous permeability coefficient was calculated using Darcy's law. The absolute and the relative filtration fineness were also determined. A statistical study of the influencing parameters on the sintering degree shows that the particle size has the greatest effect on the sintering degree compared with sintering temperature and time. The possible applications for the studied membranes are: water microfiltration, environmental technologies, filtering lubricants and cleaning agents.

Keywords: sedimentation, sintered porous membrane, porosity gradient.

1. Introduction

Topic covered by this work falls into the intense research currently carried out in the world of microfiltration inorganic membranes and of the gradual porous materials. Policy development in materials engineering and environmental protection should increase interest in developing new materials and advanced technologies for the manufacture of filter elements [1, 2]. Moreover, research and development programs for areas such as: new materials and advanced environmental protection are

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considered priority areas in research programs - development and innovation of the European Union. Ensuring a clean environment and a good quality of industrial environment and technological fluids require sophisticated solutions for filtration process as a method of pollutants separation, achievable through the use of filter materials and constructive solutions for performance filters [3].

These researches focused on designing new structures with gradual porosity, obtained by controlled powder sedimentation process, adapted to each particular area, aimed at optimizing and improving the technical and economic performance of their characteristics. Designing new structures with controlled porosity and pores size by powder sedimentation method in the micro and nanometers range can be considered an element of originality.

The membranes are selective filter mediums that allow preferential transfer of a particle, molecule, phase or substance under the action of the driving forces of transport (pressure drop, concentration gradient, temperature or potential gradient) [1]. Worldwide there is an increasing interest in the development and use of materials with gradual structure for obtaining membranes (pore size filter elements with thickness <10 mm).

The variable porous structure is characterized by the variation of structural parameters, porosity, pore size, specific surface with height, and due mainly to different particle size distribution of powders. Asymmetric membranes with porosity gradient provide more efficient separation and operation characteristics as compared to symmetric permeable porous structures. Thus, the thin porous layer with small pores provides the adequate filtration fineness, while the thicker support layer, with larger pores, provides good permeability and mechanical strength.

Gravitational sedimentation. During gravitational sedimentation the particles in suspension have different sedimentation rates due to mass difference. This difference in mass is given by the various particle sizes from a particle size fraction. Thus, based on Stokes's law one can deduce that the larger particles will have the highest rate of sedimentation, while the smallest particles will have the lowest sedimentation rate, obtaining a particle size gradient in the deposited layer (fig. 1).

The method of powder sedimentation from suspension compared to other methods of powder metallurgy, offers multiple advantages for obtaining gradual sintered porous structures, advantages like: does not require special installments and equipment and have relatively low energy consumption in comparison with alternative methods for obtaining gradual porous structures. Because of the many factors involved, the application of powder sedimentation process to obtain gradual porous materials is still problematic [1].

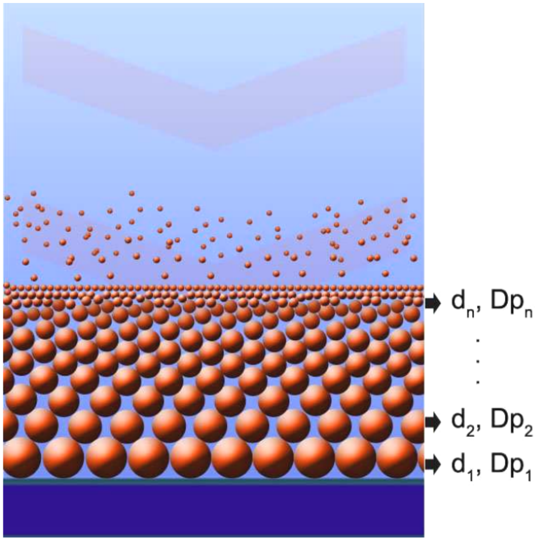


Fig. 1. The schematics of gravitational sedimentation
(d -particle diameter, Dp - pore diameter; $d_1 > d_2 > \ldots > d_n$; $Dp_1 > Dp_2 > \ldots > Dp_n$) [4].

2. Sedimented bronze structures

In the case of gradual porous structures obtained from bronze powder we used the sedimentation of a fine powder fraction on a macroporous support layer. It can provide a gradual structure with a porosity gradient in the active filter layer. In case of bronze samples the porosimetry emphasize the pore size distribution in the porous gradual structure from 2 µm to 40 µm across the sample, and SEM analysis reveals that the pore size distribution varies quasi continuously in the thickness of the sedimented layer (fig. 2).

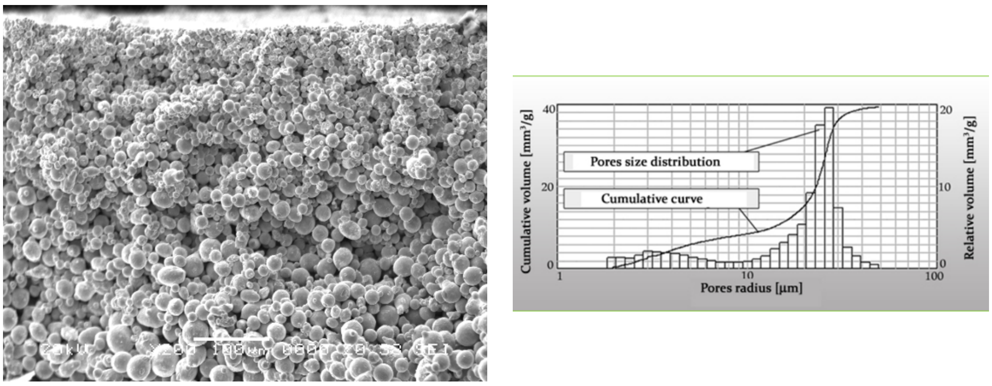


Fig. 2 Gradual porous structures obtained from bronze powder.
Cross section SEM image and pores size distribution [5].

The particle size range used for obtaining the macroporous support directly influences the permeability of the obtained samples. Therefore, the obtained macroporous support have the viscous permeability coefficient of $\Psi_v = 3.29 \cdot 10^{-12}$ m^2 for the 100-125 µm particle size range and $\Psi_v = 4.3629 \cdot 10^{-12}$ m^2 for the 125-160 µm range. It can be observed an increase of permeability with 24.5 % using a larger particle size range for support (fig. 3).

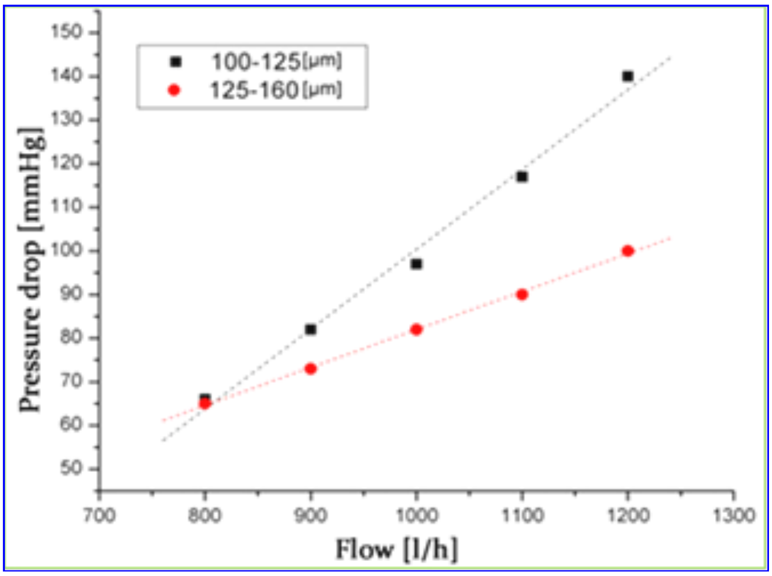


Fig. 3. Flow vs. pressure drop curves for the gradual bronze filters [5].

3. Sedimented nickel structures

For obtaining the nickel membranes, elongated and spherical nickel particles were used, with particle size in the 2-90 µm range measured by laser scattering particle size analyzer. Cross-section SEM images of the obtained nickel samples after sintering show a particle size gradient due to the gradual sedimentation of particles with different diameters and, in consequence, a pore size gradient too.

The nickel samples obtained using spherical particles evidenced a pore size distribution between 4 µm and 37 µm; the bigger pores (27-37 µm) are few and they are originating from packing defects. In the case of the samples made of irregular shaped particles, the pores size distribution is between 5 µm and 72 µm, with the majority of the pores ranging from 20 µm to 50 µm (fig.4).

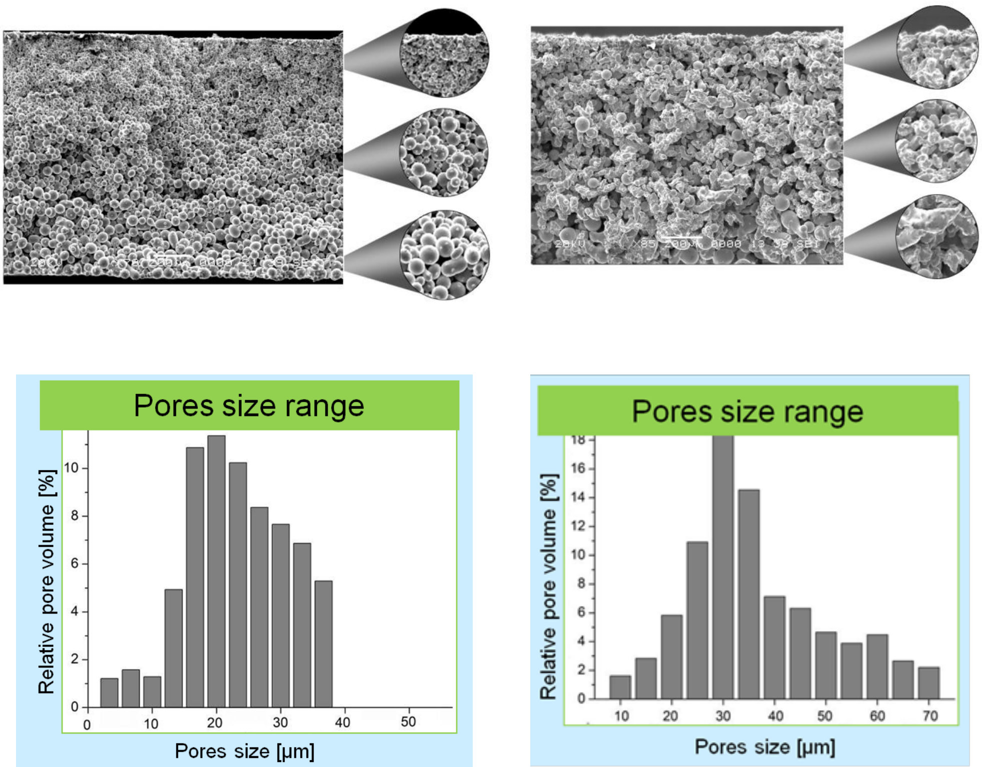


Fig. 4. Cross section SEM images and pores size distribution of sedimented structures made of spherical and elongated nickel particles [6].

With the increase of the samples thickness, for the same flow rate an increase of the pressure drop is observed (fig. 5). From the obtained curves the viscous permeability coefficient of the samples was determined using Darcy's law.

In the case of the samples made of spherical particles the mean coefficient was $\Psi_v = 1.32 \cdot 10^{-12}$ m^2 and for the samples obtained using elongated particles is $\Psi_v = 0.14 \cdot 10^{-12}$ m^2. They concluded that the higher tortuosity of the samples having elongated particles ($a_p = 6.3$) compared to the spherical shaped particles ($a_p = 1.7$) reduces the permeability of the samples.

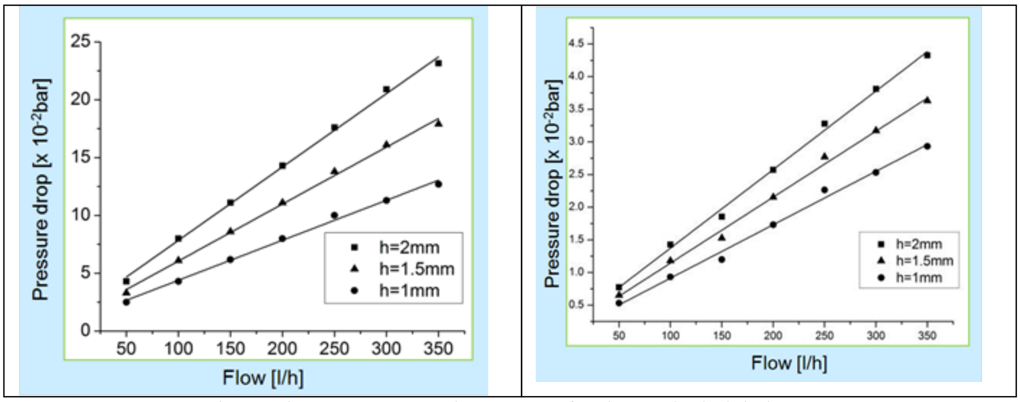


Fig. 5. Flow vs. pressure drop curves for the gradual nickel structures made of spherical and elongated particles [6].

Filtration tests were conducted to determine the filtration fineness of samples with impurities of powder Al_2O_3 particles (fig.6). The absolute filtration fineness of samples made by spherical powder is 17 µm and the relative filtration fineness (at 95 %) is 8 µm. For samples made from elongated particles the absolute filtration fineness is 20 µm and the relative filtration fineness 11 µm. It can be said from the comparative characterization of these structures that membranes made from spherical powders are superior both in terms of fineness of filtration and in terms of permeability to the membranes made of elongated particles. In addition to their characterization of gradualism is easier due to the spherical shape of particles.

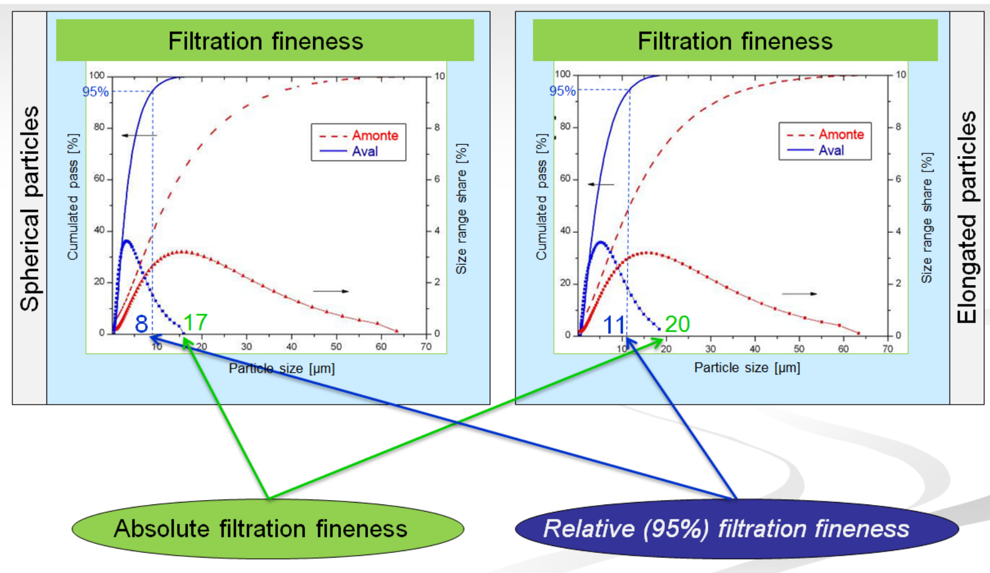
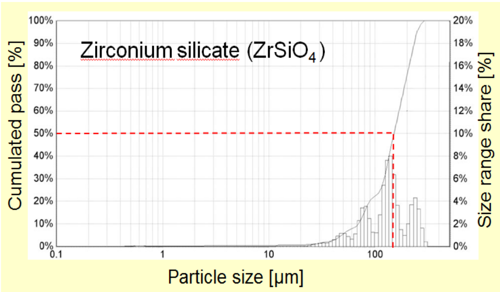


Fig. 6. Particle size distribution of the Al_2O_3 particles impurities from the feed and permeate

(samples made of spherical and elongated particles) [4, 6].

4. Sedimented ceramic structures

The ceramic membranes were obtained by sedimenting a thin, mullite layer onto a zirconium silicate support. The starting powders were characterized using a laser scattering particle size analyzer. The zirconium silicate powder was in the 20 – 300 µm range, the mullite ($3Al_2O_3 \cdot 2SiO_2$) powder was between 0.2 – 60 µm respectively (fig.7).



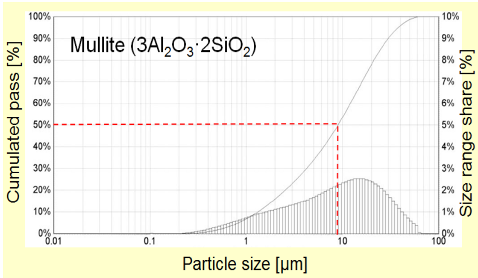


Fig. 7. Particle size distribution of the used powders:
ZrSiO4 (support), $3Al_2O_3 \cdot 2SiO_2$ (active layer) [7].

The SEM investigations show that a gradual structure was obtained in the sedimented layer after sintering. This graduality of the particles generates a quasi continuous variation of the pores size too. The sintering between the particles of the mullite active layer and the particles in the support was evidenced by SEM and EDX analyses. Between these layers mass transport occurred and sintering necks were formed (fig. 8).

The interface of the two oxide layers was also studied. The variation of the chemical composition due to diffusion was evidenced in the form of the migration of the aluminum silicon and zirconium atoms. This effect confirms a good sintering and adherence between the two layers consisting of different materials. In the top layer made by the smallest particles in the sedimented powder all pores are less than 5 µm. This mercury porosimetry analysis of the ceramic membranes evidenced a pore size distribution between 4 - 25 µm existing in the sedimented layer and a 25 - 100 µm distribution in the support layer (fig. 9, a). The filtration tests show that the absolute filtration fineness is 2.3 µm and the relative filtration fineness is 1 µm.

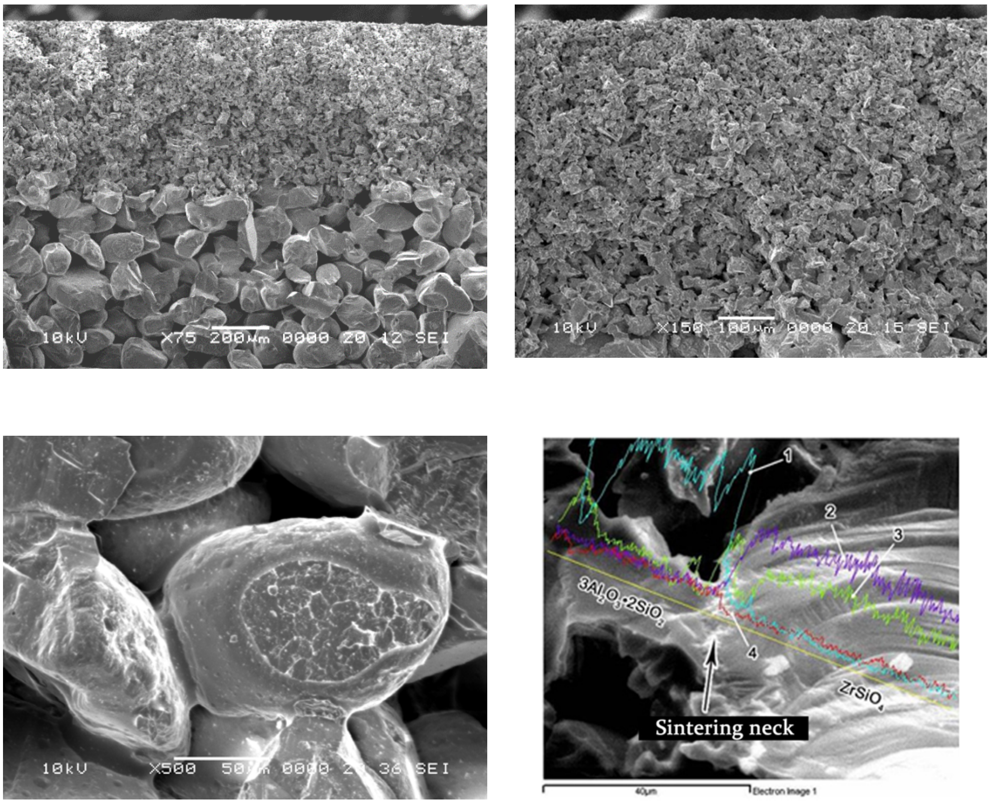
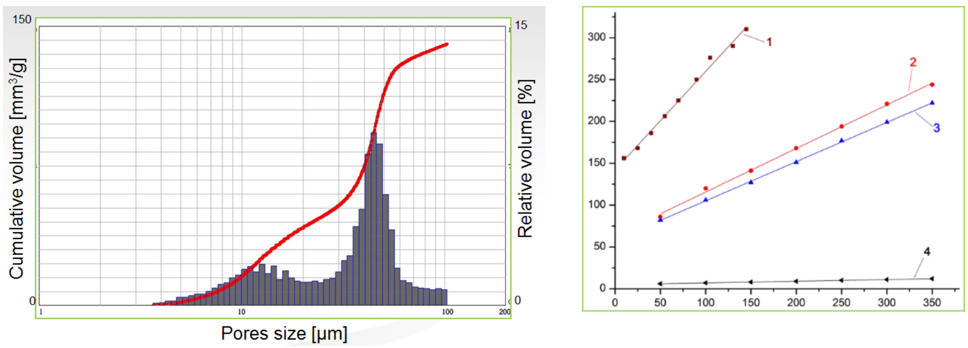


Fig. 8. Cross-section SEM images of the obtained gradual porous samples and SEM-EDX measurements of the difiusive interface between mullite and zirconium silicate particle [7].



a. ***b.***

Fig. 9. Pores size distribution and pressure drop vs flow rate curves
1 - mullite; 2 - 0.45 mm mulite+ zircon support; 3 - 0.25 mm mullite+zircon support; 4 - zircon; (all samples 2 mm thick) [7].

These findings one can conclude that the obtained porous ceramic membranes can be used in applications in the microfiltration area. Permeability tests were carried out for different samples. By combining a thin active layer deposited onto macroporous supports one can achieve porous structures with good permeability and fluid filtration fineness that can be used in applications in the microfiltration (fig. 9b). It also demonstrated that membrane permeability is influenced by the thickness of sediment active layer and the macroporous support properties.

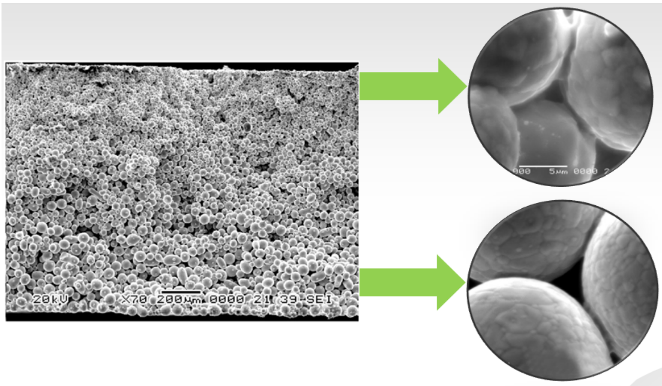


Fig. 10. Different sintering degrees for powders of different diameters [4, 8].

5. Optimisation of sintering parameters

During the experimental investigations a gradient of sintering in height of gradual porous structures it was observed (fig.10). Thus, we see that the smaller particles in the top layers of samples are over sintered (in terms of porous filter material) while the lower layers are occupied by large particles in the initial stage of sintering. We also noted that the layers occupied by fine particles suffer a contraction near the centers of the particles. From this, the cracking and exfoliation of layers with fine particles can be explained.

This was a fairly common defect in the experimental research. To highlight this phenomenon sintered samples at different temperatures and durations were made. The particle size and sintering neck size were measured by image analysis. The graphic variation was made for neck size/particle size ratio at different sintering regimes and different particle sizes (fig. 11). Through a series of equations and analysis of variance “ANOVA” the dispersions produced by different factors was calculated. These results concerning the sinterability of powders of different particle sizes contribute to the theory of study and practice of sintering process [9].

We deduced and calculated hyperplane equations for different particle sizes (6, 13 and 25 µm). A space plan was reached at the intersection of these planes. Determination of optimal parameters of the sintering zone can be deduced by intersecting the hyperplane with a plane G = 0.3 (unless they overcome stage one of sintering ... i.e. optimal degree of sintering porous materials used in filtering) (fig. 12).

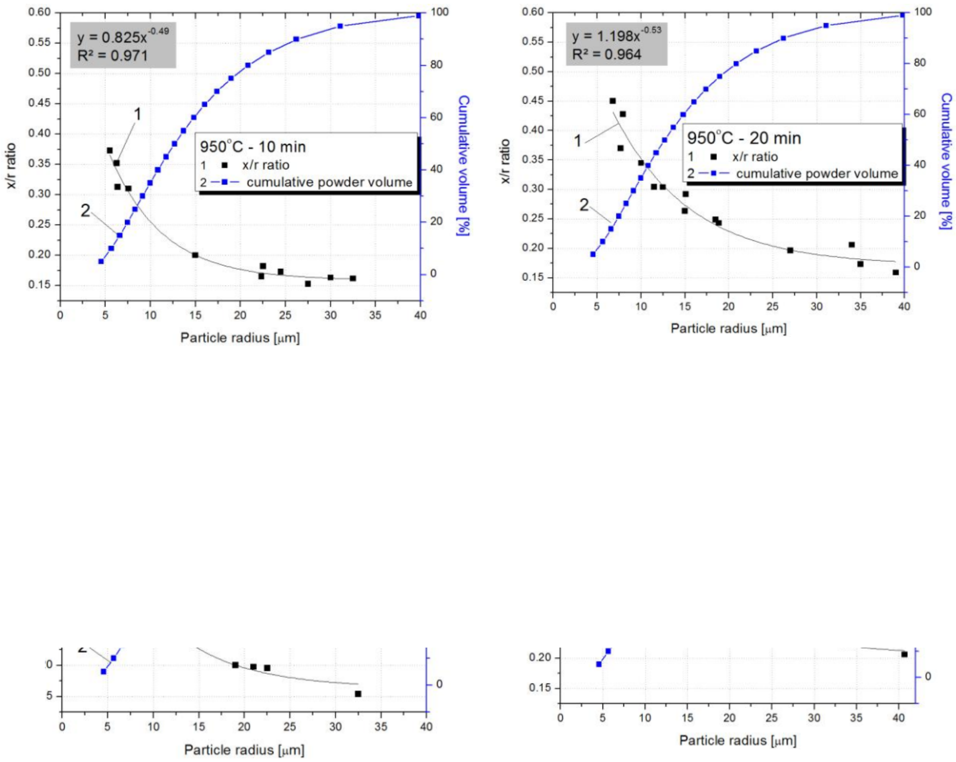


Fig. 11. The dependence of the x/r ratio on the particle size for different sintering times and temperatures: (1) - the x/r ratio (2) - cumulative particles size distribution [8].

$$G = 0.735 - 0.0006 \cdot T - 0.0487 \cdot t + 0.00006 \cdot T \cdot t \tag{1}$$

From the intersection of these planes results a curve that defines the optimal sintering parameters that should be selected from sintering temperature and time (fig. 12, b).

Fig. 12. The dependence of the sintering degree on the sintering parameters:
a - The hyperplane's intersection with the G = 0.3 plane, b - the optimum sintering zone [8].

6. Conclusions

Our group focused its research on the asymmetric membranes as presented in this review article, on two directions supported membranes for applications where good mechanical properties are also important and unsupported membranes where the main concern is the filtration fineness. As demonstrated in our previously published articles this method is applicable to a wide range of materials and can be tailored for special application requirements.
From the statistical study of influencing parameters of sintering degree, results that particle size have the greatest effect on the degree of sintering (much higher as the sintering temperature and time). The contradiction that arises between the need for a uniform degree of sintering (made with particles of powder with particle size distribution belonging to the same class) and gradual structure (particles of powder particle size distributed over several classes) requires rigorously selecting of particle size classes for gradual structure (both in terms of layer and gradualism in terms of the degree of sintering).
The presented study allows the optimization of the sintering conditions for obtaining filters with gradual porous structures so that the degree of sintering of powder particles to be about 0.3 (for a good filtering capacity).
Theoretical and experimental researches presented in this paper contribute to the development of the international researches in this field with broad applicability in the field of advanced materials and environmental protection, ensuring a clean environment and a good quality of industrial environment and technological fluids.

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