

Part 2

Composition Materials With Metal Matrix Condensed from the Vapor Phase

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Abstract: In this article, the present-day problems of microporous condensed materials obtained from the vapor phase are discussed. The pore sizes are regulated by the amount of the second phase concentration and the deposition temperature.

The oxides, fluorides, and sulfides can be used as the second phase and non-removable inclusions. The open porosity can be regulated from 0% to 50 % of the porosity and with average pore sizes of 0.1 to 8 μm . The condensed microporous materials can be deposited in coating form or the form of massive bulk sheet materials with a thickness of up to 6 mm and a diameter of 1m.

Keywords: Microporosity, Vacuum condensate, Substrate temperature, Annealing in vacuum.

INTRODUCTION

There are three technologies for getting porous materials.

Manufacturing of parts without any additives or mixers. a). molding pressure; b) hydrostatic compaction in elastic vessels; c) vibration pressing or squeezing; d). forging of foils or strips; e) sintering of free powders.

Manufacturing of parts with additives or mixers, a) which appear in the material, is further entirely removing from a sintered material; b) used for porosity creation along for sintering activation.

The presence of additives increases the strength of sintered materials. The strength increases due to inside contacts among particles and new phases' appearance.

There are other methods for porous materials production from fibbers, metallic rods, and nets.

Vapor phases technology opens new perspectives in materials obtaining within an advanced porous volume and porous sizes in manufacturing porous and microporous materials.

The evaporation process with further condensation of metals and non-metals from vapor phases in a vacuum leads to the realization of two approaches

within the additional introduction of the dispersed inclusions. That helps to get porous formation at the condensation process and keep it further in the material or remove it with the subsequent heat treatment.

At the heat treatment, dispersed inclusion can take part or not participate in the porous formation. Article [5] shows that interphase interaction can be characterized as wetting angle θ between disperse particle and molten metal. Works [6] and [7] explained no interphase interactions in the chosen condensed systems if high-temperature particles have the wetting angle in such structures $\theta = 60^{\circ} - 180^{\circ}$.

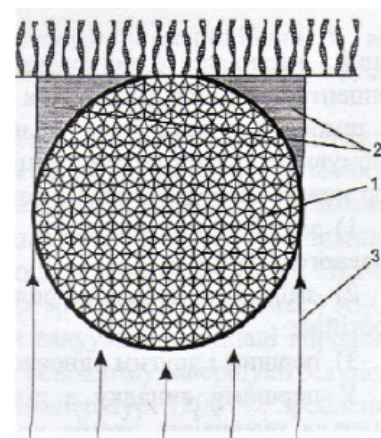


Figure 1: Schematic of porosity appearance mechanism in vacuum condensate.
1-high-temperature particle; 2-shadow zones; 3- vapor torrent.

The absence of interphase interaction and the subsequent lack of diffusion leads to shadows

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formations (porous), which appeared in the condensation process (Figure 1).

The presented results found application as a coating on special metallic filters obtained by powder metallurgy methods utilizes porous sizes gradient and thickness gradient performance.

EXPERIMENTAL PART

According to described above pores mechanism, there are conditions to satisfy a certain amount of open porosity.

It is necessary to correct the wetting angle for interphases interaction between the high-temperature particle and molten metal. This data can be obtained experimentally for the complex systems or from the literature [8.9].

A high amount of high-temperature particles with the lower limit help create enough shadow zones, which are growing and forming a considerable volume of open porosity. The upper limit detects mechanical properties and the high value of strength and hardness.

The experimental approach was based on studying porous sizes and their distribution along the substrate surface with two variables changing substrate temperatures and porosity creator material. The substrate temperature was changed during the deposition process along 500 °C to 900 °C. The porose materials creators as a characteristic influence to the porosity appearance were tested in ceramic and salt forms.

This chouse reflects the distant reference of the material's evaporation rates, and they're removing after depositions in the vacuum annealing. Two compounds Al_2O_3 and NaCl were chosen for this investigation. Both compositions evaporated along with metals evaporation from separate crucibles located in the technological chamber. The second removable phase was also an interest reflected as the third variable in thickness of the coating.

At the substrate's high temperature, in the condensation, coalescences of particles occur. The amount of coalescence regulates the increase of shadow zones. In parallel, the process of porous opening is developing.

It is essential to perform materials formation with regulated open porosity at the substrate's low

temperature (<500 °C). Additional opening channels are observed in inner crystals zones due to bad connections of the metallic matrix's border crystals that decrease the metallic grains connection's and worsening mechanical properties.

Creation of the materials with regulated open porosity is possible when the high-temperature particles contain not less than 4 % and substrate temperature 600 °C.

Taking into consideration conditions of porous formation, controlling of volume and sizes of feedthrough porous can be done in three easy ways:

- Changing of substrate temperature at a constant concentration of high-temperature composition.
- Changing of the composition of high-temperature phase at the constant substrate temperature.
- Changing both high-temperature phase concentration and substrate temperature.

At the first option, along with substrate temperature increasing, the diffusion movement grows in condensed high-temperature phase and the sizes of high-temperature particles. Small porous coagulations occur along with the opening of close pores and further joining with existing feed through pores, which depends on the dimensions of high-temperature particles.

The considerable influence on pore sizes plays high-temperature phase concentration. With the increasing high-temperature phase concentration at the constant substrate temperature, the probability of interconnecting in the condensate's high-temperature phase escalates. When the coagulation process intensifies, the pores sizes growing, and if the intensity of the input phase rises, the volume of feed through porosity develops.

The third option of porosity regulation by the last two parameters is used when porous materials demand unique physical-mechanical properties or materials with pores sizes gradient in a material body.

As mentioned above, open porosity attaining regulation technological options proves the ability to make various porous materials with complex metallic matrixes, where dispersed particles are oxides, and wetting poorly by metallic melts [5].

Studying the structure and properties of deposited porous materials from vapor phase on Nickel ($\text{Ni-Al}_2\text{O}_3$

, NiCr-Al₂O₃, NiCrY-Al₂O₃, NiCrAlTi - Al₂O₃, NiCrAl-Al₂O₃-TiC, NiCrAl-ZrO₂, and chromium (Cr-Al₂O₃, Cr-MgO-Al₂O₃) bases were presented in earlier publications [15].

In this system, the volume of porous can be regulated from 0% to 50%, and pores sizes in a range of 0 μm - 8 μm. (Figure 1). The exact value depends on choices of metallic matrix and dispersed particles, deposition temperature, the concentration of input high-temperature phase, and time and temperature of following heat processing. An example can be Ni-20%-Cr-Al₂O₃, where open porosity was created by substrate temperature 700 °C – 900 °C and vacuum heat treatment after deposition at 1200 °C. The increase of deposition temperature and heat treatment

time in the vacuum after condensation indicates open porosity volume in all systems.

The metallographic study proved that the open porosity prevails at the higher substrate temperatures in a relative balance of open-closed porosity. (Figure 2,b).

The processes of pores coalescence intensify with higher annealing temperatures. A considerable part of porosity turns to the open porosity condensate with 20%-30% Al₂O₃ after 100 hours of annealing in a vacuum. But mainly, the coalescence processes finish after 25 hours of annealing in a vacuum at a temperature of 1200 °C. Structural observations in condensate Ni – 20%Cr- 30% Al₂O₃ experimentally prove it (Figure 3). It is shown in Figure 3. that the

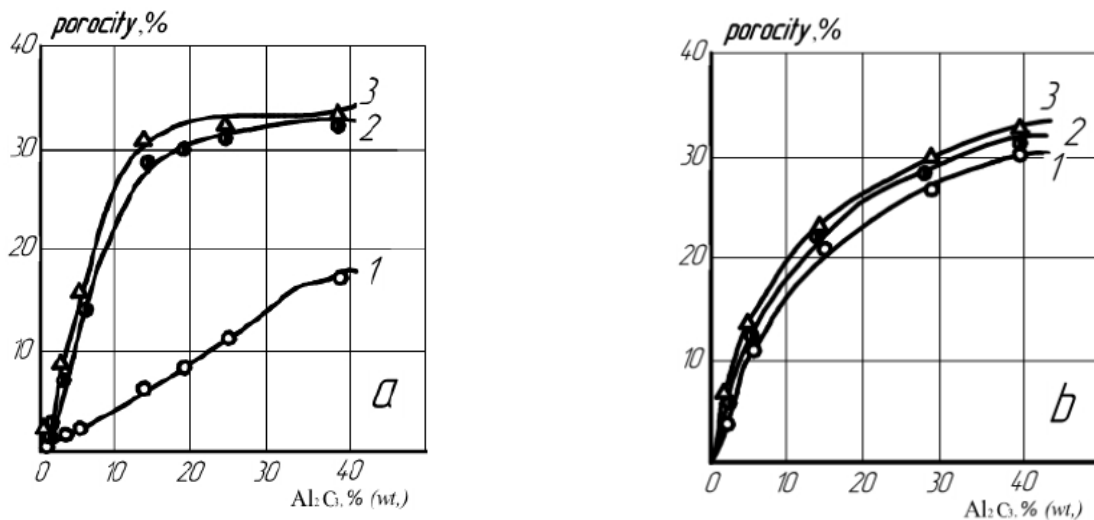


Figure 2: Open porosity dependence on Al₂O₃ concentration and time of annealing in a vacuum of Ni-Al₂O₃ condensate and substrate temperature **a**-700 °C and **b**-900 °C; 1 – initial, 2-after annealing at 1200 °C ag 25 hours; 3- after annealing at 1200 °C and time 100 hours.

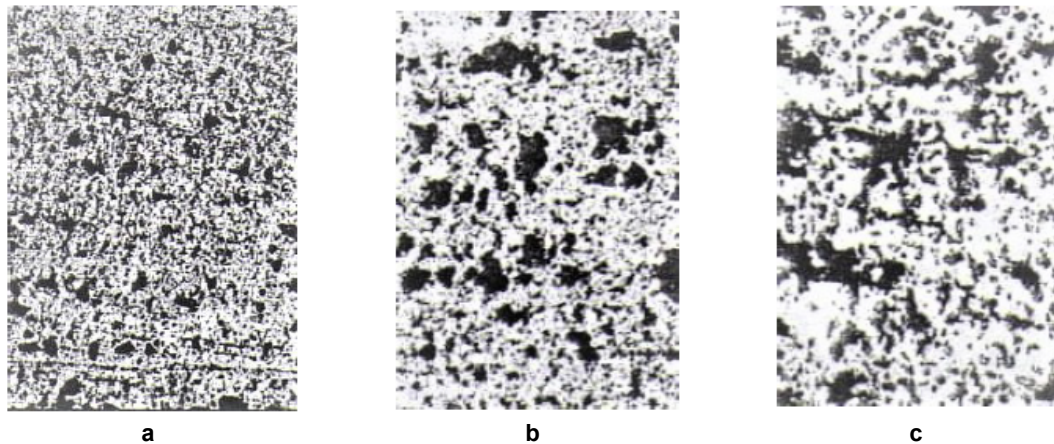


Figure 3: Microstructure of porous condensate Ni-Cr – 20% Al₂O₃ obtained substrate temperature 900 °C and annealed at 1200 °C at time **a**-5 hours, **b**- 25 hours, **c**-100 hours.

coalescence process is more active at the first 25 hours and then slows down considerably.

The Figure 4 shows average pore sizes in condensate NiCr— Al_2O_3 depends on substrate temperature $700\text{ }^\circ\text{C}$ – $900\text{ }^\circ\text{C}$. The average sizes of pores depend on substrate temperature and time of vacuum annealing of condensates. But unfortunately, this approach to get porous condensates has a lot of gaps.

More than 10 % weight of high-temperature particles' concentration in porous composite leads to lacking elasticity and insufficient strength at the high-temperature particle concentration.

The most interesting is getting porous materials from the vapor phase, where dispersed particles remove from the metallic phase after annealing or dissolution. The most suitable for that are fluoride and chloride salts. The first experimental results were received in work [16], where titanium sheets were manufactured with a diameter of 800 mm and thickness of 1 mm - 2 mm with input NaCl phase at substrate temperature $600\text{ }^\circ\text{C}$.

In initial condensates Figure 3, the average size of porous varies in the range from $0.2\text{ }\mu\text{m}$ to $0.5\text{ }\mu\text{m}$, but after vacuum annealing, this variation increases to $5\text{ }\mu\text{m}$ – $6\text{ }\mu\text{m}$ by the porous coalescence. It is shown in Figure 3. (Microstructures with this increase are attached).

Four types of condensates with different NaCl percentages compared to pure titanium condensate are presented in Table 1. Experimentally proved that more than 45% (weight) of the salts in the condensate is not desirable as it considerably damages structural architecture. Such condensates are weak conglomerates with close to zero strength and elasticity.

Samples were made of condensate for the strength and elasticity investigation at the initial state, after holding in distiller water at $20\text{ }^\circ\text{C}$ for four hours, after vacuum annealing at $850\text{ }^\circ\text{C}$ and different heating speed from $600\text{ }^\circ\text{C}$ to $850\text{ }^\circ\text{C}$. The allotropic transformation explains the choice of the temperature $850\text{ }^\circ\text{C}$ from low-temperature α -titanium to high-temperature β -titanium [17]. Phase transformation has a strong influence on the physical-mechanical properties of the material. Keeping β modification in pure titanium at room temperature is very difficult to even through reverse quenching. Second, the saturated pressure of NaCl vapors reaches 1 Pa at $850\text{ }^\circ\text{C}$. NaCl removal speed is very high (eruption removing), leading to titanium matrix bubbling. By regulating NaCl, removing speed, it is possible to control pores sizes in the condensate.

Table 1 shown the physic-mechanical properties of the condensate after processing in water and after vacuum annealing. The mechanical properties of condensate depend on salt concentration-they drop when NaCl concentration rises. Mechanical properties of pure titanium condensate close to mechanical

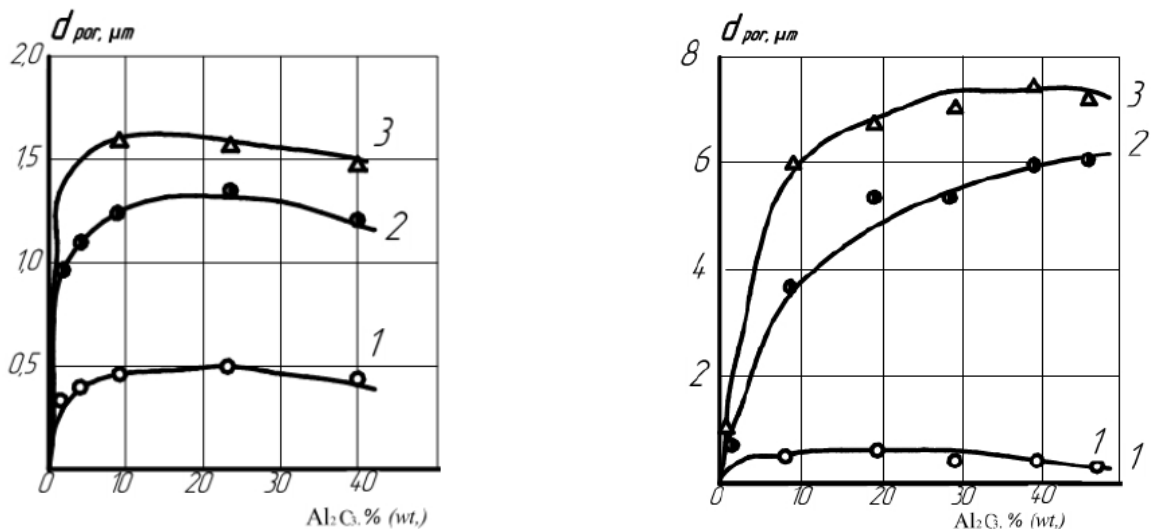


Figure 4: Dependence of average pore sizes from Al_2O_3 concentration and annealing time in condensate NiCr- Al_2O_3 got at substrates temperatures a- $700\text{ }^\circ\text{C}$, b- $900\text{ }^\circ\text{C}$. 1- initial, 2 – after annealing at $1200\text{ }^\circ\text{C}$, 3-after annealing $1200\text{ }^\circ\text{C}$ at 100 hours.

Table 1: Physical-Mechanical Properties of Porous Condensate on the Titanium Base

1	Condensate State	The Density of the Material, g/cm ³		Mechanical Properties			The Volume of Porosity, %		Average Pore Size [μm]
		Theoretical	Experimental	$\Sigma_{0.2}$ [MPa]	Σ_b [MPa]	δ %	All Pores	Open	
1	2	3	4	5	6	7	8	9	10
1	Condensate of pure titanium (deposition temperature 600 °C +_ 10 °C)	4.5	4.49	430	540	22			
2	Condensate N1 (Ti-96,3%(w) - NaCl-3.7%(w) after deposition	4.41	4.19	430	540	22	5.7		
3	Condensate N2 (Ti-88,2%(w) NaCl-11.8%(w) after deposition	4.22	3.87	190	210	1.5	8.3		
4	Condensate N3 (Ti-80,8%(w) NaCl-19.2%(w) after deposition	3.57	2.82	148	150	0.5	21.1	10.8	0.2
5	Condensate N1 after submerging in freshwater, room temperature, time 4 hours	4.41	4.07	270	30	2.46	7.8	2.8	0.25 – 0.30
6	Condensate N2 after submerging in freshwater, room temperature, time 4 hours	4.22	3.62	190	210	1.5	14.3	5.5	0.26-0.32
7	Condensate N3 after submerging in freshwater, room temperature, time 4 hours	3.57	2.43	148	150	0.5	32	26	0.3-0.4
8	Condensate N1 after vacuum [2×10^{-2} Pa] annealing. Speed of temperature rising from 600 °C to 850 °C is 10 grad/s	4.41	3.90	810	920	6.7	11.6	4.2	0.3-0.35
1	2	3	4	5	6	7	8	9	10
9	Condensate N1 after vacuum [2×10^{-2} Pa] annealing. Speed of temperature rising from 600 °C to 850 °C is 20 grad/s	4.41	3.89	760	870	5.3	11.8	5.3	0.35-0.40
10	Condensate N2 after vacuum [2×10^{-2} Pa] annealing. Speed of temperature rising from 600 °C to 850 °C is 10 grad/s	4.22	3.41	740	840	4.8	19.2	9.6	0.40-0.50
11	Condensate N2 after vacuum [2×10^{-2} Pa] annealing. Speed of temperature rising from 600 °C to 850 °C is 20 grad/s	4.22	3.40	720	830	4.5	19.5	12.7	0.45-0.70
12	Condensate N3 after vacuum [2×10^{-2} Pa] annealing. Speed of temperature rising from 600 °C to 850 °C is 10 grad/s	3.57	2.38	650	690	2.8	33.4	32.8	0.60-0.70
13	Condensate N3 after vacuum [2×10^{-2} Pa] annealing. Speed of temperature rising from 600 °C to 850 °C is 20 grad/s	3.57	2.38	630	650	2.4	33.4	33.0	0.45-0.70

properties of titanium obtained by traditional metallurgical methods.

Further holding of the samples in distilled water goes to strength degradation due to salt dissolving. Moreover, it was shown by chemical analysis that not complete salt dissolution takes place in the samples. The effectiveness of salt removal rises at higher salt concentrations in the condensate, not whole salt removal explained by salt location in closed pores of condensate. An attempt at water boiling doesn't influence the salt dissolution.

Remarkable results were obtained after vacuum annealing of condensate. Vacuum annealing dramatically expands the strength. The strength limit threshold σ_b reaches 650 MPa – 920 MPa, and the deformation limit $\sigma_{0.2}$ reaches 630 MPa – 810 MPa. And relative elongation achieves 2.4 % - 6.7 %. It is necessary to mention that the obtained porous condensate's mechanical properties overcame lithium properties, and porous titanium almost twice overcame the strength of complex titanium alloys [17]. The strength increase mechanism doesn't clear today. But one of the possible explanations that the presence of

NaCl diffusion process in the titanium matrix sharply activates.

The increase of contact surface at the sintering process is explained by diffusion movement of vacancies in contact zones Ti-NaCl, from higher concentration places to lower concentration places. The standard deviation of obtained results was around $\pm 5\%$

The interaction of titanium with NaCl can be explained as an additional strength boost. But XRD analysis of annealed condensate through the energetic dispersion method shows the absence of sodium and chloride traces.

CONCLUSION

The presented results prove an ability to get micro-porous condensate from the vapor phase of metallic, metal-ceramic with regulated mechanical properties and a porosity volume.

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