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RESEARCHES OF DIFFUSION PROCESSES IN POWDER MATERIALS AND THEIR ROLE IN STRUCTURE FORMATION

The equation of Fick's second law describing the diffusion in a porous powder body is solved in the framework of the Green's function method. The proposed mathematical model allowed the influence of the temperature, deformation rate, and porosity of a material on the diffusion coefficient to be analyzed. The microstructure of copper-titanium specimens after the sintering and a plastic deformation is studied. The increase in the temperature, as well as in the rate and the degree of a deformation, is found to promote the alloy homogenization.

Keywords: diffusion, plastic deformation, powder body, powder copper-titanium material.

1. Introduction

Researches of diffusion processes in powder systems at the sintering, as well as factors affecting them, are of large interest [1–3]. Literature data testify that the intensity of diffusion processes in powder materials is much higher than in casted ones. The authors of cited works explain such a behavior by a high distortion of crystal lattices in powders and by the defects arising in the course of the further pressing. However, the physical nature of the diffusion flow growth in materials with macroscopic defects (pores, grain boundaries, and others) has not been elucidated completely till now.

The issue concerning the influence of the porosity on diffusion processes is ambiguous. On the one hand, the presence of pores in a powder material accelerates the effective diffusion mass transfer [2] owing to the raised concentration of defects in the layer around a pore and the contribution made by the surface diffusion. On the other hand, the pores decelerate it, because the mass transfer through the gas phase is less than the flow produced by the bulk diffusion through the same cross-section.

A challenging issue is the study of the processes that intensify diffusion processes in powder materials, e.g., in Ni–Mo [4] and Cu–Ti [5] systems, which is associated with the difficulties in the preparation of homogeneous alloys of those metals. It is known that the diffusion can be activated by radiation, plastic deformation, and so forth, i.e. by the processes increasing the number of defects in the crystal structure. The researches made in the last years [4] showed that the issue of diffusion process intensification in powder materials by means of a plastic deformation is challenging, because the factors responsible for the acceleration of the homogenization under the action of a plastic deformation have not been elucidated in detail.

2. Model

The one-dimensional diffusion is analyzed using Fick's second equation [6]

$$\frac{\partial C}{\partial \tau} = -D\left(\frac{\partial^2 C}{\partial x^2}\right), \tag{1}$$

where C is the concentration of a substance, τ the time, x the coordinate reckoned along the diffusion flow direction, and D the diffusion coefficient. This is a partial differential equation of the second order in the coordinate. To solve it, let us use the Green's function method [7]. It consists in finding Green's function and checking the eligibility of its differentiation the required number of times under the integral sign.

According to work [8], Green's function for the diffusion equation looks like

$$G(x-\xi,\tau) = \frac{1}{\sqrt{4D\pi\tau}}\exp\left(-\frac{(x-\xi)^2}{4D\tau}\right). \tag{2}$$

It is a solution of Eq. (1). It depends on the coordinate x, the time τ, and an infinitesimally small quantity ξ that characterizes the accuracy of calculations. According to the definition of Green's function [8], the solution of the diffusion equation (1) under any initial condition looks like

$$C(x,\tau)=\int\limits_{-\infty}^{+\infty} G(x,\xi,\tau)\varphi(\xi)d\xi, \tag{3}$$

where $\varphi\,(\xi)$ is the function responsible for the accuracy of calculations. Equation (3) describes a change of the diffusing substance concentration C along the coordinate x and in the time τ in the general form. The representation of a solution of the differential equation (1) in the form (3) allows us to obtain an equation that describes the diffusion process under the corresponding initial and boundary conditions.

The probabilistic content of the diffusion coefficient brings us to the relation [9]

$$2D\tau=u^2(\tau), \tag{4}$$

i.e. the diffusion radius $u(\tau)$ is the root-mean-square coordinate deviation. Hence, Green's function in accordance with Eq. (4) can be presented in the form [8]

$$G(x-\xi,\tau)=\frac{1}{u(\tau)\sqrt{2\pi}}\exp\left(-\frac{(x-\xi)^2}{2u^2(\tau)}\right). \tag{5}$$

To solve the diffusion equation (1), we adopt the following initial and boundary conditions for the concentration [2, 9]:

$$\begin{aligned} &C\,(x,\;0)=C_0=\text{const}, && -\infty\leqslant x\leqslant 0,\\ &C\,(x,\;0)=0, && 0<x\leqslant\infty. \end{aligned} \tag{6}$$

Substituting Green's function (5) into Eq. (3), we obtain

$$C(x,\tau)=\int\limits_{-\infty}^{+\infty}\frac{1}{u(\tau)\sqrt{2\pi}}\exp\left(-\frac{(x-\xi)^2}{2u^2(\tau)}\right)\varphi(\xi)d\xi. \tag{7}$$

Now, substituting expression (7) to the left- and right-hand sides of Eq. (1) and taking $1/(u(\tau)\sqrt{2\pi})$ outside the integral sign, we have

$$\begin{aligned} &\frac{\partial C}{\partial\tau}=\frac{u'(\tau)}{u^4(\tau)\sqrt{2\pi}}\int\limits_{-\infty}^{+\infty}\varphi(\xi)\exp\left(-\frac{(x-\xi)^2}{2u^2(\tau)}\right)\times\\ &\times[(x-\xi)^2-u^2(\tau)]d\xi,\\ &\frac{\partial^2 C}{\partial^2\tau}=\frac{1}{u^5(\tau)\sqrt{2\pi}}\int\limits_{-\infty}^{+\infty}\varphi(\xi)\exp\left(-\frac{(x-\xi)^2}{2u^2(\tau)}\right)\times\\ &\times[(x-\xi)^2-u^2(\tau)]d\xi. \end{aligned} \tag{8}$$

Substituting formulas (8) into (1) and carrying out the corresponding transformations, we obtain

$$u'(\tau)=\frac{D}{u(\tau)}. \tag{9}$$

Then Eq. (7) can be transformed to the form

$$C(x,\tau)=\frac{1}{2\sqrt{\pi D\tau}}\int\limits_{-\infty}^{+\infty}\varphi(\xi)\exp\left(-\frac{(x-\xi)^2}{4D\tau}\right)d\xi. \tag{10}$$

With regard for the conditions [8]

$$\begin{aligned} &\varphi(\xi)=C_0,\ \xi=0,\\ &\varphi(\xi)=0,\ \xi>0, \end{aligned} \tag{11}$$

Eq. (10) takes the form

$$C(x,\tau)=\frac{C_0}{2\sqrt{\pi D\tau}}\int\limits_{-\infty}^{0}\exp\left(-\frac{(x-\xi)^2}{4D\tau}\right)d\xi. \tag{12}$$

Let us use the notation $y=(x-\xi)/(2\sqrt{D\tau})$, provided that $-\infty\leq y\leq -x/(2\sqrt{D\tau})$ [7]. Then Eq. (12) can be rewritten as follows:

$$\begin{aligned} &C(x,\tau)=\frac{C_0}{\sqrt{\pi}}\Bigg[\int\limits_{-\infty}^{0}\exp(-y^2)dy-\\ &-\int\limits_{0}^{x/(2\sqrt{D\tau})}\exp(-y^2)dy\Bigg]. \end{aligned} \tag{13}$$

The second integral in the brackets is the tabulated Gauss error function. Let us designate $z=x/(2\sqrt{D\tau}$; then the error integral looks like

$$\operatorname{erf}(z)=\frac{2}{\sqrt{\pi}}\int\limits_{0}^{z}\exp(-y^2)dy. \tag{14}$$

Since

$$\int_{0}^{+\infty} \exp(-y^2)dy = \frac{\sqrt{\pi}}{2}, \tag{15}$$

the analytical solution of Eq. (1) obtained with the use of the Green's function method is

$$C(x,\tau) = \frac{C_0}{2}\left[1 - \operatorname{erf}\left(\frac{x}{\sqrt{4D\tau}}\right)\right]. \tag{16}$$

This expression describes the diffusion in a porous powder body and satisfies the boundary conditions (6). It connects the concentration of a diffusing substance with the time of the diffusion process and the coordinate in the diffusion region. Equation (16) makes it possible to determine the concentrations of components in the diffusion zone and compare them with experimental data.

3. Application of the Model

The validity of expression (16) for powder systems was verified by comparing the calculated and experimental data on the distribution of the diffusing component concentration in the diffusion zone in the porous powder copper–titanium system. Experimental researches were carried out, by using specimens fabricated from a mechanical mixture of PMS-1 copper powder and VT1-0 titanium powder. The mass fraction of titanium was 0.5%. The specimen porosity was 5 and 10%. After the bilateral pressing, the specimens were sintered in the step-like regime for 3 h at a temperature of 900–920 °C in the generator gas environment. Then they were uniaxially compressed on a testing machine ZD-4 at temperatures of 100, 400, and 600 °C at deformation rates of 0.01 and 0.001 s^{-1} to a maximum deformation of 50%.

The chemical composition and the component concentration distribution in the diffusion zone formed at the sintering and in the course of a deformation were determined by analyzing the specimen microstructure on a raster electron microscope REMMA-102 equipped with an x-ray microanalyzer. To avoid the influence of the size effect, the diffusion zone near titanium particles with an average dimension of 20–22 μm was considered. As an inhomogeneity degree in the distribution of elements, we used the concentration variation coefficient [2]

$$V = \sqrt{\sigma^2(C)}/\bar{C}, \tag{17}$$

where $\sigma^2(C)$ is the concentration dispersion, and $\bar{C}$ the average concentration. The measurement error was equal to 20% at a significance level of 0.1.

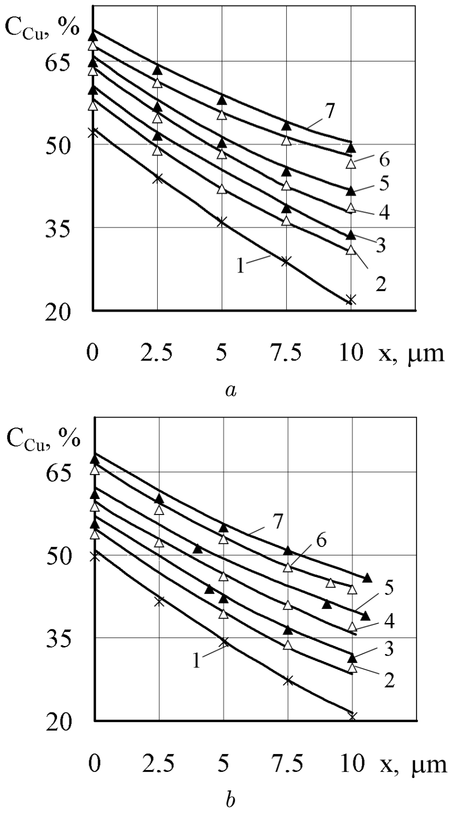
According to the experimental data on the distribution of component concentrations and Eq. (16) that connects the substance concentration with the known value of function erf (z), the diffusion coefficient D was determined. The coordinate value corresponding to the component concentration equal to $C_0/2$ was taken as a reference mark.

In Table, the calculated diffusion coefficients for copper and titanium are quoted. The coefficient D_{Cu} was 2 to 3 times larger, which testifies to the prevailing diffusion of copper into titanium. After the sintering, the diffusion coefficients became minimum, but increased a little after a deformation. As the final porosity of the sintered specimen increased, the diffusion coefficient for copper decreased and amounted to $D_{\mathrm{Cu}} = 6.5\times10^{-11}$ and 5.4×10^{-11} cm^2/s at porosities of 5 and 10%, respectively (Table).

The temperature, at which the deformation occurs, considerably affects the magnitude of diffusion coefficients. At the deformation temperature corresponding to the recovery one (100 °C), the beginning of the diffusion interaction was observed. As a result, the diffusion coefficient D_{Cu} became 1.6–2 and D_{Ti} 1.3–1.8 times as large in comparison with the corresponding values after the sintering (Table). This phenomenon results from the processes of defect reconstruction, migration, and redistribu-

Diffusion coefficients of copper in titanium, D_{Cu}, and titanium in copper, D_{Ti} under various deformation conditions

Deposition temperature, °C	$D_{\mathrm{Cu}}\times10^{-11}$, cm^2/s		$D_{\mathrm{Ti}}\times10^{-11}$, cm^2/s	
	$\dot{\varepsilon} = 0.001$ s^{-1}	0.01 s^{-1}	0.001 s^{-1}	0.01 s^{-1}
	Initial porosity of 5%			
After sintering	6.5		3.44	
100	11.4	13.2	5.25	6.21
400	21.8	29.3	7.82	8.03
600	28.6	33.1	13.3	15.3
	Initial porosity of 10%			
After sintering	5.4		2.11	
100	10.2	8.6	4.026	5.7
400	19.3	20.9	6.28	7.64
600	25.1	30.4	10.82	12.01



a

b

Fig. 1. Copper distributions in titanium particles with $\theta_0 = 5$ (*a*) and 10% (*b*). Curves exhibit theoretical data: after sintering (*1*), at 100 (*2* and *3*), 400 (*4* and *5*), and 600 °C (*6* and *7*). Symbols correspond to experimental data with the deformation rates $\dot{\varepsilon} = 0.001$ (hollow triangles) and 0.01 s^{-1} (solid triangles)

tion in the crystal structure. Under such conditions, there emerge extra vacancies that take part in the formation of the diffusion zone and activate the diffusion.

The temperature, at which the intense diffusion starts, corresponds to the temperature, at which the recrystallization begins. This correspondence of the temperatures testifies to an interrelation between the mechanisms of processes that are running simultaneously in the solid phase of a powder material [10].

The diffusion acceleration at 600 °C results in the generation of additional free vacancies owing to the increase in the number of large-angle boundaries, along which the diffusion rate is maximum, and their migration [6]. As the temperature and the deformation rate increase, the diffusion process is intensified (Table).

The growth in the powder porosity results in a reduction of the intensity of diffusion processes. This fact can be associated with a change of the ratio between the surface and bulk diffusion processes. It is evident that the surface diffusion, which takes place over the surface of particles and pores, prevails at higher porosities. At a porosity of 5%, the diffusion is of the bulk character, because the area of contacts between particles increases, and the pore dimensions decrease. For instance, if a deformation occurs at a temperature of 600 °C and at the rate $\dot{\varepsilon} = 0.001\ \mathrm{s}^{-1}$, the diffusion coefficient D_{Cu} equals 28.6×10^{-11} and $25.1 \times 10^{-11}\ \mathrm{cm}^2/\mathrm{s}$ at porosities of 5 and 10%, respectively.

The results of a comparative analysis of the theoretical and experimental data on the distribution of the concentrations of diffusing components in the diffusion zone are shown in Fig. 1. The concentration was calculated by Eq. (16), by substituting the diffusion coefficients and the time with regard for the durations of the sintering and a deformation. The copper concentration D_{Cu}, as well as the diffusion coefficient in Eq. (16), is determined by the temperature and strain-rate conditions of a deformation, as well as by the initial porosity of specimens. As the temperature and the strain rate grow, the component concentration in the diffusion zone increases, but if the initial porosity grows, it decreases.

Hence, the proposed mathematical model describes rather accurately the diffusion processes in a porous powder body and involves the influence of deformation parameters on the diffusion coefficient and the concentration of diffusing components. The deviation of theoretical values from experimental ones did not exceed 5–7%.

4. Microstructure Analysis

The process of structure formation in powder materials depends on many factors affecting the diffusion homogenization. Those factors include the initial porosity of a blank, the granulometric composition of components in a blend, the aggregate state of components in the course of sintering, the sintering atmosphere purity (the presence of water vapor and oxygen in it), the sintering temperature and duration, the purity degree of used components in a powder blend, the sequence of technological operations, the temperature, the rate of blank shape change, *etc.* The diffusion mobility of elements depends to a great extent on the mechanism of motion of atoms in the crystal lattice of metals. For instance, at the sintering of copper-titanium materials, substitutional solid solutions are formed, in which the vacancy mechanism of diffusion dominates [11].

The porous blanks were sintered at 900–920 °C. According to the state diagram of the Cu-Ti system [12], a liquid phase emerges at the sintering. The liquid phase, which accelerates the alloy homogenization, is formed only at the beginning of the sintering period; then, owing to the enrichment of copper with titanium and the transition into the solid phase, it disappears. Similar examples of the sintering process, when the transition from the liquid-phase sintering to the solid-phase one takes place, were considered in works [6, 13].

The kinetics of processes running at the sintering of powder blanks depends considerably on the initial porosity, amount of the liquid phase, linear dimensions of powder grains, degree of wetting of the solid phase by the liquid one, and the mutual solubility of phases [13]. For liquid layers to be formed in a blank, it is necessary that the separation of two solid particles, which were in the direct contact, by a liquid be energetically profitable.

As was marked by Geguzin [6], if the sintering of a blank takes place with participation of the liquid phase, there emerges a capillary pressure in the mixture Cu-Ti in the contact region of solid particles separated by a liquid layer. Our researches showed that, as a result of the surface and bulk diffusions, the formation of aa diffusion zone was observed, in which the concentration of components was different depending on the titanium content and the porosity of a specimen. At porosities of 5 and 10%, the copper concentration on the boundary of a titanium particle was maximum, equal to 52–58 and 49.7–53.98%, respectively, and decreased toward the particle center. At a higher initial porosity, the amount of copper was less. The porosity evidently interfers with the transfer of diffusing atoms [2].

The research of etched microsections carried out on an electron microscope showed that, after the sintering, no appreciable diffusion zone was formed (Fig. 2). The microstructure revealed separate copper and titanium sections, although the x-ray microanalyzer detected a change in the concentrations of components (Fig. 1). It is evident that the sintering dration (3 h)

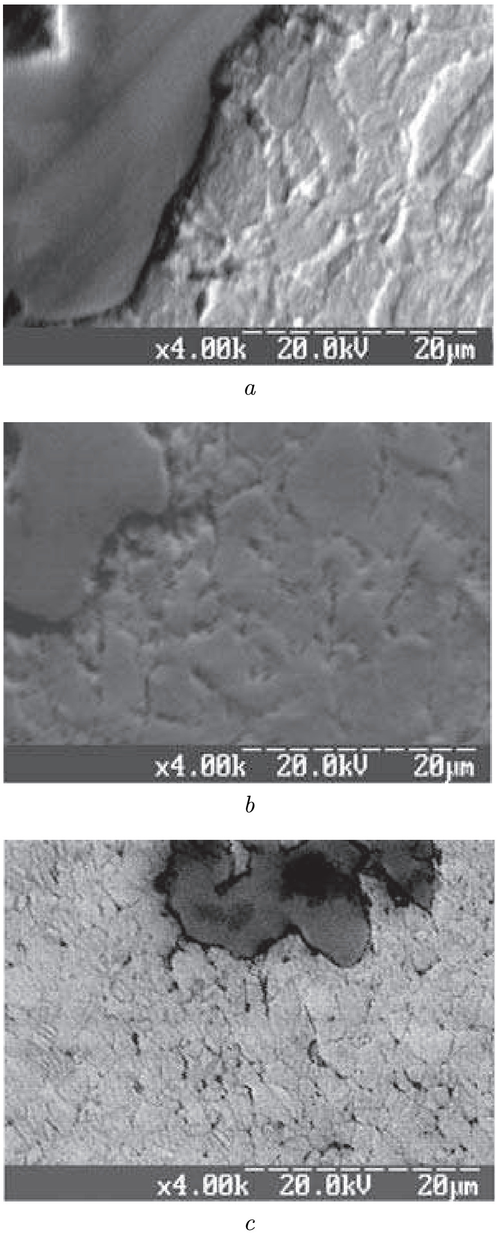


Fig. 2. Microstructures of the intergrain contact zone after the sintering (a) and the deposition at $\varepsilon_z = 0.69$, $\dot{\varepsilon} = 0.001$ s^{-1}, and temperatures of 100 (b) and 600 °C (c); $\theta_0 = 10\%$

was not enough for the complete homogenization in the alloy.

A plastic deformation promoted the activation of diffusion processes. The concentration of components in the diffusion zone increases with the temperature and the the degree and the rate of deformation (Fig. 1). In addition, the elevation of the temperature of a deformation manifested itself in the structural dispersing (Fig. 2). As the deformation temperature increases, the reduction of the copper grain size is observed: in the low-temperature interval, as a result of the deformation; and in the high-temperature one, owing to the grain nucleation in the course of dynamic recrystallization [10]. Specimens with a porosity of 10% had grains of about 21–22 μm after the sintering, 16.5 μm at 100 °C, and 5.4 μm at 600 °C (Fig. 2). Grain boundaries present the main way to accelerate the diffusion. Therefore, it is evident that a reduction in the grain size in the course of deformation favors the growth of grain boundary areas and the activation of the diffusion [14].

At dynamic recovery temperatures (100 °C), a considerable number of extra vacancies emerge owing to the processes of dislocation motion and annihilation. An increase in the deformation rate intensifies this process. The recovery kinetics is governed, to a great extent, by the mobility of atoms in the fcc lattice and, therefore, by diffusion mechanisms. The increase in the deformation temperature to 400–600 °C and the deformation rate to 0.01 s^{-1} gave rise to the appearance of recrystallized grains in the solid phase of a porous body owing to the motion or migration of their boundaries driven by diffusion mechanisms. A high migration rate between the grains is associated with a higher concentration of vacancies at the boundaries of recrystallization nuclei, created when the moving boundary absorbs dislocations and gives rise to the acceleration of the boundary diffusion [15]. The rate of vacancy migration and the speed of grain boundary motion depend on the activation energy determined by the temperature and the strain rate.

5. Conclusions

In this work, an equation describing the diffusion processes in a porous powder body is derived. On the basis of experimental data concerning the distribution of the concentrations of components in the diffusion zone in the porous powder copper-titanium system, the diffusion coefficients and the porosity are calculated (the diffusion coefficient of copper in titanium is found to equal $D_{\mathrm{Cu}} = 6.5 \times 10^{-11}$ cm^2/s after the sintering and to $D_{\mathrm{Cu}} = 28.6 \times 10^{-11}$ cm^2/s after a deformation at a rate of 0.001 s^{-1} and a temperature of 600 °C; the initial porosity is evaluated to equal 5%). It is shown that the diffusion coefficient increases at the dynamic recovery temperature (100 °C) owing to the appearance of additional vacancies, and at the temperature of dynamic recrystallization (600 °C) owing to the motion of vacancies and dislocations, as well as the dispersion of a structure. The increase of the deformation rate accelerates the diffusion process.

We have confirmed that the concentrations of diffusing elements in the diffusion zone depend on the initial porosity of a material: the porosity growth gives rise to a reduction of the concentration of components. The microstructure modifications in the powder copper-titanium materials after the sintering and after a deformation are analyzed. It is shown that no complete homogenization takes place in the alloy after the sintering. The reduction in the grain size as a result of the dynamic recrystallization is found to favor the activation of diffusion processes owing to the increase of grain boundary areas.

1. V.V. Skorokhod and S.V. Solonin, *Physico-Metallurgical Principles of Powder Sintering* (Metallurgiya, Moscow, 1984) (in Russian).
2. V.N. Antsiferov, E.Yu. Eremina, S.N. Peshcherenko, A.I. Rabinovich, and V.D. Khramtsov, Poroshk. Metallurg. **4**, 42 (1987).
3. Ya.E. Geguzin, V.V. Bogdanov, and L.N. Paritskaya, Poroshk. Metallurg. **9**, 27 (1989).
4. I.I. Ivanova, A.N. Demidik, and A.A. Sotnik, Poroshk. Metallurg. **3/4**, 58 (2001).
5. O.P. Gaponova and L.A. Ryabycheva, Visn. Skhidnoukr. Nats. Univ. **6**, 116 (2008).
6. Ya.E. Geguzin, *Physics of Sintering* (Nauka, Moscow, 1984) (in Russian).
7. M. Sucheska, A. Borisovich, and W. Serbinski, Adv. Mater. Sci. **5**, 75 (2005).
8. V.Ya. Arsenin, *Methods of Mathematical Physics and Special Functions* (Nauka, Moscow, 1984) (in Russian).
9. Ya.B. Zel'dovich and A.D. Myshkis, *Elements of Mathematical Physics* (Nauka, Moscow, 1973) (in Russian).
10. L. Ryabicheva and O. Gaponova, in *Proceedings of the Intern. Conference on Deformation and Fracture in Struc-*

tural PM Materials DF PM 2008 (Stara Lesna, High Tatras, 2008), p. 202.

11. I.B. Borovski, K.P. Gurov, I.D. Marchukova, and Y.E. Ugaste, *Interdiffusion in Alloys* (Amerind, New Delhi, 1986).
12. *Phase Diagrams of Binary Metallic Systems*, edited by N.P. Lyakishev (Mashinostroenie, Moscow, 1999 (in Russian), Vol. 2.
13. H.F. Fischmeister and L.E. Larsson, Powder Metal **17**, 227 (1974).
14. I. Kaur and W. Gust, *Fundamentals of Grain and Interphase Boundary Diffusion* (Ziegler Press, Stuttgart, 1989).
15. S.S. Gorelik, *Recrystallization in Metals and Alloys* (Mir, Moscow, 1981).

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ДОСЛІДЖЕННЯ ДИФУЗІЙНИХ ПРОЦЕСІВ В ПОРОШКОВИХ МАТЕРІАЛАХ І ЇХ РОЛЬ У ФОРМУВАННІ СТРУКТУРИ

Резюме

У роботі отримано розв'язок рівняння другого закону Фіка методом функцій Гріна, який застосований для опису процесу дифузії в порошковому пористому тілі. Представлена математична модель дозволила виконати аналіз впливу температурно-швидкісних умов деформації та пористості матеріалу на коефіцієнт дифузії. Досліджено мікроструктуру мідно-титанових зразків після спікання та пластичної деформації. Встановлено, що підвищення температури, швидкості та ступеня деформації сприяє гомогенізації сплаву.