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CONTENTS

TECHNOLOGIES

METHOD OF PERMEABLE ELEMENTS FOR SIMULATION OF POWDER METALS FORMING PROCESSES Dr.Sc. Bagliuk G.A.	376
EXOTIC BEHAVIOR OF REACTIVE-WETTING OF METAL ON METAL-ON-GLASS IN ROOM TEMPERATURE Haim Taitelbaum	380
EXPERIMENTALLY VERIFIED MATHEMATICAL MODEL OF THE POLYMER PLASTICIZATION PROCESS IN THE INJECTION MOLDING M.Sc. Iwko J. PhD., M.Sc. Wróblewski R. PhD.	382
NOVEL HYBRID POLYETHERSULFONE MEMBRANES MODIFIED WITH POLYVINYLPIRROLIDONE AND Ag/TITANATE NANOTUBES M. Sc. Sienkiewicz P., Dr. Darowna D., Prof. dr hab. eng. Mozia S.	388
THE STRUCTURE FORMATION FEATURES OF THE ALLOY Zr₄₁Ti₁₃Cu₁₂Ni₁₀Be_{22,5} DURING THE CASTING IN THE METAL MOLD AND THE FOLLOWING HEATING AMORPHOUS INGOTS Associate professor Kosynska O.L., student Hurin I.V.	392
SYNTHESIS OF THE MAGNETIC ADSORBENT BASED OF GRAPHENE OXIDE AND ZNO NANOPARTICLES FOR ENVIRONMENTAL APPLICATIONS Assoc. Prof. Abbasi S. PhD., Dr. Ahmadpoor F. PhD., M.Sc. Imani M.	395
FORMATION OF PRINCIPLES OF INVESTMENT STRATEGY OF INDUSTRIAL ENTERPRISES Ph.D., Lepekhyun O., Ph.D., Chernikova N, Ph.D., Azhazha M., Ph.D., Dashko I.	397
RESEARCH AND JUSTIFICATION OF THE POSSIBILITIES, RELEVANCE AND CORRECTNESS OF THE MONITORING AND CORRECTION OF THE STRATEGY, DIAGNOSIS OF THE PROSPECTS OF ITS FURTHER USE ON INDUSTRIAL ENTERPRISES Prof., D.Sc., Cherep A., Prof., D.Sc., Kuznetsov Yu.Prof., Ph.D., Andriukaitienė R., Ph.D., Faizullina S.	400

MATERIALS

TWO-STAGE SINTERING INVESTIGATION OF Ti-Zr-Nb BIOMEDICAL ALLOYS D. Oryshych, P. Markovsky, D. Savvakina, O. Stasiuk, V. Dekhtyarenko, V. Nevmerzhytskyi	404
THE MAGNETIC PROPERTIES OF NANO-MODIFIED COMPOSITE MATERIALS FOR MICROELECTROMECHANICAL SYSTEMS Dr., prof. Govor G.A., Dr.Vetcher A.K., Patsino E.V., Dr. Demidenko O.F., Dr. Timoshkov Yu.V., Dr.Kurmashev V.I., Grapov D.V.	408
THE CONNECTION BETWEEN COEFFICIENT CLUSTERISATION WITH TEMPERATURE Mast. of Phys. Liaushuk I., Assoc. Prof. Dr. Eng.Auchynnikau Y., Assoc. Prof. cand. Eng. Nikitin A., Prof. Dr. Phys. and Math. Liopo V.	410
FORMATION OF ZrB₂-AlN POWDER MIXTURE BY SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS H. Erdem Camurlu	414

METHOD OF PERMEABLE ELEMENTS FOR SIMULATION OF POWDER METALS FORMING PROCESSES

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Abstract. For simulation of processes of compaction or forging of products from powder materials, a method of permeable elements is proposed. The essence of the method is to use elements whose shape is regulated in advance, and, unlike the finite element method, where the elements coincide with the material volumes and their masses are unchanged, here the masses elements are variable, and material can flow between adjacent cells. Examples of using the method for modeling the processes of forging of porous preforms in closed and open dies, as well as in a closed die with a compensation cavity, are presented.

Keywords: powder materials, simulation, numerical methods, forging, porous body, plasticity criterion.

1. Introduction

Among the numerical methods for solving problems associated with finding the stress and strain fields that arise both in compact and in porous materials, the finite element method (FEM) has become widespread. Its advantages include convenience in terms of algorithmization and programming, as well as the relatively high accuracy of the resulting solutions [1-4].

However, in the study of technological processes during which large deformations develop, the use of FEM is sometimes difficult due to excessive distortions of the finite element mesh. In particular, with large axial deformations, local flattening of the cells is possible, which is especially important for bulk compressible materials, since it may not be possible to calculate the density distribution. From a purely technical point of view, this regularization necessitates the regeneration of the grid every few counting steps, significantly increases the counting time, and significantly complicates the solution algorithm.

To solve the technological problems of this type, it seems more appropriate developed in Institute for problems of materials science NAS of Ukraine so called method of permeable elements (MPE). Its essence consists in the use of elements whose shape is regulated in advance, and, unlike the FEM, where the elements coincide with the material volumes and their masses are unchanged, here the masses of the elements are variable - material can flow between adjacent cells.

2. Objects and research methods

When constructing an algorithm for modeling the processes of compaction and deformation of porous preforms during their processing by pressure using the method of permeable elements, we used the model of an ideal rigid plastic porous body. The physical and mathematical formulation of the problem is based on the following basic assumptions.

A porous preform is an isotropic compressible body to which the basic equations of continuum mechanics are applicable. In the framework of this approach, a porous body is considered as a chaotic mixture of solid and emptiness. In accordance with the basic concepts of continuum mechanics, it is also assumed that the behavior of the elements under consideration can be described using the strain rate tensor e_{ij} , stress tensor σ_{ij} , relative density ρ or porosity θ and a number of other parameters [5].

The proposed method is designed to solve problems in a quasistatic formulation and its implementation can conditionally be divided into the following three stages:

- specifying a sampling structure and determining the corresponding form functions for the velocity field;

- determination of the velocity fields all over the processed material;

- determination of the field of densities, deformations, stresses and other deformation parameters.

The first of these stages is characterized by the fact that, unlike the FEM, the movement of the mesh in the MPE (if this is realized) is not associated with the movement of particles of the pressed material, but is independent of it and is determined based on the convenience of analyzing the results. The latter is due to the use of the motion of the deformable material as the basic Eulerian idea. In this regard, the mass of each element can be variable, and the elements themselves are permeable.

The grid of permeable elements and the evolution of their shape during processing are set a priori based on known data on the nature of the movement of the processing tool, the convenience of the analytical representation of the functions of the velocity fields, and also on the basis of the possibility of further experimental verification. The foregoing also constitutes one of the advantages of the MPE, since it simplifies the procedure for comparing the results obtained by experimental and computational methods; there is no need to use averaging operations that reduce the accuracy of the obtained solution.

At the same stage, by analogy with the FEM, kinematic parameters are determined as a function of shape through their unknown values at the grid nodes. In the general case, the MPE grid can be constructed as in the FEM, however, the movement of the nodes is no longer controlled by the velocity field of the material flow.

As a basic model for describing the processes of hot deformation of porous materials, the model of a plastic porous body [5] is used based on the assumption that there is some plasticity criterion F , which relates the components of the stress tensor with porosity:

$$F = \frac{p^2}{f_1(\theta)} + \frac{T^2}{f_2(\theta)} - \sigma_s^2 = 0 \quad (1)$$

where $f_1(\theta)$ and $f_2(\theta)$ are some functions of the material porosity θ , which determine its rheological properties; σ_s is the yield strength of the base material for these temperature-strain conditions.

The basic algorithm for solving problems using the method of permeable elements, based on the application of variational methods, includes the following operations. For the investigated volume of the deformable billet, some functions of the velocity field corresponding to the boundary conditions are set in the form of polynomials:

$$v_k = a_1\varphi_1(k) + a_2\varphi_2(k) + \dots + a_n\varphi_n(k) \quad (2)$$

where k is the generalized coordinate; $\varphi_i(k)$ are some coordinate functions; a_i - numerical coefficients - unknown variable parameters, the value of which at each step of deformation is selected using one of the known optimization methods in such a way that it minimizes the value of the functional J :

$$J = \sum_{k=1}^K \iiint_V \sqrt{e^2 \cdot f_1(\Theta) + H^2 \cdot f_2(\Theta)} \cdot dV + \sum_{m=1}^M \sqrt{3} \iint_F \mu \sqrt{f_2(\Theta) \cdot (v_1^2 + v_2^2)} \cdot dF; \quad (3)$$

where $e = e_{ij}\delta_{ij}$ is the first invariant of the strain rate tensor characterizing the speed of uniform comprehensive compression (or tension), which can be defined as

$$e = \frac{1}{\Theta} \frac{d\Theta}{dt} = \frac{1}{V} \frac{dV}{dt};$$

H_i - shear strain rate intensity; dV is the elementary volume of the deformable body; μ is the coefficient of friction; v_1 and v_2 are the components of the velocities of the particles of the deformable body along the contact surfaces (at the workpiece – tool interface); dF is the elementary area of the contact surface.

Having determined the values of the varied parameters a_i , we can find the velocity field functions (2) and calculate the components of the strain rate intensity H_i and the compaction rate e , which allows us to solve the problems of final shape change and determine the force and energy parameters of the process.

The density distribution field is found from the law of conservation of mass, which for any element of a continuous medium is formulated as:

$$\frac{dm}{dt} = \int_S v_n \rho \cdot dS \quad (4)$$

where m is the mass; t is the time; v_n is the projection of the flow velocity vector of the material of a given permeable element onto the normal to the surface S bounding this element.

When assuming the existence of velocity discontinuities in a deformable body, it is also necessary to take into account the energy expenditure on deformation on the discontinuity surfaces in the main energy equation. In view of the foregoing, functional (4) takes the form [6]:

$$J = \sum_{k=1}^K \iiint_V \sigma_{ij} \cdot e_{ij} \cdot dV + \sum_{m=1}^M \sqrt{3} \iint_F \mu \sigma_s \sqrt{f_2(\Theta) \cdot (v_1^2 + v_2^2)} \cdot dF + D; \quad (5)$$

where D is the power dissipation on the discontinuity surfaces of kinematically possible displacement velocities. The rupture surface is considered as the limiting position of a thin transition layer of thickness Δn at $\Delta n \rightarrow 0$, in which the displacement velocity undergoes a fast but continuous change.

The magnitude of power dissipation on the surface of the velocity gap can be determined as [6]:

$$D = \int_{\Sigma} \sigma_s \sqrt{(\Delta v_n)^2 f_1(\Theta) + \left[\frac{4}{3} (\Delta v_n)^2 + (\Delta v_t)^2 \right] f_2(\Theta)} \cdot d\Sigma \quad (6)$$

where $d\Sigma$ is the elementary surface of the velocity gap; Δv_n and Δv_t are the normal and tangent components of the discontinuity velocity vector.

If to take the values of the functions $f_1(\Theta)$ and $f_2(\Theta)$ in the form of dependencies:

$$f_1(\Theta) = \frac{4}{9} \cdot \frac{(1-\Theta)^4}{\Theta}; \quad f_2(\Theta) = \frac{(1-\Theta)^3}{3}; \quad (7)$$

then we can write:

$$D = \int_{\Sigma} \frac{(1-\Theta)^{3/2}}{\sqrt{3}} \sigma_s \sqrt{\frac{4}{3\Theta} (\Delta v_n)^2 + (\Delta v_t)^2} \cdot d\Sigma; \quad (8)$$

3. Results and their discussion

The developed general MPE algorithm was successfully used, in particular, to simulate the processes of closed and open hot forging and forging of porous preforms in a half-open die, compaction of bimetallic porous preforms with a horizontal separation plane, precipitation of an annular porous preform in a closed die with a free centripetal radial flow of material, consolidation of step products such as a sleeve with a shoulder, etc.

In particular, we give examples of the use of the considered method for studying the mechanics of material flow during open hot forging of porous preforms (Fig. 1, a) and closed forging in a die with a compensation cavity (Fig. 1, b).

The effectiveness of the application of hot forging methods for powder products in dies with open volumes at which additional shear deformations are realized along with axial ones is shown in a number of works [7-9].

At the same time, hot forging of porous preforms in an open die, a distinctive feature of which is the presence of a height-changing section of the preform with a free lateral surface throughout the deformation process, was not widely used, since uncontrolled extrusion of the material being compacted is possible in the flake in the early stages of deformation, which may cause under-compaction of the forging material.

In this regard, questions of studying the mechanics of the flow of the workpiece material during forging in dies having additional compensation cavities are of practical interest.

The calculation model for describing the flow of a porous material during hot open forging and closed forging in dies with a compensation slit was constructed on the basis of the variational principle, while material hardening, temperature effects and inertia were neglected, and the method of permeable elements was used as a numerical method for implementing the model.

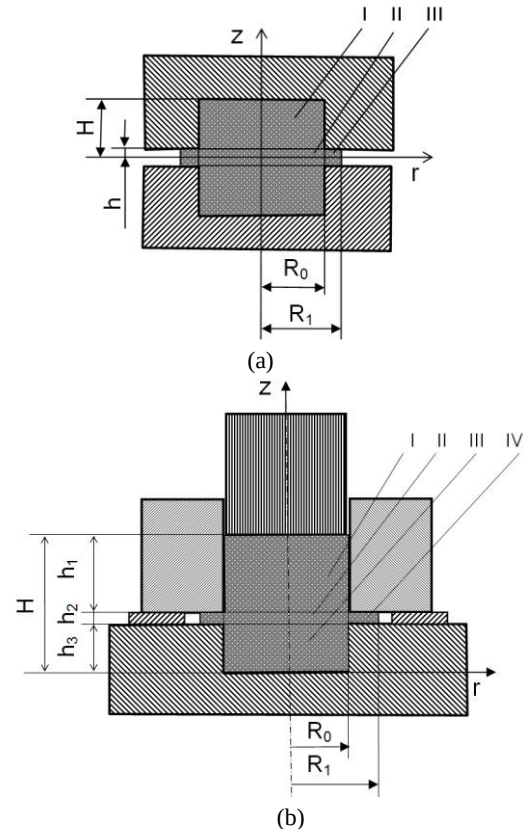


Fig. 1. The design models for the processes of open forging (a) and closed forging in a die with a compensation gap (b)

Taking into account the symmetry of the deformable workpiece relative to the vertical axis, the calculation was made for half of its cross section, which was conditionally divided into three design zones (permeable elements) for open forging (Fig. 1, a), and four zones for closed forging (Fig. 1, b). Inside each of the calculated elements, the distribution of density and strain rates at different compaction times is considered homogeneous.

The boundary conditions for the velocity components v_z and v_r can be expressed as:

$$v_z|_{z=H} = -v_0; \quad v_r|_{z=H} = 0; \quad v_z|_{z=0} = 0; \quad v_r|_{r=0} = 0; \quad v_z|_{z=h} = -v_0;$$

where v_0 is the velocity of the upper half-matrix.

Assuming that the velocities in each of the forgings calculated zones are linear functions of the r and z coordinates, taking into account the boundary conditions, we take the following expressions describing the velocity field of the material flow in each of the zones:

open forging:

$$\begin{aligned} \text{zone I: } v_z &= -v_0 \frac{z}{H}; \quad v_r = 0; \\ \text{zone II: } v_z &= -v_0 \frac{z}{H}; \quad v_r = \frac{v_0}{h} a_1 r v; \end{aligned} \quad (9)$$

zone III:

$$v_z = -v_0 \frac{z}{h}; \quad v_r = \frac{v_0}{h} a_1 R_0 v (1 + a_2 \frac{r - R_0}{R_1});$$

closed forging:

$$\begin{aligned} \text{zone I: } v_z &= v_{12} - \frac{v_0}{H} (z - h_2 - h_3); \quad v_r = 0; \\ \text{zone II: } v_z &= v_{23} - \frac{v_0}{H} (z - h_3); \quad v_r = \frac{v_0 r}{Ha_1 v}; \\ \text{zone III: } v_z &= -\frac{v_0 z}{H}; \quad v_r = 0; \\ \text{zone IV: } v_z &= 0; \quad v_r = \frac{v_0 R_0}{Ha_1 v} \left[1 + a_2 \frac{(r - R_0)}{R_1} \right]; \end{aligned} \quad (10)$$

where a_1 and a_2 are some variable parameters; v_{12} and v_{23} are the linear flow rates of material between zones I-II and II-III respectively (closed forging).

After the corresponding transformations, taking into account dependences (9) and (10), the form of the components of the functional J was determined and, taking the parameters σ , μ and v_0 as constant throughout the deformation cycle, at each calculation step we found the values of a_1 and a_2 that minimize the functional (5).

The calculation was carried out using the step loading method, in accordance with which the entire deformation period was divided into equal time intervals Δt , during which the workpiece is upsetting at $\Delta H = v_0 \Delta t$. At each i -th loading step, the parameters a_1 and a_2 were determined that minimize the functional J ; from (9) and (10) a new value of the flash radius R_1 was found from the dependence:

$$\Theta_k'' = 1 - \frac{m_k \pm \frac{dm_k}{dt} \Delta t}{V_h^k \gamma} \quad (11)$$

where Θ_k'' , V_h^k , and m_k are the porosity, volume and mass of the k -th zone of the preform, respectively, after the next step of deformation, the current values of porosity in individual zones of the preform were calculated.

Comparison of the simulation results of the hot forging process in an open die with similar data for forging in a closed die with compensators showed that while during forging in an open die the displacement of material in the flash starts already at the initial stages of deformation (Fig. 2), then in a closed die with

compensators - only after the workpiece reaches a certain threshold, sufficiently high density level (at $\theta = 2 \div 5 \%$) (Fig. 3), which leads to a decrease in the final value of the flash size during forging in a die with a compensator.

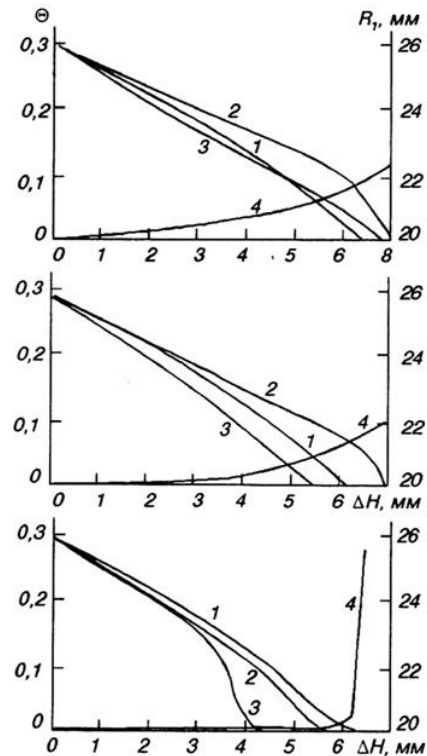


Fig. 2. The dependence of the current porosity of the material in the zones: I (1), II (2) and III (3) and the radius of the flash (4) from axial deformation at $h_0 = 11$ (a), 9 (b) and 7 (c) mm; $\theta_0 = 0.3$

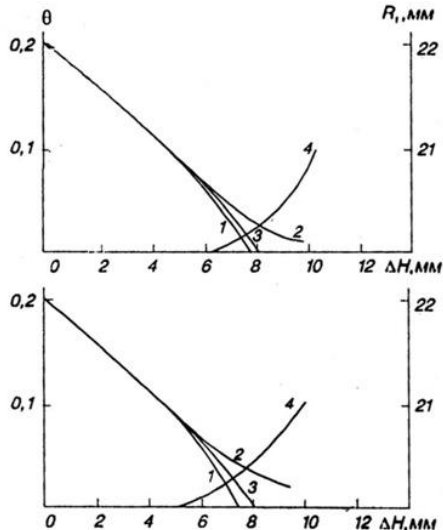


Fig. 3. The dependence of the current porosity of the material in the calculation zones I (1), II (2), III (3) and the radius of flash (4) at the axial strain ΔH for $h_2 = 3.0$ (a) and 4.0 (b) mm; $\theta_0 = 0.2$

At the same time, a sharp increase in the resistance to metal outflow in the flash at the final stage of open forging due to the gradual closure of the half-matrices, contributes to the compaction of the material in the second zone, while at closed forging with a compensator, due to the constant gap between the half-matrices, the resistance to outflow to the store changes slightly, which determines the presence of some residual porosity in zone II of the forging.

It should be noted also that, in contrast to open forging, in which the choice of optimal porosity, the ratio of the size of the workpiece and the cavity of the matrix has a significant effect on the density distribution in different parts of the forging and the final

value of the flash, then when implementing a closed forging scheme with compensators, the dependence of the qualitative characteristics forgings from the specified structural and technological parameters are significantly lower. This fact, along with the fact that the flash value is reduced during forging in a closed die with a compensator, *ceteris paribus*, allows us to conclude that the scheme under consideration is preferable to open forging. At the same time, it should be noted that the structural complexity of die tooling for the implementation of the closed forging process with compensators somewhat limits the possibility of its wider use in industry.

Information on the power parameters of the processes under consideration is essential when choosing a deformation scheme and brand of a press, as well as in calculating die tooling. Let us consider, along with the above schemes, the traditional closed powder forging scheme without compensation slots, traditional for powder metallurgy.

The forging forces for the three considered deformation schemes were calculated using the basic equation of the energy method.

Analysis of the simulation results, which are presented in Fig. 4 shows that the use of a closed forging scheme necessitates the application of significantly higher forces to obtain high-density forgings. The smallest deformation force is with open forging. These results allow us to conclude that with an increase in the rigidity of the loading circuit, the strain force increases. It is noteworthy that the difference in effort increases with increasing degree of axial deformation, and hence the average density of forgings. At the initial stages of compaction, the difference in the efforts for the considered deformation schemes is small.

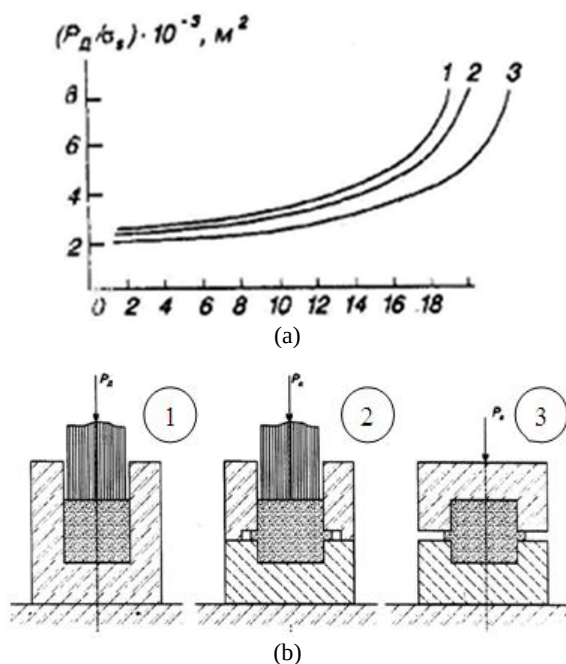


Fig. 4. The dependence of the relative value of the forging force on axial deformation (a) for deformation schemes (b): 1 - closed forging; 2 - forging in a closed die with a compensator; 3 - open forging

It should be noted that experimental studies of the processes of hot forging of powder samples lead to similar results [8-10]. The use of compensation slots allows to obtain high-density forgings with a homogeneous structure at a lower strain pressure compared to traditional closed forging.

Thus, the presented results allow us to conclude that the traditional scheme of hot forging of porous preforms in a closed die is the least preferred in terms of energy and process parameters. This indicates the advisability of using less rigid deformation schemes with partial extrusion of the workpiece material into the compensation cavities.

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EXOTIC BEHAVIOR OF REACTIVE-WETTING OF METAL ON METAL-ON-GLASS IN ROOM TEMPERATURE

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Abstract: We present non-trivial spatio-temporal patterns observed in reactive-wetting of mercury droplets spreading on thin metal (silver or gold) films on glass at room temperature. This is the only known study of reactive-wetting at room temperature. We show that there exist two main regimes, the bulk propagation regime and the interface kinetic roughening regime. In both regimes, rich spatio-temporal patterns are observed. We study and characterize these patterns using statistical physics tools, such as the growth, roughness and persistence exponents, and show the manifestation of surface tension relaxation in these statistical measures.

Keywords: Reactive-Wetting, Metal-on-Glass, Contact Angle, Surface Tension, Kinetic Roughening, Growth, Roughness, Persistence

Mercury droplets (150 microns in diameter) were placed on thin metal films (silver and gold in various thicknesses) evaporated or sputtered on glass, and their spreading has been studied using an optical microscope. The top-view images have been translated into side-view profiles, based on the various colors obtained using reflection-DIC (Differential Interference Contrast) light microscopy. The idea is that the object reflects light from different points of its surface with different colors that are indicative of its surface slope at each point.

The propagating interface of the droplet undergoes kinetic roughening. The two main regimes in the entire process, the bulk propagating and the kinetic roughening regimes, are shown in Fig. 1, for a mercury droplet spreading on a silver thin film of 4200 Å.

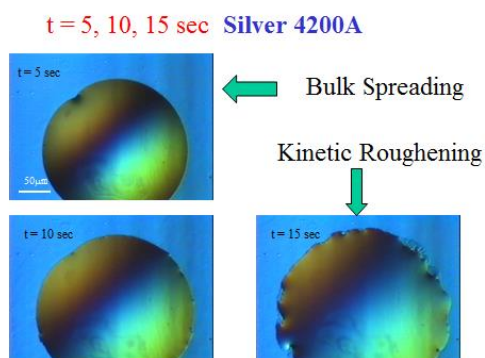


Fig. 1 The two main regimes of the process.

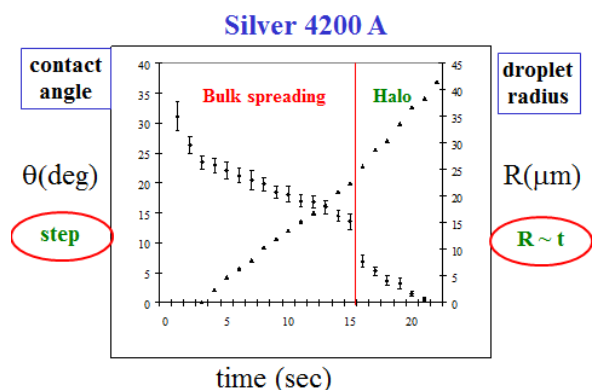


Fig. 2 The droplet radius and contact angle as a function of time in the bulk spreading regime.

Bulk Spreading

In the absence of a theoretical framework for reactive-wetting systems, we obtained empirical results for the droplet radius and the contact angle, both as a function of time. The radius was shown to grow linearly with time, and the angle exhibits a step at a time related to the glass thickness (Fig. 2).

Kinetic Roughening

Using statistical physics tools, we were able to calculate the so-called growth, roughness and persistence scaling exponents, from which we could identify three sub-regimes in the kinetic roughening of the interface – noise, non-linear growth, and surface tension relaxation, as shown in Fig. 3. The results were found similar to results in conventional high-temperature reactive-wetting systems. This universality feature is exemplified in Fig. 4.

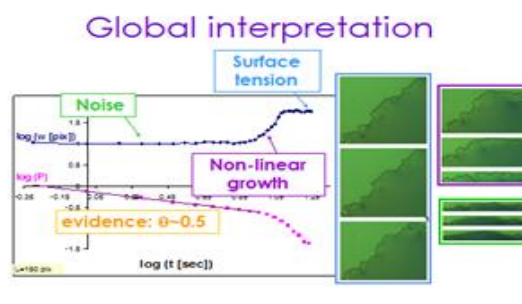


Fig. 3 Noise, non-linear growth and surface tension relaxation in the kinetic roughening regime.

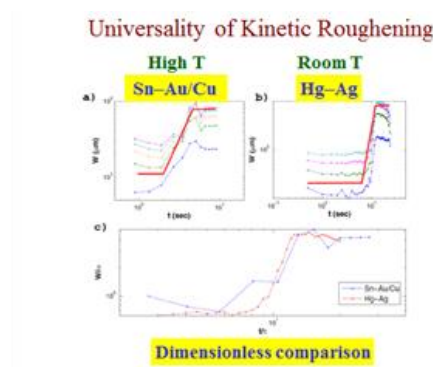


Fig. 4 Universality of kinetic roughening: High temperature vs room temperature.

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EXPERIMENTALLY VERIFIED MATHEMATICAL MODEL OF THE POLYMER PLASTICIZATION PROCESS IN THE INJECTION MOLDING

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Abstract: The mathematical model of the polymer plasticization in the reciprocating screw injection molding machine is presented. According to the mathematical model, a computer program was developed. Based on the computer program, simulation studies of the injection molding process were conducted. Next, the experimental studies, evaluating the theoretical model from the accuracy and usefulness point of view, were carried out. Important output quantities, such as the temperature and pressure profiles, the power demand by the screw, the torque on the screw and the screw rotation time were measured. The studies were performed on a specially made research office. The simulation results were compared with the experimental data measured for the most popular polymers and different operating parameters of the injection machine. The experimental studies have indicated the need to introduce some corrections to the mathematical model. Several modifications have been made to the model, related to the methods of stress determining in the polymer layer. Finally, the output characteristics of the plasticization process in the injection molding are now correctly determined by the model with an average error less than 10%.

Keywords: INJECTION MOLDING, PLASTICIZATION, POWER DEMAND, ENERGY CONSUMPTION, SEC

1. Introduction

The purpose of this article is to present the comprehensive model of the polymer plasticization process in the injection molding. The first version of this model and the simplified model verification was presented in [1,2]. Next, the experimental research which evaluates the theoretical model from the accuracy and usefulness point of view, was conducted. Important output quantities such as the temperature and pressure profiles of the polymer, the power demand of the plasticizing system, the torque of the screw and the recovery time, were measured. These tests were performed on a specially designed research office. The experimental studies indicated the need for introduction of some corrections to the mathematical model. Consequently, several modifications were made in the model. The changes were related to the methods of stress determining in the polymer layer in the screw-barrel system. Furthermore, another method for determining the temperature of the molten polymer in a slit between the top of the screw flight and the barrel was indicated. The above two groups of changes resulted in a significant improvement in determining the power demanded to the screw and the torque on the screw in the transition and melting zones. Because of these modifications, the output characteristics of the plasticization process in the injection molding are now correctly determined, with an average error less than 10%. The mathematical model and a summary of the results of its experimental verification is presented below.

2. Mathematical model

The full operation algorithm of the model is presented in Fig. 1. The model uses four groups of input data: the geometric parameters of the three-zone screw and the barrel, the adjustable operating parameters of the injection molding machine, the material data and the numerical data (rate and accuracy of calculations).

The plasticizing unit consists of a barrel with a feed hopper, a heating section and a three-zones-screw of diameter D , width W (constant on the whole screw length), lead S and flight width e . The channel depth H in feed and metering zones are constant and equal to H_f and H_m , respectively. The channel depth in a compression (transition) zone changes linearly from H_f to H_m . Additional geometric parameters of the model are flight clearance δ_s (thickness of the slit between the top of screw flight and the inner surface of the barrel) and helix angle φ . They are presented in Fig. 2.

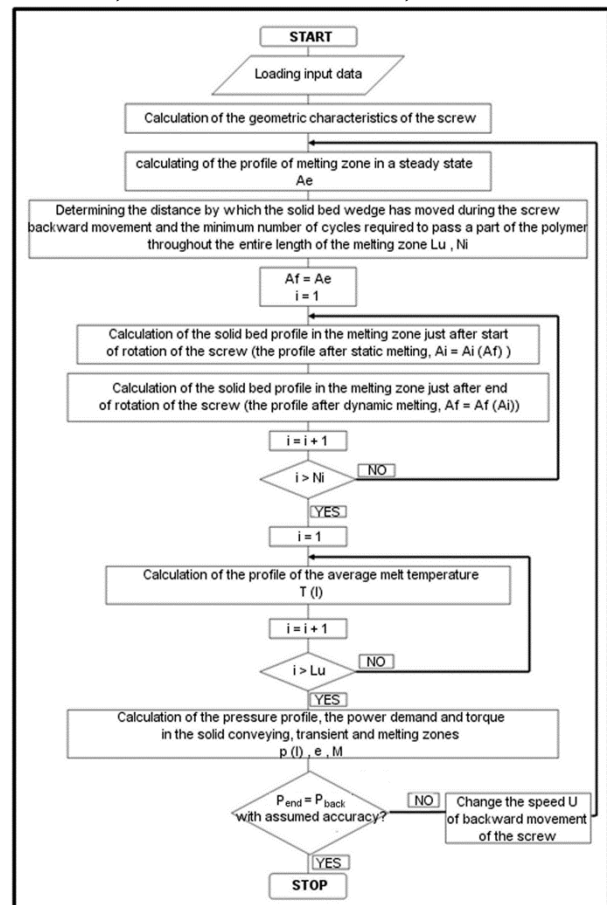


Fig. 1 The algorithm of the mathematical model of polymer plasticization in injection molding

In order to create a mathematical model of the plasticization process during the injection molding, several assumptions were made. Firstly, the existence of three dynamical zones in the plasticizing system was assumed:

1. a feed port and a solid conveying zone
2. a transient (delay) zone
3. a melting and melt conveying zone

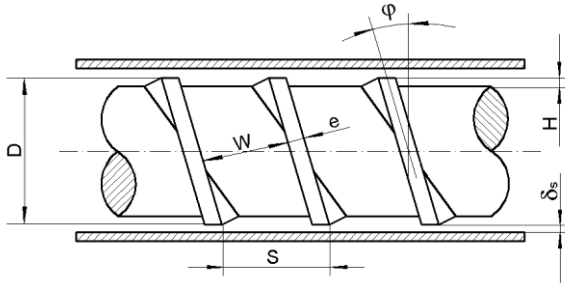


Fig. 2 Geometry of the screw-barrel system of the injection screw machine

Furthermore, the flat (rectangular) screw channel model was assumed.

The starting point for the model is the model of steady-state extrusion that is similar to the classical extrusion model of Tadmor and Klein [3]. However, in contrast to the steady conditions characteristic for extrusion, the lengths and positions of dynamical zones change in time within the injection cycle. To describe these time changes it was adopted, that two coupled states (appearing at two characteristic moments of time) are valid during the cycle:

1. at the end of screw rotation (the beginning of static melting)
2. at the beginning of screw rotation (the beginning of dynamic melting)

Moreover, it was assumed that the melt behavior can be described by the power law of the form:

$$\tau = k_0 e^{-a(T-T_0)} \left(\frac{1}{2} \Pi_d \right)^{n-1} d \quad (1)$$

where τ – the extrastress tensor, d – the rate-of-strain tensor, Π_d – the second invariant of d -tensor, T_0 – the reference temperature (usually assumed as the polymer melting temperature), k_0 , n , a – rheological parameters: k_0 – the consistency coefficient, n – the power-law exponent, a – the temperature coefficient.

solid conveying zone

It was assumed that the dynamic equilibrium in the solid conveying zone is established fast enough. Hence, its operating characteristics can be adequately described by means of relations, that are valid for the steady-state conditions [3]. However, the axial velocity component U of rotating and withdrawing screw should be taken into account.

Assuming the flow continuity, the mass flow can be calculated both from the solid bed velocity and from the screw withdraw velocity as

$$\dot{G} = H W V_{sz} \rho_s \quad (2)$$

$$\dot{G} = \frac{1}{4} \pi D^2 U \rho_m \quad (3)$$

where H – the channel height, W – the average channel width, V_{sz} – the solid bed velocity along the screw channel (in z -direction), ρ_s – the density of solid polymer, D – the outer screw diameter, U – the axial screw velocity, ρ_m – the average density of polymer melt; The V_{sz} velocity is determined as

$$V_{sz} = V_b \frac{\sin \theta}{\sin(\varphi + \theta - \gamma) \cos \gamma} \quad (4)$$

where V_b – the barrel velocity, φ – the helix angle, $\gamma = \arctan\left(\frac{U}{V_b}\right)$, θ – the solid conveying angle.

If the mass flow $\dot{G}$ is known, the values of V_{sz} and U can be calculated and this makes possible to calculate the solid conveying angle θ from Eq. (4). If this angle is known, the pressure profile in the solid conveying zone can be determined using the force and torque balance [4]. A general equation describing the pressure changes over the zone length has the form:

$$p_2 = p_1 \exp(k \Delta) \quad (5)$$

where k – the parameter determined from the balance of forces and moments of force acting on the material layer of elementary thickness dz [4], Δ – the length of one computational step in z -direction.

The initial pressure p_0 in the feed port region can be calculated according to the simple formula proposed in [5]:

$$p_0 = \rho_0 g D \quad (6)$$

where ρ_0 – the bulk density, g – the gravitational acceleration.

For the given pressure profile it is possible to determine the power demand e_s in the solid conveying zone as the sum of power dissipated at the barrel, screw root, screw flights and the power used to increase the pressure in the solid bed:

$$e_s = p(l) f_b W \Delta V_j + p(l) f_s W \Delta V_{sz} + 2p(l) f_s H \Delta V_{sz} + H W V_{sz} \frac{dp}{dl} \quad (7)$$

where $p(l)$ is the polymer pressure in l -location; l is the location on the screw channel length (in z -direction) measured by a number of computation steps from the beginning of the screw; f_b , f_s – the barrel and screw friction factors of solid polymer, respectively, V_j – the velocity of solid bed transport relative to the barrel, determined as

$$V_j = V_b \frac{\sin(\varphi - \gamma)}{\sin(\varphi + \theta - \gamma) \cos \gamma} \quad (8)$$

The torque M_s in the solid conveying zone was determined in the classical way as the product of the dry friction force and the lever arm:

$$M_s = p(l) f_b W \Delta \frac{D}{2} \quad (9)$$

From the presented relations it follows that the main difference in description of solid conveying zone action during extrusion and injection is the existence of the non-zero retraction velocity of the screw.

transient zone

The transient zone in the model starts at a point, where melt layer appears at the solid bed surface. It was adopted, that this is the place of the screw channel which corresponds with the beginning of the barrel heating zone at a given moment of time. The end of the transient zone in the screw channel corresponds with the point, where the melt film thickness reaches a critical value δ_w [3]. In contrast to the solid conveying zone, the total length of the transient zone is variable and it depends on the process conditions. The length of this zone is very short and it usually reaches half to two coils. However it is important to consider this zone, because it allows continuity of the pressure profile as well as the correct calculation of the total power demand and torque on the screw. According to [3] it was assumed that the melt film thickness changes linearly from 0 to δ_w over the zone length. These changes depend on the rate of dynamic melting, that can be calculated from [3], assuming additionally the axial screw velocity U [1].

The calculations of the pressure changes in the transient zone base on the assumption that the pressure gradient in this zone can be determined as a weighted average of the pressure gradient at the end of the solid conveying zone and the pressure gradient at the beginning of the melting zone:

$$\left(\frac{\partial p}{\partial z} \right)_t = \left(\frac{\partial p}{\partial z} \right)_s (1 - x) + \left(\frac{\partial p}{\partial z} \right)_m x \quad (10)$$

where the subscripts t , s and m mean: the transient zone, the solid conveying zone and the melting zone, respectively, x – the weight factor, changing from 0 to 1 on the length of the transient zone.

This semiempirical approach that provides a smooth pressure profile at the zone boundaries was introduced, because there is no exact method of pressure calculation in the case, if the flow is determined by both dry and viscous friction.

The power demand e_T in the transient zone was defined as the sum of the power dissipated in the thin melt film at the barrel surface, on the root surface and the flight surfaces, as well as the power desired to increase the pressure. It can be calculated for one computation step from the equation

$$e_T = [p(l) f_b (1 - x) + \tau_j x] W \Delta V_j + p(l) f_s W \Delta V_{sz} + 2p(l) f_s (H - \delta_m) \Delta V_{sz} + H W V_{sz} \frac{dp}{dl} + \tau_e e \Delta \sqrt{V_b^2 + U^2} \quad (11)$$

where τ_j – the shear stress in the polymer melt layer in the screw channel, δ_m – the melt layer thickness in the screw channel in the

transient zone, changing linearly from 0 to critical value δ_w : $\delta_m = \delta_w x$ (x – the weight factor), τ_e – the shear stress in the polymer melt layer in the slit between the top of the screw flight and the barrel surface, e – the width of the screw flight; τ_j and τ_e quantities are defined according to the power law as follows:

$$\tau_j = k_0 \exp(-a(T_b - T_m)) \left(\frac{V_b}{\delta_m} \right)^n \quad (12)$$

$$\tau_e = k_0 \exp(-a(\bar{T}_{slit} - T_m)) \left(\frac{\sqrt{(V_b^2 + U^2)}}{\delta_s} \right)^n \quad (13)$$

where k_0 , a , n – the parameters of the power law equation, δ_s – the slit thickness, T_b – the average barrel temperature in the heated zone, T_m – the melting (flow) temperature of polymer, $\bar{T}_{slit}$ – the average polymer temperature in the slit.

The first term in Eq. (11) assumes the occurrence of the polymer-barrel friction as a weighted average of dry ($p(1-x)$) and viscous (τx) friction. The last term of the Eq. (11) refers to the power dissipated in the thin polymer layer existing between the top of the screw flight and the inner barrel surface as a result of the leakage flow. The determination of the polymer temperature in the slit bases on an energy equation, which assumes neglecting of the convection and the conductivity along and across the slit for the generalized Newtonian liquid and (assuming adiabatic flow) takes the simplified form:

$$\rho_m c_m \frac{\partial \bar{T}}{\partial t} = \bar{\eta} |\dot{\gamma}|^2 \quad (14)$$

wherein, according to the power law equation, the average viscosity can be defined by the formula

$$\bar{\eta} = k_0 \cdot e^{-a(T - T_m)} |\dot{\gamma}|^{n-1} \quad (15)$$

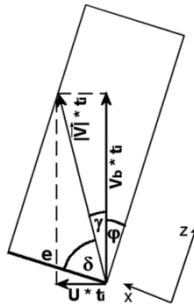


Fig. 3 The vector analysis of the polymer particle displacement in the slit

Analyzing the displacement of the polymer particle in the slit, the shear time t_i in the slit is equal to the transition time from one to the other edge of the slit with the width e and the helix angle φ in the direction and the velocity determined by the vector $\vec{V}$. The shear time can be easily calculated on the basis of the geometrical relationships from Fig. 3 as:

$$t_i = \frac{e}{|\vec{V}| \sin(\varphi + \gamma)} \quad (16)$$

$$\text{where } |\vec{V}| = \sqrt{V_b^2 + U^2} \quad (17)$$

The equation (14) with the viscosity expressed by the formula (15), integrated with the initial condition $\bar{T}(t=0) = T_b$ and taking into account the formula (18) allows to obtain the expression which describes the polymer temperature in the slit:

$$\bar{T}_{slit} = T_b + \frac{1}{a} \ln \left[\frac{k_0 a e^{-a(T_b - T_m)}}{\rho_m c_m \sin(\varphi + \gamma)} \left| \frac{\bar{V}}{\delta_s} \right|^n \frac{e}{\delta_s} + 1 \right] \quad (19)$$

where c_m – the average specific heat of the polymer melt.

The torque M_T in the transient zone was determined as

$$M_T = [p(l) f_b (1-x) + \tau x] W \Delta \frac{D}{2} \quad (20)$$

where τ is the shear stress defined as

$$\tau = k_0 \exp(-a(T_b - T_m)) \left(\frac{V_b}{\delta_m} \right)^n \quad (21)$$

Melting zone

The melting process during the injection molding is more complicated in comparison with the extrusion, mainly due to the existence of the static melting phase (for the stationary screw). Moreover, the phase of the dynamic melting must additionally take into account the axial screw motion. Both phases (static and dynamic melting) are coupled. The final conditions for one of them are the initial conditions for the second one.

Defining of the function of the solid bed width distribution in time and space (along the screw channel) is the basis for the plasticization model with the three-zone-screw. It can be described with the general relation

$$\frac{x}{w} = f(l, t) \quad (22)$$

The spatial coordinate l (along the screw channel) in the equation (22) is expressed in the number of computation steps.

It was assumed that three areas of different behavior of the polymer material, shown in Fig. 4, can be distinguished in the screw channel cross section in the melting zone [3,6]. There is an area occupied by a homogeneous wedge of solid polymer, a melted polymer layer at the barrel surface and a melt pool.

Due to the variable channel height along the screw it is convenient to express the solid bed profile as the function

$$A(l, t) = H(l) \frac{x(l, t)}{w} \quad (23)$$

where $A(l, t)$ – the ratio of the cross-sectional area of the channel occupied by the solid bed to the total cross-sectional area of the channel (see Fig. 4), $H(l)$ – the relative height of screw channel, determined as $H(l) = H/H_f$, changing from 1 (in the geometrical feed zone) to H_m/H_f (geometrical metering zone) on the screw channel length.

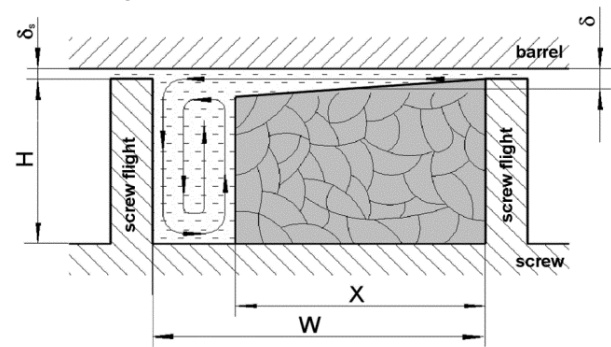


Fig. 4 The screw channel cross-section in the melting zone (δ – average thickness of the polymer melt layer)

Knowing the $A(l)$ function in the two basic moments of time, is necessary to describe of the melting process in the injection molding:

1. just after the start of the screw rotation (beginning of dynamic melting): $A(l, 0) = A_i(l)$
2. just after the finish of the screw rotation (beginning of static melting): $A(l, t_r) = A_f(l)$, where t_r is the recovery time defined as $t_r = \frac{N_s S}{U}$ (24)

where N_s is the screw stroke (expressed in number of coils).

The static melting begins after the stopping the rotational screw motion. The solid polymer is molten in a certain time interval, which is approximately equal to the cooling time, and then the screw is shifted forward on the distance of the screw stroke. The polymer is molten now in the time approximately equal to the hold time. According to the known theories of static melting [6,7] it was assumed that the time dependent melt film thickness δ_t molten in contact with the hot barrel surface is given by the equation:

$$\delta_t = \delta_0 + k \sqrt{t} \quad (25)$$

where δ_0 is the initial thickness of the melt, k is the root of the algebraic, non-linear, complex equation [6].

Assuming that the state after dynamic melting A_f is the initial state for the phase of static melting, the solid bed profile A_i after static melting can be determined as follows:

$$A_i(l) = A_f(l) \frac{H - \delta_t(l)}{H - \delta_0(l)} \quad (26)$$

Dynamic melting starts at the moment of the beginning of the screw rotation. The calculation of the solid bed profile after the screw rotation period was done using the theory of dynamic extrusion [8]. The basic equation, that describes the differential mass balance in the solid bed under unsteady conditions can be presented in the following way:

$$\frac{\partial A}{\partial \tau} + \frac{\partial A}{\partial l} = - \frac{\Phi}{V_{sz} \rho_s \sqrt{H}} \sqrt{\frac{A}{H(l)}} \quad (27)$$

where Φ - the auxiliary variable associated with the rate of dynamic melting [3], τ - the dimensionless time variable defined as

$$\tau = \frac{t V_{sz}}{\Delta} \quad (28)$$

The expression (27) is a non-linear partial differential equation of the first order, which describes the evolution of the relative cross-section area of the solid bed in time and space during the screw rotation. The equation (27) has been solved analytically for the purposes of the model with the assumption of the 3-zone screw [1]. This solution has been adapted in the model.

The quantity L_u defined by equation (29) describes the solid bed displacement due to the rotary-backward motion of the screw and it is expressed in the computation steps. The solid bed evolution during the screw rotation can be followed by changing L_u from 0 to the end value given by the equation (29).

$$L_u = \frac{t_r V_{sz}}{\Delta} = \frac{N_5 S V_{sz}}{U \Delta} \quad (29)$$

Equilibrium values of A after the static and dynamic melting can be calculated using the iteration method. The steady-state profile A_e characteristic for the extrusion process [3] taking additionally into account the backward screw motion could be assumed as the first approximation of A [1]. Hence, the approximated A_i profile after static melting can be determined. It is the initial value for the new profile of the solid bed A_f calculated for dynamic melting. The iteration is repeated until A profiles (after static and dynamic melting) will be established. It could be shown that the time required for stabilization of A_f and A_i is not shorter than the passage time of the first polymer portion over the whole channel length. It corresponds to a certain value of N_i iteration cycles [1].

If the solid bed profiles are known, the pressure and temperature profiles in screw channel can be calculated. Knowing these profiles makes it possible to calculate other quantities: the power demand, the screw torque and the energy consumption that are important for the detailed characterization of the plasticization process. All the quantities were calculated for the A_f profile after the dynamic melting, which is characterized by the maximal filling of the screw channel with the solid polymer.

The temperature profile is the result of thermal processes during the whole screw rotation phase. The methods of polymer melt temperature calculation, which are valid for the steady-state conditions, could not be applied for the calculation of the temperature profile in the injection molding. In this case, the temperature profile was determined by an approximated method described in [5], which was adapted to the model requirements.

The averaging equation of energy for the polymer melt region is represented by the expression:

$$\rho_m c_m \frac{\partial T}{\partial t} = k_m \frac{\partial^2 T}{\partial y^2} + \left(\tau_{xy} \frac{\partial v_x}{\partial y} + \tau_{zy} \frac{\partial v_z}{\partial y} \right) - \rho_m c_m \overline{V_{mz}} \frac{\partial T}{\partial z} - \rho_m c_m \overline{V_{mx}} (T - T_b) \quad (30)$$

where k_m - the average thermal conductivity of the molten polymer, $\overline{V_{mz}}$ - the average flow rate of the polymer melt along the screw channel, defined as

$$\overline{V_{mz}} = \frac{\dot{q}_z}{H W} \quad (31)$$

$\dot{q}_z$ is the volumetric flow rate. The method of the exact determination of $\dot{q}_z$ is shown later.

$\overline{V_{mx}}$ - the average inflow rate of the polymer melt from the melting layer:

$$\overline{V_{mx}} = \frac{\Phi \sqrt{\frac{A(l)}{H(l)}}}{\rho_m H (1 - \frac{A(l)}{H(l)})} \quad (32)$$

The respective terms in the equation (30) represent the following quantities: the heat accumulation rate, the heat conduction rate, the

rate of the heat generation by viscous friction, the heat convection rate and the rate of heat input from the melt film. The average values of the terms describing the energy conduction and dissipation can be calculated in a similar way as presented in [9] for the steady-state extrusion. Assuming the constant barrel temperature and the neutral screw, after several transformations the equation (30) takes the following dimensionless form:

$$\frac{\partial \theta}{\partial \tau} + \frac{\partial \theta}{\partial l} = -B(l, \tau) \theta + C(l, \tau) \exp(-a \theta) \quad (33)$$

where θ , τ , l - the dimensionless values of T , t and z , respectively; B , C - the complex variables [1], a - the temperature coefficient; the dimensionless time variable τ is defined as

$$\tau = \frac{t V_{mz}}{\Delta} \quad (34)$$

The equation (32) is a nonlinear, partial differential equation. It was solved numerically (by the similar method presented in [9]). This solution has been adapted in the model. This made it possible to calculate the temperature profile of the molten polymer in the melting zone.

For the pressure calculation we have assumed that the polymer pressure in the screw channel is stabilized fast enough. Hence, for its calculations the same methods can be used as for the steady-state conditions. The pressure was calculated according to the own method based on the results of the analysis of the two-directional, non-isothermal flow of the Ellis fluid in the rectangular channel [10]. The flow of the power law fluid is described by the following set of equations:

$$\chi \int_0^1 (\eta - \eta_x) \Psi(\eta) d\eta = U_x \quad (35a)$$

$$\int_0^1 (\eta - \eta_z) \Psi(\eta) d\eta = U_z \quad (35b)$$

$$\chi \int_0^1 \eta (\eta - \eta_x) \Psi(\eta) d\eta = U_x \quad (35c)$$

$$\int_0^1 \eta (\eta - \eta_z) \Psi(\eta) d\eta = U_z - \frac{\dot{q}_z}{W H v_0} \quad (35d)$$

where η , η_x , η_z , χ are the dimensionless quantities. η_x , η_z are the integration constants of the equation of motion and the $\Psi(\eta)$ function is defined as

$$\Psi(\eta) = \left[(\eta - \eta_z)^2 + \chi^2 (\eta - \eta_x)^2 \right]^{\frac{1-n}{2n}} \quad (36)$$

$$v_0 = H \left| \frac{\partial p}{\partial z} \right| F_p \frac{H}{k_0} \exp[a(\bar{T} - T_m)]^{\frac{1}{n}} \operatorname{sgn} \left(\frac{\partial p}{\partial z} \right) \quad (37)$$

$$U_x = \frac{V_{bx}^*}{v_0} \quad (38)$$

$$U_z = \frac{V_{bz}^*}{v_0} F_d \quad (39)$$

F_d and F_p are the shape factors for the drag and pressure flow for the Newtonian fluid [3]. $\bar{T}$ is the average temperature of the polymer melt. The transversal and longitudinal velocity components of the barrel V_{bx}^* and V_{bz}^* with respect to the screw channel in the presence of the backward screw motion can be defined by expressions:

$$V_{bx}^* = V_b \frac{\sin(\varphi - \gamma)}{\cos \gamma} \quad (40)$$

$$V_{bz}^* = V_b \frac{\cos(\varphi - \gamma)}{\cos \gamma} \quad (41)$$

For known V_{bx}^* , V_{bz}^* , $\dot{q}_z$, W and H values, the local values of η_x , η_z , χ and v_0 can be calculated by solving the system of equations (35a-d). It was solved with the iteration method. As the first approximation the Newtonian values of η_x , η_z , χ and v_0 were used [10]. The integrals were calculated by the Gaussian quadratures method with five nodes. This made it possible to calculate the local pressure gradient

$$\frac{\partial p}{\partial z} = \frac{1}{\Delta} \frac{\partial p}{\partial l} \quad (42)$$

from the equation (37) and then to calculate the pressure profile, if the average polymer melt temperature $\bar{T}$ is determined.

The total power demand in melting zone e_M is the sum of the power dissipated in the melt region due to the longitudinal and transversal flow, the power dissipated in the slit between top of screw flight and the barrel inner surface and the power required for pressure changes:

$$e_M = \tau_z W \Delta V_{bz}^* F_d + \tau_x W \Delta V_{bx}^* + \tau_e e \Delta \sqrt{V_b^2 + U^2} + H W \overline{V_{mz}} \frac{dp}{dl} \quad (45)$$

where

$$\tau_z = k_0 \exp[-a(\bar{T} - T_m)] \left(\frac{V_{bz}^* F_d}{H} \right) \quad (46)$$

$$\tau_x = k_0 \exp[-a(\bar{T} - T_m)] \left(\frac{V_{bx}^*}{H} \right) \quad (47)$$

τ_e – the shear stress in the polymer melt layer in the slit, defined by eq. (13).

The torque M_M in the melting zone was determined as a sum:

$$M_M = \tau_{xz} W \Delta \frac{D}{2} + \tau_e e \Delta \frac{D}{2} \quad (48)$$

where τ_{xz} and τ_e are defined respectively as

$$\tau_{xz} = \sqrt{\tau_x^2 + \tau_z^2} \quad (49)$$

$$\tau_e = k_0 \exp(-a(\bar{T}_{slit} - T_m)) \left(\frac{V_b}{\delta_s} \right)^n \quad (50)$$

One of the most fundamental questions in the model is the determination of the screw retraction velocity U and the pressure profile, where the pressure value at the screw end is equal to the known back pressure (operating parameter). Both quantities are strictly coupled and their determination closes the computation cycle. Hereafter, that makes it possible to calculate the most important process characteristics such as the plasticization rate, the power requirement, the screw torque, the average melt temperature and the specific energy consumption. The choice of the proper backward velocity U for a given back pressure was done with the iteration method using a special control algorithm. It increases or decreases the U value depending on the calculated pressure on the screw end and the assumed back pressure, until both pressures become equal with a desired accuracy.

3. Experimental results and discussion

The test office for the measurements of the output parameters of the plasticization process during the injection molding consists of the suitably instrumented injection molding machine linked to the collecting and processing data module and the computer for imaging and saving of the collected data. The test office shown in Fig. 5 consists of:

1. the injection molding machine Battenfeld Plus 350/70,
2. four pressure/temperature sensors (analog CDTAI200-1/2-1500-1-1-1J (Bagsik Sp. z o.o.), range 0-150 MPa, 0-300 °C, OE: $\pm 0.5\%$ FS),
3. the torque - measuring device (analog sensor DMF2X-250 (MEGATRON Elektronik GmbH & co. KG), range 0-250Nm, OE: $\pm 1\%$ FS),
4. the inductive sensor for the screw rotational velocity measurements (induction detector E2A-S08KS02-WP-B1, Omron Corp.),
5. the screw linear displacement sensor (analog sensor LWH 0150 (Novotechnik U.S. Inc.), range 0-150 mm, LE: $\pm 0.08\%$),
6. the control cabinet with the touch screen.

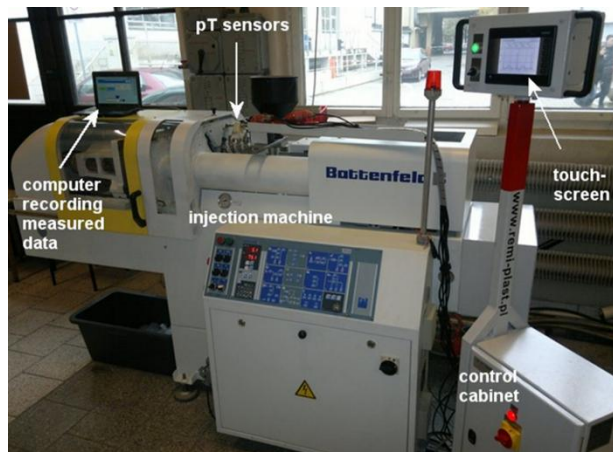


Fig. 5 The test office for the plasticization process in the injection molding

The results presented below are related to the studies involving selected examples from five typical thermoplastic polymers characterized in Table 1. The variable parameters of the injection molding machine during the plasticization process study were the following:

1. the back pressure (changed in range of 4-24 MPa)
2. the screw velocity (changed in range of 30-70% of the maximal screw velocity)
3. the dwell time (changed in range of 8-50 s) - approximately equal to the cooling time of the product in the mold
4. the average barrel temperature in the heated section

Tab. 1 The types of tested polymers

PE-LD	PE-HD	PP	POM	PS
Malen E	Hostalen	HP 515M	Schulaform	Krasten
FABS	GC 7260		9A	154
23D022				

Table 2 shows the values of the adjustable parameters of the injection molding machine used in the experiments. Other process parameters were kept constant.

Tab. 2 The adjustable parameters of the injection molding process

	back pressure [MPa]				
	3	6	10	16	24
	screw rotational velocity [rpm]				
	154	200	240	286	333
	dwell time [s]				
	8	12	20	30	50
	average barrel temperature [°C]				
	T1	T2	T3	T4	T5
PE-LD	140	160	180	200	220
PE-HD	150	170	190	210	230
PP	190	210	230	250	270
POM	-	-	210	-	-
PS	-	180	200	220	240

The studies on the plasticization process in the injection molding were carried out as two independent series of experiments:

1. The study by changing only one of the parameters listed in Tab. 3, and keeping constant the values of the other parameters, which were always equal to the third value in Tab. 2. The back pressure, the screw velocity and the dwell time were the same for all polymers. The symbols of T1-T5 were introduced due to the different average barrel temperature for processing of five polymers mentioned above. All three heating zones of the barrel were kept at the same (constant) temperature during experiments.

2. The study by changing simultaneously two of the adjustable parameters listed in Tab. 2 and keeping constant the values of the other parameters, which were always equal to the third (middle) value from Tab. 2.

During the experiment, all the most important characteristics of the process were measured: the pressure and temperature profiles on the screw length, the torque on the screw, the power supplied to the heaters, the mass yield of the plasticization process and the recovery time.

Because there is a lot of results and they are very similar for different polymers in aspect of the shape of curves and the differences for the relevant theoretical and experimental characteristics, it was decided to present the output characteristics of one polymer for the study with simultaneously two of the adjustable parameters changing. In order to standardize the charts, the characteristics obtained from the model are shown as thick lines without markers, while the experimental profiles represent the markers indicating the measurement points.

In the analyzed example, the rotational velocity of the screw and the plasticizing pressure in the tests were changed at the same time. These parameters are presented in Table 3. Other working parameters of the injection machine were constant, as in the first part of the studies. The tests were performed for PE-LD, PP and PS. The exemplary results are shown for PP.

Tab. 2 Changed parameters in the second part of the studies

screw rotation velocity [rpm]	back pressure [MPa]
60	1.0
154	4.0
240	10
333	16
400	21

A comparison of the output characteristics for the injection molding of PP is presented in Figs. 6 and 7. We can see a very good agreement between the model curves and the experimental points. The model provides a very good pressure profile as well as the power demand, the torque and the process yield. Only the temperature profile is predicted by the model with the differences of approx. 5-7% for high screw rotational velocity. The same situation occurs for PE-LD and PS. In order to generalize these results, similar tests should be performed by changing other pairs of the injection working parameters. Research works in this area are continued.

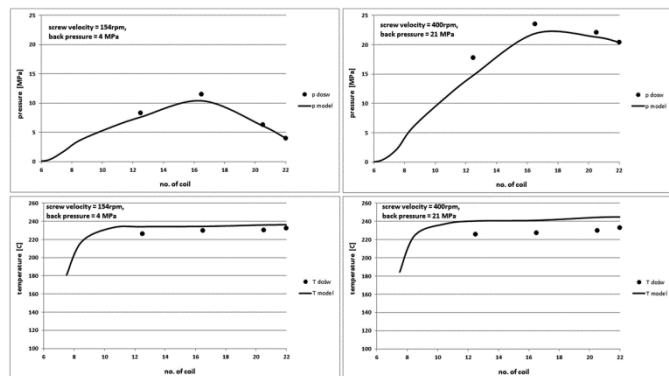


Fig. 6 Comparison of the theoretical and experimental characteristics of the pressure (top) and temperature profiles (bottom) on the screw channel length in PP injection process for the screw rotational velocity of 154 rpm and back pressure of 4 MPa (left) and 400 rpm and 21 MPa (right)

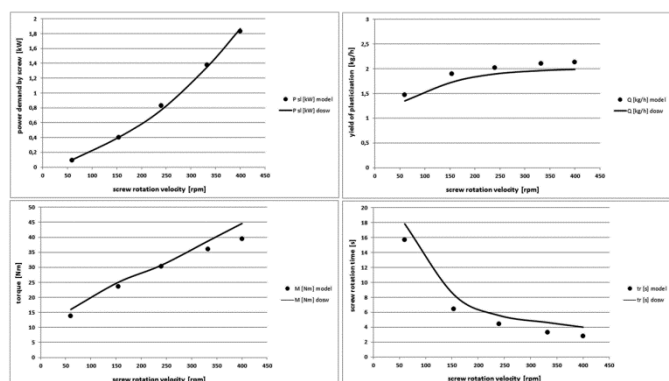


Fig. 7 Comparison of the other theoretical and experimental characteristics (power demand, torque, yield of plasticization and screw rotation time) for the different screw rotation velocity and back pressure values in PP injection process

4. Conclusions

The paper presents the comprehensive model of the plasticization process during the injection molding. The experimental verification of the model using the specially designed and built research office was described. The plasticization studies of five typical thermoplastic polymers during the injection molding with different values of the back pressure, the screw rotational velocity, the dwell time and the barrel temperature were carried out. The values of experimental characteristics with the results generated by the simulation model were compared. It was found that the model correctly determines the dynamics of the plasticization process under the changes of the most important input parameters. The model predicts well the power demand and the torque values as well as the process yield. The average differences in the theoretical and experimental values do not exceed 10%. Slightly larger average differences (about 20%) occur in the determination of the pressure and temperature characteristics. It is worth noting, however, that the knowledge of the pT profiles is scientific and cognitive in nature. On the other hand, the results such as the power demand, the torque, the process yield and the SEC are of a practical importance. Here the model shows the results more compatible with the experience.

The model uses three groups of input parameters: geometrical parameters of the plasticizing system (mainly the screw), working parameters of the injection molding machine and material parameters of the polymer being processed. In the experimental verification of the model, the second and third parameter groups are changed. All tests were conducted using one injection molding machine and one screw. It is worth performing similar studies for a larger injection molding machine as well as at least two different screws with the different length of feed, compression and metering zones to generalize or detail the results presented in this work.

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NOVEL HYBRID POLYETHERSULFONE MEMBRANES MODIFIED WITH POLYVINYLPIRROLIDONE AND Ag/TITANATE NANOTUBES

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Abstract: In this work, the influence of addition of polyvinylpyrrolidone (PVP, 10kDa, 1-4.8wt%) and Ag-modified titanate nanotubes (Ag/TNTs, 0.1wt%) on physicochemical and transport properties of polyethersulfone (PES) ultrafiltration membranes was studied. The membranes were prepared via wet phase inversion method using *N,N*-dimethylformamide (DMF) as a solvent and water as a non-solvent. The Ag/TNTs nanocomposite was obtained via photodeposition method using AgNO_3 as a precursor. It was found that the addition of PVP into the casting dope affected the cross-section structure of the membranes and their surface topography. The presence of PVP improved the dispersion Ag/TNTs agglomerates in the membranes structure. A positive influence of the introduction of the nanocomposite into the membranes matrix on their permeability was also proved.

Keywords: TITANATE NANOTUBES, SILVER, POLYVINYLPIRROLIDONE, POLYETHERSULFONE, MEMBRANE

1. Introduction

Due to many advantages such as low energy or chemical consumption, automation and modularity of installations as well as high and stable quality of permeate the membrane processes are widely used for water and wastewater treatment. Despite these benefits, they have some drawbacks, and the main of them is the decrease of the permeate flux in time, resulting from the so-called fouling and biofouling phenomena, especially in case of micro- (MF) and ultrafiltration (UF) processes. A promising attempt to solve this problem is introduction of different types of (nano) fillers and modifiers into the membrane structure. There are some reports regarding the use of TiO_2 , Al_2O_3 , SiO_2 , halloysite nanotubes (HNTs), carbon nanomaterials (e.g. graphene, fullerenes, carbon nanotubes (CNTs) and different metal nanoparticles such as Ag, Au, Cu and Pd [1-4]. The application of Ag has attracted special attention due to its antibacterial properties and a positive effect on membranes hydrophilicity.

Silver can be introduced into the membrane structure by itself [5], or deposited on a carrier, such as CNTs, HNTs, zeolites or SiO_2 [6-8]. Likewise, TiO_2 nanotubes or titanate nanotubes (TNTs) can be used as carriers of Ag nanoparticles [9]. There are some reports indicating the positive effect of titanate nanotubes on membrane properties such as hydrophilicity, pure water flux and antifouling performance. Padaki et al. [10] observed that the favorable effect of TNTs on the properties of polymer membranes may be caused by a large amount of hydroxyl groups present on the surface of the nanotube, which contributes to improvement of the hydrophilic properties of the membranes. The effect of TNTs functionalized with sulfonic acid on the performance of polyethersulfone (PES) UF membranes was examined by Alsohaimi et al. [11]. It was reported that the modified membrane was characterized by the improved bacteriostatic and separation properties.

A positive influence of modification of membranes with hybrid Ag/TNTs was reported in our earlier works on PES UF membranes [12,13]. However, we have applied a simple casting dope solution containing the polymer and solvent only. Although the presence of Ag/TNTs improved the permeability of the membranes, they were still characterized by moderate permeate fluxes due to the absence of any pore forming agent. One of well-known porogens is polyvinylpyrrolidone (PVP). In literature there are reports proving a positive impact of PVP on membrane transport properties [14]. Since the effect of PVP on the characteristics and performance of PES UF membranes modified with Ag/TNTs is unexplored, the aim of the present work was investigation on that subject. The research were focused on the influence of Ag/TNTs (0.1wt%) and PVP (10kDa, 1-4.8wt%) on physicochemical and transport properties of PES ultrafiltration membranes.

2. Materials and methods

2.1. Materials

Polyethersulfone was supplied by BASF (Germany). Anatase TiO_2 powder, PVP (10kDa) was purchased from Sigma Aldrich Chemicals (USA). DMF, HCl (35-38wt%), AgNO_3 , NaOH, $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 (96wt%) were provided by Avantor Performance Materials Poland S.A.

2.1 Preparation of titanate and silver-modified titanate nanotubes

Pure TNTs were prepared using hydrothermal treatment of anatase TiO_2 . In the first step, 2g of TiO_2 were ultrasonicated with 60 cm^3 of 10M NaOH for 1 h at room temperature. Then, the suspension was transferred to the autoclave and treated at 140°C for 24h. After washing with HCl and deionized water, the final powder was dried at 80°C for 12 h and ground using agate mortar.

The Ag/TNTs were prepared using photodeposition method [14]. A defined amount of pure TNTs was introduced into 100mM solution of AgNO_3 in a glass reactor and stirred (2 h, 250 rpm) at ambient temperature and pressure. Next, the suspension was irradiated with a UVC lamp (TNN 15/32, Heraeus Noblelight GmbH, 15 W, $\lambda_{\text{max}} = 254 \text{ nm}$) for 2h with continuous stirring. Afterwards, the slurry was centrifuged and washed with deionized water. Then, the product was dried at 80°C for 12 h and ground using agate mortar.

2.2. Preparation of membranes

The membranes were prepared using casting dopes with compositions presented in Table 1.

Table 1: Composition of casting solutions.

Sample name	PES [wt%]	DMF [wt%]	PVP [wt%]	Ag/TNTs [wt%]
M0	15	85	-	-
M1	15	84.9		0.1
M2	15	84	1	-
M3	15	83.9		0.1
M4	14.8	82.8	2.4	-
M5	14.8	82.7		0.1
M6	14.4	80.8	4.8	-
M7	14.4	80.7		0.1

First, the unmodified membranes (M2, M4, M6) were obtained by dissolution of a defined amount of the polymer and 0.56; 1.40 or

2.80 g of PVP in DMF (50 cm³). For comparison purpose, a solution without PVP addition was also prepared to cast the unmodified M0 membrane. Next, the casting dopes were left for degassing (2 h) and cast on a glass plate using the applicator (Elcometer 4340, Elcometer Ltd., UK) equipped with the casting knife (gap set at 0.1mm). Finally, the films were immersed in the non-solvent (pure water (Elix, Millipore), 20°C) for 24 h. The hybrid membranes (M1, M3, M5, M7) were obtained as follows. First, PES and of PVP (where applicable) were dissolved in 40 cm³ of DMF. Next, the suspensions of NPs in 10 cm³ DMF (NPs/DMF) were sonicated for 30 min using Vibra-cell VCX-130 ultrasonic liquid processor (Sonics, USA; output power 130 W, frequency 20 kHz, amplitude 80%). Subsequently, the suspension of NPs/DMF was dispersed in the dissolved polymer by stirring (200 rpm) with heating at 55-60°C and sonication at 20-25°C for 15 min. Both steps (stirring and sonication) were carried out by turns for 2 h.

2.3. Characterization of Ag/TNTs nanocomposite and membranes

The morphology of TNTs and Ag/TNTs nanocomposite was examined via transmission electron microscope (TEM) FEI TecnaiF20. The topography of the membranes surface was studied using atomic force microscopy (AFM). NanoScope V Multimode 8 scanning probe microscope (Bruker Corp.) equipped with the silicon nitride ScanAsyst – Air probe was applied. The scanned area was 10 µm × 10 µm. The measurements were executed in the ScanAsyst mode. The cross-sections of the membranes were examined using Hitachi SU8020 Ultra-High Resolution Field Emission Scanning Electron Microscope (UHR FE-SEM). The membranes samples were coated with a 10 nm thick chromium layer (Q150T ES coater, Quorum Technologies Ltd., UK). Two types of techniques were used i.e. analysis using secondary (SE) and back scattered electrons (BSE). The accelerating voltage was 5 kV and 15 kV for SE and BSE, respectively.

The transport and separation properties of the membranes were examined using a laboratory scale UF installation (Fig 1). The installation consisted of a suction pump, two stainless steel membrane modules (with a 1.194 mm feed spacer) and manometers with needle valves. The transmembrane pressure (TMP) applied during pure water ultrafiltration experiments was set at 1, 2 and 3 bar, and the temperature was maintained at 20±1°C. The membrane separation area was 0.0025 m². All the experiments were carried out at least three times.

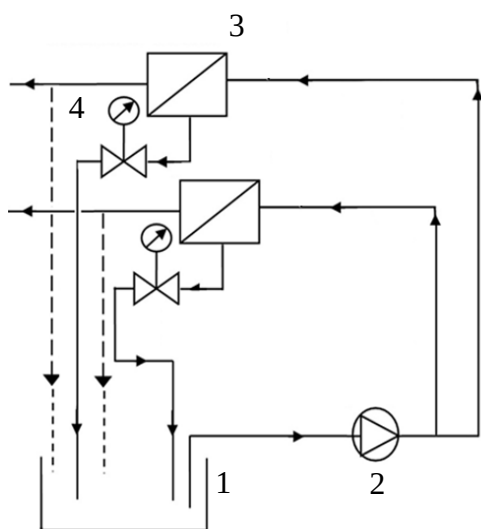


Fig. 1 Scheme of ultrafiltration installation; 1-feed tank; 2-pump; 3 – membrane module; 4-needle valve with manometer.

3. Results and discussion

3.1.Characterization of obtained nanomaterials

Fig. 2 A and B shows microstructure of pure TNTs and Ag/TNTs obtained by the photodeposition method, respectively.

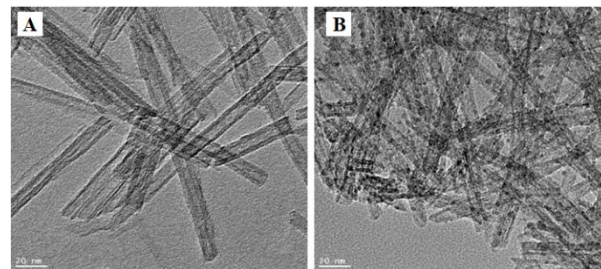


Fig. 2 TEM images of (A) pure TNTs and (B) Ag/TNTs.

The pure TNTs have multi-walled tubular structure with a length in the range from 50 to 200 nm and diameter of 6-8 nm. Fig. 2(B) shows that the Ag nanoparticles are evenly distributed on the TNTs surface. Most of the silver nanoparticles have diameters of 2-5 nm.

3.2.Characterization of the prepared membranes

In Fig. 4 the SEM-SE and SEM-BSE images are presented. The membranes without PVP addition are much thinner than the membranes prepared using the pore forming agent. Moreover, the porous structure of both types of membranes (with and without PVP) differs significantly. The cross section of M1 membrane is asymmetric and exhibits a dense top layer and a porous bottom layer, with large finger-like and some round-shaped pores surrounded by a spongy structure. In case of the membrane prepared with application of 1wt% of PVP (M3) the relatively narrow finger-like and the large oval pores in the bottom part turned into the long, slanted macrovoids. In the cross sections of M5 and M7 membranes, under the thin skin layer, a middle layer with narrow finger-like pores and the loose bottom layer with large shapeless macrovoids surrounded by a spongy structure can be seen. The obtained results revealed that the increase of the concentration of PVP up to 2.4 and 4.8wt% resulted in a delamination of the membranes structure. Similar results were described in other works [15-17]. Amirilargani et al. [16] explained the formation of the large pores in the bottom part of the membranes cross-section by high affinity of PVP for the solvent and low in relation to the polymer. These properties are the reason of increasing the thermodynamic instability of the casting solution. That leads to the instantaneous demixing in the non-solvent bath, which results in formation of macrovoids. In other words, PVP is a hydrophilic and water- soluble pore- forming polymer, therefore its addition into the casting doped increases the solvent (DMF) – non-solvent (water) exchange rate at the stage of phase inversion. This leads to a loose structure of a membrane and formation of macrovoids [17].

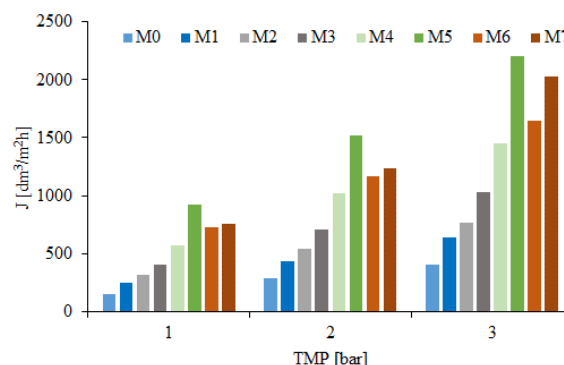


Fig. 3 Influence of transmembrane pressure on pure water fluxes (PWF) of the prepared membranes.

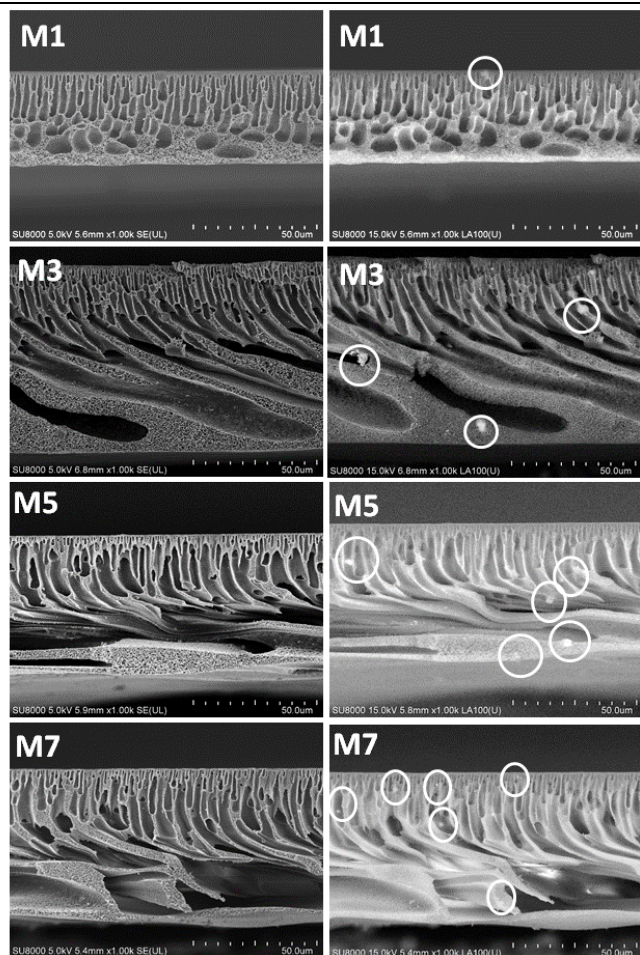


Fig. 4 SEM-SE (left side) and SEM-BSE (right side) microphotographs of M1, M3, M5 and M7 membranes.

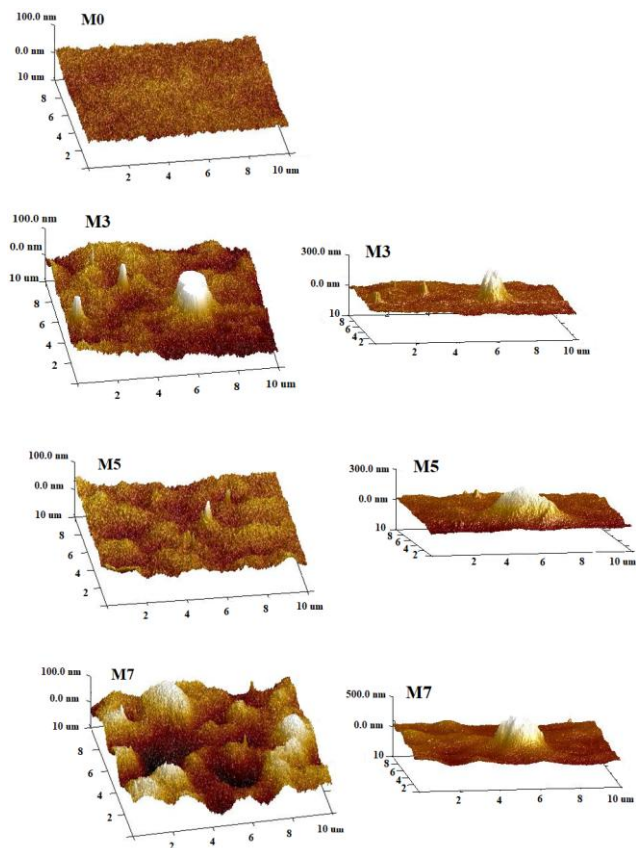


Fig. 5 The topography of the surface of the obtained M0, M3, M5 and M7 membranes.

Fig. 5 presents AFM images of the surface of the membrane without PVP addition (M0) and the mixed matrix membranes prepared using various amount of the porogen. The topography of M0 membrane is relatively smooth and uniform. The incorporation of even a small dose of PVP resulted in the corrugation of membranes surface. The increasing PVP amount caused a further increase of roughness, therefore the M7 membrane has a more non-uniform surface with numerous valleys and hills compared to M5. Regardless of the PVP content, both small and large Ag/TNTs agglomerates were observed.

It was noticed based on Fig. 4 that the addition of PVP may improve the dispersion of Ag/TNTs agglomerates. For M1 the amount of agglomerates visible in the cross-section was low (only one agglomerate in Fig. 4) which means that the dispersion of Ag/TNTs was not very good. Moreover, the average size of agglomerates was larger ($4.7 \mu\text{m}$ ($\text{SD}=1.5 \mu\text{m}$)) than for the membranes with addition of PVP (4.6 ($\text{SD}=0.6 \mu\text{m}$); 2.8 ($\text{SD}=1.1 \mu\text{m}$) and $2.6 \mu\text{m}$ ($\text{SD}=1.4 \mu\text{m}$) for M3, M5 and M7)). The addition of PVP not only had impact on the dimensions of NPs agglomerates but improved their dispersion through the whole membrane matrix. The white circles in Fig. 4 show the places where Ag/TNTs were detected. It can be seen that the increasing amount of PVP results in increasing amount of white dots on SEM-BSE images, which correspond to the NPs agglomerates. For M7 membrane with the highest amount of PVP the number of dots was also the highest in comparison to the other membranes obtained with lower dose of PVP.

Fig. 3 summarizes the water permeability of the prepared membranes. Generally, in all cases the addition of PVP resulted in an increase of pure water flux (PWF) values. Compared to the M0 membrane, the PWF for M2, M4 and M6 membranes measured at $\text{TMP} = 3$ bar increased by about 1.9, 3.6 and 4.1 times, respectively. The obtained results are associated with the loose structure of the membranes observed in Fig. 4, as well as their improved hydrophilicity due to PVP addition [15-17].

The incorporation of Ag/TNTs nanocomposite into the membranes matrix resulted in further improvement of their permeability. Analyzing the PWF values at $\text{TMP} = 3$ bar for M3, M5 and M7 in comparison with M2, M4 and M6 membranes, respectively, an increase of the flux for about 260, 750 and $380 \text{ dm}^3/\text{m}^2\text{h}$ was found. The observed improvement can be attributed to further increase of membranes hydrophilicity due to the presence of hydrophilic nanoparticles. Moreover, the Ag/TNTs can act as additional channels for water transport through the membranes.

The results presented in Fig. 3 revealed that the highest improvement of water permeability was obtained when both Ag/TNTs and PVP were applied. The PWF at $\text{TMP} = 3$ bar reached the values around $2250 \text{ dm}^3/\text{m}^2\text{h}$ for M5 and $2050 \text{ dm}^3/\text{m}^2\text{h}$ for M7 membrane.

4. Conclusions

In this study the polyethersulfone membranes prepared by the wet phase inversion method and modified with Ag/TNTs and PVP were obtained successfully. The physiochemical and transport properties of the membranes were investigated. The changes in the membranes cross-section appearance due to the application of PVP and NPs were noticed. An asymmetric structure of M1 membrane characterized by a dense top layer and narrow finger-like pores was significantly affected by the addition of PVP. The mixed matrix membranes fabricated with application of PVP at the highest concentrations (2.4 and 4.8wt%) exhibited large macrovoids and visible delamination in the bottom part of their cross-sections. The addition of PVP led also to an increase of the membranes thickness. Moreover, the incorporation of PVP improved the dispersion of Ag/TNT agglomerates inside membrane. The highest water permeability was observed for the membrane modified with both Ag/TNTs and PVP at a concentration of 2.5wt%.

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THE STRUCTURE FORMATION FEATURES OF THE ALLOY $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ DURING THE CASTING IN THE METAL MOLD AND THE FOLLOWING HEATING AMORPHOUS INGOTS

ОСОБЕННОСТИ ФОРМИРОВАНИЯ СТРУКТУРЫ СПЛАВА $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ ПРИ ЛИТЬЕ В МЕТАЛЛИЧЕСКУЮ ИЗЛОЖНИЦУ И ПОСЛЕДУЮЩЕМ НАГРЕВЕ АМОРФНЫХ СЛИТКОВ

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Abstract: The structure formation features of the bulk glass alloy $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ under conditions of melt casting in a copper mold and subsequent heating of amorphous ingots, are studied. It is shown that for certain parameters of the model (the thickness of the ingot and its heating rate), the main contribution to the total crystallized volume fraction passes from frozen crystal growth processes to the processes of nucleation and growth of new crystals. Regardless of the dominant crystallization process during heating, amorphous ingots of the $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ alloy are crystallized to form a coarse crystalline structure.

Keywords: MELT CASTING INTO THE MOLD, SOLIDIFICATION, THERMAL CONDITION, CRYSTALLIZATION KINETICS, MICROSTRUCTURE PARAMETERS

1. Introduction

It is known that under conditions of quenching from the melt in the structure of amorphous metal alloys, it is possible to obtain nanoscale crystallization centers. The volume density of such crystals and their average sizes depend on the conditions for the preparation of such materials [1, 2] and determine their final properties, thermal stability and transformation features upon heating [3-5]. In this regard, in this work, the main purpose was to study the features of the formation $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ alloy structure during cooling under conditions of melt casting into a copper mold and during heating amorphous ingots.

2. Method of calculation

Studies were performed using computer simulation methods. In studies, a previously developed model of melts and glasses crystallization [6] was used.

According to the used model, two stages of structure formation were considered. The first stage takes place under conditions of melt cooling in a massive copper mold. At this stage, crystallized the volume fraction x_-^e (in studies chose the thickness of the ingots, which provide the formation x_-^e no more $5 \cdot 10^{-2}$) and in a unit of volume formed N_-^S crystallization centers with average sizes $\bar{R}_-^e$. At the second stage, the processes of crystallization that occur during the heating of amorphous ingots are modeled. It was considered that they are carried out both by the growth of already existing frozen-in crystals, and by homogeneous nucleation and further growth of new crystals. As a result of the frozen crystals growth formed a fraction of the transformed volume x_{-+}^e , which consists of N_-^S crystals with sizes $\bar{R}_{-+}^e$. Simultaneously with the growth of crystals formed as a result of cooling, the processes of nucleation and growth of new crystallization centers occur. The result of this process is the formation N_+^S crystals having a size $\bar{R}_+^e$, which contribute to the total crystallized volume the part of x_+^e . The resulting volume fraction of the crystalline phase, formed at different stages of the process:

$$x_-^e + x_{-+}^e + x_+^e = 1. \quad (1)$$

Calculations x_-^e , x_{-+}^e и x_+^e carried out by the kinetic equations obtained in the approximation of the effective rates of nucleation and growth of crystals [7].

For spherical crystals formed by nucleation and further isotropic growth in a supercooled melt with effective rates, the fraction of the crystallized volume can be determined using the equation:

$$x_-(t_-) = \frac{4}{3} \pi \int_{t_-^m}^{t_-} (1 - x(t'_-)) I(t'_-) \left[R_c(t'_-) + \int_{t'_-}^{t_-} (1 - x(t''_-)) u(t''_-) dt''_- \right]^3 dt'_-, \quad (2)$$

where t_-^m – the melting point temperature T_m at melt cooling; R_c – the critical nucleus radius; t_- , t'_- , t''_- – current times, belonging to the time interval of crystallization $[t_-^m, t_-]$: $t_-^m \leq t'_- \leq t''_- \leq t_- \leq t_-^e$.

A similar kinetic equation was used for the formation of new crystals during the heating of metallic glass:

$$x_+(t_+) = \frac{4}{3} \pi \int_{t_+^b}^{t_+} (1 - x(t'_+)) I(t'_+) \left[R_c(t'_+) + \int_{t'_+}^{t_+} (1 - x(t''_+)) u(t''_+) dt''_+ \right]^3 dt'_+, \quad (3)$$

where $t_+^b \geq t_-^e$ – heating start time; t_+ , t'_+ , t''_+ – current time points corresponding to the heating stage: $t_+^b \leq t'_+ \leq t''_+ \leq t_+ \leq t_+^e$; t_+^e – time of crystallization completion during heating.

The volume fraction of the crystalline phase x_{-+} , which is formed due to the growth of frozen centers, was calculated as follows:

$$x_{-+}(t_+) = 4\pi N_-^S \int_{t_+^b}^{t_+} \bar{R}_{-+}^{-2}(t'_+) [1 - x(t'_+)] u(t'_+) dt'_+. \quad (4)$$

Calculations of the crystallization kinetics under the conditions of melt cooling were performed by a consistent numerical solution of equation (2) with the Fourier heat conduction equations [8] for melt with a half-thickness l_1 and copper mold with wall thickness l_2 using the algorithm described in detail in the work [9]. The calculations were performed by the finite difference method in an implicit scheme [10].

The crystallization processes during heating were modeled, assuming that an amorphous ingot having an initial temperature T_+^b is heated by heat exchange with the working medium, the temperature of which rises linearly with a predetermined velocity v_+ . The part of crystallized volume $x(t_+)$, included in the integrands of the equations (3) and (4), calculated taking into account the relative contributions of all the transformation mechanisms analyzed in the model:

$$x(t_+) = x_-^e + x_{-+}(t_+) + x_+(t_+). \quad (5)$$

3. Results and analysis

Figure 1 shows the results of the calculated analysis of the crystallization kinetics of the alloy $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$, performed using equation (2) for castings with half-thickness ranging from 0,25 to 500 mm. For all values l_1 determined the cooling rate ν_c at melting point T_m , the final value of the crystallized volume fraction x^e , nucleation rate I and growth rate u , as well as structural parameters N_-^s and $\bar{R}^e$, fixed at the end of the cooling process.

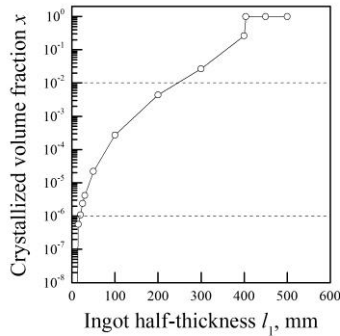


Figure 1 – The calculated dependence of the crystallized volume fraction, obtained during casting of the melt $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ in the copper mold, from the ingot half-thickness.

As the results of calculations show, with an increase in the half-thickness of the ingots under study, the proportion of the crystallized volume fraction during the entire cooling period increases from 10^{-21} ($l_1 \approx 0,25$ mm) to $\sim 0,99$ ($l_1 \geq 404$ mm). It should be noted that the general nature of dependencies $x^e(l_1)$, as well as critical cooling rate values ($\nu_c = 0,97$ K·s⁻¹) and critical half-thickness mold casting ($l_1 = 20$ mm), at which the volume fraction of the crystalline phase becomes 10^{-6} , correlates well with experimental data [11,12]. According to the calculated analysis, in the conditions of melt casting $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ in a copper mold it is possible to obtain a wide range of structural states, for which the density of nuclei of crystals can vary from $6 \cdot 10^5$ to $6,5 \cdot 10^{14}$ m⁻³, and their average sizes are from $1,2 \cdot 10^{-9}$ to $6,9 \cdot 10^{-5}$ m.

Obtaining such a wide range of structural states with different volume density and sizes of crystallization makes it possible to analyze the influence of the thermal history of the alloy on the crystallization kinetics of castings during subsequent heating. For this purpose, different half-thickness castings (0,25 – 300 mm), according to equations (3) and (4), the volume fractions of the crystalline phase were calculated, one of which (x_-^e) formed by nucleation and growth of new crystals in an amorphous matrix, and the second (x_+^e) formed due to the growth of frozen crystals. Calculations were performed for heating rates 0,017, 0,03, 0,7 and 1,67 K·s⁻¹.

As an example, fig. 2 shows the calculated kinetic curves $x_+(t_+)$, $x_-(t_-)$, $x(t)$ for ingots with half-thickness 0,5 mm, 7 mm and 10 mm, heated at rate 0,7 K·s⁻¹. As can be seen, depending on the half-thickness of the ingots, the crystallization mechanisms considered in the model make different contributions to the total crystallized volume fraction x . So when heating ingot with a half-thickness 0,5 mm (fig.2a) crystallization is carried out due to the mechanism of formation of new crystals ($x_-^e \approx 0,97$, $x_+^e \approx 2,2 \cdot 10^{-2}$). However, with increasing casting thickness x_-^e and x_+^e changing to the opposite so when $l_1 = 10$ mm $x_+^e \approx 6,4 \cdot 10^{-2}$, and $x_-^e \approx 0,93$ (fig.2c). In ingots with a half-thickness $l_1 = 7$ mm there is an approximate equality of the volume fractions of the phases formed by different mechanisms: $x_+^e \approx 0,57$, $x_-^e \approx 0,42$ (fig.2b).

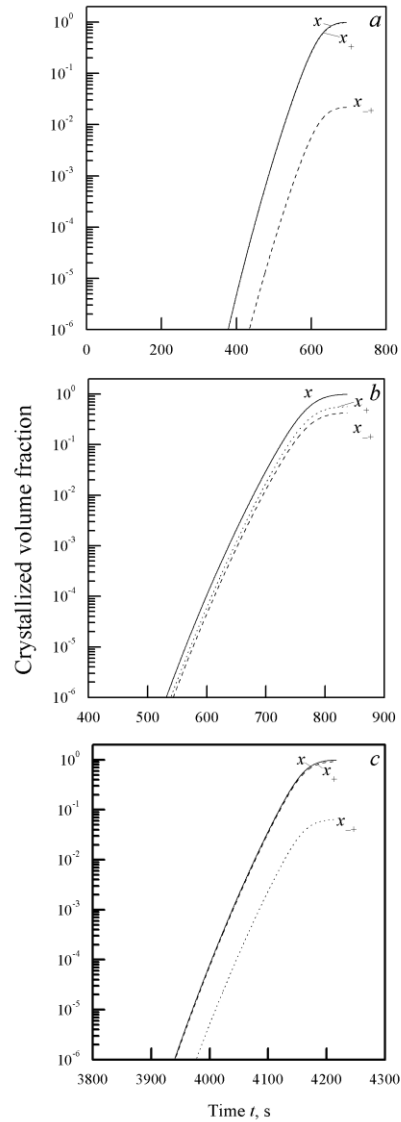


Figure 2 – Dependence of the volume fraction of the crystalline phase on the heating time for amorphous castings $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$ with half-thickness (mm): 0,5 (a), 7 (b), 10 (c), appropriate heating rate $\nu_+ = 0,7$ K·s⁻¹.

With a decrease in the heating rate, the growth processes of quenched nuclei dominate in wider intervals of ingot half-thicknesses l_1 , the half-thicknesses, in which both mechanisms make equal contributions to the total fraction of the crystallized volume, are shifted towards smaller thicknesses (fig. 3).

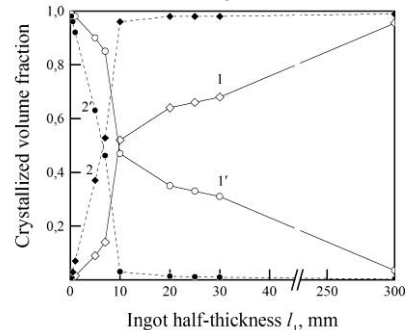


Figure 3 – Calculated dependencies of contributions to the crystallized volume fraction of two competing crystallization mechanisms on the half-thickness of amorphous castings $Zr_{41,2}Ti_{13,8}Cu_{12,5}Ni_{10}Be_{22,5}$, corresponding to the heating rates 0,017 K·s⁻¹ (light symbols) and 1,67 K·s⁻¹ (dark characters): 1, 2 – x_+ ; 1', 2' – x_- .

According to the calculated data, crystallization processes occur during supercooling 100–200 K relative to the melting point. Under these conditions, nucleation processes occur at a rates of 0–10⁷

$\text{m}^{-3}\cdot\text{s}^{-1}$, and the crystal growth rate varies within $\sim 10^{-7}\text{--}10^{-9}\text{ m}\cdot\text{s}^{-1}$. But, despite such low values I and u , due to very long crystallization time intervals ($10^2\text{--}10^5\text{ s}$), during the heating time in a unit of volume crystallize $\sim 10^{11}\text{--}10^{14}\text{ m}^{-3}$ new crystals, the final size of which ($\bar{R}_t^e \sim 10^{-5}\text{ m}$) not inferior to the size of crystals growing from frozen-in crystallization centers. This result of computational analysis confirms the need to take into account the two mechanisms of crystallization of metal glasses.

4. Conclusions

1. Through modeling studies alloy $\text{Zr}_{41,2}\text{Ti}_{13,8}\text{Cu}_{12,5}\text{Ni}_{10}\text{Be}_{22,5}$ It was found that, with an increase in the half-thickness of amorphous ingots and a decrease in the heating rate, the main contribution to the total fraction of the crystallized volume is made by the growth of frozen-in crystallization centers.
2. It has been established that the equal contribution of the growth processes of frozen crystals and the processes of nucleation of new crystallization centers during heating in the range of $\nu_t=0,017\text{--}1,67\text{ K}\cdot\text{s}^{-1}$ observed in castings with a half-thickness from 10 to 6,5 mm.
3. It is shown that upon heating the amorphous alloy ingot $\text{Zr}_{41,2}\text{Ti}_{13,8}\text{Cu}_{12,5}\text{Ni}_{10}\text{Be}_{22,5}$ possible to obtain structures with mean crystal size of 10 μm .

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SYNTHESIS OF THE MAGNETIC ADSORBENT BASED OF GRAPHENE OXIDE AND ZnO NANOPARTICLES FOR ENVIRONMENTAL APPLICATIONS

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Abstract: In this study Fe₃O₄-ZnO and GO-Fe₃O₄-ZnO are synthesized as photocatalysis for decomposition of methyl orange (MO) as organic dye pollutant model. The XRD results show that the prepared nanocomposites contain the modified GO with cubic structure of Fe₃O₄ and hexagonal wurtzite structure of ZnO nanoparticles. The photocatalytic results show that the degradation of MO using both of the synthesized photocatalysts enhances with respect to the time and weight fraction. The removal efficiency of MO using GO-Fe₃O₄-ZnO at each concentration and irradiation time is more than that of Fe₃O₄-ZnO.

Keywords: GRAPHENE OXIDE; Fe₃O₄; ZnO; REMOVAL EFFICIENCY

1. Introduction

The application of different semiconductors as photocatalyst has been widely investigated for elimination of organic pollutants from the wastewater. The importance of the semiconductor photocatalysts such as TiO₂, SnO₂ and ZnO in the environmental purification may be due to the application of them in the ambient conditions [1]. The decomposition of the organic pollutants such as methylene blue (MB) and methyl orange (MO) using semiconductor photocatalysts can be initiated in the presence of a light supply and oxidant acting such as O₂ [2]. Among different kinds of the semiconductor photocatalysts, ZnO nanoparticles are known as more applicable photocatalyst. It can be due to its environmental friendly, wide band gap, inexpensive and chemical stability[3]. The illumination of the photocatalysts leads to the production of the electron and hole in the valence band and conduction band, respectively [4, 5].

The produced electron hole pairs (h⁺ - e⁻) in the dye organic solution can spread on the surface of the semiconductors and contribute into the reaction between organic pollutants and donor and acceptor of electron [6]. Because of this reaction, the different kinds of the oxidant species such as hydroxyl radicals are produce. Therefore, the surface enhancement of the photocatalysts can be effective in the separation of the generated electron hole pairs and degradation of the dye pollutants. Graphene is one of the carbon materials that have been great deal of interests due to the excellent properties such as electronic properties and high specific surface area. Thus, the presence of the graphene oxide (GO, containing functional groups such as hydroxyl and carboxyl) in the magnetic photocatalysts matrix can enhance the active surface area of the photocatalysts.

2. Experimental

2.1. Materials

For the synthesis of GO-Fe₃O₄, 45 mg of GO is dispersed into 45 ml of Ethylene glycol and agitated for about 30 min. Then, 0.225 g of Fe(acac)₃ is dispersed to the suspension and mixed for about 30 min using an ultrasound bath at room temperature. Subsequently, 1.5 g NH₄Ac is dissolved in the solution, followed by stirring for 30 min. Then, the obtained mixture is transferred into a 100 ml Teflon lined autoclave. The autoclave is sealed and kept at 200°C for 24 h. Afterward the autoclave is cooled to ambient temperature. The synthesized products are separated from the suspension using an external magnetic field. Finally, the separated powders are washed several times with distilled water and dried at 60°C for 12 h. For the synthesis of ZnO nanoparticles, 0.5 g of ZnCl₂ is dispersed in a suspension containing 0.1g of GO-Fe₃O₄. After increasing the temperature to 90°C, 5.3 ml of aqueous solution of NaOH (5 M) is added drop wise under vigorous agitation. Subsequently, the precipitated powder is separated from suspension, washed several times with distilled water and dried at 80°C for 12 h. Finally, the dried powder is calcined at 300°C for about 3 h.

The photocatalytic measurements are carried out for degradation of MO (10 ppm MO aqueous solution) using a Hg vapor lamp (150 W) at different concentration of synthesized photocatalysts (0.1, 0.2 and 0.3 %wt). The concentration of MO at any intervals can be calculated according to the Equation 1[7].

$$\text{Photocatalytic performance (\%)} = \frac{A_0 - A_t}{A_0} \times 100 = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

The A and C refer to the absorbance and concentration of MO. The subscript of 0 and t refer to the initial and remainder parameter.

3. Results and discussion

In the XRD pattern of the synthesized GO-Fe₃O₄-ZnO (Fig. 1), the presence peaks at $2\theta = 30.21^\circ$, 35.27° , 56.81° and 62.45° are assigned to the (220), (311), (511) and (440) reflections, respectively. The mentioned peaks are in agreement with the XRD pattern of Fe₃O₄ nanoparticles with a cubic structure. Meanwhile, the characteristic peak of GO can be observed at 2θ value of 10.75° . In addition to the mentioned peaks, several peaks are centered at 2θ values of 31.65° , 34.3° , 36.2° , 47.4° , 56.5° and 62.7° are assigned to the ZnO nanoparticles with the hexagonal wurtzite structure.

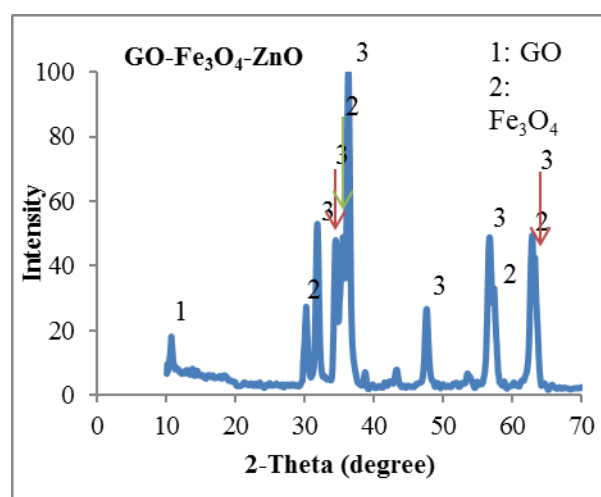


Fig. 1. XRD pattern of the synthesized GO-Fe₃O₄-ZnO.

Fig. 2 and Fig. 3 show the variation of the removal efficiency of MO using Fe₃O₄-ZnO and GO-Fe₃O₄-ZnO, respectively. As can be seen, the removal efficiency of MO using both of the synthesized photocatalysts enhance with respect to the irradiation time and weight fraction of the applied photocatalyst. The enhancement of the removal efficiency of MO with respect to the irradiation time can be attributed to the production the large amount of excited electrons[8]. The variation of the removal efficiency of MO with

weight fraction of $\text{Fe}_3\text{O}_4\text{-ZnO}$ and $\text{GO-Fe}_3\text{O}_4\text{-ZnO}$ in the range of 0.1 %wt to 0.3 %wt reveals that the removal percentage of MO enhances by increasing the concentration of $\text{Fe}_3\text{O}_4\text{-ZnO}$ and $\text{GO-Fe}_3\text{O}_4\text{-ZnO}$. It may be due to the enhancement of active sites of photocatalysts that are exposed to MO [9].

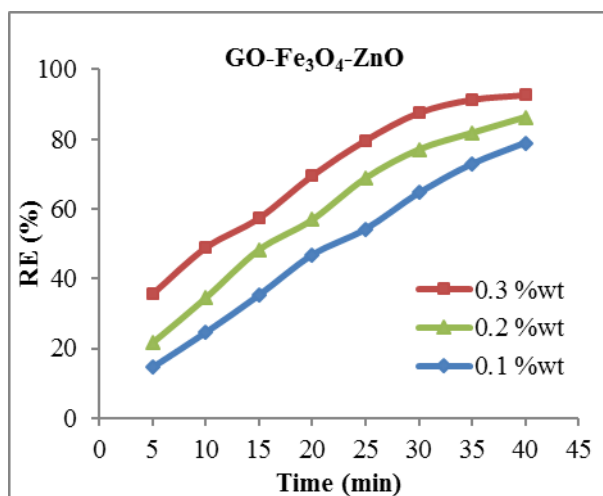


Fig. 2. Removal efficiency variation of MO using $\text{Fe}_3\text{O}_4\text{-ZnO}$, influence of weight fraction.

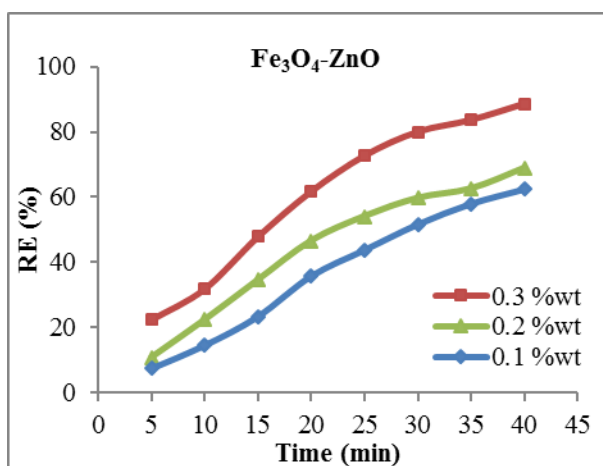


Fig. 3. Removal efficiency variation of MO using $\text{GO-Fe}_3\text{O}_4\text{-ZnO}$, influence of weight fraction.

The comparison between removal efficiency of MO using $\text{Fe}_3\text{O}_4\text{-ZnO}$ and $\text{GO-Fe}_3\text{O}_4\text{-ZnO}$ is presented in Fig. 4. Based on this Figure, it can be seen that at concentration equal to 0.2 %wt and each interval of irradiation time, the removal efficiency of MO using $\text{GO-Fe}_3\text{O}_4\text{-ZnO}$ is higher than that of $\text{Fe}_3\text{O}_4\text{-ZnO}$ (the same results are obtained at the other concentrations). The higher photocatalytic activity of the synthesized $\text{GO-Fe}_3\text{O}_4\text{-ZnO}$ is related to the presence of GO in the matrix of the photocatalyst. The produce electron-hole pairs in $\text{Fe}_3\text{O}_4\text{-ZnO}$ are not stable and can be recombined and produce heat. It can decrease the photocatalytic performance of $\text{Fe}_3\text{O}_4\text{-ZnO}$. However, the presence of GO in the matrix of $\text{GO-Fe}_3\text{O}_4\text{-ZnO}$ reduces the rate of electron-hole pairs recombination.

4. Conclusions

Here, we applied magnetics adsorbents for degradation of MO. The synthesized adsorbents are characterized using XRD and the results confirm that ZnO nanoparticles and Fe_3O_4 nanoparticles are synthesized successfully on the GO sheets. The photocatalytic results reveals that irradiation time and weight fraction have a significant effect on the decomposition of MO. Meanwhile, the presence of GO in the structure of $\text{Fe}_3\text{O}_4\text{-ZnO}$ leads to the enhancemet of removal efficiency of Mo.

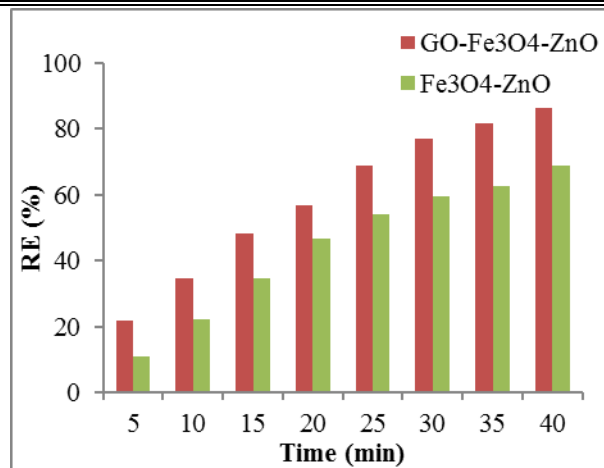


Fig. 4. Comparison between removal efficiency of MO using $\text{Fe}_3\text{O}_4\text{-ZnO}$ and $\text{GO-Fe}_3\text{O}_4\text{-ZnO}$ at 0.2 %wt.

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FORMATION OF PRINCIPLES OF INVESTMENT STRATEGY OF INDUSTRIAL ENTERPRISES

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Annotation. *The types of entrepreneurial activity and form of enterprises are investigational. Described business system and her elements. Sequence of executions and in accordance with principles which provide the acceptance of effective administrative decisions aimed at realization of investment strategy of industrial enterprises is offered. Tasks which must be the strategies of industrial enterprise taken into account in the process of choice are certain. The stages of life cycle of industrial enterprises are set from the period of "birth" to the period of "expansion". Expediency of different forms of strategy of diversification of investment activity of industrial enterprises is reasonable.*

KEYWORDS. *Forms, strategy, diversification, investment activity, task, life cycle, stages, decisions, systems, principles.*

Results. A business system being an economic system has such elements: entrepreneurial business; state business; consumer business.

The subjects of entrepreneurial business are businessmen - legal entities and individuals- who are interested in getting income through production and selling, fulfilling work and delivering services.

The types of entrepreneurial activity depend on the forms of ownership and organization.

There are different organizational forms of enterprise: state, rent, individual, private, domestic, different societies, and joint ventures. There are big, medium, and small companies. The companies differ in their relation to property. The functions of a businessman and an owner are separated at a large enterprise; that means that the capital function is separated from the capital owner. The functions of the owner and the businessman coincide at the small company. The middle business is on border of the large and the small enterprise and combines the features of the first and the second one [1, p.13].

The combination of such types of enterprises creates market environment, in which every businessman occupies the niche, finds the place and solves the management problems considering the criteria of production efficiency, own interest, and commercial success.

A small enterprise is accessible to population. Small business must be encouraged by the state for strengthening entrepreneurial environment. Development of small business creates bigger employment opportunities and is the main "supplier" of workplaces for the state.

Entrepreneurial business is subdivided also into production, commercial and financial.

Production business is the production, consumption of commodities and services and is represented by enterprises, firms, establishments.

Commercial business is the exchange, distribution and consumption of commodities through trade establishments and exchanges.

Financial business is circulation and exchange of costs through banks and stock exchanges.

State business is carried out by state bodies; that means they enter the market with business propositions. State business interest is providing the priority of national scientific and technical, production, and other objectives which satisfy interests of national economy. The state encourages firms participating in these programs, to provide their performance. The basis of state business is national property on capital goods, information, money resources, and securities.

Consumer business is carried out by public with the aim of getting commodities and services by the independent selection of producers and salespeople on the basis of maximal benefit. For the consumers of commodities a benefit is a commodity (favour) which satisfies their needs the best way. The basis of such business is the property for consumer goods and services.

Business strategy is maximization of benefit (profit, income) in the process of realization of various agreements. This

strategy is realized depending on a definite case considering the terms of realization, period and subject of an agreement [2, p.77].

An entrepreneurial environment is a complex of external terms and strengths, which effect the opportunities and results of entrepreneurial activity of subjects of market relations. It is divided into external and internal environment.

External environment is foremost legislative and regulative bases, competition, market infrastructure, stimuli, and features of economic development of the state, socio-political terms and so on [3, p.94].

Internal environment is the presence of outset capital, the system of doing business (marketing, management).

Entrepreneurial environment can be favourable, or unfavourable. The level of favourableness of entrepreneurial environment depends on the following factors:

- property rights of a businessman to capital goods, product and incomes;
- certain rights and freedoms, choice of type of economic activity;
- favourable psychological climate;
- the level of market competition development;
- the reliability of protection of a businessman rights;
- the state support [4, p.15].

An unfavourable environment is the absence of the above-mentioned conditions. Partially favourable environment exists in the case of instability of economy and society. Entrepreneurial environment constantly changes due to various cyclical and not cyclical factors

Cyclical factors are divided into evolutionary and wave, and not cyclical – into constantly operating and not constantly operating.

Evolutional factors are irreversible factors which in the absence of other influences operate in a certain direction (for example, the tendency of increase of population, increase of general production).

Wave factors change an entrepreneurial environment in the different intervals of time with an identical or similar conditions (for example, labour productivity, price, interests on a capital, rate of unemployment and so on).

Constantly operating not cyclical factors signify the change of level of economic development, scientific and technical progress, monopolization, government control, militarization of economy, competition. Inconstantly operating non-cyclical factors are seasonal fluctuations, social conflicts, political crises, calamities.

The driving force of business development is the needs and personal economic interest which is the basis of needs.

Business development is impossible without corresponding operating conditions. They provide a legislative and normative base, competition environment, market infrastructure and stimuli of entrepreneurial activity.

The methodological basis of business is a theory of market management.

A market is a form of economy functioning, and a market mechanism is an important regulator of economic development.

Functioning of market mechanism has some conditions, which allow to make important conclusions about the character, type and level of organization of market:

- independence and freedom of action of businesses;
- an opportunity to independently place an order and to freely dispose of own incomes;
- responsibility for the use of resources, for possible losses and ineffective decisions;
- the opportunity of mutual choice of partners at the market;
- competition as a result of sufficient amount of producers and consumers of commodities.

Forming of enterprise environment and effective market mechanism need taking the following measures: denationalization and privatization; reformation of financial, credit money system and pricing; demonopolization of economy; creation of the effective system of population protection.

Forming of market environment presupposes the encouragement of such activity by tax deductions, direct state grants, financing of important innovative projects [5, 69].

The specification of investment strategy according to the periods of its realization means sequencing the terms of achievement of definite goals and strategic tasks. In the process of this specification external and internal synchronization in time is provided. External synchronization means synchronization of the investment strategy with the general strategy of economic development of a corporate structure, and also with the forecast changes of the investment market. Internal synchronization means synchronization of separate directions of investing, as well as synchronization with forming the necessary investment resources.

The last stage is the estimation of the developed investment strategy and its correspondence to the principles of the investment strategy forming.

The basis of the process of the choice of strategic directions of investment activity is the aims of this activity. The following tasks must be taken into account in the process of choice:

- 1) determination of correlation of different forms of investing on the definite stages of the considered period;
- 2) determination of branch orientation of investment activity;
- 3) determination of regional orientation of investment activity.

Correlation of different forms of investing on the definite stages is related to directions of activity of a corporate structure.

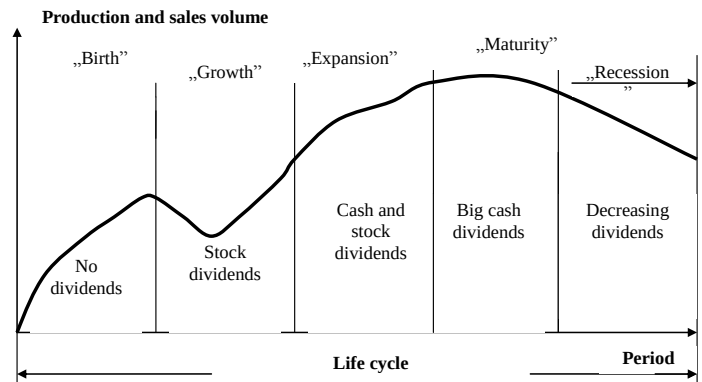
Institutional investors carry out the investment activity mainly at the stock market. Thus the main form of a long-term investment activity is investing in stocks, bonds, saving certificates and other financial instruments. Real investing in such structures can fluctuate within the limits set by norms and regulations developed for each of the group of investors.

Production corporate structures have real investments as the basic form of investing. This form of investing allows such structures to develop in the highest pace, to master new products, to penetrate into new commodity and regional markets. Financial investments of such structures are short-term investments of temporally free money carried out with the purpose of instituting control (or influence) over the activity of definite companies (partners, competitors and so on).

Solving this task substantially depends on the stages of life cycle of a corporate structure (Picture 1). On the stages of "birth" and "growth" most part of investments is the real, on the stage of "expansion" the real investments (capital and circulating capital) prevail as well; and only on the later stages of the life cycle ("maturity") corporate structures can increase the share of financial investments. In order to avoid the period of "recession" and prolong the period of "maturity", it is necessary to diversify the activity of the corporation; that means to give up those directions of activity, which do not bring income, and to develop new directions of activity, which bring income.

Besides the basic directions of production or financial activity many corporate structures (holdings, financial industrial groups, multinational corporations) buy publishing organizations, TV and radio companies, participate in show business as sponsors or direct shareholders, organize tour operators and so on.

The business timely diversified allows to avoid the period of "recession" of a corporate structure. Instead the duty stage of the life cycle of a corporation starts but not from the period of "birth", but from the period of "expansion".



Picture 1 Character of stages of the life cycle of a corporation

Note: Created by the author on the basis of [6, p. 120]

There is a correlation between forms of investing and the size of a corporate structure. Investment activity of small and medium size structures is related to the real investments, when large corporations perform mostly financial investments. The general economic situation which determines the situation at investment market influences the correlation of the real and financial investments. When the economy is unstable, the inflation is high, permanent change of tax rates takes place the efficiency of the real investing is low and the investment risks are high. Financial investments especially short-term are more effective in such periods (on condition that the profitability of these investments exceeds inflation rates).

Taking into account these terms of estimation of different forms of investing differentiate according to the separate stages of investment activity of a corporate structure.

The experience of investment activity of the corporate systems in the second half 1990s shows that a branch orientation is the most difficult task of the investment strategy development. This decision requires the stage-by-stage approach to forecasting the investment activity together with the general strategy of economic development of a corporate structure. On the first stage the expediency of two basic strategic directions of investment activity is investigated: Branch concentration. Investment activity diversification.

As a rule, the initial stages of activity of a corporate structure are related to its concentration on the industry which is most familiar to investors.

The review of the western practice shows that many of the most successful investors attained the high level of welfare using the strategy of concentration that is staying within the diversified activity. Especially bright examples are provided by the production of separate types of technological products (computer technique, computer software and so on) or products that meet the needs of a larger circle of consumers. At the same time there is the biggest amount of bankruptcies among investors which use this strategy. It is determined by the fact that the concentration is connected with the higher level of investment risks, than can be afforded by most investors.

The strategy of branch concentration (if chosen by an investor regardless the high level of risk) can be used only on the first three stages of the life cycle of a corporate structure, because under favourable circumstances it provides the highest rates of

production development of capital increase. On the next stages of the life cycle as the demand satisfaction in the products is reached the strategy of branch diversification of the investment activity is to be developed.

On the second stage the expediency of different forms of branch diversification of the investment activity is investigated within the framework of a certain group of industries, for example, of agricultural industry, food industry, transport and so on. Such branch diversification allows an investor to use the accumulated experience in the field of marketing, production technologies and so on and to determine the efficiency of investment. In addition, the use of branch diversification even within these limits allows to substantially reduce the level of investment risks.

The diversification of investment activity of a corporate structure within the certain group of industries is connected with forming the so-called "strategic areas of business". Such formation is carried out in the process of the development of the general strategy of economic development of a structure and is an independent economic segment, which carries out the activity in a number of contiguous industries, united by consumer demand, raw material or technology. The strategic area of business is responsible for the development of the list of competitive products, effective sale strategy, and also providing the investment strategy.

At the same time, such strategy of investment activity has some drawbacks. The basic is the fact that contiguous industries have similar in time branch life cycle within their group. This increases investment risk, especially in traditional industries of economy. In addition, the products of such industries are effected by identical cycles, that increase investment risk in certain unfavourable periods. Therefore the use of the strategy of diversification of investment activity within the certain group of industries is effective only at the favourable prognosis at corresponding commodity markets.

On the third stage the expediency of sharp forms of diversification of investment activity is investigated from the point of view of different, unconnected with each other groups of industries. The necessity of use of such strategy is determined by the fact that for many large and medium size companies which perform for a long period, the traditionally chosen industries (separate or within the certain groups) slow down the rates of perspective development, high yield from investments, and sometimes cause strategic vulnerability in competitive activity. The condition of such diversification of investment activity, as the analysis shows, is forming "the strategic economic centres".

Conclusions. A strategic economic centre is an independent structural unit of CS, which includes a few strategic areas of business (the system of such strategic economic centres was first realized at the American firm "General electric", that allowed the company to considerably increase the efficiency of the investment and economic activity). A strategic economic centre fully develops the investment strategy which is an independent element of investment strategy of a corporation. Due to the choice of industries with the different stages of the life cycle and with the different fluctuations periods the level of investment risks substantially goes down.

Diversification of the investment activity, carried out in the process of the second and third stages of the investment strategy development, is carried out considering the forecast estimations of development of separate industries (or groups of industries).

Regional orientation of investment activity when developing the corresponding strategy of CS is determined by two basic factors: the size of corporate structure; performance period.

Most of medium size firms and considerable part of small firms carry out the activity within the limits of the region of investors' residency. For such firms the opportunity of regional diversification of investment activity (especially real investments) is limited due to the insufficient volume of investment resources and substantial complication of the investment and economic activity management. The fundamental opportunity of regional diversification is possible only for financial investments, however their volume is small; that is why investment decisions can be made

not within the developed strategy but when developing the investment portfolio (that is on the stage of investment activity tactical management).

The second factor which determines the necessity of such development is the corporate systems performance period. On the first stages of its life cycle the economic and investment activity is concentrated, as a rule, within one region, and only with further development of CS there come a need in regional diversification of the investment activity.

The basis of development of regional investment activity is the estimation of investment attractiveness of different regions. Due to stability of many regional development factors the results of estimation of investment attractiveness of regions usually is not subject to dramatic changes and can be used for development of investment strategy.

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RESEARCH AND JUSTIFICATION OF THE POSSIBILITIES, RELEVANCE AND CORRECTNESS OF THE MONITORING AND CORRECTION OF THE STRATEGY, DIAGNOSIS OF THE PROSPECTS OF ITS FURTHER USE ON INDUSTRIAL ENTERPRISES

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Annotation. It is established that the main activities include: exercising control over the rational use of resources; reducing the cost of using and maintaining outdated equipment; increasing of production capacity; upgrading of equipment; improvement of production technology; production of unique products and improvement of their quality; diversification; automation of the production process by eliminating manual labor; reduction of pollutant emissions, search for new sources of raw materials; rational use of working capital and fixed assets. It is noted that marketing directions in the process of monitoring and adjusting the strategy, diagnostics and finding prospects for its further use include a set of actions concerning: exploring new markets for products; use of discount system for goods and services; application of modern pricing methods; product updates; production of new products according to existing orders; new methods of product promotion; improving customer service. The financial directions in the process of monitoring and adjusting the strategy, diagnostics and finding prospects for its further use are determined, they are aimed at providing the process of development and implementation of the IA strategy with sufficient financial resources, correlation of the planned effect with the achieved, estimation of the amount of expenses for carrying out research works, development technologies, their introduction into production, production of new products, its supply, search for consumers. The justified use of financial directions in the process of monitoring and adjusting the strategy, diagnostics and finding prospects for its further use allows to create some methods of protection from risks impact, to improve financial activity of the enterprise, to rise the effectiveness of IA organization, to increase sales volumes.. The factors of influence on the development of innovation strategy and the development of innovation activity of industrial enterprises are suggested.

KEYWORDS. STRATEGY, INNOVATION ACTIVITY, MONITORING, IMPLEMENTATION PROCESS, REGULATION, FACTORS OF INFLUENCE, DEVELOPMENT, FACTORS.

Formulation of the problem. Important role in the development of the IA strategy is played by motivational actions aimed at creating a friendly atmosphere in the team, using social programs, improving working conditions, increasing the interest of staff in the production of products with new properties, improving their well-being and productivity, rational distribution of responsibilities, increasing qualifications, exchange of experience with innovative developed enterprises.

Results. Analytical actions include the subsystem of collection, processing and analysis of information, the subsystem of risk assessment, the subsystem of diagnostics. The use of these subsystems allows to receive timely information, respond to changes in the regulatory framework, determine the list of risks, predict the outcome of the strategy, adjust the process of strategy development.

Regulatory actions should be considered as a set of measures for the legislative regulation of enterprise IA and they include: internal documents of the company, which are aimed at regulating the IA; regulations, state provisions that form innovation potential and on the basis of which business entities develop an IA strategy; state IA development programs.

Before deciding on the implementation of the IA strategy, a study of the resource base, the level of competition and the investment potential at the sixth stage is carried out. These studies are necessary to clarify the possibility of obtaining financial, innovative, social effects from the implementation of IEIS. Accordingly, obtaining the desired result is possible if there are sufficient resources available, risk assessment, forecasting the advantages and disadvantages of implementing the strategy, the ability to use the available potential.

Implementation of the Industrial Enterprise Innovation System (IEIS) occurs when the expected benefits are significant, there are prospects for the use of innovative ideas and the outcome of using the chosen strategy will be higher than that of other strategies. At the seventh stage, the existing IA strategy is used and its compliance with the established criteria is established. It is also possible at this stage to adjust the strategy according to the variability of environmental factors and the needs of the enterprise. The process of developing an IA strategy must meet a number of criteria defined by the subjects of the strategy and include: a time parameter, that is, the use of the strategy is long-term, but the process of strategy development and implementation must have time limits; nature of risk - the need to reduce the impact of risk on

strategy use; production of new products; investment character - the need to attract investment as a basis for implementing IA; long-term success, that is, the value of success from strategy implementation; the cost of strategy implementation; advantages and disadvantages of the chosen type of strategy, validity of the strategy choice; its social nature, i.e. improving the well-being of employees; degree of researches, frequency of use of innovations; the cost of the strategy chosen and the quality of information on strategy selection; readiness of the enterprise for the implementation of the strategy, availability of resources, technologies.

Monitoring the process of strategy implementation, that is, control over the implementation of each stage of the development of IEIS, adherence to the sequence of actions and determines the level of achievement of goals, effectiveness of the strategy. At this stage, there is an opportunity to minimize the risks that affect the implementation of the chosen strategy. Note that the effectiveness of the IEI strategy is being evaluated. Carrying out the evaluation of the strategy's effectiveness includes the following actions: alignment of the IA strategy with the overall strategy, i.e. defining the targets, objectives, goals; interaction of the IA strategy with the external environment; sufficiency of resource provision; completeness of the goals of the activity; assessment of the existing level of risk; analysis of the sequence of development and efficiency.

At the last stage, the results of the use of the IAE strategy determine the financial status of the enterprise, set changes in its development, compare the results of economic, innovation, investment, production activities before the implementation of the strategy and after its use, assesses the prospects for operation. On the basis of the analysis, a decision is made regarding the possibility of extending the term of the IA strategy at the enterprise.

The generated IA strategy must meet the following requirements: resource supply, acceptable level of risk; taking into account the effect of external factors; long-term nature; the consistency of the established goals and objectives; the time period for using the strategy; the sequence of actions. The development of an IAE strategy is a complex process, which is explained by the variability of the external and internal environmental factors, the complexity of predicting the results of the IA, the need to make adjustments to the strategy, since the development of industrial enterprises is also changing [1, p. 28-29; 2, p. 68-74]. Thus, the use of IA strategy in industrial enterprises will achieve the following results: production automation; introduction of technologies;

attraction of investments; conservation of resource potential; reduction of waste emissions; raising wages; coverage of new markets; production of new products; reducing the number of risks. Considering the improved IA strategy, it is necessary to analyze in more detail the factors influencing the process of its development and implementation. Exactly the factors of external and internal environment depends on the correct development of IA strategy and the ability to obtain the desired result and, as a result, the efficiency of the enterprise, the development of methods of protection against the effects of threats and risks [3, p. 74-75].

In the writings of Semeniuk O.M. [4, p. 221-222] factors of influence on the development of enterprise IA are considered in detail. In particular, the following factors were analyzed: financing of innovative development; credit system of the country; security of investment resources; information support; organization of marketing work; productivity of staff; the level of competition; production process; the effectiveness of the motivational system; relations with partners; directions of activity of the enterprise. In our opinion, taking into account the above group of factors in the development of the strategy will contribute to the effective development of the enterprise, the introduction of innovations, the improvement of innovation activity.

Another author Chernobai L. [5, p. 32] examined the factors of influence on the renewal of the IA of industrial enterprises, among which identified: macroeconomic; microeconomic. The

macroeconomic group includes the activities of regional and state authorities, the regulation of IA, the existence of effective legislative acts. Among the microeconomic factors were highlighted: low level of consumer awareness of innovative products, uncertain demand for new products, outdated and energy-intensive equipment, high level of equipment wear and tear, reduction in the proportion of skilled workers. The factors analyzed influence the development of the IA and, accordingly, the process of strategy development, since without considering these factors the effectiveness of the IA strategy may be low.

Bezus A.M., Bezus P.I. [6, p. 63-67] in their study suggested the factors of influence on the implementation of the innovation strategy and identified the factor of external environment (economic, scientific, technical, state-legal, natural-resource, socio-political) and internal environment (Fig. 1). The economic factors include the development of the state, inflationary processes, employment of the population, the fullness of the country's budget, investment development, and the reduction of skills of workers. The scientific and technical factors are: carrying out research works; innovative developments at the international level; conducting research at regional and national levels; financing of innovative development. State-legal factors included: tax burden and simplified taxation system; preferential lending; development of state innovation programs; regulatory and legal regulation

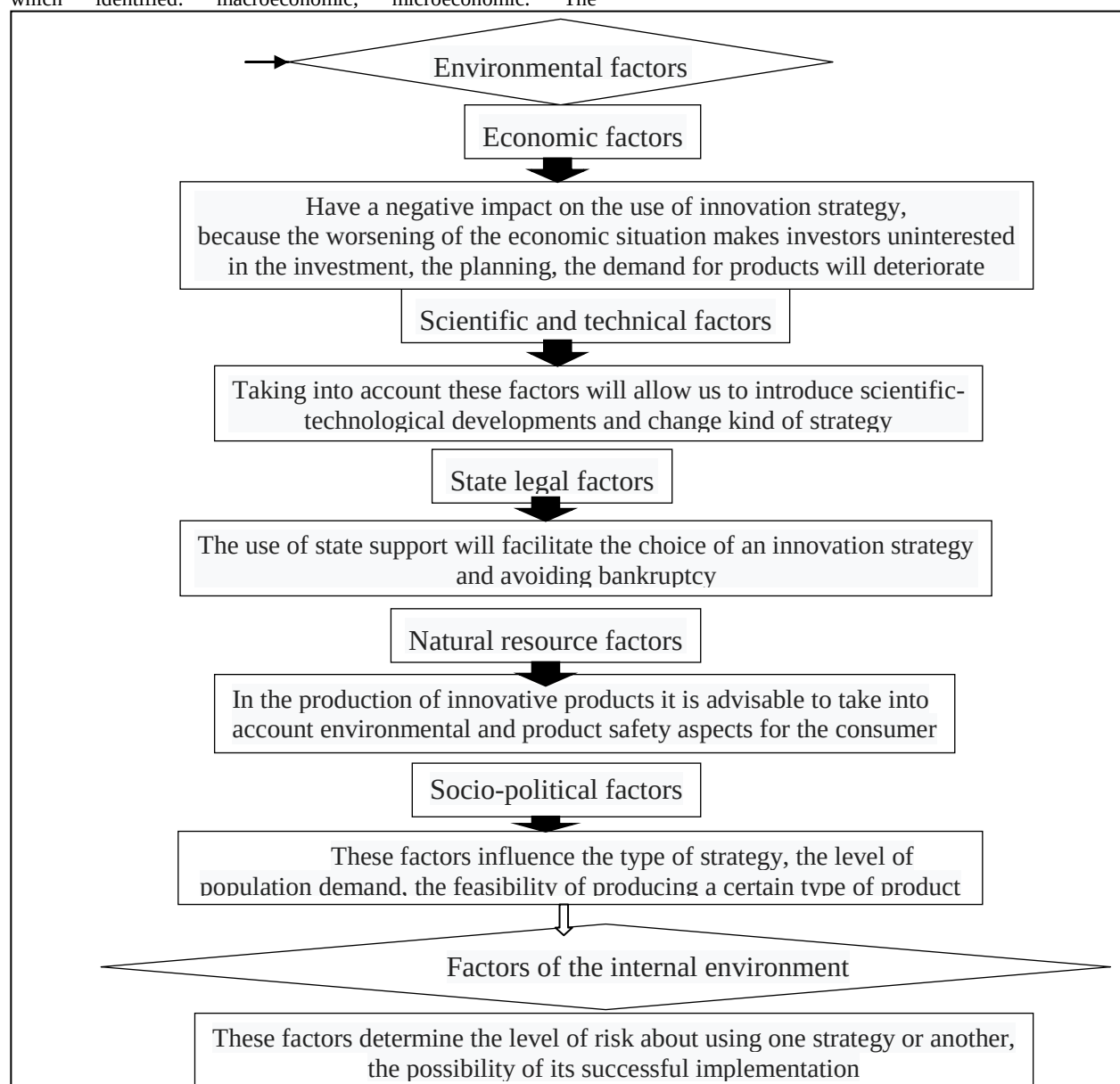


Fig. 1. Factors influencing the development of enterprise innovation strategy
Note: Created by the author on the basis of [6, p. 63-67]

Natural-resource factors are the geographical location of the enterprise, favorable climatic conditions, and the level of environmental safety in the region. Socio-political factors include: aggravation of conflicts in the country; instability of the political situation; the level of minimum wage of the population; consumer needs; productivity; attitude of staff to work. The main factors of the internal environment are: the task of the enterprise; the effectiveness of the overall strategy; the level of competitiveness; timing of tasks; covered markets; company image; availability of resources; information environment; security of technology; production process; the level of innovative development. Taking into account the analyzed group of factors will allow developing an effective innovation strategy, to skillfully use it in the activity of the enterprise, to avoid unforeseen threats in the implementation of the strategy, to bring the organization to a new level of development.

It should be noted that Zakharkin O.O. [7, p. 277-279] analyzed a group of factors influencing the debugging of IA, which included: endogenous; exogenous. Exogenous factors were understood as: ineffective regulation of innovation, lack of mechanism for protection of intellectual rights, incentives for the development of IA; instability of the political situation; low level of financial support from the state. The group of endogenous factors include: equipment wear; centralization of power, inefficient business organization, limited access to information; lack of incentives for IA; reduction of skilled workers. In order to neutralize the influence of the group of factors described above, it is necessary to develop measures to stimulate innovative development, update the technological base, and introduce into the production of innovations.

Verminska O.M. [8, p. 194] carried out a thorough analysis of the factors influencing the process of innovation implementation and IA development. The main factors of influence were: price, i.e. the opportunity to finance innovation, research, the amount of spending on IA; information - availability of information, qualification of staff; market - search for new markets for products, demand for goods, competition; the innovative downturn is the

reduction in demand for products, the absence of the need to produce a new product. Note that the definition of the analyzed group of factors in the implementation of IA is appropriate, and should be taken into account when developing an IA strategy.

Tiutchenko Iu.Iu. [9, p. 122-124] proposed a group of factors influencing the development of IA and divided them into two groups: factors aimed at improving IA; factors that impede the development of IA. These groups of factors include technical, economic, organizational, managerial, legal, socio-psychological factors, but for each group the values of the selected factors will be different. Thus, the factors that contribute to IA will be characterized by: availability of reserves for financing innovation, sufficient competition, state support; preferential taxation system, effective legislation; creation of innovative programs, independence of enterprises, international cooperation; motivational activities, productivity, interest in technology development. The opposite is the case with the factors that impede IA: the ineffectiveness of the legislative framework; lack of proper working conditions; deterioration of the country's innovation potential, insufficient financial resources, lack of information; short-term nature of the activity, lack of relationships with partners, centralization of power. Note that the development of enterprise IA depends on the policy of the state, which will contribute to the development of an effective strategy of IA, improvement of innovative development, indicators of financial activity.

Krush N.P. [10, p. 63] adhered to a similar opinion and suggested factors of influence on the development of the innovative strategy of the enterprise, to which he referred (Fig. 2): demand for products (political, social, environmental, climate); state regulation (control of activity of enterprises, regulation of IA, legal basis); factors that depend on the functioning of the enterprise (production organization, financial support, technological). It should be noted that every enterprise has peculiarities of functioning for it, and when developing an IAE strategy it is necessary to take into account the factors of influence, which will allow improving the process of planning, regulation, control and adjustment of the strategy.

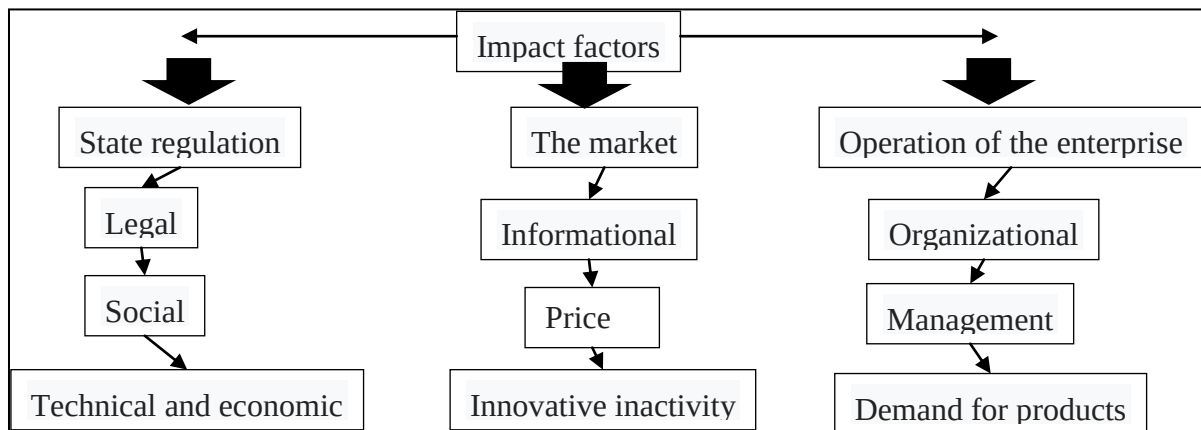


Fig. 2. Factors influencing the development of innovation

Note: Created by the author on the basis of [10, p. 63; 11, p. 84-86; 12, p. 49-50; 8, p. 194; 9, p. 122-124].

Conclusions. According to the results of the analysis, it can be noted that the set of analyzed factors should be taken into account in the development of improved IEIS, which is appropriate for the correct formation of stages of the strategy, justification of its feasibility, exploring the capabilities of the enterprise, reducing the number of risks for the implementation of innovation strategy, diagnostics of prospects for its further use.

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TWO-STAGE SINTERING INVESTIGATION OF Ti-Zr-Nb BIOMEDICAL ALLOYS

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Abstract: Biomedical alloys 19Ti-59Zr-22Nb and 40 Ti-35Zr-25Nb were produced by blended elemental powder metallurgy approach using TiH_2 , ZrH_2 and Nb powders. Usage of hydrogen as temporary alloying element for titanium and zirconium leads to activated sintering and decreased residual porosity of the alloys produced. Contrary, large amount of Nb powder negatively affects sintering and 6-9% residual porosity is observed in sintered alloys. Two-stage sintering (TSS) approach which includes preliminary sintering of powder blends, hydrogenation of sintered products, crushed in powder and sintering again, was used to obtain uniform alloys with reduced porosity. Volume changes of sintering of noted powder blends and prealloyed powders were investigated together with microstructure of sintered materials. Using prealloyed hydrogenated powders in TSS process resulted in activated densification, improved homogeneity of alloy microstructures and low (~2%) residual porosity.

Keywords: BIOMEDICAL ALLOYS, TWO-STAGE SINTERING, MICROSTRUCTURE, POWDERS.

Introduction

Titanium and Ti-based alloys are widely used for biomedical applications due to its promising mechanical properties and non-toxicity [1-2]. A number of biocompatible titanium-based alloying systems were developed to achieve microstructure, phase composition and mechanical properties desirable for medical applications [3].

Alloys based on titanium, niobium and zirconium are popular in some biomedical applications such as orthodontic arch wires, bone plates and stents due to their high corrosion resistance and sufficient strength and elasticity [4-11]. Alloying of titanium with zirconium provides improvement of the mechanical properties of the material [12], including high strength, as well as good corrosion resistance and biocompatibility [12, 13]. One of the main requirements for medical implant materials is their low Young's modulus close to the corresponding parameter of human bone (30 GPa) to avoid stress shielding effect [14-16]. It was shown [17], that additions of sufficient amount of β -stabilizer Nb to Ti-Zr alloys causes decrease of Young's modulus to 50-60 GPa owing to formation of β -BCC Ti-Zr-Nb phase [18-22].

The powder metallurgy (PM) manufacturing approach has significant advantages over ingot metallurgy one for various alloys, giving opportunities for smaller grain size, improved chemical and structure uniformity, economical efficiency and creation of controlled porosity which in some cases is desirable for medical implants.

It was shown [23-24] that alloys based on Ti-Zr-Nb system can be produced by press-and-sinter blended elemental powder metallurgy using blends of titanium hydride, zirconium hydride and niobium powders. In this approach hydrogen was used as temporary alloying element for titanium and zirconium that causes the sintering activation, reduction of residual porosity and decrease in oxygen content in the final material. However, despite positive influence of hydrogen on alloy manufacturing process, the residual porosity of Ti-Zr-Nb materials could not be reduced below 5-8% [25] thus leading to degradation of mechanical properties [22]. It was established [26] that niobium powder addition causes increased as-sintered porosity while relatively slow diffusion dissolution of niobium particles delays formation of uniform ternary Ti-Zr-Nb alloys. Improved sintering kinetics with decrease in residual porosity down to 2% and faster homogenization was achieved with usage of Zr-Nb and Ti-Nb master alloy powders instead of Nb powder. However, melting of master alloys and their crushing to powders are additional processing operations which reduce technological and economy advantages of powder metallurgy approach.

The goal of present study was to form sintered Ti-Zr-Nb alloys with reduced residual porosity and sufficient uniformity using TiH_2 , ZrH_2 and Nb powders as starting materials. Such approach allows exclusion of master alloys production and provides cost effectiveness of alloy manufacturing process.

Materials and experimental procedure

Production of two low-modulus Ti-Zr-Nb alloys promising for medical applications [22] was investigated. The first composition is based on titanium (40Ti-35Zr-25Nb mass%), while another one is based on zirconium (59Zr-19Ti-22Nb mass%). The corresponding alloys were named according to the base element (Zr or Ti) and were produced using two processing which are designated as Zr1;2 and Ti1;2 (Table 1).

We used zirconium TS-1 grade, titanium sponge TG-110 and industrial niobium powder as starting materials for alloys production. Zirconium and titanium were hydrogenated to produce single phase brittle TiH_2 and ZrH_2 hydrides which then were easy crushed in powders. Both hydride powders and niobium powder less than 100 μm in size were blended in corresponding ratios to produce starting blends of noted total compositions.

Table 1
Alloy compositions and manufacturing processes

No	Manufacturing process	40Ti-35Zr-25Nb	59Zr-19Ti-22Nb
1	Compaction and sintering of elemental powder blends of TiH_2 , ZrH_2 and Nb	Ti1	Zr1
2	Process 1 followed by alloy hydrogenation, production hydrogenated prealloyed Ti-Zr-Nb powders; compaction and sintering	Ti2	Zr2

According to manufacturing process No1 (Table 1), these blends were compacted at pressure of 640 MPa, room temperature. The powder compacts were heated in vacuum at rate of 10 °C / min to 1250°C and exposed at this temperature for 4 hours. Such heating cycle causes the removal of hydrogen from the powders, sintering and homogenization of powder blends thus transforming them in bulk alloys.

In order to reduce material porosity and to improve homogeneity, two stage sintering process (process No2, Table 1) was also tested. Both alloys manufactured using process No1 were hydrogenated again and grinded in a planetary mill to produce prealloyed hydrogenated powders of two noted compositions (Table 1, process No2). Prealloyed hydrogenated powders less than 100 μm in size were pressed at 640 MPa, heated 10°C /min to 1250°C and sintered at this temperature for 4 hours.

Hydrogenation of materials and investigation of hydrogenation kinetic was performed by Sieverts method. Materials were heated (rate 0.125°C/s) up to 600°C under hydrogen atmosphere (starting pressure of 0.6 MPa).

The sintering kinetic and volume changes on sintering of powder compacts were studied with high temperature vacuum dilatometry on continuous heating (rate of 10 °C/min) up to 1250°C. The structure of the sintered material was investigated by scanning electron microscopy (SEM). Phase composition was evaluated using X-ray analysis. The Vickers hardness tests and Young

modulus measurement with impulse excitation technique were performed to evaluate mechanical properties of the alloys obtained using various powders.

Results and discussion

X-ray analysis showed formation of single phase BCC alloys after 4 hours sintering of both Zr1 and Ti1 powder blends (fig.1).

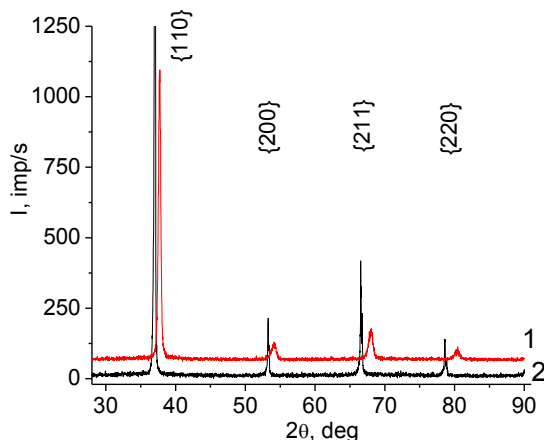


Fig. 1. Typical X-ray diffraction patterns of as-sintered 40Ti-35Zr-25Nb (1) and 59Zr-19Ti-22Nb (2) alloys.

At the same time, some local inhomogeneities and a huge (up to 9%) residual porosity were observed in alloys produced using process No 1 (Fig. 2 a, b). The inhomogeneities were caused with the coarsest (~100 μm) niobium particles which were not completely dissolved even during 4 hours sintering at 1250°C. It was established that coarse residual pores of non spherical elongated shape were formed due to following reasons. Difference in volume changes on heating of both hydride powder particles (thermal expansion and then considerable shrinkage during hydrogen emission at 300-800°C) and Nb powders (thermal expansion only) created additional voids between hydride particles and Nb ones in compacted blends [27]. Moreover, high elastic energy accumulated in compacted ZrH_2 powder resulted in particle rearrangement and formation of gaps between particles on hydrogen emission [28] with visible swelling effects at 400-600 °C (Fig. 3, curves 1 and 2). Development of diffusion between Nb particles and Ti-Zr matrix at higher temperatures [27, 28] led to development of Kirkendall's porosity on homogenization stage. Due to above described reasons, the retarded shrinkage of powder compacts on heating (curves 1 and 2, Fig.3) and preservation of significant porosity after further isothermal exposure were observed. It can be also concluded that Nb powder quite less in size than 100 μm is necessary to achieve completed uniformity of alloys at used time-temperature sintering parameters.

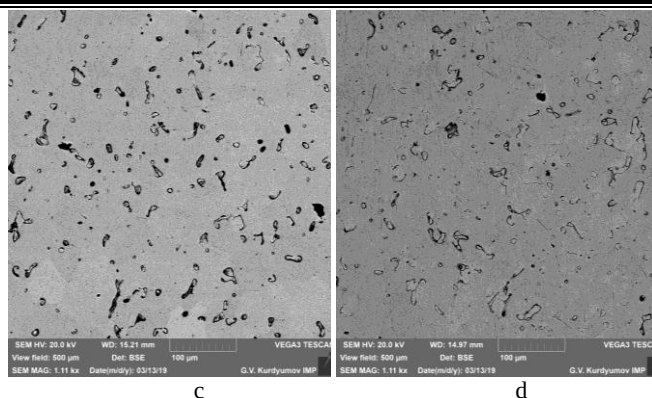
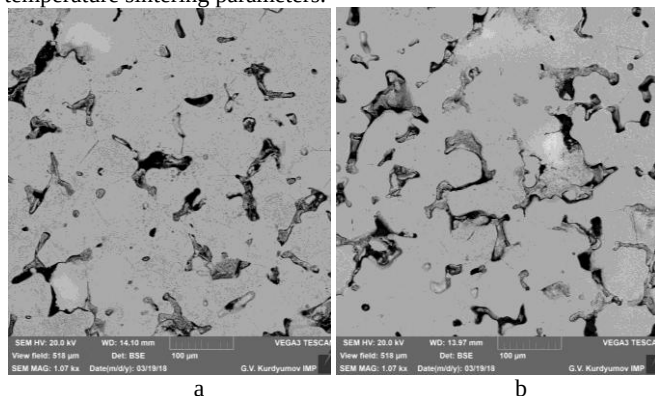


Fig. 2. As-sintered microstructures of Zr1(a), Ti1(b), Zr2(c), Ti2(d) alloys.

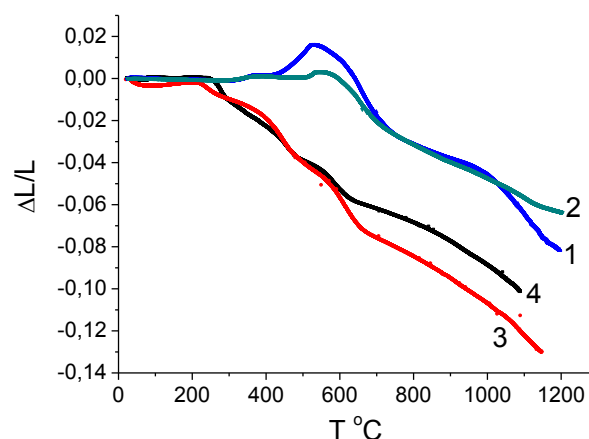


Fig. 3. Dilatometric heating curves for compacted powder blends of Zr1 (1) and Ti1 (2) compositions as well as for compacted prealloyed hydrogenated powders Zr2 (3) and Ti2 (4).

To reduce residual porosity and to achieve better uniformity of sintered alloys, two stage sintering process (manufacturing process No2) was proposed. Hydrogenation of the produced alloys makes them brittle and suitable for crushing to produce prealloyed hydrogenated powders of desirable sizes. Sintering of prealloyed powders should result in better densification and accelerated finishing of homogenization as compared to elemental powder blends. Moreover, positive influence of hydrogen on powder compact densification should also take place at second sintering stage.

To realize this processing scheme, hydrogenation of both alloys was investigated. Sintered alloys were heated under hydrogen atmosphere to 600°C with monitoring of hydrogen pressure raise in heating chamber with temperature (Fig. 4). Temperature at which pressure-temperature dependence curve deviated from straight line shows the beginning of hydrogen absorption by alloys (Fig. 4). Temperatures of hydrogen absorption starting and the calculated amounts of hydrogen absorbed are shown in Table 2 for both alloys.

Table 2 Beginning of hydrogen sorption temperatures and concentrations of hydrogen absorbed by two sintered alloys

Alloy	$T_{\text{sorb}}, ^\circ\text{C}$	$C_H, \text{mass.}\%$
59Zr-19Ti-22Nb	375	2,45
40Ti-35Zr-25Nb	395	2,87

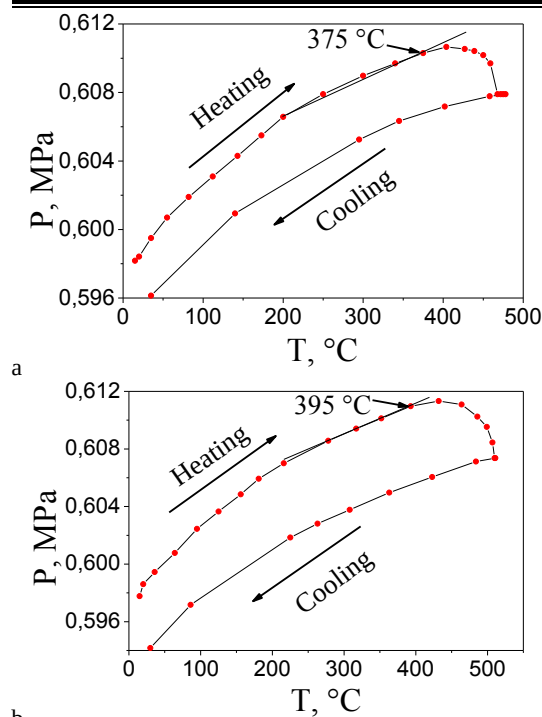


Fig. 4. Correlation between pressure and temperature raise during: 59Zr-19Ti-22Nb(a) and 40Ti-35Zr-25Nb (b) alloys heating under hydrogen atmosphere. The temperatures of hydrogen absorption beginning are noted.

The both alloys were saturated with hydrogen at temperatures below 500-530°C. The noted amount of hydrogen absorbed is quite enough to become both alloys brittle and easy crushed them to powder particles of desirable sizes. Produced powders were compacted and sintered again, a volume changes versus temperature on sintering of both hydrogenated prealloyed powders are shown at Fig. 3 (curves 3, 4). Like for TiH₂ and for ZrH₂ powders, hydrogen desorption from both prealloyed powder compacts resulted in intensive shrinkage above ~250°C, while further heating led to shrinkage due to development of powder sintering. It is clearly seen the differences between shrinkage behavior caused by powder type (prealloyed hydrogenated powders versus blends of TiH₂, ZrH₂ and Nb powders) within 250-700°C interval. At the same time, the total chemical composition of the compacts slightly affects volume changes. It should be noted that harmful swelling effect at dilatometric curves is absent for prealloyed hydrogenated powders of both compositions in contrast to blends contained ZrH₂ powder [26]. Moreover, shrinkage process begins at significantly lower temperatures for prealloyed powder compacts, thus making contribution to reduced porosity. It can be seen from fig. 2 c, d and fig. 3 that using prealloyed powders provides minimization of the total porosity of materials with markedly smaller sizes of individual pores. X-ray diffraction patterns of final sintered materials confirm their single phase BCC structures, while microstructure observations did not reveal residual inhomogeneities for both compositions (Fig. 2 c, d).

The hardness of all sintered materials was evaluated to make preliminary conclusion about validity of proposed powder manufacturing approach for practice applications. Vickers hardness test (Fig. 5) demonstrated that manufacturing process No 2 provided much better results with approximately twice higher hardness values as compared to processing route No 1. It was caused by reduction in total residual porosity, formation of smaller individual pores and improved uniformity of alloys produced with two-step sintering approach. Zirconium based composition possessed markedly higher hardness than titanium based one for both manufacturing processes; the highest value of 380 HV was achieved for process No2. Excessive residual porosity is harmful for material hardness as well as for strength and ductile characteristics. Contrary, highly porous structures are promising for reduction of

Young modulus to meet requirements of medical applications. Evaluation of Young modulus was performed for high-porous Zr1 and Ti1 materials. The promising values of 55,0 GPa (Ti1 alloy) and 56,3 GPa (Zr1 alloy) were obtained, thus the present approach can be considered for medical implant materials manufacturing. More detailed investigations and testing of materials produced with this approach is planned in our further studies.

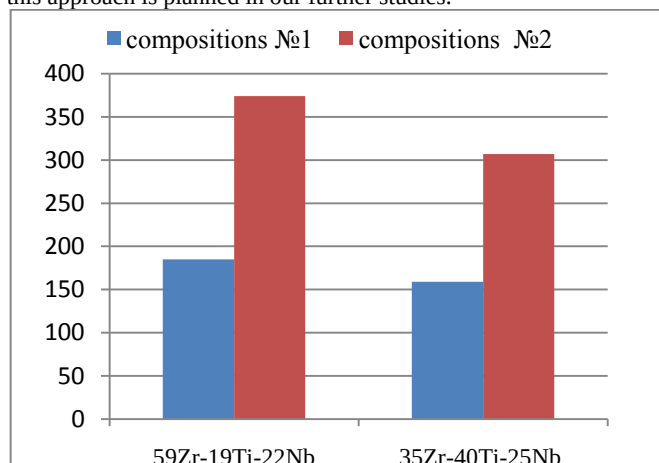


Fig. 5. Vickers hardness of the materials produced.

Conclusions.

1. Two BCC low-modulus Ti-Zr-Nb alloys were produced with press-and-sinter approach using hydrogenated powders.
2. Sintering kinetic and residual porosity markedly depend on type of starting powders used to achieve prescribed alloy composition.
3. Blends of TiH₂, ZrH₂ and Nb powders demonstrated worse densification than hydrogenated prealloyed Ti-Zr-Nb, which provides formation of completely uniform low-porous materials.
4. Proposed two stages solid-state powder processing allowed formation of uniform Ti-Zr-Nb alloys with small residual pores and higher hardness values.

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THE MAGNETIC PROPERTIES OF NANO-MODIFIED COMPOSITE MATERIALS FOR MICROELECTROMECHANICAL SYSTEMS

МАГНИТНЫЕ СВОЙСТВА НАНОМОДИФИЦИРОВАННЫХ КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ ДЛЯ МИКРОЭЛЕКТРОМЕХАНИЧЕСКИХ СИСТЕМ

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Abstract: Magnetic matrices for SMC powders by nanocomposite magnetic materials electroplating on copper foil rings with 50 μm thick were obtained. For each type of magnetic SMC matrices were measured magnetic properties in a transformer mode on a sinusoidal signal. As a result of the conducted research, it was shown that the application of the technique of applying composite nanomodified materials to a special substrate will allow the formation of heterogeneous composite magnetic components with the use of SMC material for microelectronics.

KEYWORDS: NANOCOMPOSITES, MAGNETIC MATRICES, MAGNETIC PROPERTIES

1. Introduction

Modern electromagnetic machines and systems require new materials with improved properties. Heterogeneous three-dimensional nano-modified magnetic material can be effectively used in such systems. A good opportunity to improve their reliability is the use of nanocomposite materials. To obtain samples for the study, we used the method of electroplating deposition of nanocomposite magnetic materials on special substrates. The combined deposition of soft magnetic alloys with inert solid nanoparticles makes it possible to obtain materials with magnetic permeability up to $\mu_m = 104$, magnetic induction $B_s = (0,62-1,3)$ T with improved physical properties.

2. Experimental technique

Were manufactured 6 sets of rings of the following compositions:

- 1) 80 / 20A –80% nickel 20% iron.
- 2) 82 / 18B –82% nickel 18% iron.
- 3) 50 / 50A –50% nickel 50% iron.
- 4) 50 / 50B –50% nickel 50% iron.
- 5) CoP – cobalt-phosphorus
- 6) SMC in a magnetically soft matrix based on a nickel-iron alloy.

Magnetic matrices for SMC powders are electrochemically deposited onto rings of copper foil 50 μm thick, the base. For the manufacture of copper rings, a laser machine for high-precision cutting of thin-sheet metal FMC 280 was used.



Fig.1. Measuring copper rings

Unilateral and bilateral deposition of magnetically soft SMC matrices was carried out. This is explained by the internal stresses of the deposited films and, as a result, the deformation of the copper base and the deposited magnetic soft SMC matrices themselves. Two layers of SMC (Magnetic Soft Powder) powder were applied. Number of layers: two. The dielectric layer is phosphorus oxide, the conductive layer is Co and Ni.

Table 1. Magnetic properties of SMC powder

Magnetic properties of powders					
$\mu_i(k)$	$\mu_m(k)$	$B_s(T)$ @4000A/m	$B_s(T)$ @10000A/m	$B_r(T)$	$H_c(A/m)$
0.087095	0.23165	0.9284	1.3165	0.2097	464.75

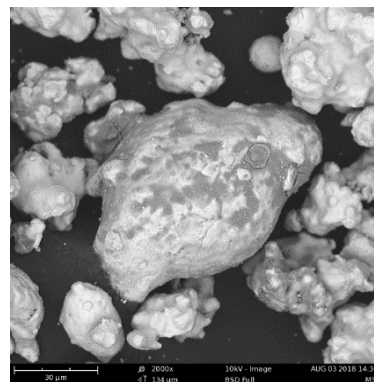
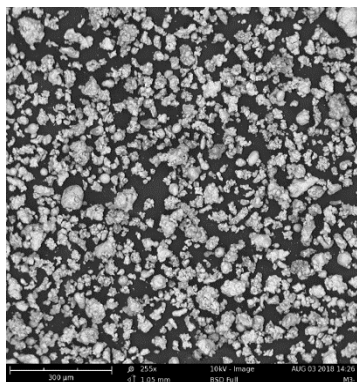


Fig.2 SEM photos of SMC powders

3. Results and discussion

To ensure the effective introduction of SMC powders and integration into the coprecipitation process, SMC powders must be a) inert and stable in electrolytes and b) have a conductive surface. Both of these conditions can be fulfilled by encapsulating SMC particles into a conductive shell, for example, Ni or Co.

For each type of magnetic SMC matrices, magnetic properties were measured in a transformer mode on a sinusoidal signal. The frequency of the signal during measurements is 200 Hz. The measurement results are shown in table 2.

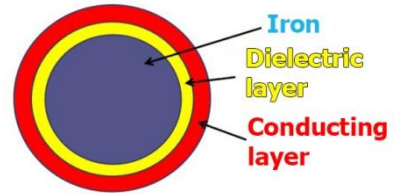


Fig.3 Structure of an individual particle of SMC powder for the coprecipitation process.

Table 2. The results of measurements of the magnetic properties of magnetic SMC matrices.

Sample	B_p , T	H , A/m	H_c , A/m	B_r , T
80/20A	1,65	6960	150	0,67
82/18B	0,74	6750	1150	0,53
50/50A	1,04	6880	520	0,63
50/50B	0,77	6820	510	0,21
CoP	0,54	6920	100	0,15
Fe/Ni-SMC	0,86	7000	460	0,55

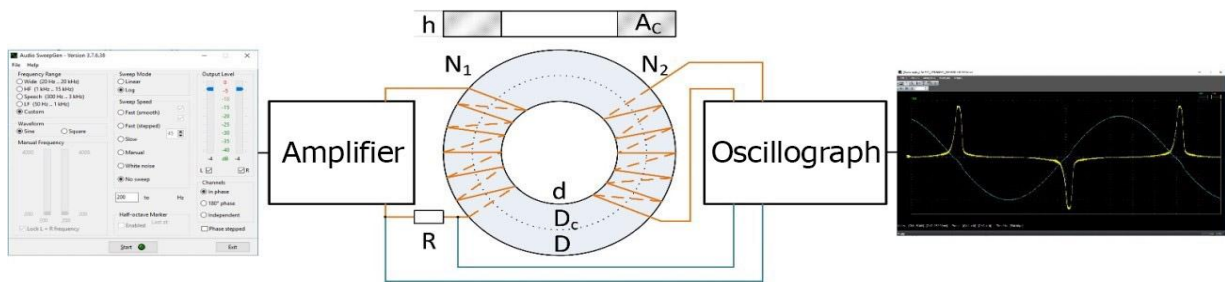


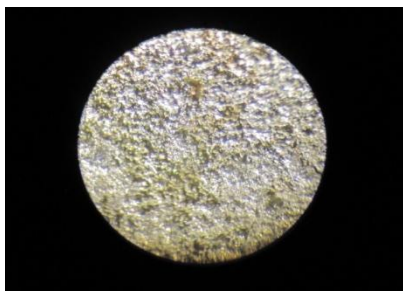
Fig. 4 Installation diagram for measuring magnetic parameters of rings.

A ring prepared for measurements was connected to a system for measuring magnetic parameters. The measuring system consists of a sinusoidal signal generator and an amplifier. The current in the inducing winding N_1 is measured by the voltage drop across the current-limiting resistor $R = 4 \Omega$ (Fig. 20). The voltage in the measuring winding is directly measured by the second channel of the oscilloscope.

The oscilloscope is connected to a computer, which makes it possible to save the waveform for further processing. To automate

the processing of the stored waveforms, a specialized program was written that allows to recalculate the waveforms taking into account the geometric parameters of the sample and the number of turns of the inducing and measuring windings. The conversion results are hysteresis curves stored in the csv format.

It is important to note that samples of a heterogeneous material with a magnetically soft Fe-Ni matrix and SMC powders embedded in it were obtained.



(a)



(b)

Fig. 5 Photo of the surface of the copper ring after the operation of the SMC powder capture (a) after the overgrowth of Fe-Ni matrix (b). High-quality overgrowth of SMC powder with a soft-magnetic matrix is clearly visible.

4. Conclusion

As a result of the research, it was shown that the application of the technique of applying composite nanomodified materials to a special substrate will allow the formation of heterogeneous composite magnetic components with the use of SMC material for microelectronics.

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THE CONNECTION BETWEEN COEFFICIENT CLUSTERISATION WITH TEMPERATURE

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Abstract: A statistical model is proposed to analyze the relationship between the clustering coefficient (CC) and the temperature and atom-atom interaction potential. CC is defined as the ratio of the number of atoms in clusters to the total number of atoms in a system. The proposed technique is based on the statistical concept of entropy. The clustering coefficient is considered for the equilibrium state.

KEYWORDS: CLUSTERED LIQUID, CLUSTERING, FREE ENERGY, INTERATOMIC POTENTIAL, ENTROPY.

1. Introduction

In various liquids there are regions with a large number of atoms with degree of ordering more than the average for the whole volume of the liquid. Such regions are called as clusters, and the fluids in which they emerge are called as clustered. At a temperature close to the evaporation one temperature, the concentration of clusters is minimal, and at crystallization their concentration has maximal value. If the number of atoms in the system is N and the number of atoms in the clusters is C , the ratio $q = C/N$ is a clustering coefficient (CC). Each cluster is a dynamic system with a lifetime τ . But the total number of atoms C remains unchanged if $T = \text{const}$. The value q at a fixed temperature depends on the properties of the liquid, which are individual for each liquid substance. It means that cluster have possibility to appear and to disappear. But the dependence $q = q(T)$ has common form.

This fact may be explained on the basis of methods of physical kinetics.

The aim of the research is to create a mathematical model based on the minimization of free energy at the equilibrium state of the cluster system.

The object of the investigation is the Helmholtz equation, which includes the potential of atom-atom interaction and entropy of the system.

The object of the research is the relationship between CC, temperature and potential of atom-atom interaction.

There are following research tasks:

1. To constructed a model for calculating the entropy of a cluster system at a fixed free energy when $T = \text{const}$;
2. To look for a connection between the CC and the internal energy for isothermal conditions at equilibrium;
3. To show that the CC in liquids monotonically decreases if temperature changes from the melting point of the crystal (T_{cr}) to the point of evaporation of the liquid (T_{ev}).

2. Degree of atomic-molecular ordering

Crystalline objects are atomic-molecular systems with regular arrangement of homologous points in any direction. This means that if one selects any point in the crystal and draw a straight line through it, then on this straight line, at a distance from the initial point equal to a , there's a point absolutely identical in structural and chemical relation to the starting point. For an ideal crystal, the distance from the initial point to n -th point (a_n) is described by the condition:

$$a_n / n \equiv a \quad (1)$$

In real crystals, the distance from the starting point to the n -th one equals to:

$$a_n / a = n + \Delta \quad (2)$$

This is explained by the fact that the distances between neighboring atoms fluctuate. As repulsive forces are significantly stronger than attractive forces at the same change $a_n - a_{n-1}$, then Δ in formula (2) is always positive. If the Δ exceeds any fixed value, for example $a/2$, the value of n determines the degree of ordering. For perfect crystals $n \Rightarrow \infty$, for gases $n=1$.

The degree of ordering is a subjective characteristic to some extent, since Δ can take other values. For example, if Δ_1 is accepted as equal to $a/2$ or $\Delta_2 = \frac{a}{4}$, that the degree of ordering in the first case "will appear" higher.

However if the same limit value is taken for a number of samples with the same structure and composition but different concentrations of defects, then regardless of its magnitude a hierarchical series is constructed from the sample with the highest degree of ordering to the sample with a lower value q or vice versa.

If the substance in the crystalline state is described by the $Fm3m$ group, which corresponds to a three-layer closed sphere package, for an ideal crystal, the radius of the n -th coordination sphere is equal to:

$$R_n = \sqrt{n} \cdot d, \quad (3)$$

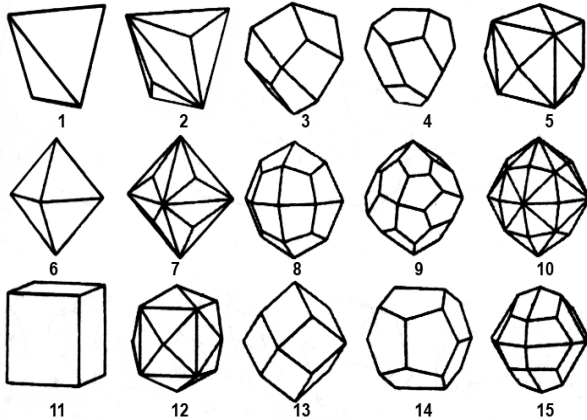
where d is the diameter of the atom.

That is, a monoatomic substance is considered, in which, within the framework of the model of the densest sphere packing, the degree of ordering determines the defect of the crystal due to various factors.

The example of these objects is metallic crystals [1]. In this case, the criterion of the degree of ordering is the difference of the radius of the n -th coordination sphere and its number for metals of the corresponding point $Fm3m$ group or other groups. In particular for metals with $Fm3m$, $Im3m$, $6/mmm$ point groups. These three groups describe the structures of almost all metals, ice and other substances.

In liquid environment, the average atom-atom distance is almost equal to the value for crystalline objects. But the degree of atomic ordering in liquids is much lower than in crystals. So for liquids the notion of middle and even closest order applies. At the same time, groups of atoms can interact with each other to create a three-dimensional configuration similar to a nanocrystalline particle.

As the temperature decreases, the stability of this system increases. At the point of crystallization, each system of this kind which is called a cluster, becomes the center of crystallization. That is why metals create polycrystalline objects during crystallization. Let's consider the correct forms of crystals of the $Fm3m$ group.



1. Tetrahedron
2. Trigontrioctahedron
3. Tetragontritetrahedron
4. Pentagontritetratetrahedron
5. Hexatetrahedron
6. Octahedron
7. Trigontrioctahedron
8. Tetragontritetrahedron
9. Pentagontritetratetrahedron
10. Hexaoctahedron
11. Hexahedron
12. Tetrahexahedron
13. Rhombododecahedron
14. Dodecahedron
15. Didodecahedron

Fig. 1. - The cubic crystals polyhedral right forms

Figure 1 shows the names of possible polyhedra.

These habitus are preserved for the nanocrystals. As the particle size increases, the polyhedral form takes the shape of a sphere, as the $Fm3m$ group in the limiting transition from a polyhedron to a sphere becomes a group of infinite order $\infty : \infty \cdot \infty$.

In general case, clusters are the objects with the following characteristics. The first, the degree of atomic ordering is greater than the average volume of the cluster fluid; secondly, they are a dynamic system, which even in thermostatic conditions disappear and occur in other parts of the system.

The total number of atoms in the cluster state remains unchanged.



Fig. 2. – Macroscopic model of the atomic cluster

An example of a cluster system is shown in figure 3, which demonstrates that clusters with structural characteristics different from non-clustered matrix are visible in the electron-microscopic image of the pure metal.

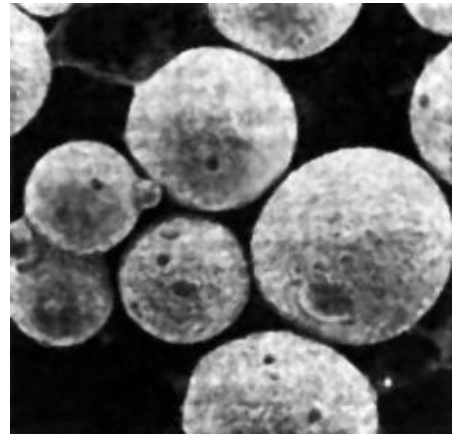


Fig. 3. – Electron microscopic image of copper particles, magnification $5.2 \cdot 10^{-7} \text{ m}$ [2].

3. The Helmholtz equation for cluster liquids

To determine the relationship of the clustering coefficient for liquids, the Helmholtz equation was used which is applicable for solids, liquids and gases, especially for cases with high pressure.

This equation has the form:

$$F = U - TS, \quad (4)$$

where F is the free energy of Helmholtz or the isochoric-isothermal thermodynamic potential determined by the difference between the total energy and the parameter configuration, depending on the number of States in thermodynamic equilibrium.

The total energy U is the sum of the kinetic energy of the motion of atoms (ions, molecules) and potential energy of atom-atom interaction. The kinetic energy of one atom modeled by a sphere with three degrees of freedom is:

$$K = 3kT, \quad (5)$$

where k is Boltzmann's constant.

For polyatomic molecules

$$K = f kT, \quad (6)$$

where f is a factor depending on the number of degrees of freedom of an atom (ion, molecule).

The potential energy of the pair atom-atom interaction (P) in the general case can be represented as:

$$P = \alpha \exp \frac{E}{kT}, \quad (7)$$

When α , E are energetical parameters which depends on properties of matter and start temperature point.

If is consider the following temperature range:

$$T_{cr} < T < T_{ev}, \quad (8)$$

where T_{cr} , T_{ev} , – crystallization and evaporation temperatures respectively.

For specific situations, the form of the potential may be different [3]. The potentials of Lennard – Jones, Morse, of Sutherland, Yukawa, models of hard spheres, quantum wells with different parameters [4, 5]. All these potentials can be considered as constants for fixed interatomic distances. If the temperature increases, the atom-atom distance increases. This means that the parameter of atom-atom interaction decreases with increasing temperature. That is, this degree of approximation is applicable to the analyzed temperature range.

Entropy $S = k \ln \Omega$, where Ω is the number of the system states. In this case entropy as thermodynamic function has statistical sense. General number of atoms (ions, molecules) equal N in the system. From N atoms C atoms are displaced in clusters. That is,

$$C/N = q, \quad (9)$$

it is a clustering coefficient with $0 \leq q \leq 1$.

Atoms in a cluster interact with each other.

The total potential energy for all clusters is equal to

$$U_C = \frac{C}{2} \alpha \exp \frac{E}{kT}, \quad (10)$$

For atoms outside the cluster system, the gas model is applicable, when atoms interact only in a collision.

This model is used not only for liquids but also for solids [6]. On its basis it is proved that

$$C_V(T)_{T > \theta_D} = 3R, \quad (11)$$

where θ_D – Debye temperature.

This conclusion is in good agreement with the experiment, which indicates that classical concepts are applied legitimately.

The total energy in the Helmholtz equation (4) for the system under consideration is

$$U(T, C) = (N - C) f k T + \frac{C}{2} \alpha \exp \frac{E}{kT}, \quad (12)$$

The scheme of change of the clustering coefficient for any cluster systems is shown in figure 4.

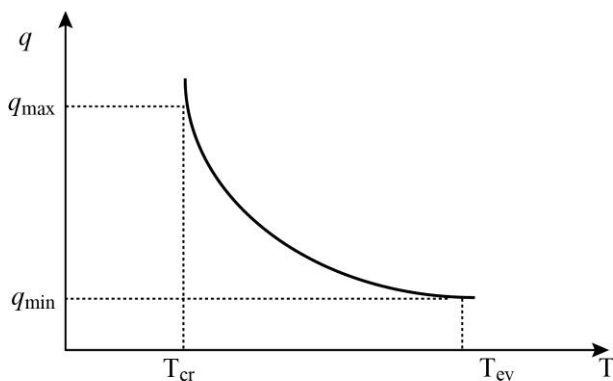


Fig. 4 – The scheme relation between coefficient of clusterization (q) and the temperature (T) [2].

From this scheme clearly visible, that $q_{\max}$ meets the requirements T_{cr} , and $q_{\min}$ – T_{ev} .

The numerical values of these parameters depend on the properties of the substance and the methods of temperature change. For example, the sudden cooling of the melt (method of

spinningovye or punching through the capillary) can be fixed clustering for intermediate temperatures of the melt.

4. The entropy of a cluster system

The cluster system can be considered as a two-phase substance with phase concentration $(N-C)/N$, C/N .

In the framework of the classical kinetic model atoms are distinguishable, that is, the number of States in the system (Ω) is determined by the condition:

$$\Omega = \Pi_{(N-C)} \cdot \Pi_C = (N - C)! C!$$

$$S = k \ln \Omega = k \cdot \ln(N - C)! + \ln C!, \quad (13)$$

When $\Pi_{(N-C)}$ is according to Stirling's formula and $(X \gg 1)$

$$\ln X! = X \ln X - 1 = X \ln X, \quad (14)$$

and considering that N , $N-C$, C immeasurably more than one, we get:

$$S = k \ln \Omega = k((N - C) \ln(N - C) + C \ln C) = k[N(1 - q) \ln N(1 - q) + qN \ln qN] \quad (15)$$

According to formulas (13 – 15) the Helmholtz equation (4) will take the form:

$$F(T, q) = N(1 - q) f \cdot kT + q \frac{N}{2} \alpha \exp \frac{E}{kT} - kT \{ N(1 - q) \ln N(1 - q) + q \cdot N \ln qN \} \quad (16)$$

Free energy at a constant temperature depends only on the degree of clustering determined by the value of the clustering coefficient q . When the system is in the equilibrium state the following ratio must be true

$$\frac{dF}{dq} = 0. \text{ Then}$$

$$\frac{1 - q}{q} = \left(0,5 \exp \frac{E_0}{kT} - f k T \right). \text{ Then}$$

$$F(q) = (1 - q) f k T + \frac{q}{2} \cdot \alpha \exp \frac{E}{kT} + (1 - q) \ln N(1 - q) + q \cdot \ln Nq \quad (17)$$

At a constant temperature, the equilibrium state of the system is determined by condition:

$$\frac{dF}{dq} = 0. (T = \text{const}).$$

That is:

$$\left(-f k T + \frac{1}{2} \alpha \exp \frac{E}{kT} + k T \ln \frac{q}{(1 - q)} \right) = 0, \quad (18)$$

From here

$$\ln \frac{q}{1-q} = \frac{\alpha}{2kT} \cdot \exp \frac{E}{kT} - f, \quad (19)$$

In thermostatic conditions, the clustering coefficient of the system depends on only the potential of atom-atom interaction.

In the quasi-stationary transition to higher temperatures, the right side of the equation (19) decreases, hence the clustering coefficient also decreases. Using the model the size of clusters and their shape cannot be determined. Because it needs property of matter.

However, given the dynamic processes of cluster formation, we can understand why, for example, it is very difficult to obtain single crystals during solidification of cluster fluids.

Each cluster at a lower temperature is characterized by a longer lifespan and can become the embryo of the crystal.

At sharp cooling of metal melts, when relaxation in the cluster is not achieved, the metal solidifies.

Since the cluster does not necessarily reflect the symmetry of the crystal state, structures can occur even with non-crystallographic symmetry.

This may explain the example of quasi-crystalline objects with pentagonal symmetry.

5. Conclusion

The model of calculation of entropy of cluster system for conditions of thermostatic equilibrium has been constructed.

The relationship between the clustering coefficient and the internal energy for isothermal conditions at equilibrium has been analyzed.

The focus of the study has been the dependence of energy freedoms on temperature, the parameters of the atom-atom interaction potential and the ratio of the number of atoms in clusters to the total number of atoms in the system, also known as the clustering coefficient.

It is found that the clustering coefficient in liquids monotonically decreases with temperature change from the melting point of the crystal to the point of evaporation of the liquid.

The proposed model for determining the dependence of the clustering coefficient (q) in cluster fluids, based on the method of physical kinetics, explains the dependence of the clustering coefficient (q) on temperature T , and is applicable to all types of atom-atom interaction potentials.

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FORMATION OF ZrB_2 -AlN POWDER MIXTURE BY SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS

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Abstract: Formation of ZrB_2 -AlN mixed powder by self-propagating high-temperature synthesis (SHS) was investigated. Powders of Zr, B, BN and Al (purity >99 %) was used as the starting materials. Two initial mixtures were prepared and mixed at specific ratios. The first mixture was made of Zr and B, which were weighed at stoichiometric amounts to form ZrB_2 . The second mixture contained Zr, BN and Al; amounts of which were calculated so as to form ZrB_2 and AlN.

The starting powders were mixed in a mortar and pestle, and then the reactant mixture was slightly pressed in a steel die. The SHS reactions were conducted in high purity argon atmosphere, in an SHS chamber. The reactant pellet was ignited from one end with a tungsten wire. The reaction products were examined with scanning electron microscopy and they were subjected to X-ray diffraction analyses.

It was found that when the reactants contained 40 % mixture-1 and 60 % mixture-2, according to the XRD results of the products, the peaks related to ZrB_2 were dominant. The product contained some AlN and ZrN. When the amount of mixture-2 was increased to 90 %, the amounts of AlN and ZrN both were observed to increase. When Al amount in mixture-2 was increased by 30 % and mixture-2 was added as 90% into mixture-1, amount of AlN in the reaction products increased and amount of ZrN decreased. According to SEM examinations, ZrB_2 particles were seen to be mixed with AlN particles in the reaction products. Size of ZrB_2 particles were about 1 micron and AlN particles were larger.

Keywords: ZAMAK 3 ALLOY, AGING, MECHANICAL PROPERTIES

1. Introduction

Aluminum nitride (AlN) is important for electronic industry due to its good properties such as high electrical resistivity, thermal conductivity and low thermal expansion. In addition, its corrosion resistance and oxidation resistance make it a suitable material for high temperature boats that are used in various metal melting and similar processes [1].

Zirconium diboride (ZrB_2) is in the class of ultra-high temperature ceramics. It has also high thermal conductivity and thermal shock resistance. It is used in high temperature applications and as high temperature boats [2].

Self-propagating high-temperature synthesis (SHS) is a procedure that utilizes the exothermic character of the reactions for sustaining the formation of the products. One chief benefit of this practice is that it requires little amount of energy, which is necessary to initiate the reaction. Low equipment cost, uncontamination of the products, fast production rate are a few of the other rewards [3].

AlN was prepared through combustion synthesis by heating Al powder in high pressure nitrogen atmosphere. AlN was used as diluent. It was reported that reaction did not take place when the Al content of the mixture was less than 20 wt % [1].

For high temperature applications, there are some disadvantages of single phase ceramic materials, such as low ablation resistance. Therefore, they are combined with other ceramics. Addition of secondary or tertiary compounds enhances their properties and density [2]. Addition of SiC to ZrB_2 increases its strength and addition of MoSi_2 to ZrB_2 increases its high temperature strength [2].

In the study of Liu, ZrB_2 based ceramics were produced by reactive spark plasma sintering [4]. Zr, ZrH_2 , Si, B_4C , BN were used as the starting materials and ZrB_2 and SiC or AlN or ZrN containing ceramics were obtained.

In the study of Zhang et al. [4], boron carbide and boron nitride were used as reactants for producing boride containing ceramic composites. ZrB_2 and AlN ceramics were obtained by in situ reactive hot pressing technique.

In this study, formation of ZrB_2 -AlN mixed powder by self-propagating high-temperature synthesis (SHS) by using of Zr, B, BN and Al powders, was investigated.

2. Experimental Procedure

Formation of ZrB_2 -AlN mixed powder by self-propagating high-temperature synthesis (SHS) was investigated. Powders of Zr, B, BN and Al (purity >99 %) was used as the starting materials. Two initial mixtures were prepared and mixed at specific ratios. The first mixture (mixture-1) was made of Zr and B, which were weighed at stoichiometric amounts to form ZrB_2 according to Reaction (1).



The second mixture (mixture-2) contained Zr, BN and Al; amounts of which were calculated so as to form ZrB_2 and AlN according to Reaction (2).



Three samples were produced by using different amounts of starting materials. The first composition was contained 40 wt % of mixture-1 and 60 wt % of mixture-2. The second composition contained 10 wt % of mixture-1 and 90 wt % of mixture-2. The third composition contained 10 wt % of mixture-1 and 90 wt % of mixture-2, but the amount of Al in mixture-2 was 30 % in excess of the stoichiometric amount (Table 1).

Table 1: Produced samples and amounts of the reactants powders in them

Sample	Amounts of Reactants (g)			
	Zr	B	BN	Al
Sample-1 (%60M1-%40M2)	0.4525	0.0575	0.1146	0.1247
Sample-2 (%10M1-%90M2)	0.37	0.0134	0.1604	0.1746
Sample-3 (%10M1-%90M2 (Al 30%xs))	0.37	0.0134	0.1604	0.2275

The starting powders were mixed in a mortar and pestle, and then the reactant mixture was slightly pressed in a steel die. The SHS reactions were conducted in high purity argon atmosphere, in an SHS chamber. The reactant pellet was ignited from one end with a tungsten wire. The reaction products were examined with scanning electron microscopy and they were subjected to X-ray diffraction analyses.

3. Results and Discussion

After self-propagating high-temperature synthesis reaction the pellets preserved their shapes. Some swelling was observed, along with increase in the porosity. In addition, the pellets had a lamellar morphology, a typical result of the SHS reaction. The pellets were ground in a mortar and pestle into powder form.

XRD Analyses

The ground samples were subjected to XRD analyses at a rate of 2 °/min. XRD patterns of the product obtained from the sample containing 40% mixture-1 and 60% mixture-2 (Sample-1) is presented in Fig. 1(a). The peaks related to ZrB₂ were dominant. The product contained some AlN and ZrN. The intensity of AlN peaks are much lower as compared to that of ZrB₂ peaks. The intensity of the AlN peaks are believed to be not directly proportional with the amount of AlN phase in the products.

The reaction was conducted in argon atmosphere. Thus, the only source of nitrogen in the system is BN. There was no sign of unreacted aluminum or boron nitride in the system, indicating that the reaction was completed. In the present study, BN was used to provide nitrogen, whereas in literature AlN production by combustion synthesis is frequently performed in high pressure nitrogen [1].

When the amount of mixture-2 was increased to 90 % in the reactants (Sample 2), the amounts of AlN and ZrN both were observed to increase (Fig 1(b)). Mixture-2 contains BN, which is the nitrogen source in the system, and the products of Reaction (2) are ZrB₂ and AlN. Therefore AlN is expected to increase in the products, as a result of increase in the amount of mixture-2 in the reactants. On the other hand, amount of ZrN also increased in the products, due to increase in the amount of BN in the reactants.

In the third sample, Al amount in mixture-2 was increased by 30 % and mixture-2 was added as 90% into mixture-1, (Sample 3). It was seen that the amount of AlN in the reaction products increased and amount of ZrN decreased (Fig. 1(c)). It can be deduced that in sample-2, there was a loss of aluminum during the SHS reaction. Adding excess aluminum into the reactants may have compensated for the loss of aluminum from the system and led to formation of more AlN. In addition, this decreased the formation of ZrN. According to XRD pattern given in Fig. 1(c), there was trace amount of unreacted aluminum in the reactants, when 30 % excess aluminum was used in mixture-2.

Microstructure

Scanning electron micrographs of the products are given in Figs 2-4. These images were obtained in the backscatter electron mode. Therefore, compositional contrast was obtained. The white particles are believed to be ZrB₂ (or ZrN in some cases), with higher average atomic weight. Gray particles are believed to be AlN (or Al), with lower average atomic weight.

According to SEM examinations, ZrB₂ particles were seen to be mixed with AlN particles in the reaction products. The microstructure is very similar to the ZrB₂-AlN system synthesized by in situ reactive hot pressing [5]. Size of ZrB₂ particles were about 1 micron and AlN particles were larger.

Amount of AlN phase was seen to be higher in Sample-3 (Fig. 4), as compared to other samples.

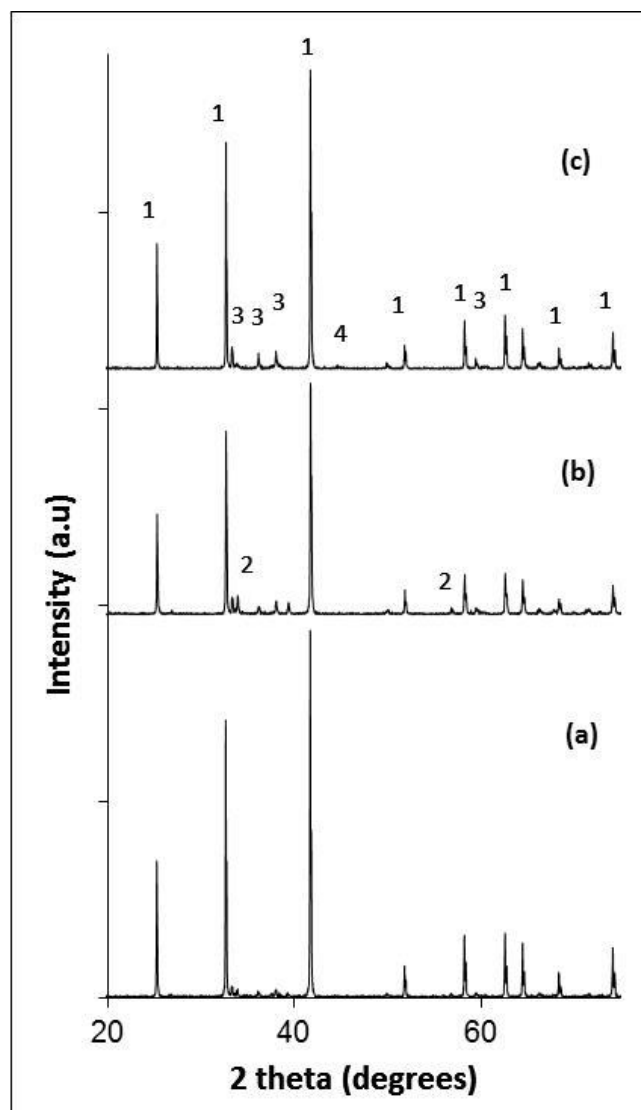


Fig. 1 XRD patterns of the products (a) S1 (%60M1-%40M2) (b) S2 (%10M1-%90M2) (c) S3 (%10M1-%90M2 (Al 30%xs)), 1. ZrB₂, 2. ZrN, 3. AlN, 4. Al

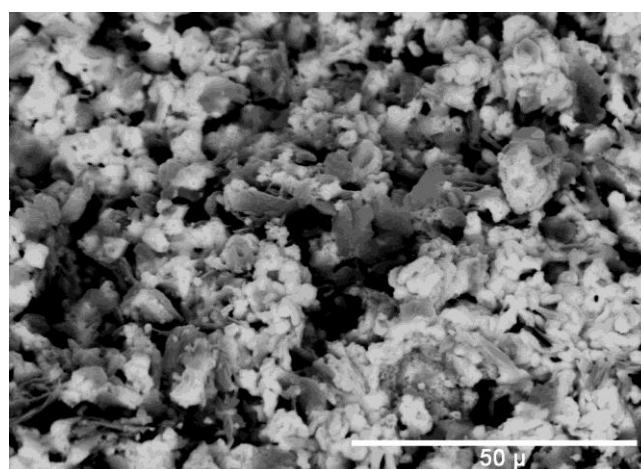


Fig. 2 Scanning electron micrograph of the products obtained from reactants containing 40% mixture-1 and 60% mixture-2 (Sample-1).

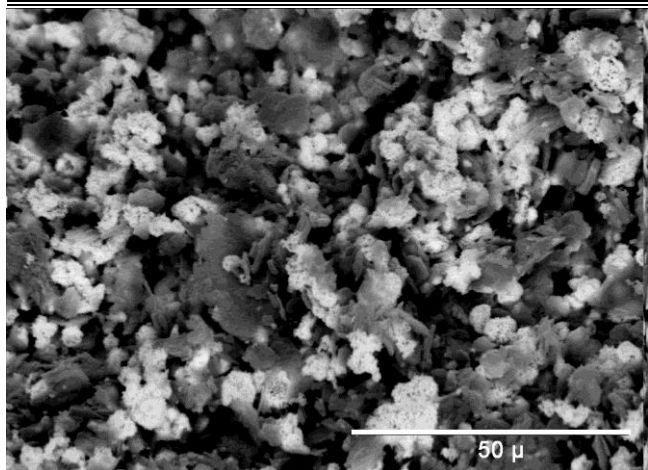


Fig. 3 Scanning electron micrograph of the products obtained from reactants containing 10% mixture-1 and 90% mixture-2 (Sample-2).

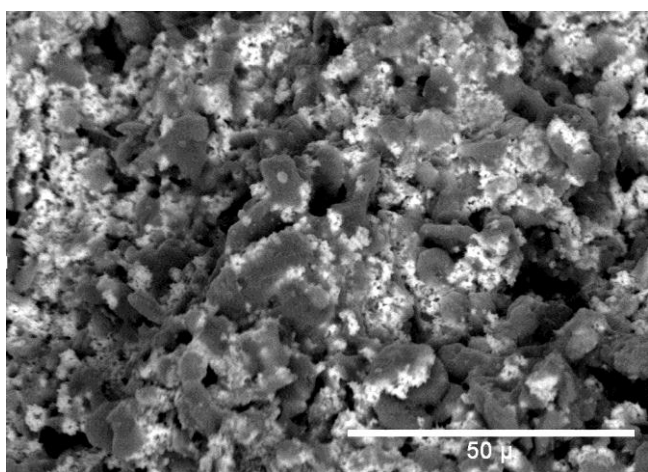


Fig. 4 Scanning electron micrograph of the products obtained from reactants containing 10% mixture-1 and 90% mixture-2 (Al 30%xs) (Sample-3).

4. Conclusion

ZrB₂-AlN powder mixture was produced from Zr, B, BN and Al reactant mixtures by self-propagating high-temperature synthesis. Increase in the amount of BN and Al in the reactants, resulted in an increase in the amount of AlN in the products.

ZrB₂ and AlN particles could be visualized by compositional contrast in SEM. ZrB₂ particles were seen to be mixed with AlN particles in the reaction products. Size of ZrB₂ particles were about 1 micron and AlN particles were larger.

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