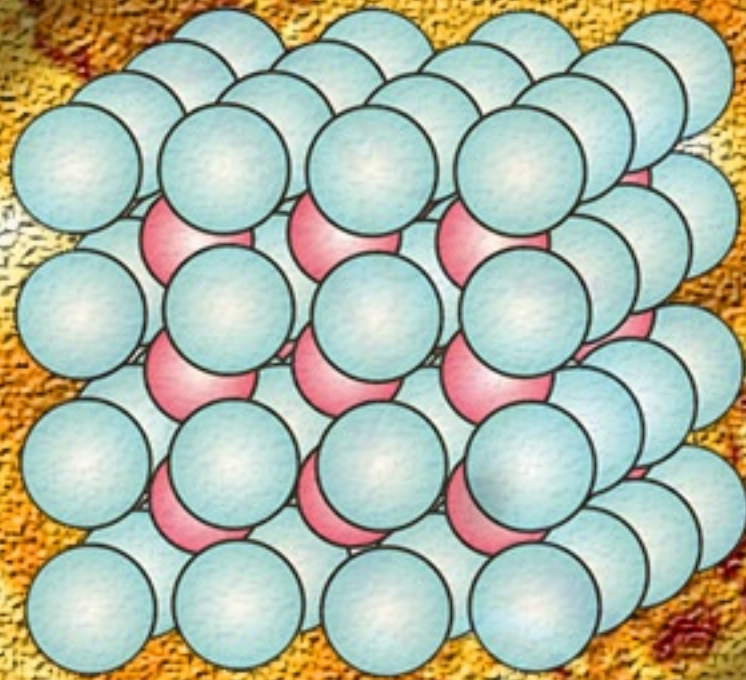


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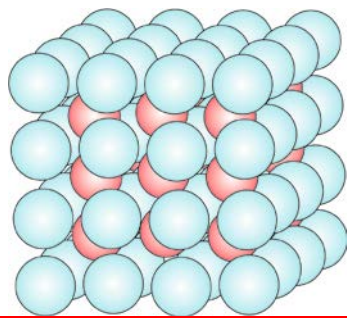
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MODELING OF THE METAL POWDER PRESSING PROCESS WITH A POROGEN

МОДЕЛИРОВАНИЕ ПРОЦЕССА ПРЕССОВАНИЯ МЕТАЛЛИЧЕСКИХ ПОРОШКОВ В ПРИСУТСТВИИ ПОРООБРАЗОВАТЕЛЯ

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Abstract: A model for calculating the metal powder pressing process with a porogen is proposed. An approximate method and algorithm have been developed that make it possible to take into account the presence of a porogen in the calculation of the pressing process and reflect all types of bonds at the contact boundaries of metal powder particles. Based on the constructed model, an approximate method and algorithm for calculating the properties of powder filter material (PFM) produced by pressing granular metal powders using a porogen have been developed. The advantage of the proposed mathematical model is the possibility of its development to describe the sintering process, as well as the possibility of its use for calculating the modified elementary cells used by researchers in modeling the structure of PFM with a porogen.

KEYWORDS: POWDER FILTER MATERIALS (PFMs), CALCULATION MODEL, METAL POWDER PRESSING, POROGEN

1. Introduction

Taking into account the influence of the use of porogens on expanding the range of PFM properties, modeling of a porous body with the presence of porogens is of interest. An analysis of the given models of the PFM structure shows that the model that most fully describing the structural features of the metal frame of the material and at the same time enabling to determine filtering properties is an elementary cell in which the properties of each element of the PFM volume are set by the elementary cell parameters in the form of a parallelepiped isolated from 8 powder particles. According to [1, 2], the presence of a porogen in this model is taken into account by shearing 1/4 of one of the faces in the direction of the corresponding axis of the nonorthogonal coordinate system (Figure 1).

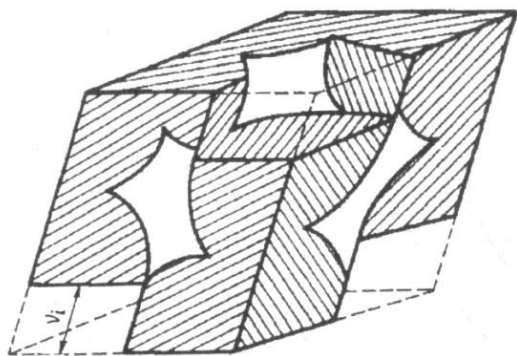


Figure 1 Scheme of powder particle displacement;
 v_i – Shearing area

The authors of Ref. [3] used the idealized (geometrically ordered) PFM structural model to define the relationship between various structural characteristics and determine the role of a porogen in the formation of a porous structure. It is assumed in a first approximation that the porogen particles, and therefore the cavities formed after their decomposition, have a spherical shape. These cavities in the finished material are uniformly distributed and form a simple cubic lattice with a step a . The gaps between the spherical cavities (the walls of these cavities) are formed by sintered metal powder and have a corresponding porosity, in the formation of which a porogen is not involved (the case is considered when the particle size of a porogen is much larger than the particles of the metal powder).

However, the first of given models does not take into account the particle size of a porogen, the second one – the particle size of the metal powder.

The purpose of this paper is to develop a mathematical model for calculating the PFM properties produced by pressing metal powders with a porogen.

2. Results and discussion

Let's consider the process of molding metal powders with porogen particles using mathematical modeling methods. This, in essence, means determining the properties and characteristics of the phenomenon or process by solving with a computer a system of certain equations – a mathematical model [4].

The main stages of the numerical solution of tasks in continuum mechanics are: 1) a choice of a model of a physical process; 2) a choice of a mathematical model or mathematical formulation of a task; 3) a choice and development of a numerical method for solving the corresponding mathematical problem; 4) development of a method for implementing an algorithm on a computer and conducting serial calculations, accumulation of experience, evaluation of the effectiveness and applicability limits of the algorithm.

In this paper, following the above stages, a mathematical model is developed to calculate the PFM properties obtained by pressing granules formed by particles of a porogen and metal powders.

Let's consider a cell as an elementary volume characterized by a cubic volume-centered packing of particles, with a porogen particle located in the center of the cube (Figure 2).

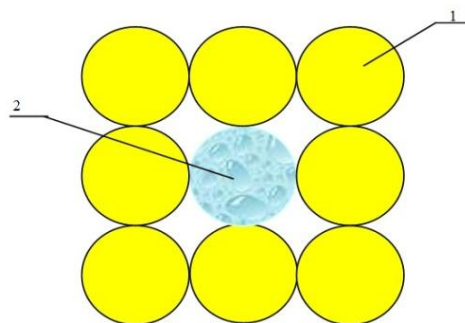


Figure 2 Elementary cell cross section
1 – metal powder, 2 – porogen

It was assumed that each particle is homogeneous and consists of a substance, which, as a separate compact body, obeys all the laws of classical mechanics. The mechanism of crumbling (pressing) of four particles under a given load was considered and a numerical model for calculating the resulting cavity (pore) was proposed. It should be noted that in the general case, the particles can be from different materials.

We show that the choice of a model with a porogen presented in Figure 2 expands the possibilities of obtaining a porous structure and makes it possible to predict the quality of PFM.

Based on the laws of continuum mechanics [5, 6] using static equations (the equilibrium equation of the selected medium element), geometric equations that determine deformations by the displacements of its points and the physical group of equations that take into account the mechanical properties of the material and determine the relationship between stresses and deformations of the element (Hooke's law), a mathematical model was proposed and an approximate algorithm for numerical calculation was described, which makes it possible to calculate pores and their sizes. The geometry of the pore was determined by a combination of some points M_k , called boundary with coordinates (r_i^k, z_j^k) , according to which it is easy to restore the closed curve that defines the pore.

When deriving the equations, Hooke's linear law [5] was used in the form:

$$T = \lambda_m D E^1 + 2\mu_m \varepsilon, \quad (1)$$

or in another form

$$T = 2\mu_m \left(\frac{\nu_m}{1-2\nu_m} D E^1 + \varepsilon \right), \quad (2)$$

where T – stress tensor, ε – deformation tensor, E^1 – unit matrix, $D = \nabla \cdot \vec{v} = \text{div } \vec{v} = \frac{\partial u}{\partial r} + \frac{u}{r} + \frac{1}{r} \frac{\partial v}{\partial \varphi} + \frac{\partial w}{\partial z}$ – divergence of the displacement vector, the index m indicates the properties of either metal ($m=1$) or the properties of a porogen ($m=2$), λ_m, μ_m – constant elastic moduli or Lamé coefficients for m – material, which are determined through the Young's modulus E_m and Poisson's coefficient ν_m using formulas

$$\mu_m = \frac{E_m}{2(1+\nu_m)}, \quad \lambda_m = 2\mu_m \frac{\nu_m}{1-2\nu_m}.$$

Thus, for the displacement vector $\vec{u}$ arising in the m particle under the applied load, we have a system of nonlinear partial differential equations:

$$\frac{1}{1-2\nu_m} \text{grad } \text{div } \vec{u} + \nabla^2 \vec{u} + \frac{\rho_m}{\mu_m} \vec{Q} = 0, \quad (3)$$

where $\vec{Q}$ – volume or mass forces. In our case, the volume force is its own weight.

Taking into account cylindrical symmetry (when considering the task) and the assumption that the unknown quantities are independent of the angle φ , in the projections on the corresponding axes for the components of the displacement vector, we have system of equations

$$\begin{cases} \frac{1}{1-2\nu_m} \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (ru) + \frac{\partial w}{\partial z} \right) + \nabla^2 u = 0 \\ \frac{1}{1-2\nu_m} \frac{\partial}{\partial z} \left(\frac{1}{r} \frac{\partial}{\partial r} (ru) + \frac{\partial w}{\partial z} \right) + \nabla^2 w - \frac{\rho_m}{\mu_m} g = 0 \end{cases}, \quad (4)$$

$$\text{where } \nabla^2 u = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u}{\partial r} \right) + \frac{\partial^2 u}{\partial z^2},$$

$$\nabla^2 w = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial w}{\partial r} \right) + \frac{\partial^2 w}{\partial z^2},$$

u, v – projections of the displacement vector on the corresponding r and z axes.

Since the obtained system of equations contains partial derivatives, to uniquely determine the unknowns to the system of equations that determine the behavior of a linearly elastic body at points of its volume, it is necessary to add conditions on the surface S bounding it, which include particle surfaces, points of application of loads, points of contact with the solid surface (the base of the mold), and the points of contact or contact of the particles.

The boundary conditions are determined by the task or external surface forces or displacements of surface points, depending on the specific task. The points of the free surface are those points of the boundary of the particle contour that border gas (air) and the distribution of surface forces F is specified in them and the boundary condition is the equation of equilibrium on the surface

$$\vec{n} \cdot T|_S = \vec{F}, \quad (5)$$

where T – stress tensor at surface points; $\vec{n}$ – unit vector of the external normal to the surface of the body.

Guide cosines of the outer normal $n_r = \cos(r, \vec{n})$, $n_z = \cos(z, \vec{n})$ to the curve $z = z(r)$, determining the boundary of the surface are found by the formulas:

$$n_r = \frac{|z'|}{\sqrt{1+(z')^2}}, \quad (6)$$

$$n_z = -\frac{z'}{\sqrt{1+(z')^2}|z'|}. \quad (7)$$

Since the free surface S of the particle at the initial moment is known and in the dimensionless form on the plane (r, z) has the form

$$r^2 + (z-1)^2 = 1, \quad (8)$$

then according to formulas (2.24) and (2.25) it is easy to determine the direction cosines of the normal at the points of the boundary M^k

$$n_{r,M^k} = r^k, \quad (9)$$

$$n_{z,M^k} = \pm \sqrt{1-r^k}. \quad (10)$$

Task of 5 types of boundary conditions [7] leads to a closed system of differential equations, from the solution of which the stress state realized in the body and the displacement vector of the medium points realized in the body are determined. We formulate preliminary boundary conditions on the initial geometry of the body. Thus, the system of partial differential equations was finally obtained for the displacement vector $\vec{u}(u, w)$.

To numerically solve the system of equations (4) - (10) taking into account the boundary conditions [7], we will use the finite difference method. The solution is not found analytically, but on some selected set of points, called a difference mesh. The solution region is divided by coordinate lines with uniform nodes

$M_{ij} = M_{(i,j)} = (r_i, z_j)$, $z_j = (j-1)h_z$ into cells (volumes), as a result of which we obtain a constant Eulerian mesh.

In the cells of the region, we specify the sign of filling the cell with substance according to the principle of the volume function, i.e. for a cell not fully filled with the substance, a scalar function F is introduced, the value of which is equal to the fractional volume of the cell filled with the substance. It is assumed that $F = 1$ when the cell is completely filled with the substance, and $F = 0$ in the case of an empty cell. Cells with values $0 < F < 1$ contain a free surface. Using this feature, a decision algorithm is built taking into account the relevant conditions.

The system of difference equations for the numerical solution obtained by the integro-differential method [6] (by integrating the system of equations over the elementary volume or over the cell of the difference mesh) taking into account the dimensionlessness has the following form

$$\begin{cases} \frac{1}{\bar{r}}(r_{-0.5}u_r)_r + u_{zz} + \frac{1}{1-2\nu_m} \left(\frac{1}{\bar{r}}(r_{-0.5}u)_{\bar{r}} + w_z \right)_r = 0, \\ \frac{1}{\bar{r}}(r_{-0.5}w_r)_r + w_{zz} + \frac{1}{1-2\nu_m} \left(\frac{1}{\bar{r}}(r_{-0.5}u)_{\bar{r}} + w_z \right)_r - \frac{\rho_m}{\mu_m} gr_0 = 0, \end{cases} \quad (11)$$

for points $M_{ij} = M_{(i,j)} \in$ particle from m material.

The system is solved by the iterative method of establishing using the method of variable directions by iteration.

$$\begin{cases} \frac{u^{s+1} - u^s}{\tau_s} + \frac{1}{\bar{r}}(r_{-0.5}^{s+1}u_r)_{\bar{r}} + u_{zz}^{s+1} + \frac{1}{1-2\nu_m} \left(\frac{1}{\bar{r}}(r_{-0.5}^{s+1}u)_{\bar{r}} + w_z^{s+1} \right)_r = 0, \\ \frac{w^{s+1} - w^s}{\tau_s} + \frac{1}{\bar{r}}(r_{-0.5}^{s+1}w_r)_{\bar{r}} + w_{zz}^{s+1} + \frac{1}{1-2\nu_m} \left(\frac{1}{\bar{r}}(r_{-0.5}^{s+1}u)_{\bar{r}} + w_z^{s+1} \right)_r - \frac{\rho_m}{\mu_m} gr_0 = 0, \end{cases} \quad (12)$$

where τ_s - iterative parameter.

The method is based on explicitly finding the type of intersection of the boundary of the particle material with the coordinate lines of a constant Eulerian mesh.

We will focus on some stages of the system solution.

Stage 1: Solving an iterative system with respect to unknown displacements, we find a set of values $u = u_{ij}$, $w = w_{ij}$, which represent the values of the displacement vector in the nodes of the chosen mesh $u_{ij} = u(M_{ij}) = u(r_i, z_j)$,

$$w_{ij} = w(M_{ij}) = w(r_i, z_j).$$

Stage 2: Knowing the displacements found, it is easy to determine the coordinates of the displaced points $M^* = (r_i^*, z_j^*)$ by the formulas:

$$r_i^* = (r_i + u_{ij})r_0, \quad (13)$$

$$z_j^* = (z_j + w_{ij})z_0, \quad (14)$$

which determine the position of the deformable body. Finding new values $M^{*k} = (r_i^{*k}, z_j^{*k})$ of the boundary points $M^k = (r_i^k, z_j^k)$, we find a new surface of the deformable particle..

Stage 3: Next, we redistribute the cells along a given constant Eulerian mesh, taking into account the new position of the deformed particles. We form, based on the new coordinates of the points, a function indicating the filling of the volume in the cell, and introduce new markers, and etc.

When constructing a solution algorithm, to describe the behavior of a substance in an incomplete cell under the assumption of a linear

nature of the substance change in the cell, 2 markers were introduced in incomplete cells located in the boundary cells at the points of intersection of the substance with the Eulerian mesh coordinate lines. Such a number of markers were enough to determine the normals and radii of curve at points on the free surface. The numbering (in ascending order) of the particle markers

M^k in fractional cells is made so that the area filled with the substance is on the left.

The calculation algorithm considers 12 types of fractional cells, which differ from each other in the type of intersection of the free surface of the cell particles of the mesh region. Their configuration is shown in Ref. [7].

With the introduction of new coordinates of markers and signs of filling the cells, the algorithm is then repeated, but on a modified region. On its boundary conditions and the coupling conditions of various substances are determined according to the type of points.

The stress state at each point of the body (from the chosen system of points – the difference mesh) is determined by the stress tensor. We determine the components of the stress tensor through the found displacements using the following difference formulas:

$$\begin{cases} \sigma_{r,ij} = 2\mu_m \left(\frac{\nu_m}{1-2\nu_m} D_{ij} + (u_{ij} - u_{i-1,j})/h_r \right), \\ \sigma_{\varphi,ij} = 2\mu_m \left(\frac{\nu}{1-2\nu} D_{ij} + \frac{u_{ij}}{r} \right), \quad \sigma_{z,ij} = 2\mu_m \left(\frac{\nu_m}{1-2\nu_m} D_{ij} + (w_{ij} - w_{i-1,j})/h_z \right), \\ \sigma_{rz,ij} = \mu_m ((u_{ij} - u_{i-1,j})/h_z + (w_{ij} - w_{i-1,j})/h_r), \quad \sigma_{r\varphi,ij} = 0, \quad \sigma_{z\varphi,ij} = 0, \\ D_{ij} = (u_{ij} - u_{i-1,j})/h_r + \frac{u_i}{r_i} + (w_{ij} - w_{i-1,j})/h_z. \end{cases} \quad (15)$$

Stresses in the medium can be represented as consisting of stresses associated with uniform hydrostatic pressure (all three normal stress components are equal), plus stresses characterizing the resistance of the material to shear deformations. Therefore, if we decompose each stress $\sigma_r, \sigma_\varphi, \sigma_z$ into the hydrostatic component P and the deviator component S , then we will have the following ratios

$$\sigma_r = -P + S_r, \quad (16)$$

$$\sigma_\varphi = -P + S_\varphi, \quad (17)$$

$$\sigma_z = -P + S_z. \quad (18)$$

where P – arithmetic average of three stresses.

$$P = (\sigma_r + \sigma_\varphi + \sigma_z). \quad (19)$$

We will use Mises yield criterion to describe the yield stress. If the principal stresses are known, then the yield criterion is written as follows:

$$(\sigma_r - \sigma_\varphi)^2 + (\sigma_\varphi - \sigma_z)^2 + (\sigma_r - \sigma_z)^2 = 2(Y_0^m)^2, \quad (20)$$

where Y_0^m – yield stress for simple stretching for a particle of m material. We continue the calculations until the stress values on the left side become less $2(Y_0^m)^2$.

The solution of a nonlinear system of differential equations allows one to determine displacements that describe the pore space of the simulated cell and make it possible to determine the specific surface, pore size, and porosity with subsequent calculation of permeability according to known techniques [2].

The advantage of the developed mathematical model is the possibility of its development to describe the sintering process.

Schematically, the option of pore formation as a result of pressing and sintering is shown in Figure 3.

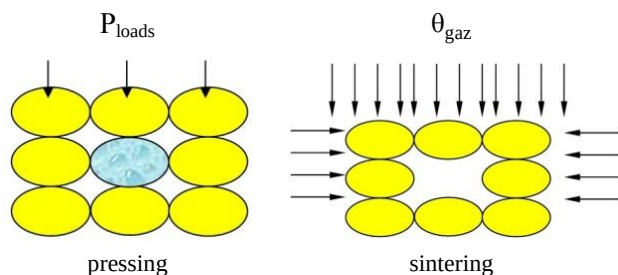


Figure 3 Scheme of pore formation during pressing and sintering:

P_{loads} – sample load, θ – sintering temperature

Moreover, the developed mathematical model can be used to calculate modified elementary cells. One of the options for such a modification is presented below in Figure 4, which schematically shows a granule formed by a metal powder and a porogen.

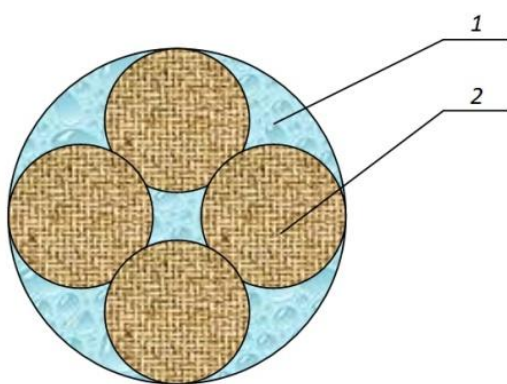


Figure 4 Granule scheme (homogeneous metal particles in porogen media):

1 – a porogen, 2 – metal

3. Conclusion. PFM model is proposed, which enables to take into account the presence of a porogen when calculating the pressing process and reflects all types of bonds at the contact boundaries of metal powder particles. Based on the constructed model, an approximate method and algorithm for calculating the properties of PFM obtained by pressing granular metal powders using a porogen were developed.

The advantage of the proposed mathematical model is the possibility of its development to describe the sintering process, as well as the possibility of its use for calculating the modified elementary cells used by researchers in modeling the structure of PFM with a porogen.

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THE IMPACT OF FREQUENCY COMPOSITION OF CONSOLIDATION CURRENT ON THE STRUCTURE AND PHYSICAL-MECHANICAL PROPERTIES OF Ti-Al-C SYSTEM METAL MATRIX COMPOSITES

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Abstract: The impact of industrial frequency (50 Hz) current with the voltage of $U = 10$ V while using the Field Activated Pressure Assisted Synthesis (FAPAS) method as well as the impact of superposition of direct and alternating (with 10 kHz frequency) currents with the voltage of $U = 2$ V while using Spark Plasmas Sintering (SPS) method on the phase composition, structure and properties of Ti-Al-C system metal-matrix composites, consolidated from the powder mixtures, prepared by high voltage electric discharge, is experimentally studied. It is shown, that using SPS and FAPAS methods allows synthesis of materials, dispersion-strengthened by phases of TiC and Al_4C_3 carbides and Ti_3AlC_2 MAX-phase. It is found out, that using FAPAS method allows obtainment of Ti-Al-C system composites with higher values of density, hardness and wear-resistance, than those of materials obtained by SPS due to more homogeneous structure. Such a differences can be explained by the fact that high frequency (10 kHz) current component promotes movement of disperse phase inside the matrix, which leads to the agglomeration of strengthening particles as well as to increase of obtained composite porosity up to ~ 8 %.

Keywords: metal-matrix composite, MAX-phases, high voltage electric discharge, synthesis, spark plasma sintering.

1. Introduction

Metal-matrix composite materials (MMC) are such materials, in which matrix consists of metal or metal alloy. Ultrafine powder particles or fiber materials of different origins in most cases are acting as a reinforcing components.

MMC's are characterized by a combination of high physical and mechanical properties that are inherent to metals (plasticity and viscosity) and those that are inherent to ceramics (high strength and high elastic modulus) [1, 2]. During the recent years, the interest to metal-matrix composites from the companies of aerospace, automotive, machine building and other industries increases steadily.

Usage of relatively low-cost reinforcing components and development of different technological approaches can lead to less costly and simpler technology of MMC's production [3]. Thus the development of new physical principles of such materials production is an urgent task for scientists and engineers. Methods of high energy preparation of powders and their consolidation by passage of electric current are actively developing nowadays. This allows obtainment of materials with higher values of physical and mechanical properties than those of materials obtained by conventional metallurgy methods.

2. Problem discussion

The universal complex for electric sintering of powder materials, which can use two different current sources of power up to 10 kW, was created at the Institute of Pulse Processes and Technologies of NAS of Ukraine [4]. First electric current source for this complex is based on the superposition of direct and alternating (with frequency of 10 kHz) currents at the working voltage of $U = 2$ V (this source allows realization of Spark Plasmas Sintering (SPS) method), and the second source is based on alternating current with industrial frequency of 50 Hz at the voltage of $U = 10$ V and allows realization of Field Activated Pressure Assisted Synthesis (FAPAS) method.

The possibility of creation of metal-matrix composites of Ti-Al-C, reinforced with MAX-phases, by preliminary treatment of powder material with high voltage electric discharge (HVED) and subsequent high-frequency low-voltage sintering by SPS method was shown in work [5]. According to [6], these composites can compete on the market with industrial alloys, based on Ti_3Al (α -2, 57 % Ti + 25 % Al + 17 % Nb + 1 % Mo) and TiAl (γ , 50.8 % Ti + 45 % Al + 1 % Nb + 2.5 % Cr + 0.2 % B + 0.5 % Ta) intermetallic compounds.

Thus the studies of impact of frequency current composition during the consolidation of powder mixtures with SPS and FAPAS methods on the physical and mechanical properties of obtained materials are of high scientific urgency.

The goal of present work is the studies of impact of frequency current composition during the consolidation on the physical and mechanical properties of Ti-Al-C system materials specimens.

3. Objective and research methodologies

The approach, in which synthesis of reinforcing components occurs in two stages, was used for obtainment of Ti-Al-C system metal-matrix composites. On the first stage (powders preparation) dispersion and surface preparation of powders as well as the synthesis of dispersion-strengthening inclusions takes place. On the second stage (consolidation) synthesis of materials with dispersion-strengthening additives with the preservation of nanostructure occurs.

High voltage electric discharge treatment of powders of 85 % Ti + 15 % Al initial composition in hydrocarbon liquid was used on the first stage [7].

4. Results and discussion

Obtained powders were studied with "Biolam-I" («Биолам-И») optic microscope using Image-J software according to [8]. As a result, histograms of particles distribution by their size and form factor (see Fig. 1 and Fig. 2) were obtained. It is found out that more than 70 % of particles have size less than 10 μ m, while 35 % of particles have size of ~ 3 μ m and 5 % of particles have size of ~ 0.6 μ m. The predominant forms of particles are spongy (35 %) and spherical (30 %). Mean diameter of particles in initial powder mixture was 30-50 μ m. Most particles of initial powder mixture had spongy form.

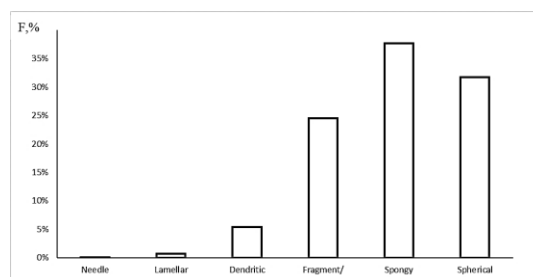


Fig. 1 – Distribution of particles of powder mixture of Ti-Al-C system after HVED treatment by their form

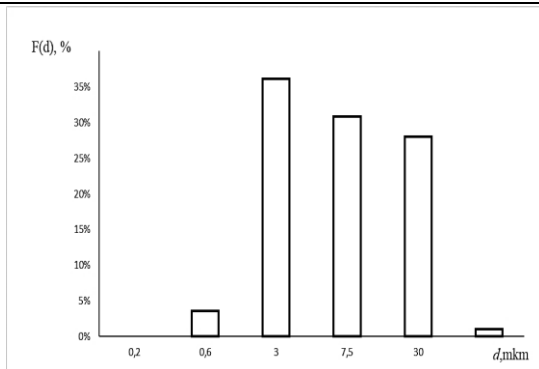


Fig. 2 – Distribution of particles of powder mixture of Ti-Al-C system after HVED treatment by their diameter

The usage of hydrocarbon liquid (kerosene) as a working medium during HVED treatment of initial Ti-Al-C system powder mixture allows excluding the introduction of additional carbon during powders preparation [5].

According to results of X-ray diffraction analysis of Ti – Al powder system after HVED treatment (X-ray diffraction patterns were obtained on Rigaku Ultima IV X-ray diffractometer), content of Titanium carbide in obtained powder mixture is ~ 25 % (see Fig. 3).

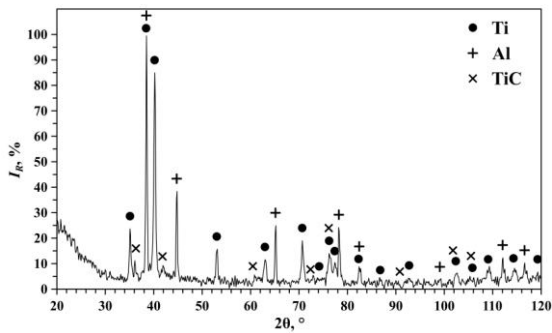


Fig. 3 – X-ray diffraction pattern of powder mixture of Ti-Al-C system after HVED treatment

The impact of current of different frequency composition on the properties of consolidated cylindrical specimens with diameter of 10 mm was studied by comparison of physical and mechanical properties of composites that were obtained from powder mixture of Ti-Al-C system, synthesized by HVED, that was consolidated using SPS and FAPAS methods. Consolidation by both methods was performed under pressure of 60 MPa in vacuum with isothermal holding at 1100 °C during 300 s.

Physical, mechanical and performance properties of obtained materials, such as density, wear resistance, Vickers hardness and dynamic strength, were studied.

Studies of abrasive wear resistance were performed on SMC-2 (CMI-2) friction machine using “roller – block” scheme [9]. Pair of friction consisted of immovable cylindrical specimen ($d = 10 \text{ mm}$, $h = 6 \text{ mm}$) of studied material (block) and roller (counter-body) made from quenched and tempered 1045 steel (Сталь 45). Friction conditions: no lubricant, peripheral speed – 0.785 m/s, specific pressure – 0.75 MPa, distance – 5 km.

Roller was rotated by machine operating axis with frequency of 300 spins/min. Specific load on the block was 60 kg/cm^2 . Studies were preceded by the preparation of contact surfaces that was performed by fitting with pre-friction during $30 \cdot 10^3$ work cycles.

During the studies, control of the load on the block and the way, which the specimen has passed, was performed. control of the wear was performed by the determination of specimens mass (using “Tehnovagy-TVE-0.21” («Техноваги-ТВЕ-0.21») lab scales of 2 accuracy class after each 0.5 km of the way. Dynamic compressive strength was studied using specimens compression

diagrams, obtained on split Hopkinson (Kolsky) bar experimental stand for dynamic studies [10]. Values of ultimate dynamic compressive strength and deformation energy during the destruction were determined using the obtained data.

X-ray diffraction analysis of consolidated specimens have shown that after consolidation of powder mixtures, prepared by HVED, using SPS (see Fig. 4) and FAPAS (see Fig. 5) methods the intensity of TiC peaks have increased, which indicates the significant increase of this phase concentration.

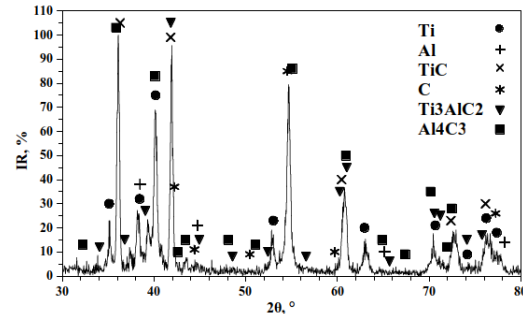


Fig. 4 – X-ray diffraction pattern of specimens, consolidated using SPS method

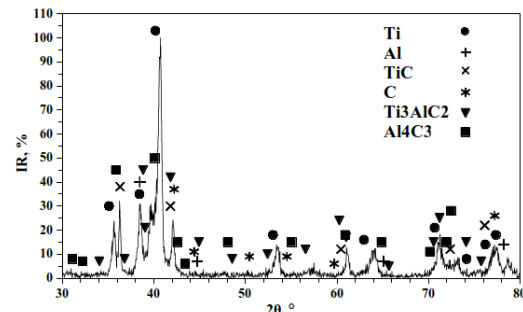


Fig. 5 – X-ray diffraction pattern of specimens, consolidated using FAPAS method

The intensity of Ti and Al peaks have notably decreased. Also, synthesis of such dispersion-strengthening phases, as TiC, Al_4C_3 and Ti_3AlC_2 MAX-phase takes place. It should be noted that intensity of dispersion-strengthening phases peaks is higher in case of using SPS than in case of using FAPAS method, which indicates that SPS ensures higher efficiency of their synthesis.

Properties of composite materials, based on Ti-Al-C system, obtained using SPS and FAPAS method are given in Table 1.

Table 1 – Properties of specimens, obtained by FAPAS and SPS methods

Sintering method	Porosity, %	Hardness HV, GPa	Dynamic strength, MPa	Loss of mass during abrasive wear, %
FAPAS	1	6.7	970	0.7
SPS	8	5	490	1.8

As it can be seen from this table, physical and mechanical properties of composite materials, obtained using FAPAS method, are significantly higher than those of composite materials, obtained using SPS method. Such significant difference of their characteristics can be explained by the fact that high-frequency component of current (frequency of 10 kHz) promotes movement of disperse phase inside the matrix, which leads to the agglomeration of strengthening particles (see Fig. 6, b) as well as to increase of obtained composite porosity up to ~ 8 %. sintering with the industrial frequency current allows obtaining of the material with homogeneously distributed structure (see Fig. 6, a) and porosity of ~ 1 % and less.

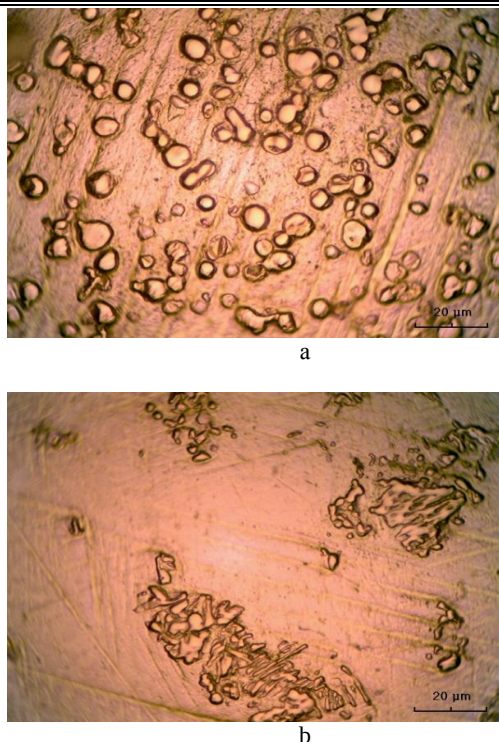


Fig. 6 – Optic microphotographs ($\times 1000$) of consolidated specimens of HVED-treated powders of initial 15 % Al + 85 % Ti composition, obtained using FAPAS (A) and SPS (b) methods

Characteristic diagrams of stress, strain rate and strain energy density of the specimen, made by FAPAS of powder mixture of Al – Ti after HVED treatment, are shown on Fig. 7. According to the curve 1 of Fig. 7, dynamic stress in the specimen σ^{cs} was around 970 MPa, while strain rate $\dot{\nu}^{\text{d}}$ was around 580 s^{-1} (see Fig. 7, curve 2) and energy density E_{d} was 10 MJ/cm^3 . Loss of mass during abrasive of this specimen was $\sim 0.7 \%$ after way of 5 km.

It is clear that the use of electric current of different frequency composition for consolidation of powder mixtures allows influencing the processes of liquid metal transfer and diffusion as wells as the size of strengthening phase in obtained specimens.

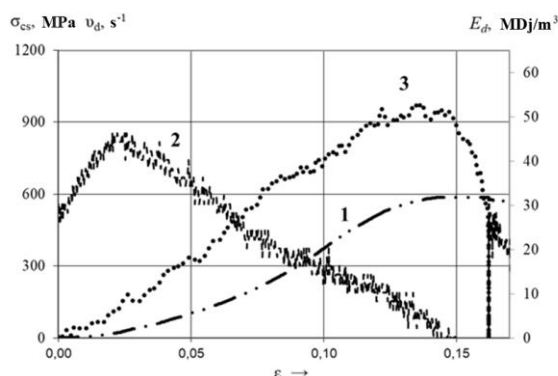


Fig. 7 – Diagram of compressive stress (1), strain rate (2) and strain energy density (3) of the specimen, obtained using FAPAS method

5. Conclusions

1. It is found out, that the use of currents of different frequency composition (superposition of direct current and alternating current with 10 kHz frequency or alternating current with industrial frequency of 50 Hz) during the consolidation of Ti – Al – C powder mixture can influence the processes of liquid metal transfer and diffusion as wells as the size of strengthening

phase in obtained specimens, which impact physical and mechanical properties of obtained specimens.

2. It is shown, that the use of SPS and FAPAS methods allows synthesizing of the materials, dispersion-strengthened by TiC and Al_4C_3 carbides and Ti_3AlC_2 MAX-phase. Intensity of dispersion-strengthening phases on the X-ray diffractograms is higher in case of using SPS method, yet their agglomeration is observed.

3. It is found out, that the use of FAPAS method allows obtaining of Ti – Al – C system MMC's with higher values of hardness and wear resistance, than of those obtained using SPS method. This is due to the formation of more homogeneous structure.

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IMPROVING THE MECHANICAL PROPERTIES OF CONVENTIONAL MATERIALS BY NANO-COATING, PART-1

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Abstract: The use of an advanced nanotechnology coating process is absolutely helpful in immensely optimizing the efficiency of mechanical properties of materials such as: Longer service life, ability to tolerate greater loads, ease and low cost of maintenance, the environmental gain in the conservation of resources, improved response in kinetic systems, lower energy consumption, resistance to corrosion, low friction, use of low-cost base material, etc. Metal materials are usually subjected to various surface conditions that might cause stress, strain, deformation, and corrosion. Accordingly, Nano-coating technology is used to enhance the performance of mechanical properties in addition to reduce mechanical failure as much as possible. This research, a simulation of Nano coating effect on some mechanical properties performance using Finite Element Analysis (FEA) software was carried out. The prime focus here was on exposing a thin Aluminum (Al7075-T6) walled spherical vessel to internal pressure before and after coating, this spherical vessel was coated by nano- layer using two different materials such as Titanium (Ti) and Nickel (Ni) with thicknesses ranging (100 nm, 500 nm, and 900 nm). Then a comparison of the obtained results was made before and after coating, the results showed that the aluminum 7075-T6 thin walled spherical vessel was successfully coated with Titanium and Nickel separately using ANSYS software. Also the results showed that 900 nm Nickel coated aluminum 7075-T6 thin walled spherical vessel has a better improvement in mechanical properties. These improvements in mechanical properties were varied between 4.5225% to 20.724% depending on coating thickness and coating material. The Nickel coating has shown higher improvements in comparison with Titanium were observed.

Keywords: MECHANICAL PROPERTIES, NANO, COATING, T_i , N_i , and AL 70705-T₆

List of Abbreviations: Al: Aluminum, ASM: American Society for Metals, FEA: Finite Element Analysis, GPT: General Purpose Technology, Ni : Nickel, PAS: Publicly Available Specification, Ti: Titanium, nm : nanometer, ϵ_c : the circumferential strain, ϵ_r : radial strain, ϵ_t : tangential strain , P : Resultant Pressure Force, P : Pascal , r: radius of the sphere , t : thickness, σ : sigma (tensile stresses), E : Modulus of elasticity , p: Fluid Pressure, v: Poisson ratio

Background: Nanotechnology is a nascent, vibrant, and burgeoning scientific discipline that is predicted to have important implications for an extraordinarily broad array of applications encompassing almost every industrial sector. It is surmised that virtually no facet of the industry will be left uninfluenced by its seemingly ubiquitous reach. Nanotechnology is defined as the capacity for the controllable manipulation of matter at the molecular and atomic levels, typically from 1 nm to 100 nm. It allows for and encompasses the fundamental ability to synthesize novel materials and to create devices that exhibit extraordinary properties with enhanced functionality. One compelling driver of this technology lies in the premise that matter behaves in radically different ways for nano scale materials in contrast to their bulk material counterparts. Nano scale materials can possess innumerable components that are endowed with exponentially greater surface areas, which are critical in many industrial processes. Nano materials or Nano scale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair as shown in figure-1. Nano materials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields. (A, Alagarasi, 2011). Nano coatings have the potential for enhancing the performance and durability of an extensive array of manufacturing processes, in addition to improving the items that they produce. They may thus enable significant energy savings to be realized across just about every market sector. Nano coating imparts multifunctional attributes to many everyday consumer and industrial products.



Figure 1: Nano-material (National Center for Electron Microscopy, Lawrence Berkeley Lab, US. Department of Energy)

Nanotechnology: Richard Feynman gave flight to the concept of nanotechnology via his 1959 introductory lecture “There’s Plenty of Room at the Bottom.” Sited in 1986 K. Eric Drexler’s book *Engines of Creation* articulated the promise of this new science in the diverse range of future scenarios. An important development that transitioned many “Nano visions” into tangible reality was the development of Scanning Tunneling Microscopy (1981) and Atomic Force Microscopy (1986). These instruments enabled imaging at a Nano metric resolution and the manipulation of individual atoms. (Boehm, Frank. 2010) Nanotechnology is a newly emerging branch of technology, which incur high expectations of its possibility to change the world fundamentally. Some policymakers and technology developers even speak about “the Next Industrial Revolution”, which advancing nanotechnology is supposed to bring along (Schummer, 2004). Others argue that nanotechnology is just a new label put on research projects in conventional fields of science – such as chemistry, physics, biomedical engineering, materials science and electrical engineering to gain more research funding. However, there have been also efforts to define various terms in the field of nanotechnology, and thus build a common understanding about the issue.

Research objectives: The main objectives of this work are:

- 1- Studying and analyzing the mechanical properties improvement when using a Nano coating of Al 7075-T6 alloy. The following stresses will be studied and analyzed includes, which are:
 - a) Normal Stresses in X and Y axis.
 - b) Shear Stresses in XY and XZ plane.
 - c) Equivalent (Von-Misses) stresses
- 2- Studying and analyzing normal elastic strain in X and Y axis
- 3- Studying and analyzing total deformation

Research methodology: In this work a simulation of the Nano coating effect on mechanical properties for optimizing its performance using FEA software were carried out. The prime focus here was on exposing a thin walled spherical vessel made of Aluminum (Al7075-T6) under internal pressure before and after

coating with Nano coated materials such as Titanium (Ti) and Nickel (Ni) with different thicknesses .A comparison of the results before and after coating will be made. In the same fashion prepared electro-deposition of composite coatings containing Nano particles in a metal matrix. It was showed that the inclusion of Nano sized particles can give rise to increased micro hardness and corrosion resistance and modified growth to form a Nano crystalline metal deposit and shifted reduction potential of a metal ion. (Low et al, 2006). The above observations motivated the present investigation, where an attempt will be made to develop and characterize the mechanical, chemical properties, micro structural and compositional features of the coating in present work.

Theoretical analysis: The proposed work as a comparison of the performance analysis of mechanical properties of Nano coated and uncoated for the Al7075-T6 alloy. The work will be intend to enhance the mechanical properties, life time, ability of carrying high stress and the resistance to deformation of aluminum alloy AL 7075-T6. The finite element analysis (FEA) will be performed on thin walled spherical pressure vessels geometry under internal pressure compared with the uncoated and coated with Nano thicknesses of Titanium and Nickel separately by using surface coating function in ANSYS software (Products Release 19.0).

Pressure Vessel: Pressure vessel is a tank contains pressures, either internal or external. This pressure may be obtained from an external source, or by the application of heat from a direct or indirect source, or any combination thereof. (Boiler, ASME and Code, P.V.1989). Spherical shells as structural parts are used extensively in many applications, like nuclear, offshore, fossil oil and transport, because they can be subjected to variable loading conditions like external pressures or internal or both (V. Prasad and B. Praveen Kumar, 2017) for the following advantages:

1. The stress resistance considered to be uniform
2. The distribution of pressure is uniform upon the tank storage.
3. Sphere contains more volume for the surface area.
4. Also metal thickness is sometimes about half as much as a cylinder of the same diameter for the same pressure rating.
5. The stresses and strains are spreading more uniformly.
6. The cost of the wall thickness of a spherical shell will be about half the wall thickness needed for a cylindrical shell for holding in the same pressure. So, in a spherical container use a thinner shell which means lesser cost and weight.
7. Area to volume ratio is the area that a sphere occupies will be lesser compared to a cylindrical container of the same volume.

But in spite of the above advantages spherical pressure vessels are more expensive than cylindrical pressure vessels to fabricate, and this higher price is only justifiable for large vessels.

The Geometric modeling of the case study: One finite element model is created, it is a thin walled spherical pressure vessel coated with different Nano thickness of Titanium and Nickel separately. As seen in figures (2 to 5).

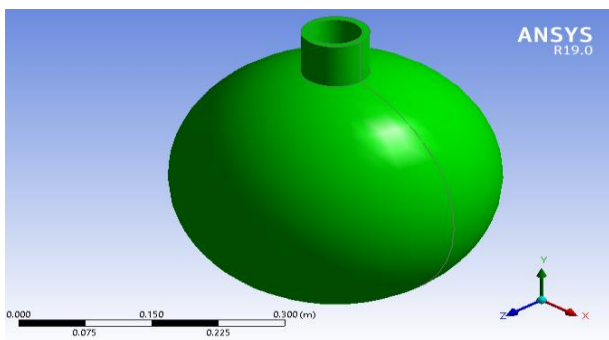


Figure 2: 3D Thin walled Spherical vessel

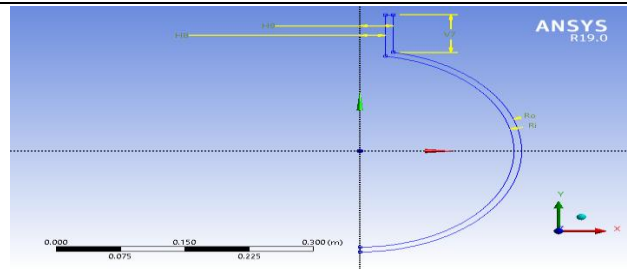


Figure 3: Front view thin spherical vessel with dimensions

Where: H8 = 0.03 m, H9 = 0.039 m, Ri = 0.18 m, Ro= 0.189 m, V7= 0.07 m

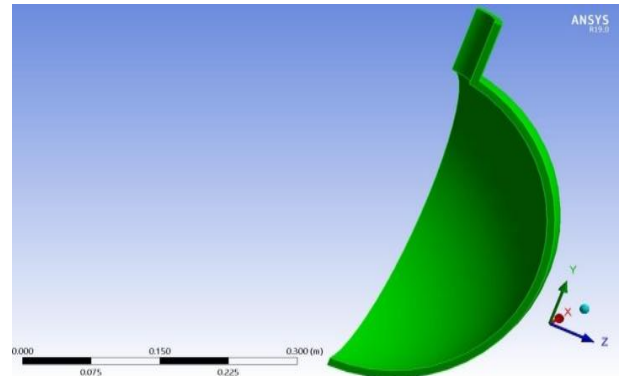


Figure 4: 90° Thin walled Spherical vessel

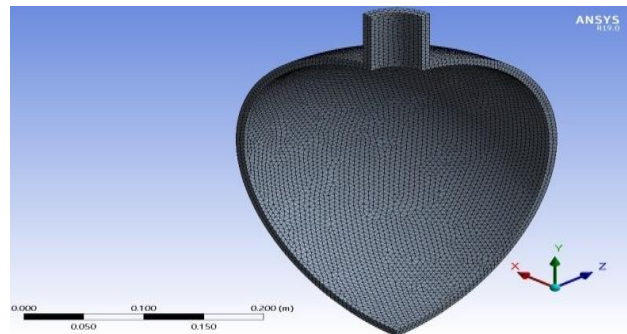


Figure 5: 90° Thin walled spherical vessel with 5 mm elements size of mesh

Stress analysis in the thin-walled spherical pressure vessel:

Theoretically, spherical shape it is the ideal shape for a vessel that resists internal pressure. To derive the stresses in a spherical vessel, a cut through the sphere on a vertical diametric plane as in Fig. 6a and isolate half of the shell and its fluid contents as a single free body (Fig. 6b), was made acting on this free body is the tensile stresses σ in the wall of the vessel and the fluid pressure p . This pressure acts horizontally against the plane circular area of fluid remaining inside the hemisphere. Since the pressure is uniform, the resultant pressure force P as in Fig. 6b (Gere and Goodno, 2008)

$$P = p(\pi r^2) \quad (1)$$

Where, r : is the inner radius of the sphere, p : net internal pressure, or the gage pressure. Because of the symmetry of the vessel and its loading (Fig. 6b), the tensile stress σ is uniform around the circumference. Moreover, since the wall is thin, an assumption with good accuracy may be used in which the stress is uniformly distributed across the thickness t . The accuracy of this approximation rise as the shell becomes thinner and lowers as it becomes thicker. The resultant of the tensile stresses σ in the wall is a horizontal force equal to the stress σ times the area over which it acts, or

$$\sigma(2\pi r_m t) \quad (2)$$

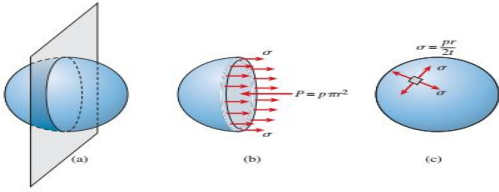


Figure 6: Tensile stresses σ in the wall of a spherical pressure vessel (Gere and Goodno, 2008)

Where, t : the thickness of the wall, r_m : It's the mean radius where, $r_m = r + \frac{t}{2}$ (3)

Thus, equilibrium of forces in the horizontal direction (Fig. 6b) gives $\sum F_{horiz} = 0$ $\sigma(2\pi r_m t) - p(\pi r^2) = 0$ (4)

Will get the tensile stresses in the wall of the vessel

$$\sigma = \frac{pr^2}{2r_m t} \quad (5)$$

This analysis is valid only for thin shells, disregarding the small difference between the two radii appearing in equation (4) and replace r by r_m or replace r_m by r . While either choice is satisfactory for this approximate analysis, it turns out that the stresses are closer to the theoretically exact stresses if using the inner radius r instead of the mean radius r_m . Therefore, will adopt the following formula for calculating the tensile stresses in the wall of a spherical shell:

$$\sigma = \frac{pr}{2t} \quad (6)$$

As is evident from the symmetry of a spherical shell, it will obtain the same equation for the tensile stresses when cutting a plane through the center of the sphere in any direction. So, we have the following conclusion: The wall of a pressurized spherical vessel is subjected to uniform tensile stresses σ in all directions. This stress condition is represented in Fig. 6c, by the small stress element with stresses σ acting in mutually perpendicular directions (Gere and Goodno, 2008). Because of the symmetry of the sphere and of the pressure loading, the circumferential (or tangential or hoop) stress at any location and in any tangential orientation must be the same and there will be zero Shear Stresses. (Kelly, P., 2013).

Strain analysis of the thin-walled spherical pressure vessel:

The thin-walled pressure vessel will extend when it is internally pressurized. These results in three principal strains, the circumferential strain ϵ_c (or tangential strain ϵ_t) in two perpendicular in-plane directions, and the radial strain ϵ_r . referring to Fig. (7), these strains are:

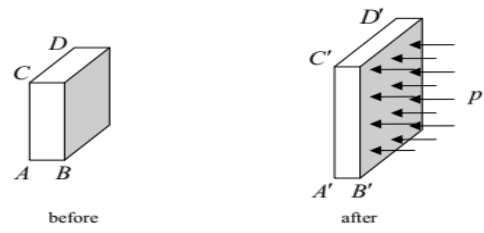


Figure 7: Strain of an element at the surface of a spherical pressure vessel (Kelly, P., 2013).

$$\epsilon_c = \frac{A'C' - AC}{AC} = \frac{C'D' - CD}{CD}, \epsilon_r = \frac{A'B' - AB}{AB} \quad (7)$$

$$\epsilon_{xx} = \frac{1}{E} [\sigma_{xx} - \nu(\sigma_{yy} + \sigma_{zz})] \quad (8)$$

$$\epsilon_{yy} = \frac{1}{E} [\sigma_{yy} - \nu(\sigma_{xx} + \sigma_{zz})] \quad (9)$$

$$\epsilon_{zz} = \frac{1}{E} [\sigma_{zz} - \nu(\sigma_{xx} + \sigma_{yy})] \quad (10)$$

$$\epsilon_{xy} = \frac{1+\nu}{E} \sigma_{xy} \quad (11)$$

$$\epsilon_{xz} = \frac{1+\nu}{E} \sigma_{xz} \quad (12)$$

$$\epsilon_{yz} = \frac{1+\nu}{E} \sigma_{yz} \quad (13)$$

From Hooke's law (equations: 8- 13) with z the radial direction, with $\sigma_r = 0$:

$$\begin{bmatrix} \epsilon_c \\ \epsilon_c \\ \epsilon_r \end{bmatrix} = \begin{bmatrix} 1/E & -\nu/E & -\nu/E \\ -\nu/E & 1/E & -\nu/E \\ -\nu/E & -\nu/E & 1/E \end{bmatrix} \begin{bmatrix} \sigma_t \\ \sigma_t \\ \sigma_r \end{bmatrix} = \frac{1}{E} \frac{pr}{2t} \begin{bmatrix} 1-\nu \\ 1-\nu \\ 1-\nu \end{bmatrix} \quad (14)$$

Equations (7 to 14) are from (Kelly, P., 2013). To calculate the amount by which the vessel expands, consider a circumference at average radius r which moves out with a displacement δr , Fig.8. From the definition of normal strain

$$\epsilon_c = \frac{(r+\delta r)\Delta\theta - r\Delta\theta}{r\Delta\theta} = \frac{\delta r}{r} \quad (15)$$

This is the circumferential strain for points on the mid-radius. The strain at other points in the vessel can be approximated by this value.

The expansion of the sphere is thus

$$\delta r = r\epsilon_c = \frac{1-\nu}{E} \frac{pr^2}{2t} \quad (16)$$

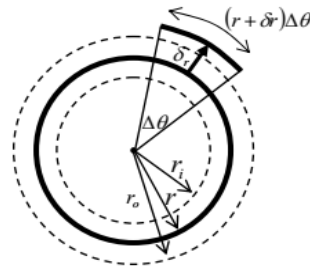


Figure 8: Deformation in the thin-walled sphere as it expands (Kelly, P., 2013).

To determine the amount by which the circumference increases in size, consider Fig. 9, which shows the original circumference at radius r of length c increase in size by an amount δc . One has

$$\delta_c = c\epsilon_c = 2\pi r\epsilon_c = 2\pi \frac{1-\nu}{E} \frac{pr^2}{2t} \quad (17)$$

It follows from equations (16 and 17) that the circumference and radius increases are related through. (Kelly, P., 2013).

$$\delta_c = 2\pi\delta_r \quad (18)$$

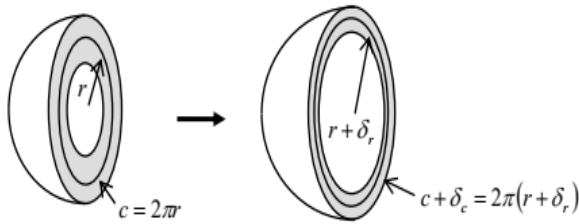


Figure 9: Increase in circumference length as the vessel expands (Kelly, P., 2013).

Results and discussions: The improvement in mechanical properties such as , lifetime, ability of carrying high stress and the resistance to deformation, done on aluminum alloy (Al 7075-T6) as a thin-walled spherical vessel, coated with different Nano thicknesses of Titanium (Ti) and Nickel (Ni) using surface coating technique in ANSYS Software, Product Release 19.0. This work began by applying internal pressure (1 bar) to a thin-walled spherical vessel made from (Al 7075-T6) without coating and finding the effects on mechanical properties, after which the internal pressure value was kept at (1 bar) and surfaces coating was applied in the range of (100 nm, 500 nm and 900 nm) thicknesses of a Titanium and Nickel separately, these mechanical properties at each stage, as follows:

a) Total Deformation: Total Deformation used to obtain displacements due to internal pressure (stress) in X, Y, and Z directions, figures (10 to 16), and table (1) show the value of the improvement in Total Deformation in thin-walled spherical pressure vessel, before and after coating with different Nano thicknesses of Titanium and Nickel separately.

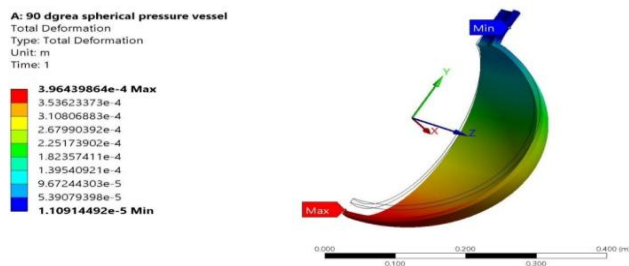


Figure 10: Total Deformation of Al7075-T6 without coating

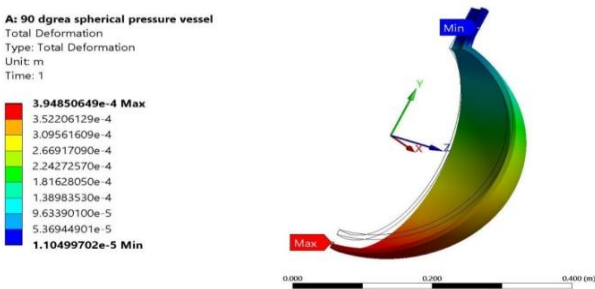


Figure 11: Total Deformation of Al7075-T6 with 100 Nanometers of Titanium

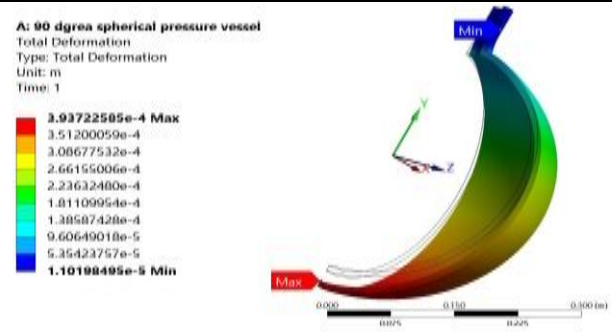


Figure 12: Total Deformation of Al7075-T6 with 100 Nanometers of Nickel.

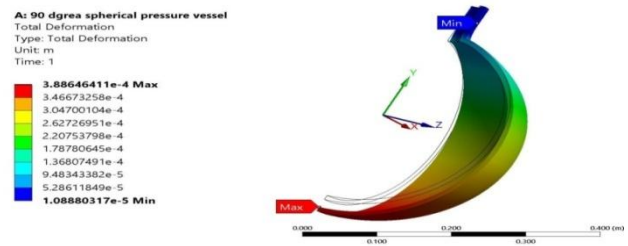


Figure 13: Total Deformation of Al7075-T6 with 500 Nanometers of Titanium

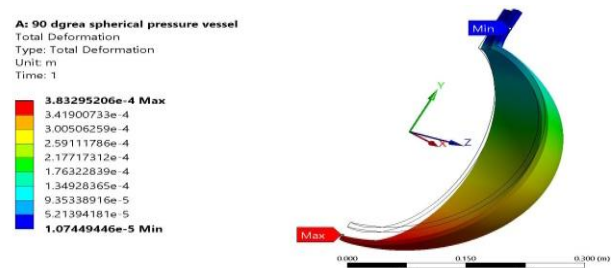


Figure 14: Total Deformation of Al7075-T6 with 500 Nanometers of Nickel.

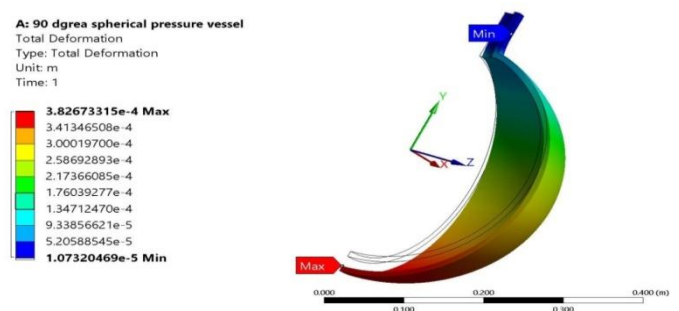


Figure 15: Total Deformation of Al7075-T6 with 900 Nanometers of Titanium.

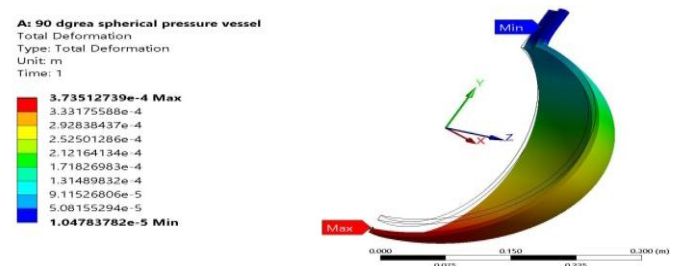


Figure 16: Total Deformation of Al7075-T6 with 900 Nanometers of Nickel.

Table-1: Improvement percentage in Maximum Total Deformation

	Titanium (Ti)		Nickel (Ni)	
	value	Improvement %	value	Improvement %
0.0 nm	3.96439864e-4	0.0	3.96439864e-4	0.0
100 nm	3.94850649e-4	0.4009	3.93722585e-4	0.6902
500 nm	3.88646411e-4	1.9659	3.83295206e-4	3.4294
900 nm	3.82673315e-4	3.4725	3.73512739e-4	6.1382

$$\text{The improvement percentage} = \left| \frac{\text{old value} - \text{new value}}{\text{old value}} \right| * 100\% \dots (19)$$

Where, Old value: value before coating.

New value: value after coating.

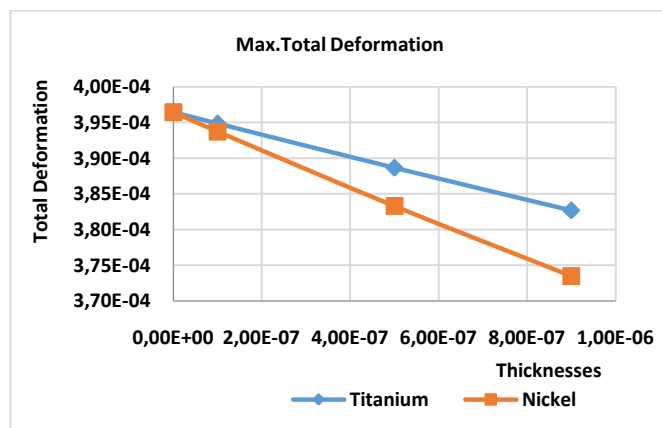
**Figure 17:** Comparison between Titanium and Nickel Nano coating thickness improvement on maximum Total Deformation.

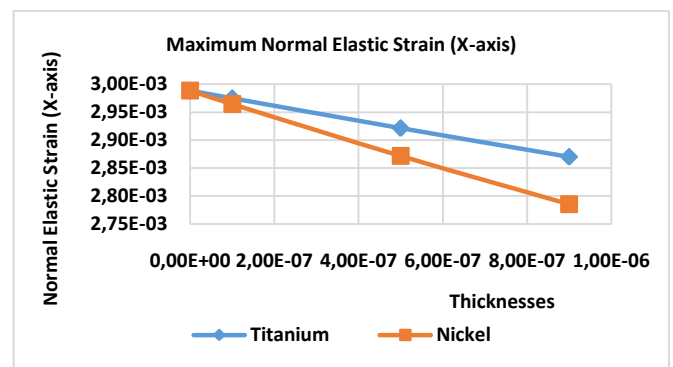
Figure (17) shows the value of improvement on thin-walled spherical vessel for increasing the resistance to Total Deformation after coating the surface of thin-walled spherical vessel which made of (Al 7075-T6) by different Nano thicknesses of Titanium and Nickel separately, starting coating from 100 Nanometers thickness of (Titanium and Nickel), the increasing the thicknesses of coating to (500 and 900 Nanometers) the lowest value of improvement in decreasing the Total Deformation is (0.4009%) for Titanium and the highest improvement in decreasing the Total Deformation is for Nickel about (6.1382%) between these two values the advantage of improvement it is for Nickel, it can make improvements (56.6%) more than Titanium.

b) Normal Elastic Strain: Elongation or contraction of a line segment due to stress it is the normal elastic strain was studied longitudinally and normally (hoop), as follows:

1) Normal Elastic Strain (longitudinal strain): By the same way which had been done with total deformation discussed above, table (2) shows the value of improvement in Normal Elastic Strain in the (X-axis) direction for a thin-walled spherical vessel, it is obvious that the maximum and minimum value of strain which is located in the vessel neck, increasing in one direction means decreasing in the other direction, negative values mean that a contraction in this region is occurred.

Table 2: Improvement percentage in Maximum Normal Elastic Strain (X-axis)

	Titanium (Ti)		Nickel (Ni)	
	value	Improvement %	value	Improvement %
0.0 nm	2.98887594e-3	0.0	2.98887594e-3	0.0
100 nm	2.97514615e-3	0.4615	2.96454998e-3	0.8206
500 nm	2.92165568e-3	2.3008	2.87164939e-3	4.0822
900 nm	2.87032658e-3	4.1302	2.78514992e-3	7.3147

**Figure 18:** comparison between Titanium and Nickel Nano coating thickness in maximum Normal Elastic Strain (X-axis)

While, Figure (18) shows the value of improvement on thin-walled spherical vessel for increasing the resistance to Normal Elastic Strain (longitudinal strain) after coating the surface of thin-walled spherical vessel which made of Al 7075-T6 by different Nano thicknesses of Titanium and Nickel separately, started coating from 100 Nanometers of (Titanium and Nickel) thicknesses, then increasing the thicknesses of coating to (500 and 900 Nanometers). It can be seen that the lowest value of improvement in Normal Elastic Strain (longitudinal strain) is (0.4615%) for Titanium, and the highest improvement it is for Nickel (7.3147%), also the larger improvement can be seen in Nickel coating, which is about (56.4%) higher than Titanium.

2) Normal Elastic Strain (hoop strain): Table (3) shows the improvements in Normal Elastic Strain in the (Y-axis) direction for a thin-walled spherical vessel, it is evident that the maximum value of strain which is located at the middle of the vessel and the minimum value at the vessel neck.

Table 3: Improvement percentage in Maximum Normal Elastic Strain (Y-axis)

	Titanium (Ti)		Nickel (Ni)	
	value	Improvement %	value	Improvement %
0.0 nm	9.82097024e-4	0.0	9.82097024e-4	0.0
100 nm	9.78520897e-4	0.3655	9.76008701e-4	0.6238
500 nm	9.64471383e-4	1.8275	9.52388661e-4	3.1194
900 nm	9.50816693e-4	3.2898	9.29879822e-4	5.6155

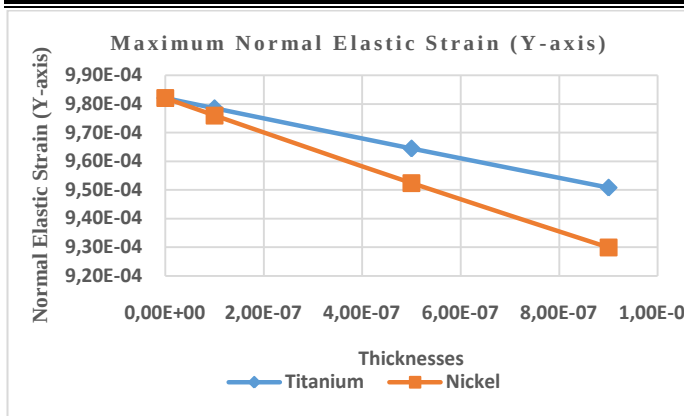


Figure 19: comparison between Titanium and Nickel Nano coating thickness improvement maximum Normal Elastic Strain (Y-axis).

Figure (19) shows the value of improvement on thin-walled spherical vessel for increasing the resistance to Normal Elastic Strain (hoop strain) after coating the surface of thin-walled spherical vessel. It is clear that the lowest value of improvement in Normal Elastic Strain (hoop strain) is (0.3655%) for Titanium, and the highest improvement it is for Nickel (5.6155%), also again the larger improvement is found in Nickel coating, which is about (58.6%) higher than Titanium.

c) Normal Stress: Normal Stress is the stress which acts in a direction perpendicular to the area [Bansal, R.K., 2010.]. Also by the same procedure as above was analyzed longitudinally and normally l(hoop) as follows:

1) Normal Stress (longitudinal stress, X-axis): Longitudinal Normal Stress is the stress acting in a spherical vessel wall along the longitudinal axis, table (4) shows the improvement in longitudinal stress in a thin-walled spherical vessel.

Table 4: Improvement percentage in Maximum Normal Stress (X-axis)

	Titanium (Ti)		Nickel (Ni)	
	value	Improve nt %	value	Improve nt %
0.0n m	2.06153552 e6	0.0	2.06153552 e6	0.0
100n m	2.05191643 e6	0.4688	2.04519670 e6	0.7989
500n m	2.01453305 e6	2.3332	1.98284223 e6	3.9687
900n m	1.97878315 e6	4.1812	1.92481780 e6	7.1029

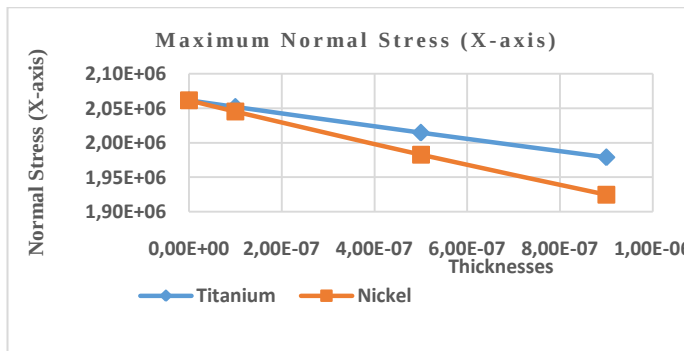


Figure 20: Comparison between Titanium and Nickel Nano coating thickness improvement maximum Normal Stress (X-axis)

Figure-20 shows the value of improvement on thin-walled spherical vessel for increasing the resistance to Normal Stress (longitudinal stress) after coating the surface of thin-walled spherical vessel, it is clear that the lowest value of improvement in Normal Stress (longitudinal stress) is (0.4688%) for Titanium, and the highest improvement it is for Nickel (7.1029%), also the larger improvement is found in Nickel coating, which is about (58.86%) higher than Titanium.

2) Normal Stress (hoop stress, y-axis)

Hoop stress is the stress in a spherical vessel wall, acting circumstantially in a plane perpendicular to the longitudinal axis of the vessel, table (5) and figure-21 show the improvement in Normal Stress (hoop stress). Figure (21) indicates that the spherical vessel coated with Ni 900 Nano meters has the highest percentage of improvement in decreasing the Normal Stress (hoop stress), about 5.7471% compared to all other coatings. Also, it depicts that with the increase in the coating thickness there is an appreciable increase in the improvement. The larger improvement is found in Nickel coating, which is about (58.6%) higher than Titanium.

Table 5: Improvement percentage in Maximum Normal Stress (Y-axis)

	Titanium (Ti)		Nickel (Ni)	
	value	Improve nt %	value	Improve nt %
0.0n m	1.00175610e 6	0.0	1.00175610e 6	0.0
100 nm	9.98024075e 5	0.3739	9.95402406e 5	0.6383
500 nm	9.83366919e 5	1.87	9.70767044e 5	3.1922
900 nm	9.69131450e 5	3.3664	9.47312896e 5	5.7471

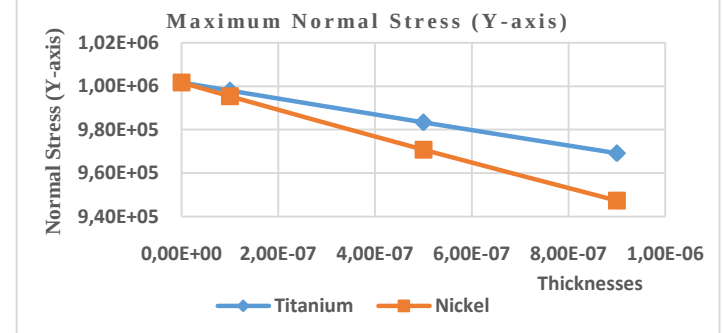


Figure 21: comparison between Titanium and Nickel Nano coating thickness in maximum Normal Stress (Y-axis).

d) Equivalent Stress: Equivalent Stress (also called Von Misses stress) is often used in design work because it allows any arbitrary three-dimensional stress state to be represented as a single positive stress value. Equivalent Stress is part of the maximum Equivalent Stress failure theory used to predict yielding in a ductile material. The test results for Equivalent Stress are tabulated in the table (6) and figure (22) indicate that the spherical vessel coated with Ni 900 Nano meters has the highest percentage of improvement in decreasing the Equivalent Stress (7.3358%) compared to all other coatings. Also, they depict that with the increase in the coating thickness there is an appreciable increase the improvement. Again the larger improvement is found in Nickel coating, which is about (55.3%) higher than Titanium.

Table 6: Decreasing percentage in Maximum Equivalent Stress

	Titanium (Ti)		Nickel (Ni)	
	value	Improvement %	value	Improvement %
0.0nm	2.20215702e6	0.0	2.20215702e6	0.0
100nm	2.19220712e6	0.4539	2.18416913e6	0.8236
500nm	2.15339847e6	2.2643	2.11550008e6	4.0963
900nm	2.11610677e6	4.0664	2.05165105e6	7.3358

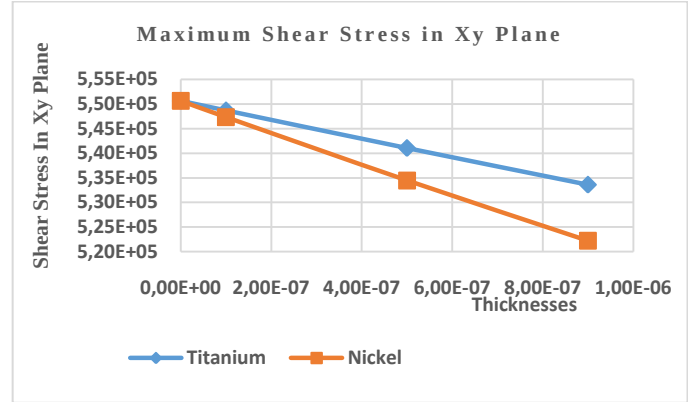


Figure 23: Comparison between Titanium and Nickel Nano coating thickness in maximum Shear Stress in the XY plane

The test results for Shear Stress in the XY plane are also shown in figure (23), which illustrates that the spherical vessel coated with Ni 900 Nanometers has the highest percentage of improvement in decreasing the Shear Stress in XY plane (5.4464%) compared to all the other coatings. Also, it depicts that with the increase in the coating thickness there is an appreciable increase in the improvement. Again the Nickel has improvements (58.6%) higher than Titanium.

2) Shear Stress in XZ plane: Table (8) and figure-24 show the improvement in Shear Stress in the XZ plane. The results show that the spherical vessel coated with Ni 900 Nanometers has the highest percentage of improvement in decreasing the Shear Stress in XZ plane (20.7240%) compared to all the other coatings, and the Nickel has improvements (56.1%) more than Titanium.

Table (9) shows a summary for all types of stresses which have been analysed and the improvement percentage on these stresses after coating with Nano thicknesses of Titanium and Nickel.

Table 8: Decreasing percentage in Maximum Shear Stress in XZ plane

	Titanium (Ti)		Nickel (Ni)	
	value	Improvement %	value	Improvement %
0.0nm	9.55220253e3	0.0	9.55220253e3	0.0
100nm	9.43021767e3	1.2936	9.33437257e3	2.3336
500nm	8.97289643e3	6.4562	8.56243172e3	11.5595
900nm	8.55764045e3	11.6219	7.91243169e3	20.7240

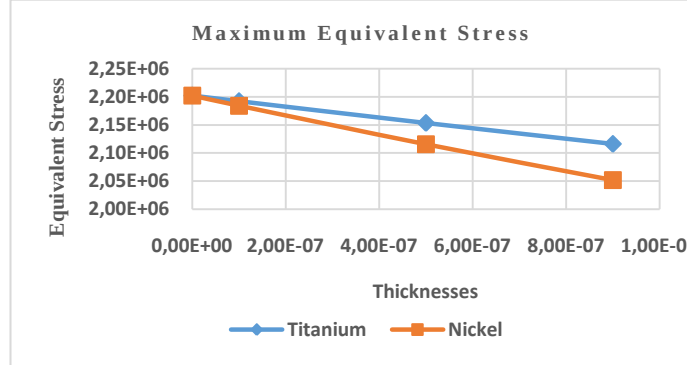


Figure 22: comparison between Titanium and Nickel Nano coating thickness in maximum Equivalent Stress.

c) Shear Stress: Shear stress is the stress induced in a body when subjected to two equal and opposite forces which are acting tangentially across the resisting section (Bansal, R.K., 2010).

1) Shear Stress in XY plane

Table (7) shows the improvement in Shear Stress in XY plane

Table 7: Decreasing percentage in Maximum Shear Stress in XY plane

	Titanium (Ti)		Nickel (Ni)	
	value	Improvement %	value	Improvement %
0.0nm	5.50635833e5	0.0	5.50635833e5	0.0
100nm	5.48691844e5	0.3543	5.47325146e5	0.6049
500nm	5.41048542e5	1.7720	5.34468677e5	3.0249
900nm	5.33608417e5	3.1910	5.22194865e5	5.4464

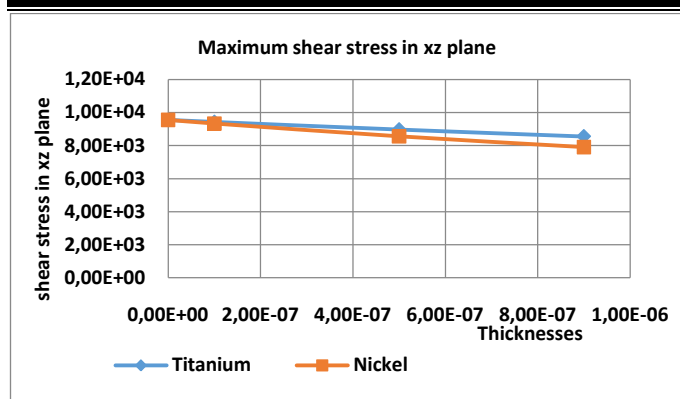


Figure 24: comparison between Titanium and Nickel Nano coating thickness in maximum Shear Stress in the XZ plane.

Table 9: Summary of improvement percentage

Conclusions:

From the results of this work, the following conclusions can be drawn.

- 1- The aluminum 7075-T6 thin walled spherical vessel was successfully coated theoretically by modeling with Titanium and Nickel by using ANSYS software with different Nano thicknesses of 100nm, 500nm, and 900nm respectively.
- 2- The 900nm Nickel coated aluminum 7075-T6 thin walled spherical vessel showed a better improvement in their mechanical properties, where: The percentage of improvement in increasing the resistance in Total Deformation (6.1382%), the Normal Elastic Strain X-axis (7.3147%), the Normal Elastic Strain Y-axis (5.6155%), the Normal Stress-axis(7.1029%), the Normal Stress-axis(5.7471%), the Equivalent Stress(7.3358%), the Shear Stress XY- plane(5.4464%) and the Shear Stress XZ- plane(20.724%).
- 3- The improvement percentage of the coated thin-walled spherical vessel by 500nm Nickel it is approximately equal to the improvement percentage of the coated thin-walled spherical vessel by 900nm Titanium.
- 4- Nickel and Titanium can helping in protecting against corrosion and improve wear resistance, as well as increasing the thickness of a surface.
- 5- Nickel and Titanium can enhance the appearance of the spherical vessel by adding brightness.
- 6-The Spherical vessel with Nickel coated exhibited the highest percentage of improvement in comparison with Titanium under the conditions.

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WARM COMPACTION OF IRON POWDER

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Abstract: Iron powder metallurgy is a method that is widely used in production of steel parts that are utilized as machine components or as parts in automotive industry. Milling is extensively used in powder metallurgy of iron, for purposes of mixing. The hardness and yield strength of milled iron powders increase due to work hardening. This leads to low green density of the cold pressed green parts, prior to sintering. In powder metallurgy, warm compaction is utilized for enhancing the green density and green strength.

In the present study, effect of warm compaction of milled iron powders was investigated. For warm compaction of iron powders, 600 MPa pressure was applied in a steel die at 150 °C. The microstructure of the milled samples was examined by scanning electron microscopy. Hardness values of the cold pressed and warm compacted samples were determined by a Brinell hardness tester. Bending strength values of the samples were determined by a universal testing machine. It was found that the hardness of the cold compacted green samples increased considerably, from about 40 Brinell10 to about 140 Brinell10, as a result of warm compaction. Bending strength values increased to over 100 MPa after warm compaction; whereas the bending strength of the cold compacted green samples were in 10-20 MPa range.

Keywords: POWDER METALLURGY, WARM COMPACTION, IRON POWDER

1. Introduction

In the method of powder metallurgy, metals in powder form are mixed, compacted and sintered. In comparison to other manufacturing methods, it has some benefits such as very high utilization rate of starting powders, capability of net shaped production, etc.

Microstructural control is another outcome of powder metallurgy. Due to the fact that the process starts from powdered metal, particle size of which is generally 10 microns or less, the distribution and size of the microstructural constituents such as phases and pores in the final product can be arranged, in a much better manner than the other production techniques.

Mixing and milling is one of the initial steps in powder metallurgy, which is used for blending powders, as well as for powder production and particle size reduction [1]. During milling, especially when the impact of the balls is large, such as in high energy milling, a high amount of plastic deformation of the particles occurs. Ductile metallic particles become flake shaped. In addition, due to cold welding of the flakes, agglomerates form and particle size increases [2]. During milling, the hardness and yield strength of milled metal powders increase due to work hardening. This leads to low green density of the cold pressed green parts, prior to sintering.

In powder metallurgy, warm compaction is utilized for enhancing the green density and green strength. Warm compaction of iron is conducted mostly in 150-180 °C temperatures range. During warm compaction, polymer binder and lubricant melts and solidifies, giving the pressed article a higher density and strength [1,3,4]. In addition, it was reported that the properties of the articles that are warm compacted and sintered are superior to those of the articles that are cold compacted and sintered [5].

In the present study, effect of warm compaction of milled iron powders was investigated. After milling, iron powders were warm compacted at 150 °C. Mechanical properties and microstructure of the warm compacted specimens were compared with the properties of cold compacted green samples.

2. Experimental Procedure

In the present study, effect of warm compaction of milled iron powders was investigated. Milling of the Fe powder was conducted in a planetary ball mill having a 250 ml capacity stainless steel grinding jar. Process control agent was not used.

In each run, 10 g Fe powder was milled. The grinding jar was equipped with an aeration cover, which made it possible vacuuming and back filling the jar with argon. This provided the milling

operation to be conducted in argon atmosphere. Thus, oxidation of the Fe powder during milling was prevented.

The diameter of the milling balls were 6 mm. Ball to powder weight ratio was kept as 10. Milling was conducted for various durations up to 1 hour. Milling was interrupted at definite durations such as 2 minutes, and after 2 minutes of cooling period, milling was continued.

In order to characterize the milled Fe powders, particle size analyses were performed. A scanning electron microscope (SEM) was employed for morphological and dimensional investigations after milling.

For warm compaction of iron powders, 600 MPa pressure was applied in a steel die at 150 °C, in a hot press. Milled powders were subjected to scanning electron microscopy examinations and particle size analyses. The microstructure of the compacted samples was examined by optical microscopy (Nikon Eclipse LV 150). Hardness values of the samples were determined by a Brinell hardness tester (Bulut Makine RBOV). Bending strength values of the samples were determined by a universal testing machine (Shimadzu AG-IC, capacity: 50 kN).

3. Results and Discussion

Powders, which were milled for 0, 15, 30 and 60 min were subjected to SEM examinations and particle size measurements.

SEM micrograph of Fe powder which was milled for 15 min is given in Fig. 1. It can be seen that size of the particles are mostly about 10 microns and the particles have sphere-like morphology. There are a few large particles which have flat surfaces. It can be inferred that in 15 minutes milling duration, the effect of milling is quite low.

Average particle size of the Fe powder prior to milling was 10 microns. Particle size distribution plot of the Fe powder which was milled for 15 minutes is given in Fig.2. It can be seen that the size distribution has 3 modes. Most of the particles are about 10 microns, some are about 70 microns and very few are about 300 microns.

During milling flattening of the Fe particles takes place with the squeezing action of the milling balls and vial. The increase in the particle size may be attributed to sticking and cold welding of the flattened Fe particles to each other with the repeated impact of the milling balls.

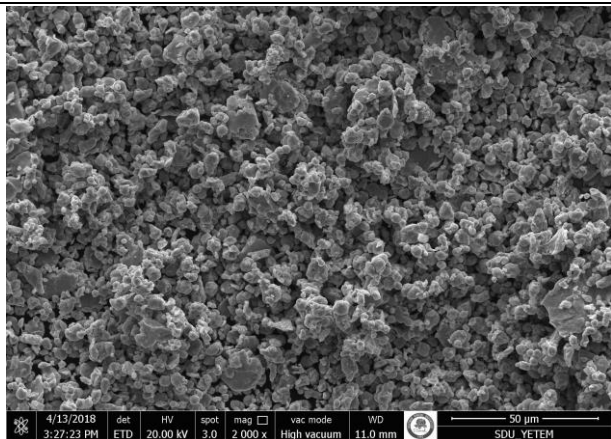


Fig. 1 Scanning electron micrograph of the Fe powder which was milled for 15 minutes.

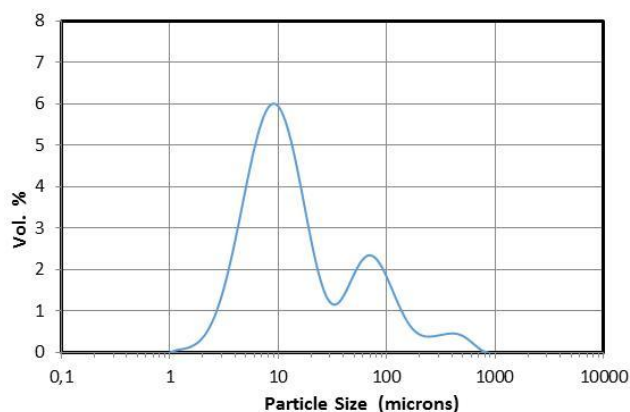


Fig. 2 Particle size distribution plot of the Fe powder which was milled for 15 minutes

SEM micrograph of Fe powder which was milled for 60 min is given in Fig. 3. It can be seen that size of the particles are mostly larger than 50 microns and the particles have flake-like morphology. It can be inferred that in 60 minutes milling duration, almost all of the particles are affected from the milling operation.

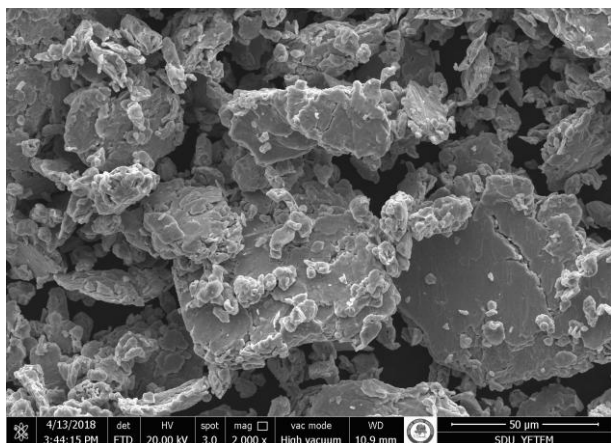


Fig. 3 Scanning electron micrograph of the Fe powder which was milled for 1 hour.

Particle size distribution plot of the Fe powder which was milled for 60 minutes is given in Fig. 4. It can be seen that the average particle size is about 70 microns. There is a slight second mode at about 10 micron size. It can be inferred when compared with the particle size of Fe powder milled for 15 min that the average particle size increases during milling.

Unalloyed Fe particles are quite ductile and they plastically deform easily. As a result of the cold welding of the flattened Fe particles, formation of large agglomerates takes place. There is a second effect of milling on Fe particles, which are strain hardening due to plastic deformation. There is the possibility that the hardened agglomerates break up upon excessive plastic deformation during milling. The disappearance of the mode at about 300 microns after 1 h milling, that was present after 15 min milling, can be attributed to this effect.

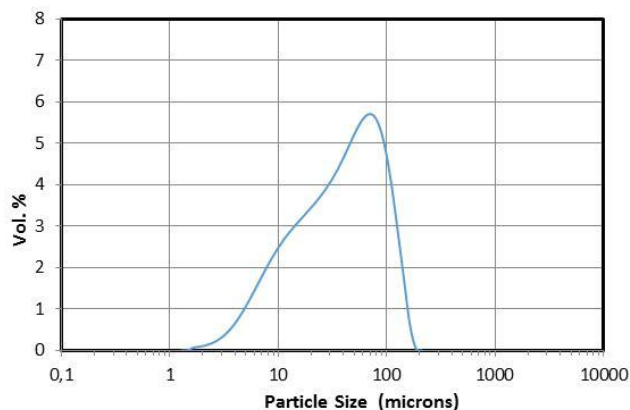


Fig. 4 Particle size distribution plot of the Fe powder which was milled for 1 hour.

The unmilled and milled Fe powders were shaped by cold pressing and warm compaction. After that, hardness and bending strength of the green samples were determined. Hardness and bending strength values of the samples are presented in Table 1, Fig. 5 and Fig. 6. Some of the hardness values, that are not present in Table 1, could not be determined since the samples were broken apart during hardness measurements.

Table 1: Hardness and bending strength values of the samples after cold pressing and after warm compaction.

Milling Duration (min)	Cold Pressed		Warm Compacted	
	Hardness (HB10)	Bending Strength (MPa)	Hardness (HB10)	Bending Strength (MPa)
0		22,49	134,72	94,87
15		18,91	152,97	117,95
30			159,00	
60	44,00	8,57	152,03	135,00

Hardness values of the cold pressed and warm compacted samples were determined by a Brinell hardness tester. The hardness of the sample that was prepared by cold pressing of the 60 min milled Fe powder, was 44 HB10. It was found that the hardness of the cold compacted green samples increased considerably, to about 150 Brinell10, as a result of warm compaction.

This can be attributed to the increase in the density of the samples when warm compaction is employed. It was reported in literature that the density of the samples are about 3 % higher when warm compaction is applied, as compared to cold pressing [5,6].

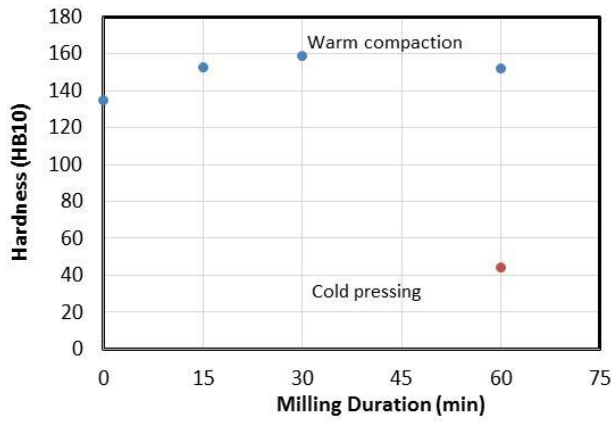


Fig. 5 Hardness values of the samples after cold pressing and after warm compaction.

Bending strength values of the samples were determined by a universal testing machine. Bending strength values after cold pressing were about 20 MPa and less. Bending strength increased to over 100 MPa after warm compaction. It can be seen that warm compaction has a significant effect on green strength of Fe articles.

The increase in the bending strength may be attributed to increase in green density after warm compaction. In the present study, warm compaction was applied at 150 °C. At this temperature, the yield strength of Fe particles is expected to decrease. This leads to higher amount of plastic deformation. Therefore, more void is filled in the article, providing a higher green density and better interlocking of the Fe particles. These effects may be the reasons for the increase in the green strength after warm compaction.

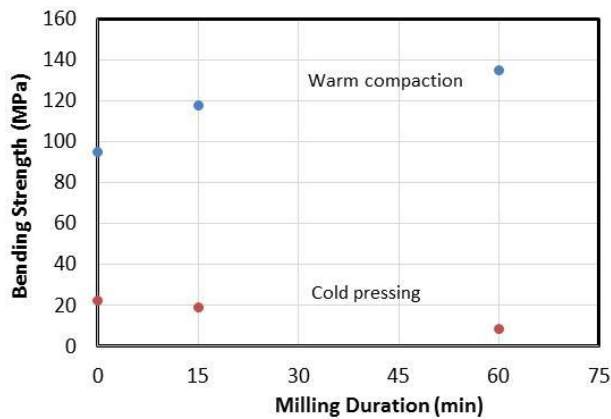


Fig. 6 Bending strength values of the samples after cold pressing and after warm compaction.

4. Conclusion

The milled powders are more difficult to compact, due to strain hardening of the particles. Higher pressures are necessary for compacting milled powders, as compared to unmilled powders. Warm compaction is believed to help to reduce the strain hardening effect on milled powders and provide higher density. This leads to higher hardness and higher green strength.

Acknowledgements

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FEATURES OF STRUCTURE, PHASE COMPOSITION AND PROPERTIES OF HOT-FORGED HIGH-ENTROPY ALLOYS OF Ti-Cr-Fe-Ni-C SYSTEM

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Abstract. Powder high-entropy alloys (HEA) of TiCrFeNiC equiatomic composition were synthesized by hot forging (HF). The phase composition and parameters of the fine structure of the alloys are determined. It is shown that at all annealing temperatures of the alloys their phase composition does not change significantly and consists of two solid solutions of substitution - FCC and BCC and two carbide phases - TiC and Cr₃C₂. The mechanical properties of the alloys are at a rather high level - so the maximum strength of the alloy was 2243 MPa and the hardness is more than 62 HRC, which can be explained by the effect of high entropy and in situ synthesis of carbides in the manufacture of alloys.

Keywords: powder high-entropy alloy, phase composition, microstructure, hot forging, hardness, compressive strength

1. Introduction

A characteristic feature of high-entropy alloys is the content in their composition of at least 5 basic elements in the equiatomic ratio. The presence of a large number of heterogeneous but equal number of atoms with different individual properties imposes its specificity on the formation of solid solutions in these alloys [3]. The high entropy of mixing elements in the alloys causes the Gibbs free energy to be minimized and leads to the predominant formation of solid solutions with BCC, FCC or FCC + BCC structure. Reduced free energy of the alloy provides the stability of the solid solution during further heat treatment [1, 2]. Increased characteristics at high temperatures are ensured by the strong distortion of the crystal lattice due to differences in the atomic radii of the substitution elements [3, 4].

The purpose of the study is to study the phase composition, microstructure, structural imperfections of the crystal lattice and properties of high-entropy TiCrFeNiC powder alloys in the process of their synthesis.

2. Experimental materials and methods

The microstructure of the alloys was studied on an XJL-17 optical microscope as well as on a JEOL Superprobe 733 scanning electron microscope. Investigations of phase composition and structural component defects were performed by X-rays methods. X-rays of the samples were carried out on a DRON-3 diffractometer in filtered cobalt radiation by a stepwise scanning method in the range of angles $20 \div 130^\circ$. The scanning step was 0.05 deg, the angular velocity of the goniometer was $\frac{1}{4}$ deg/min. Quantitative micro-X-ray spectral analysis was performed on a CAMECA MS-46 x-ray microprobe at 20 kV, 12 nA probe mode and 3 μ m probe diameter.

Fe, Cr, Ti, Ni and C (graphite) powders with a purity of 99.5 - 99.9% were used as starting elements for obtaining equiatomic alloys of the Ti-Cr-Fe-Ni-C system. The original powders were dosed on an electronic scales. The mechanical activation of the powder mixture was carried out in a planetary mill at a ratio of the mass of the mixture to the mass of grinding bodies 1: 10. The speed of rotation of the drums of the mill was about 800 rpm, the grinding time - 60 minutes. In order to prevent oxidation and segregation of the powder particles, this process was carried out in ethyl alcohol. The drums were periodically cooled in water.

From the resulting mixture in a steel matrix pressed cylindrical blanks with a diameter of 40 mm at a pressure of 700 MPa. The consolidation of the powder blanks by hot forging was carried out on an forging press FB1732 at a temperature of 1100 °C in argon atmosphere. The annealing of the alloys after forging was carried out in an induction furnace in argon at temperatures of 1200, 1250 and 1300 °C. Annealing time is 2 hours. The density and porosity of the alloys were determined by hydrostatic weighing. The hardness was measured on a TK-14-250 hardness meter according to GOST 9013-75, and the micromechanical characteristics were measured on PMT-3. The strength characteristics were determined by the compression method according to GOST 25.503-97.

3. Results of the experiments and their discussion

Analysis of the X-ray spectrum of the mixture of TiCrFeNiC composition after grinding in a planetary mill for 60 min showed (Fig. 1) that it consists of the reflexes of the individual components that are part of the alloy being developed. Therefore, chemical interaction between the components does not occur, but the nature of the profile of the reflexes of the components of the alloy changes dramatically. Significant expansion of the reflexes indicates the distortion of the crystal lattice of elements, overlapping of x-ray reflections of elements having close angles of reflection, eliminates the possibility of profile selection for calculating the parameters of the fine structure. Defects in the crystal structure, intensify the sintering processes and greatly affect the peculiarities of the formation of the phase composition.

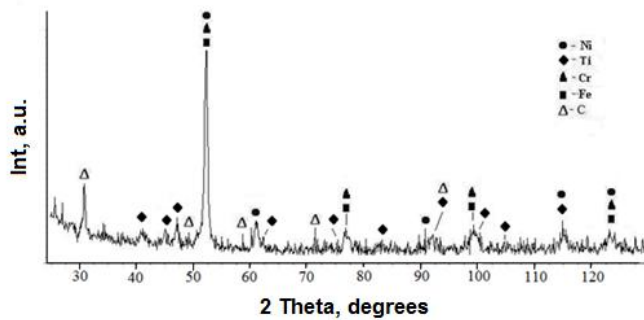


Fig. 1. Diffraction pattern of equiatomic TiCrFeNiC powder mixture after grinding for 60 min in a planetary mill

The X-ray spectrum of the TiCrFeNiC alloy synthesized by grinding the original charge for 60 min and subsequent hot forging at 1100 °C is mainly represented by the reflexes characterizing the FCC structure (Fig. 2 a). Significantly expanded lines of titanium carbide are clearly recorded on the X-ray of the alloy. The crystal lattice parameter of titanium carbide is 0,43267 nm, which corresponds to the ratio $C / Me = 0,82$. Many of the weak reflexes characteristic of this type of lattice are represented by Cr_3C_2 chromium carbide. Intermittent Cr_2Ti and Fe_2Ti interfaces with cubic and hexagonal structure are present in a small amount, respectively.

The use of hot forging after grinding showed a high defect of the solid solution based on the phase with the structure of the FCC: $\beta_{111} = 7,37$ mrad, $CSR = 24$ nm; $\beta_{311} = 21,79$ mrad, $\rho = 9,49 \cdot 10^{12} \text{ cm}^{-2}$, micro-distortion = $21,11 \cdot 10^{-2}$. In the course of hot deformation, at the same time as the introduction into the alloy of dislocations, their transformation into orderly groups always occurs. Hot stamping of porous blanks can be considered as one of the cycles of thermomechanical treatment, in the process of which a developed substructure is created. This developed substructure is the primary factor that determines all other structural causes of thermomechanical strengthening of the alloy and can contribute to the formation of solid solutions structures [5, 6].

On the X-ray spectrum of the alloy, no phase with the BCC structure is detected, but using the mathematical approach to decompose the maximum (111) of the FCC phase, the presence of two phases was found simultaneously (Fig. 1b). This can be explained by the significant slander of the BCC phase, which is associated with the blurring of the lines of this phase, which makes it impossible to distinguish from the low intensity line background.

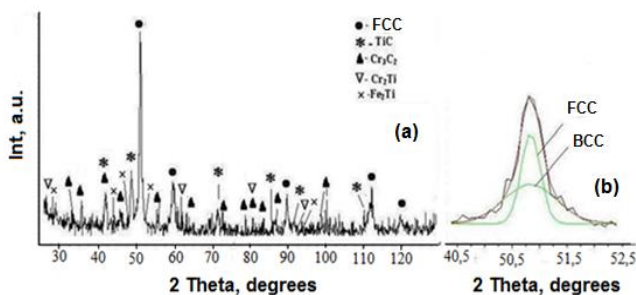


Fig. 2. Diffraction pattern of equiatomic TiCrFeNiC alloy after 60 min grinding and hot forging at 1100 °C (a) and the results of the decomposition of the FCC reflex (111) (b)

The performed calculations of the parameters of the fine structure according to the maxima of the component phases indicate

the significant imperfection of the crystal lattice of the structural components of the alloys.

At an annealing temperature of 1300 °C, the HEA is formed on the basis of a phase with the FCC structure. The FCC lattice parameter of 0,3597 nm is the largest compared to similar parameters in all technological modes. However, increasing the lattice parameter did not lead to an increase in hardness, which decreased to 49,1 HRC (Table 1). A similar feature of WEC alloys was observed by the authors of [4], explaining that one of the reasons may be the redistribution of the elements of substitution in the alloy with FCC structure. The defect in the HEA based on the FCC structure is characterized by the following values $\beta_{111} = 6,8$ mrad, $CSR = 25,8$ nm, $\beta_{311} = 17,76$ mrad, $\rho = 5,24 \cdot 10^{12} \text{ cm}^{-2}$, micro-distortion = $17,39 \cdot 10^{-2}$.

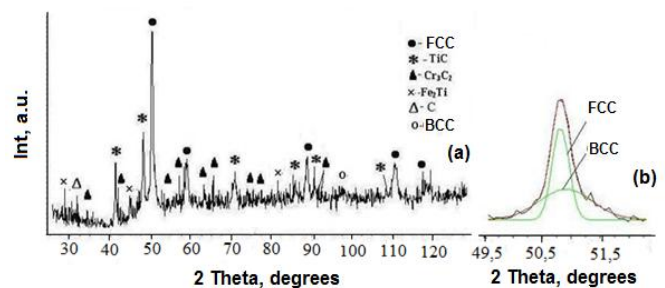


Fig. 3. Diffraction pattern of equiatomic TiCrFeNiC alloy after grinding, hot forging and annealing at 1300 °C (a) and the results of the decomposition of the FCC reflex (111) (b)

Structural formation during hot forging of porous powder blanks occurs under conditions of intense plastic deformation and accelerated cooling from contact with a relatively cold press tool, which provides a manifestation of the effect of thermomechanical treatment. The temperature and duration of heating before forging accelerate the flow of interparticle splicing processes when compacting the blanks and forming a finished product from it. In the case of HF, there is a partial annihilation of the dislocations acquired during the grinding process and the simultaneous introduction of dislocations. The heating temperature under forging ensures the alignment of the structure defect in the sample volume, the processes of structure formation are activated [7].

According to metallographic and micro-X-ray spectral analyzes, two solid-solution phases of substitution with FCC and BCC lattices and two carbide phases are present after annealing at all temperatures at TiCrFeNiC alloys (Figs. 4, 5). There is a layered structure, the layers of which are directed perpendicular to the direction of stamping, which is characteristic of hot-forged alloys. It is only after annealing at 1300 °C (Fig. 4, d) that a regular matrix structure is formed, in which a gray and light gray matrix and dark inclusions are present. The light area is a solid solution of iron with chromium in which there are gray inclusions of chromium carbide Cr_3C_2 . The dark gray area formed by the lattice of nickel contains the inclusion of titanium carbide TiC and a small fraction of iron and chromium (Fig. 5).

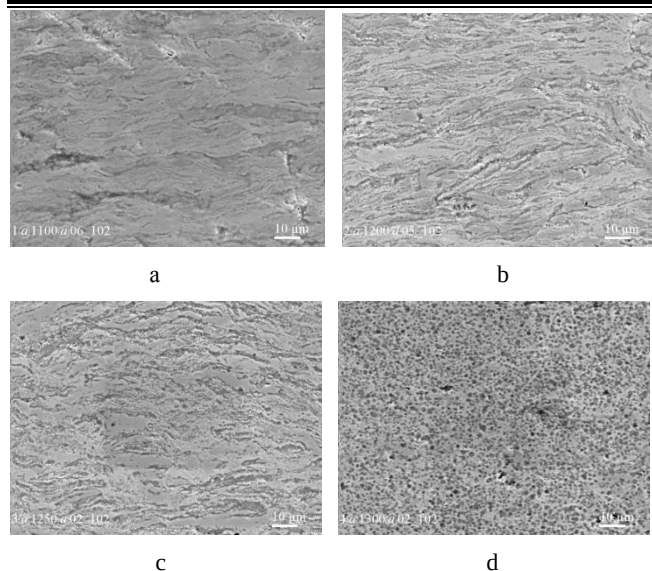


Fig. 4. SEM image of the microstructure of equiatomic TiCrFeNiC alloys after HF (a), after HF and annealing at 1200 °C (b), after HF and annealing at 1250 °C (c), after HF and annealing at 1300 °C (d)

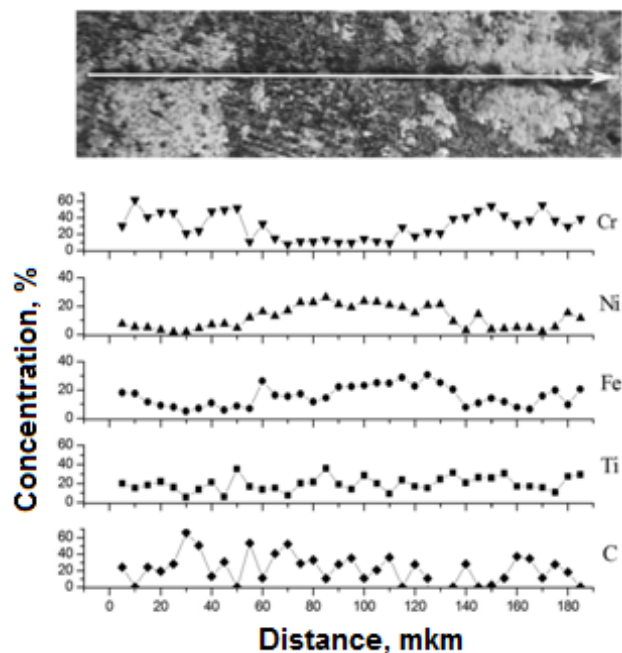


Fig. 5. The distribution of elements in the TiCrFeNiC alloy phases after annealing at 1300 °C

Therefore, a solid solution of substitution on the basis of the FCC structure is formed on the basis of the Nickel lattice. In the smaller volume of the bright region, the formation of a solid solution of substitution occurs when the mutual dissolution of chromium and iron with the formation of BCC structure on the basis of the chromium lattice. The data of the micro-X-ray spectral analysis confirm the results of the X-ray structural study on the formation of a high-entropy solid solution of substitution with the BCC structure.

In the table. 1 shows the density, porosity and hardness of the synthesized alloys. The theoretical density of the alloy is 6,65 g/cm³. The use of hot forging has yielded almost non-porous alloys, which is known to significantly affect their properties.

Table 1

Density, porosity and hardness of synthesized high-entropy TiCrFeNiC alloys

№	T _{annealing} , °C	Density, g/cm ³	Porosity, %	Hardness, HRC
1	without annealing	6,55	1,5	62,4
2	1200	6,51	2,1	58,2
3	1250	6,50	2,2	55,5
4	1300	6,48	2,5	49,1

Samples that were annealed have slightly higher porosity than non-annealed ones. This can be explained by the Frenkel II kind of effect due to the difference in the heterodiffusion coefficients of the alloy elements. The hardness of the samples decreases naturally with increasing annealing temperature, although this decrease is negligible due to the high entropy effect.

The results of tests for uniaxial compression are presented in table. 2. The high values of the mechanical characteristics of the alloys can be related to the effect of high entropy of element mixing in the alloys, as well as to the synthesis of carbides in situ during the process operations. The nature of the destruction of the samples is fragile, as evidenced by the low values of relative deformations. In the first three specimens, there is actually a microplastic deformation that does not exceed 0,7 %, and only in the last specimen does the plasticity increase significantly compared to other specimens. In general, the mechanical properties are clearly correlated with the annealing temperature of the alloys.

Table 2

Mechanical properties of synthesized high-entropy TiCrFeNiC alloys

№	T _{annealing} , °C	σ _{pr} , MPa	σ _{0,2} , MPa	σ _r , MPa	ε, %
1	without annealing	1381	1978	2243	0,41
2	1200	1081	1567	1971	0,65
3	1250	1055	1507	1663	0,69
4	1300	890	1266	1551	1,64

4. Conclusions

1. The synthesized high-entropy alloys of the TiCrFeNiC system are formed into solid solutions with FCC and BCC structures. The preferred phase is a solid solution based on the structure of the FCC.

2. Quantitative characteristics of the imperfections of the crystal lattice of HEAs indicate a significant distortion of the lattice of a solid solution with the BCC structure.

3. Along with the phases of the FCC and BCC structures, high-entropy chemical compounds are formed: TiC and Cr₃C₂ carbides, Fe₂Ti, Ni₃Ti, Cr₂Ti intermetallides, which play a large role in the solid solution formation on the basis of the FCC structure.

4. The high values of the mechanical characteristics of the alloys can be related to the effect of high entropy of element mixing in the alloys, as well as to the synthesis of carbides in situ during the process operations.

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THE EFFECT OF THE MAX-PHASE Ti_3AlC_2 ON HYDROGEN STORAGE PROPERTIES OF Mg

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Abstract: The MAX-phase Ti_3AlC_2 was synthesized by sintering method. The study of sorption properties of the sample was carried out under conditions continuous heating. It was established that desorption of hydrogen begins at a temperature of $\sim 210^\circ\text{C}$. After complete desorption, the sample was re-heated in an atmosphere of hydrogen. It was found that Mg-5 wt% Ti_3AlC_2 composite begins absorb hydrogen at a temperature of $\sim 76^\circ\text{C}$. As a result of cycling, the temperature of desorption has shifted towards lower values $\sim 186^\circ\text{C}$.

KEYWORDS: MAX-PHASE, Ti_3AlC_2 , HYDROGEN STORAGE

1. Introduction

The last years more attention is a pay to the search of the clean energy sources. The most promising area in this field is hydrogen power. Developing safe, efficient and affordable approaches of hydrogen storage is especially important for practical application. Compared to gaseous or cryogenic methods [1], the storage of hydrogen in a bonded state in the form of various compounds attracts great attention due to their unique characteristics, safety and high volumetric energy density. Metal hydrides attract a special attention [2]. Metal-hydrogen compounds have a high mass and volumetric density of hydrogen. However, the hydrogen content of the vast majority of hydrides is $\sim 2\%$, which makes them economically unprofitable. Moreover, the temperature at which the release of hydrogen for the vast majority of hydrides is several hundred degrees. Hydrides based on intermetallic compounds exhibit significantly lower desorption temperatures of hydrogen. But their hydrogen capacity is small and does not exceed 1-2%. In contrast to the materials pointed out above, magnesium capable to absorb up to 7.67% hydrogen. Therefore magnesium is a most promising material for use in hydrogen energetic [3]. But there are crucial disadvantages must be overcome for widespread use of magnesium as a hydrogen storage media: high storage/release temperatures, slow hydrogen sorption/desorption kinetics and low cyclic stability. A wide range of different methods has been applied over the past decades. Mechanical grinding magnesium with a various additives cause a great practical interest since allows to synthesize high active powders with improved hydrogen sorption/desorption kinetics [4-7]. Further development of this approach may be the use of new type of catalysts - MAX phases [8] and their derivative 2D structures – MXene [9-11]. To prepare magnesium based hydrogen storage materials the ball milling under hydrogen atmosphere [12, 13] (so-called reactive grinding) is also widely used.

In this paper we propose to use the MAX-phase Ti_3AlC_2 as a catalyst additive to the magnesium powder. The samples were prepared by reactive ball milling under hydrogen atmosphere.

2. Materials and method

The MAX-phase Ti_3AlC_2 was synthesized by sintering method. The initial powders Ti, Al and spectrally pure graphite in atomic ratio of 3:1.1:2 with additive 5 wt% B_2O_3 were homogenized using the laboratory planetary ball mill Fritsch Pulverisette P-6 for 1 h. The milling speed was 200

rpm. The balls to powder ratio was 10:1. Then the homogeneous mixture was cold-pressed under 640 MPa and sintered at 1400°C during 1 hr in Ar atmosphere.

Samples Mg-5 wt% Ti_3AlC_2 were prepared by ball milling under hydrogen atmosphere at 400 rpm for 10 hr. Initial hydrogen pressure in the milling vial was ~ 1 MPa. Every two hours the grinding process was stopped and a new portion of hydrogen gas was added. This technique allowed the control of the hydrogen absorption process. During grinding the mixture exhibited high activity of interaction with hydrogen.

X-ray diffraction studies are carried out on the standard diffractometer HZG-4 with filtered CoK_α radiations in the Bragg-Brentano geometry. Rietveld refinement of the XRD patterns was performed by the MAUD software [14]. Investigation of the hydrogen sorption properties of the magnesium based composites was performed out on a homemade Sievert's type apparatus.

3. Result and discussion

The diffraction pattern of synthesized MAX-phase Ti_3AlC_2 is shown on the Fig. 1. From the Rietveld refinement has been found that the sintered pellets contain ~ 98.5 wt% of Ti_3AlC_2 phase and ~ 1.5 wt% TiC.

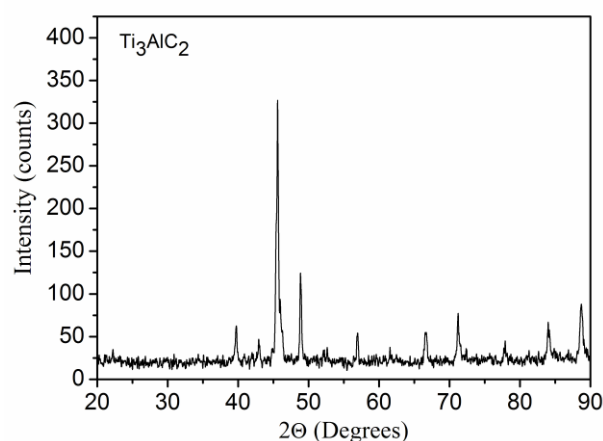


Fig. 1 XRD pattern of MAX-phase Ti_3AlC_2 .

The prepared MAX-phase Ti_3AlC_2 was used as a catalyst additive to magnesium. The XRD of as-milled Mg-5 wt% Ti_3AlC_2 compositions is shown on Fig. 2. It should be immediately noted that sample have diffraction peaks whose positions are very close to those for the Mg, MgH_2 and MAX-phase Ti_3AlC_2 .

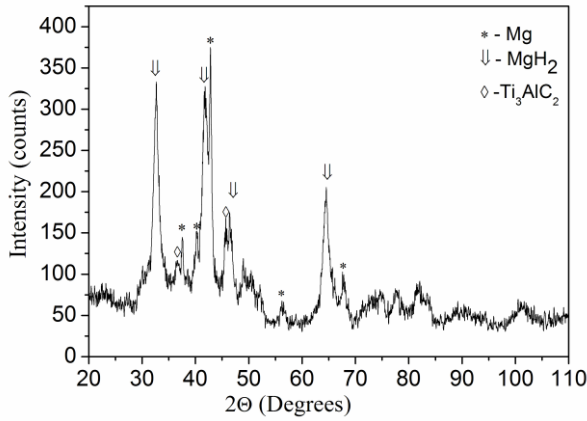


Fig. 2. The as-milled Mg-5 wt% Ti_3AlC_2 composite after the reactive ball milling during 10 h.

The sorption properties of the composite Mg-5wt% Ti_3AlC_2 after reactive ball milling have been tested by the Sievert's technique. A powder sample was placed in a reactor. Then as-milled sample was continuously heated from the room temperature up to 400 °C to estimate quantity hydrogen absorbed during the reactive grinding. After the first heating cycle from thermal desorption curve it was found that the decomposition of magnesium hydride starts at 210 °C and finished at a temperature of 310 °C (Fig. 3, a). As a result of cycling, the temperature of desorption is shifted towards the lower values of 186 °C (Fig. 3, b). The amount of hydrogen released from the sample under these conditions is about 4.8%. The release of hydrogen occurs in a wide range of temperatures. It could be seen use Ti_3AlC_2 MAX-phase as catalyst additive promotes to a remarkable decrease in the hydrogen desorption temperature from the magnesium hydride. It is one of the important moments at the development of materials for hydrogen energy. According to the literature data, the temperature of the beginning of decomposition of magnesium hydride is ~ 283 °C [15].

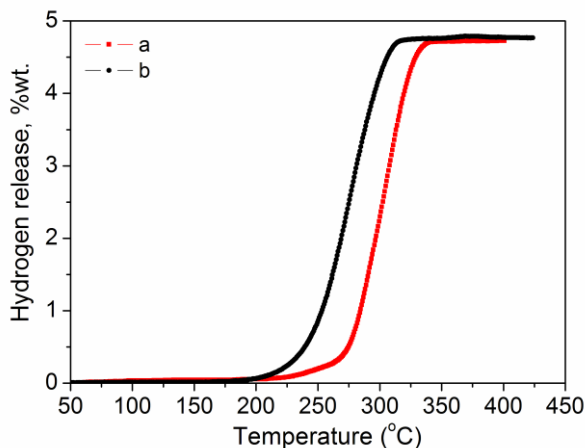


Fig. 3 The thermal desorption curves of composite Mg - 5wt% Ti_3AlC_2 : (a) – as-milled in hydrogen atmosphere and (b) - after second cycle.

After complete desorption, the sample was re-heated in an atmosphere of hydrogen. From the sorption curve (Fig. 4) was established that Mg-5 wt% Ti_3AlC_2 composite begins absorb hydrogen at a temperature of ~ 76 °C. The amount of hydrogen absorbed after full saturation is 4.8%. It is corresponds to the amount of desorbed hydrogen.

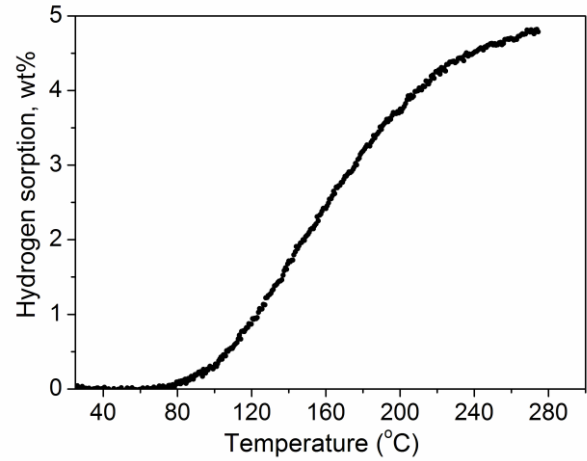


Fig. 4. Typical hydrogen sorption curve by Mg-5wt% Ti_3AlC_2 composite after cycling.

The studies of the hydrogen desorption kinetics under isothermal conditions at a temperature of 300 °C have been carried out. It was shown that the Mg-5wt.% Ti_3AlC_2 composite at this temperature desorption 4.5% hydrogen for 200 s (Fig. 5).

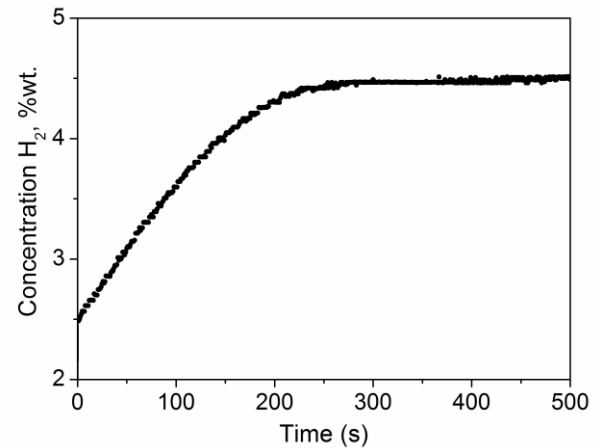


Fig. 5 Desorption of hydrogen in isothermal conditions at $T=300$ °C.

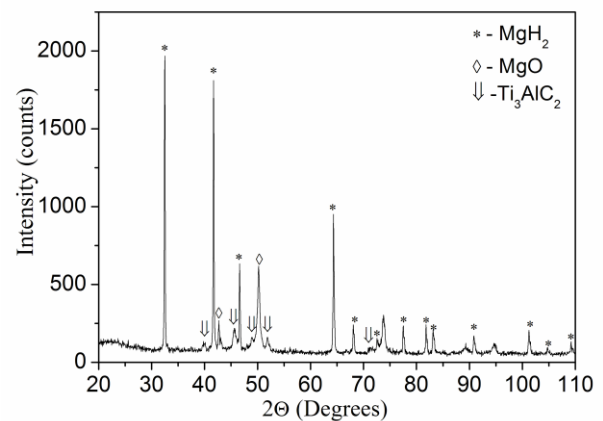


Fig. 6 XRD pattern of composite Mg - 5wt.% Ti_3AlC_2 after cycling.

The X-ray diffraction pattern of the composite Mg-5wt.% Ti_3AlC_2 after saturation is show on Fig. 6. According to the results of the phase analysis it is established that after the last saturation cycle the materials contains mainly MgH_2 with the preservation of the initial MAX-phase Ti_3AlC_2 and a

relatively small amount of MgO. Magnesium oxide was formed as a result of oxidation of the sample during X-ray diffraction studies in the air.

4. Conclusion

The use of the MAX-phase Ti_3AlC_2 as an active additive to magnesium at reactive ball-milling treatment results to the formation of a composite with a sorption/desorption temperature of $\sim 76^\circ\text{C}/186^\circ\text{C}$, which is significantly lower than that of pure magnesium hydride.

The hydrogen capacity of the composite Mg-5wt.% Ti_3AlC_2 is 4.8%.

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TRANSFORMATION OF NON-METALLIC INCLUSIONS “EUTECTICS” IN STEELS UNDER LASER ACTION

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Abstract. Melting and crystallization of heterophase non-metallic inclusions “eutectics” was investigated. Mechanism of melting of the eutectic inclusions and inclusion-matrix boundaries under contact laser melting with steel matrix in the conditions of abnormal mass transfer connecting with formation of zones with high dislocation density and also with electron and electro-magnetic interaction between inclusion and steel matrix was proposed. That allows to create the possibilities for the influence on the inclusion-matrix boundaries and also on the chemical and phase composition of surface layer of non-metallic inclusions. Peculiarities of structure of non-metallic inclusions after speed crystallization were investigated. It was shown that under laser action the initial composite colonial structure of inclusions transits into abnormal eutectic structure. Also it was shown that under laser action the initial structure of inclusion-steel matrix boundaries transits into unstable equilibrium high-energy condition that cause development of the dissipation processes connecting with aspiration of system inclusion-matrix to the state with minimum of the free energy. In the result of the system eutectic inclusion-matrix transits to the state of unstable equilibrium which determines structure and properties of laser-quenched interphase boundary. Processes of melting, fusion and dissolution of non-metallic inclusions “eutectics” and also of the melting of steel matrix play the great role in transformation of interphase inclusion-matrix boundaries under laser action.

KEYWORDS: NON-METALLIC INCLUSIONS “EUTECTICS”, STEEL, STRENGTHENING, LASER TREATMENT

1. Introduction.

In steels, heterophase types of inclusions are often present [1 - 7]. For heterophase inclusions, the presence of internal interphase boundaries is characteristic, which, along with the inclusion-matrix interphase boundaries, play an important role in the formation of defects, which is very important when analyzing the reliability and durability of products operating in different conditions [4, 8 - 11]. Heterophase inclusions of the “eutectics” type are formed as a result of simultaneous crystallization of the phases during eutectic transformation. Such inclusions have a eutectic structure and are colonies of eutectic phases eu1 and eu2 — composite formations of different types depending on the composition and nature of these eutectic phases (Fig. 1), although conglomerates of eutectic phases are possible. Accordingly, it is possible to designate the interphase boundaries inclusion-matrix $eu1 \leftrightarrow m$ and $eu2 \leftrightarrow m$. Eutectic inclusions with phases eu1 and eu2: sulfide $FeS-MnS$, $FeS-(Mn, Fe)S$, $FeS-Al_2S_3$, $(Fe, Mn)S-FeS$, $(Fe, Cr, Mn)S-FeS$, $(Fe, Cr, Mn)S-(Fe, Mn)S$, oxysulfide $FeS-FeO$, $MnS-MnO$, $MnO-FeS$, $(Fe, Mn)O-$

$(Fe, Mn)S$, $(Fe, Mn, Cr)S-FeO$, oxide $MnO-Mn_3O_4$, $Fe_2O_3-CaO-Fe_2O_3$, $MgO-Al_2O_3-2MgO-SiO_2$, $MgO-Al_2O_3-2MgO-Al_2O_3-MgO$, $5CaO-Al_2O_3-CaO-Al_2O_3$, $CaO-Al_2O_3-CaO-2Al_2O_3$, $CaO-Al_2O_3-CaO-2Al_2O_3-CaF_2$, silicate $FeO-SiO_2-MnO-SiO_2$, $2FeO-SiO_2-MnO-SiO_2$, $2FeO-SiO_2-CaO-MgO-SiO_2$, $FeO-SiO_2-CaO-FeO-SiO_2$, $2CaO-Al_2O_3-SiO_2-CaO-MgO-SiO_2$, $CaO-FeO-SiO_2$, nitride $TiN-TiCN$, sulfosilicate $FeS-FeO-SiO_2$, oxilicate $FeO-FeO-SiO_2$. In the structure of such inclusions, due to the joint crystallization of the phases, a certain regularity is observed in their arrangement, typical of eutectics, although phase conglomerates are possible, and the second phase can form layers with an oval cross section or films along the grain boundaries of the first phase.

The goal of this investigation was to research the processes of melting, dissolution, crystallization of the heterophase non-metallic inclusions “eutectics” in hypernonequilibrium conditions and the influence of these inclusions on the peculiarities of structural changes in steel matrix and its strengthening under laser treatment.

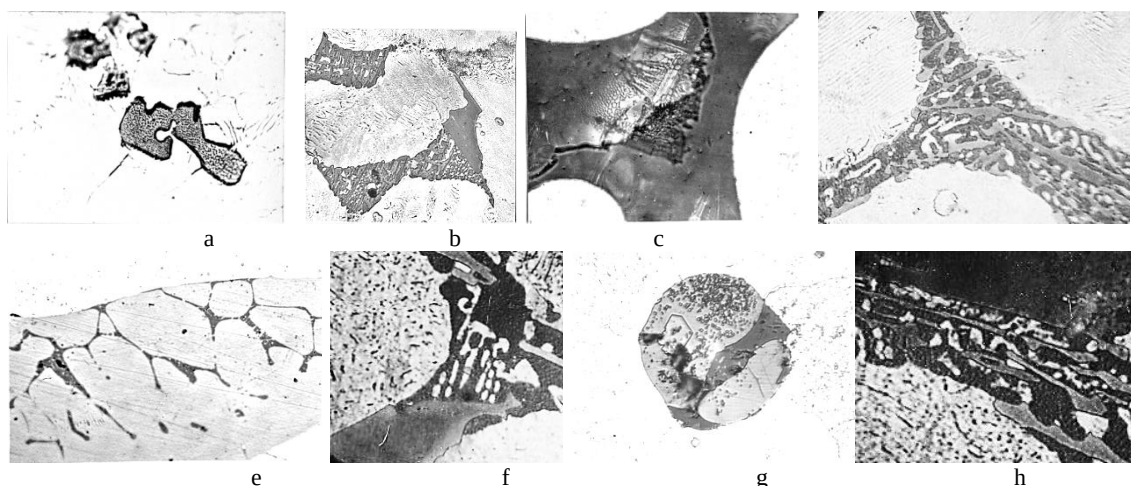


Figure 1. Non-metallic inclusions “eutectics” before laser action; x600

2. Materials and Procedures.

Specimens made of wheel steel R7, 08Yu, 08T, 08Kp, 08Ch18N10T, ShCh15, NB-57, 12GS, E3 were irradiated by laser in GOS-30M installation with an excitation voltage of 2,5kV and pulse energy of 10, 18, 25 and 30J at heating rate of 10^5 °C/s and cooling rate of 10^6 °C/s with action time of (1,0, 2,5, 3,6, 4,2 и

$6,0) \cdot 10^{-3}$ s. heterophase non-metallic inclusions “phases are beside” were identified by metallographic, X-ray microspectral and petrographic methods, [1, 12]. Distribution of elements and nanohardness of steel matrix near inclusions were determined.

3. Results and discussion.

Most of inclusions of “eutectics” are low-melting and both their phases must to melt almost simultaneously. But eutectics with high-melting phases exist too [1, 4]. Inclusions of eutectics are differed from heterophase non-metallic inclusions “high-melting phase surrounding with low-melting cover” and “phases are beside” with the presence of more dispersed phases and more branching net of interphase boundaries $eu1 \leftrightarrow eu2$ inside inclusions. Molten inclusions “eutectics” is been in molten steel matrix and micrometallurgical bath is formed. Hydrodynamics flows in the conditions of vortex thermocapillary mixing and temperature gradients are originated and that causes displacement of inclusion phases. In the result of high-speed melting of inclusions “eutectics” heavy oversaturated liquid solution or two liquid solutions on the base of inclusion and steel matrix differing by concentration heterogeneity are formed. In such liquid systems nonbalanced mass transfer is happened that suppresses of cooperative growth of phases and formation of cooperative structures of non-metallic inclusion.

Evidently under laser melting and contact interaction of eutectic inclusion with liquid steel matrix advantageous the dissolution (melting) of interphase boundaries $eu1 \leftrightarrow eu2$ must to happen. Just distribution of surface tensions in the zone of contact interaction when heavy disordered state in surface areas of eutectic phases is created and diffusive composition equalizing do not happened the heavy nonequilibrium conditions and thermodynamic stimulus for rapid simultaneous or selective dissolution of phases of inclusion are appeared. Besides since speed of mass transfer and degree of saturation of eutectic phases with elements of steel matrix (in first turn with iron) is different. That phase of inclusion with more degree of saturation by iron is dissolved more quickly.

Inclusions of “eutectics” containing both low-melting and high-melting phases after high-speed crystallization in the conditions of laser action were investigated. They had regular colony structure in the initial state. In the most of them such structure was not kept after laser action. Evidently transformation of type of eutectic was happened. Regular colony structure was transformed into abnormal eutectic without regular distribution of components (Fig. 2, a - d). In such inclusions no regular distribution of the elements of the eutectic phases is observed (Fig. 3, a). According to reference [5], abnormal eutectics are formed in conditions when conjugational growth of crystals of eutectic phases do not possible and also when eutectic is formed with high-entropy phases. It is evidently the absence of possibility for conjugational growth of crystals of eutectic phases in the conditions of laser action. For the structure of abnormal eutectics the presence of phase areas with different shape chaotically disposing in inclusion is typical. Abnormal eutectic structures after laser action with energy of impulse W_{pulse} 10 – 25 J were observed. In the resort of W_{pulse} 30 J together with abnormal eutectics the sulphide and silicate eutectics inclusions with amorphous structure were observed (Fig. 2, e), which have significant chemical heterogeneity (Fig. 3, b). As a rule, these were sulphide or silicate eutectics, i.e. inclusions consisting of fusible phases. Some inclusions have signs of colony structure (Fig. 2, f). Various of structures of inclusions of “eutectics” is explained with differences of nature of eutectic phases and also with heterogeneity of laser radiation promoting appearance of different conditions of their crystallization. Steel matrix under laser melting is saturated with elements of phases of inclusions of “eutectics” independently on the type of inclusion.

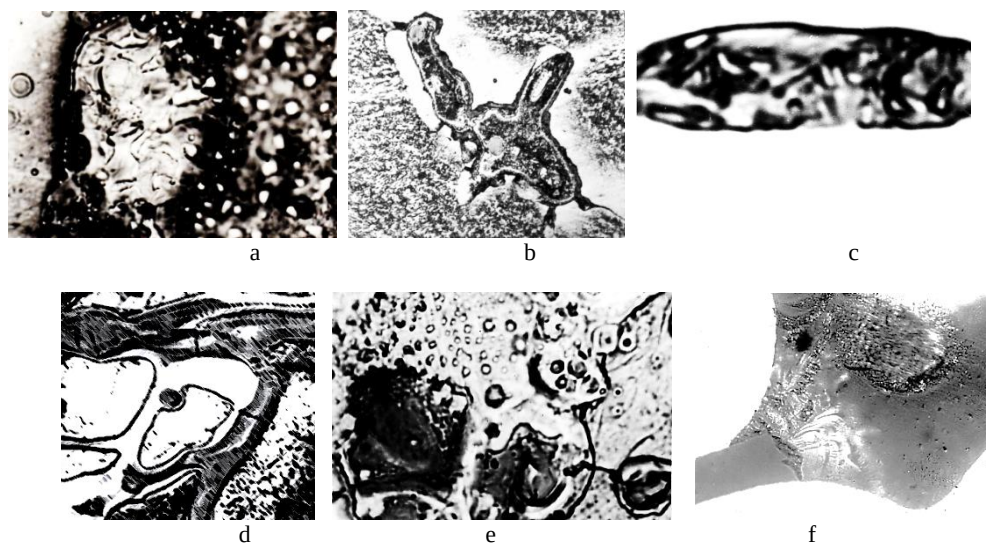
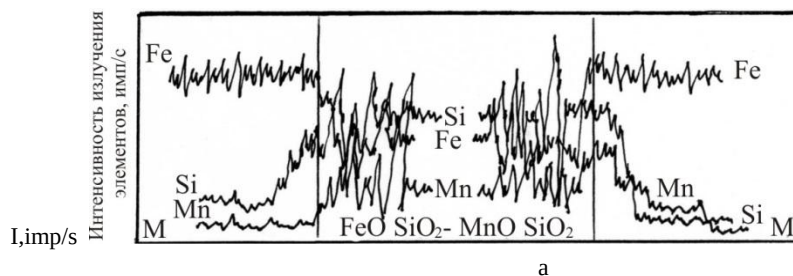


Figure 2. Dissolution and melting of heterophase non-metallic inclusions of “eutectics” under laser action; $\times 2000$



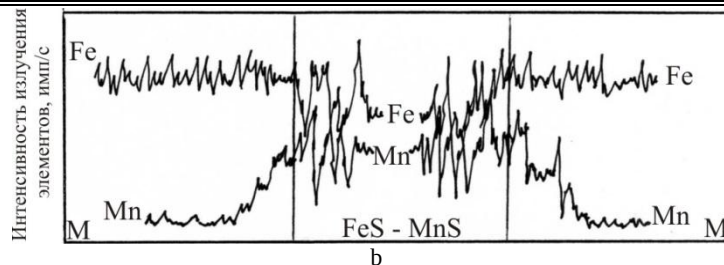


Figure 3. Distribution of elements near inclusions of the "eutectics" type after laser action

In anomalous eutectic inclusions, the interphase boundaries of $eu1 \leftrightarrow eu2$ inclusions appear somewhat "blurred"; X-ray microscopic analysis showed that the content of elements of the neighboring phase in both phases of inclusion was increased near these boundaries (Fig. 3, a). This indicates the mutual exchange of atoms between the inclusion phases at the moment of eutectic melting, which occurs through their disordered transitions across the $eu1 \leftrightarrow eu2$ boundaries, as well as through the boundaries with the molten steel matrix. Considering the features of laser melting of two-phase inclusions of "eutectic", it should be noted that each phase of the inclusion contacts both the steel matrix and the other phase of the inclusion, i.e. It has two interphase boundaries (the inclusion-matrix $eu1 \leftrightarrow m$, $eu2 \leftrightarrow m$ and the inclusion-inclusion $eu1 \leftrightarrow eu2$), which differ in structure [4].

Contact dissolution and melting of phases $eu1$ and $eu2$ of inclusions "eutectics" and also of interphase boundaries $eu1 \leftrightarrow eu2$, $eu1 \leftrightarrow m$, $eu2 \leftrightarrow m$ in molten steel matrix in nonequilibrium conditions under laser action is energetically excused because surface layers of both phases of inclusion being in stress state with high energy are replaced with liquid phase with less energy. Decrease of surface energy owing to contact interaction of eutectic phases and steel matrix and also owing to interaction of phases $eu1$ and $eu2$ of inclusion in the moment of melting is rather considerably that system "phase $eu1$ of inclusion" – "boundary $eu1 \leftrightarrow eu2$ " – "phase $eu2$ of inclusion" –

"interphase boundaries $eu1 \leftrightarrow m$, $eu2 \leftrightarrow m$ " – "steel matrix" was thermodynamically unstable after laser action. Realization of such mechanism of melting and dissolution of inclusions of "eutectics" is determined with value of stresses creating in surface layers of both phases of inclusion. Evidently owing to formation of big stresses in surface layers of matrix and both phases of inclusion "eutectics" in the conditions of high-speed laser action it is possible nonactivated transformation of heavy disordered surface layers of both phases of inclusion into liquid state with formation of liquid phase.

Consistency of formation of heavy disordered areas on the surface layers of both phases of inclusion "eutectics" and also movement of interphase boundaries is shown on Fig. 4. In the moment of melting (dissolution) of eutectic type of inclusions the both their phases must to dissolve practically simultaneously. Evidently owing to contact interaction of inclusions with liquid steel matrix advantage melting (dissolution) of interphase boundaries of eutectics takes place. On Fig. 4 surface tensions on interface boundaries are shown. Distribution of surface tensions in zone of contact interaction then heavy disordered state in surface areas of eutectic phases is formed and diffusive equalizing of composition do not have time for happen the heavy nonequilibrium conditions are created and thermodynamics stimulus for rapid simultaneous or selective dissolution of inclusion phases is appeared.

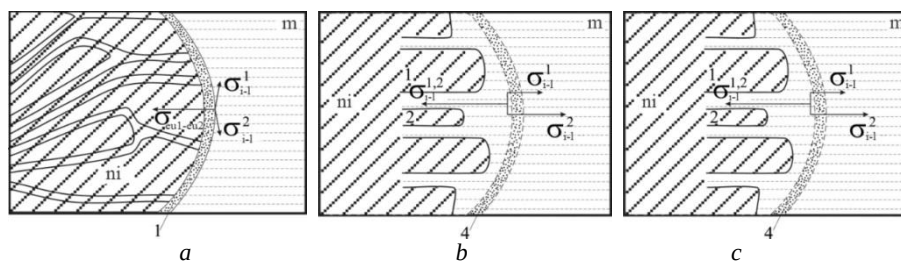


Figure 4. Schemes of laser melting of inclusions of "eutectics": σ_{i-1} – stresses on boundary between hard heavy distortion area of inclusion and liquid steel matrix, $\sigma_{1,2}$ – stresses between eutectic inclusion and molten steel matrix, σ_{1-1} and σ_{2-1} – surface tensions between phase $eu1$ and phase $eu2$ of inclusion and molten steel matrix accordingly, $\sigma_{eu1-eu2}$ – surface tensions between phase $eu1$ and phase $eu2$ of inclusion, $\sigma_{1,2}$ – stresses between molten eutectic inclusion and molten steel matrix, 1 – inclusion-matrix boundary, 2 – initial position of inclusion-matrix boundary

Under quenching from liquid state in both phases of inclusion the zones of high-speed crystallization with columnar shape of grains and liquation are formed. Silicate and sulphide inclusions of "eutectics" were inclined for amorphization.

When studying the features of the microstructure of the steel matrix near inclusions of eutectic type, it is necessary to take into account that two different phases, $eu1$ and $eu2$, are in contact with the steel matrix, which are much more dispersive and often have closer chemical composition and properties. In this study, we are talking about inclusions, which in the initial

state have the structure of eutectic colonies. Analysis of the steel matrix areas adjacent to eutectic inclusions was showed that their structure is heterogeneous. Near the inclusions, one, or two or three saturation zones of the cascade-type, columnar or the saturation zones of the spotted type were detected (Fig. 5). The formation of saturation zones of the steel matrix is associated with the exchange of the phases of inclusion and the steel matrix with atoms of various elements as a result of anomalous mass transfer [1, 4]

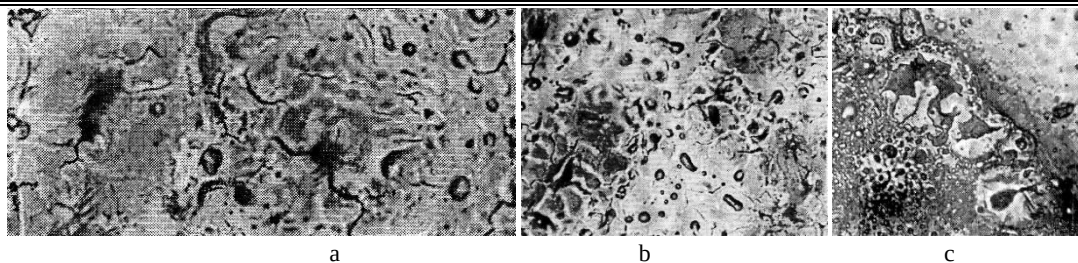


Figure 5. Saturation zones of the steel matrix near the "eutectic" inclusions $\times 500\times 3$

The results of a study of the distribution of nanohardness in the zones of saturation of the steel matrix adjacent to the phases of eu1 and eu2 inclusions of the "eutectics" type showed that the nanohardness is much higher than its average value for the matrix far from the inclusions (Table 1). The level of nanohardness of each zone of the metal matrix is determined by the type of steel, since the degree of hardening in the process of laser action depends on its composition and structure. In the first saturation zone, the values of (H_M^e) at a pulse energy of 25 J and an exposure time of $3.6 \cdot 10^{-3}$ s at 1.46 ... 1.95 times higher than in the steel matrix far from the inclusion. In the second and third

saturation zones, the values of the nanohardness of the steel matrix are lower than in the first zone, but exceed the values of H_M for the matrix far from the inclusions, respectively, in 1.39 ... 1.58 and 1.29 ... 1.42 times at a pulse energy of 25 J and exposure time $3.6 \cdot 10^{-3}$ sec. Bursts of the nanohardness of the steel matrix were observed, which under the same conditions of laser action in the saturation zones 1, 2, 3 were respectively the excess of the nanohardness of the steel matrix far from the inclusion of 1.75 ... 2.41; 1.61 ... 1.85; 1.55 ... 1.63 times. Obviously, a cascade distribution of the values of the nanohardness of the metallic matrix is observed at a distance from the phases eu1 and eu2 of the inclusion.

Table 1. The values of the nanohardness of the saturation zones of steel matrix near the "eutectic" type of inclusions H_M^e and far from them, H_M , as well as the coefficient (K_i) at a pulse energy of 25 J and an exposure time of $3.6 \cdot 10^{-3}$ s

inclusion eu1-eu2, steel, H_M , x 10, MPa	Phases of inclusion (state under laser action: *L – liquid; M – melted)	Condition and type of saturation zone in steel matrix of steel matrix under laser action	H_M^e , x 10, MPa and (K_i) in zones		
			1	2	3
FeS-(Fe,Mn)S, 08Kp, 260	FeS (L)	Liquid; columnar, spotted	379(1,46); "bursts" 455(1,75)	-	-
	(Fe,Mn)S (L)		429(1,65); "bursts" 494(1,9)	-	-
TiN-TiCN, 08T, 280	TiN (M)	solid / liquid; cascade with "bursts"	518 (1,85); "bursts" 616(2,2)	389(1,39), "bursts" 476(1,7)	-
	TiCN (M)		549 (1,96); "bursts" 675 (2,41)	423 (1,51), "bursts" 518 (1,85)	-
FeO·SiO ₂ -MnO·SiO ₂ , 08Uy, 290	FeO·SiO ₂ (L)	Liquid; columnar, spotted	508 (1,75); "bursts" 609 (2,1)	-	-
	MnO·SiO ₂ (L)		574 (1,98); "bursts" 670 (2,31)	-	-
MgO·Al ₂ O ₃ -2MgO·SiO ₂ , ShH15, 750	MgO·Al ₂ O ₃ (M)	Liquid; cascade with "bursts"	1185 (1,58); "bursts" 1350 (1,8)	1058 (1,41), "bursts" 1208 (1,61)	968 (1,29), "bursts" 1163 (1,55)
	2MgO·SiO ₂ (L)		1343 (1,79); "bursts" 1440 (1,92)	1185 (1,58), "bursts" 1358 (1,81)	1065 (1,42), "bursts" 1223 (1,63)

The main factor for strengthening the phase-adjacent type of "eutectics" the steel matrix is its microalloying from internal sources, which are the phases of eu1 and eu2 of nonmetallic inclusion. In this case, by forming local liquation zones near each inclusion phase, saturation zones of a cascade-type steel matrix are created, which are layered composite regions near the phase differences of nonmetallic inclusions.

4. Conclusions.

The mechanism of melting of inclusions "eutectics" under laser action depends on their type. In this case, as a rule, their composite colonial microstructure is transformed into the structure of anomalous eutectics. Near the heterophase inclusions of the type of "eutectics", the formation of the saturation zones of

the matrix is controlled by both phases eu1 and eu2 of inclusions, which are sources of internal doping of the steel matrix. In the vicinity of both phases of inclusions, we observed composite liquation zones of saturation of a steel matrix of several types. A characteristic feature of the saturation zones of the steel matrix for heterophase inclusions of this type is that near the different phases of the ph1 and ph2 inclusions saturation zones of the matrix with different structures were encountered. Therefore, their formation of the saturation zones of the steel matrix near inclusions "eutectics" under laser action depends on the behavior of different phases of inclusion, as well as the ability to speed mass transfer of the elements of these phases to the surrounding steel matrix under conditions of pulsed laser action.

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THE OBTAINING OF Sn–Ag POWDER ALLOY BY CONTACT DISPLACEMENT IN AQUEOUS SOLUTIONS

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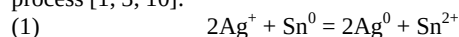
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Abstract: Sn–Ag powder alloy of eutectic composition is demanded in the production of powders for soldering pastes used in electronics. Non-eutectic alloy has found its application in catalysis for CO₂ reduction, in 3D printing, as the promising material for lithium ion batteries. In this work the way of synthesis of Sn–Ag nanostructured powder alloy with near-eutectic composition based of cementation reaction in the system Sn⁰/Ag⁺ in aqueous solutions was proposed. The peculiarities of alloy powder synthesis in acid and slightly acid solutions were studied. Factors influencing on powder microstructure, phase and elemental composition were identified. Electrochemical behavior of tin in aqueous solutions for silver deposition was studied by potentiometric method.

KEYWORDS: CEMENTATION, POWDER, Sn–Ag EUTECTIC ALLOY, PHASE COMPOSITION, MELTING POINT.

1. Introduction/Введенне

Ultra- and nano-dispersed powders from Sn–Ag alloy with different metal content are used in catalysis, electrocatalysis, in printed electronics, as the promising material for lithium ion batteries [1–4]. Powder alloys with eutectic or close to eutectic compositions (Sn96.5Ag3.5 (wt.%); phases β-Sn, Ag₃Sn) are in demand in the production of solder pastes, due to the low melting point of 221°C [5] and the correspondence to a number of physicochemical requirements for solders [6]. Powders from the Sn–Ag alloy are obtained by thermal and plasma chemical spraying [7, 8], by mechanochemical treatment of high-purity tin and silver powders [9], in the way of Sn(II) chemical reduction in aqueous and non-aqueous solutions with subsequent Ag(I) reduction on the surface of tin in the result of contact displacement (cementation) process [1, 3, 10]:



Contact displacement is proceeded in case of the reduction of metal ions in solution with more negative metal of the substrate ($E(\text{Ag}^+/\text{Ag}^0) = +0.08 \text{ V}$, $E(\text{Sn}^{2+}/\text{Sn}^0) = -0.76 \text{ V}$).

In the work [10] the possibility of synthesis an ultrafine powder alloy Sn–Ag, close in composition to the eutectic, Ag(I) cementation with tin powder (99.9 wt.%) is shown. Two strongly acidic solutions containing thiourea or citrate- and iodide- ions simultaneously as ligands for inhibition of oxidation of Sn(II) to Sn(IV) with oxygen dissolved in water and hydrolysis of Sn(II, IV) were used for alloy synthesis.

The purpose of this work was to evaluate the effect of pH, the duration of tin powder treatment in cementation solution, the role of side processes accompanied cementation on the elemental, phase compositions and microstructure of the alloy in the solution with thiourea as ligand.

2. Experimental

For Sn–Ag alloy synthesis the cementation solution with next composition was used (mol·dm⁻³): silver nitrate(I), thiourea, sulphuric acid (pH 0.5, 4.0). Deposition of silver coating was proceeded on tin powder (99.9 wt.%) with molar ratio Sn : Ag(I) equal to 56 : 1 (or on the surface of tin foil). Duration of tin powder or tin foil treatment in the solution was 1–16 min. The experiment with tin foil was needed to assess the role of side processes accompanying Ag(I) reduction.

Electrochemical measurements were conducted in standard electrochemical cell with tin working, platinum counter and Ag/AgCl reference electrodes with PG Autolab, controlled by Nova 2.1. Concentrations of Ag(I) and Sn(II, IV) ions in the solutions after the tin foil treatment were determined by X-ray fluorescence spectroscopy (XFS) (PANalitical); error of concentration determination was 3% for Ag(I) and 17% for Sn(II, IV). The obtained powder alloys washed repeatedly with distilled water and air dried were analyzed by energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) (LEO 1420), differential scanning calorimetry (DSC) (NETZSCH SRA 449 F 3), X-ray phase analysis (DRON-3.0, CuKα).

3. Results and discussion

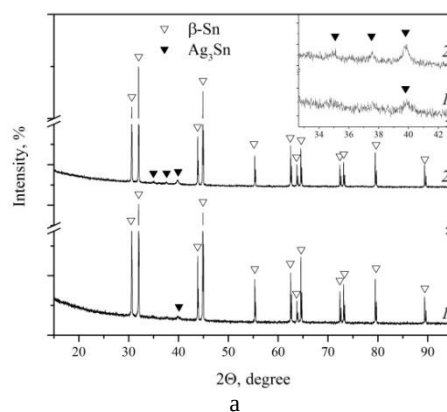
The elemental analysis results of Sn–Ag powders show that the quota of silver in the alloys does not depend on the duration of tin powder treatment in cementation solution, but depend on the solution pH, Table 1. So, silver content in the obtained alloys after two minutes of tin treatment in the solutions with pH 0.5 and 4.0 reaches 11.4 and 6.0 wt.%, accordingly, and changes little with the increase of treatment time.

Table 1. The dependence of the silver content in Sn–Ag alloys obtained in the solutions with pH 0.5 and 4.0 on the duration of tin powder treatment.

Time, min	Silver content, wt.%	
	pH = 0.5	pH = 4.0
2	11.4 ± 1.1	6.0 ± 0.5
5	14.2 ± 1.3	6.6 ± 0.4
10	13.4 ± 1.1	6.8 ± 0.4
15	14.3 ± 1.2	6.3 ± 0.5

X-ray phase analysis showed that powders with silver content 11.4–14.3 wt.% consist of two crystalline phases which are β-Sn and Ag₃Sn. Low intensity peaks at 36.0, 38.11 and 39.59 2θ correspond to Ag₃Sn phase (Fig. 1, a). The powders with silver content 6.0–6.8 wt.% formed in cementation solution with pH 4.0 consist of β-Sn phase only (Fig. 1, b).

DSC analysis in nitrogen atmosphere (Fig. 2, curve 1) shows that the alloy obtained from the solution with pH 0.5 with silver content 11.4 wt.% starts to melt at 220.4 °C, which corresponds to the melting point of the eutectic Sn–Ag alloy. It is necessary to note that the DSC curves for all alloys with a silver content 11.4–14.3 wt.% were the same. Powders containing silver in quota 6.0–6.8 wt.% obtained from the solution with pH 4.0 wt.% (Fig. 2, curve 2) melt at 230.9 °C, at melting point of tin.



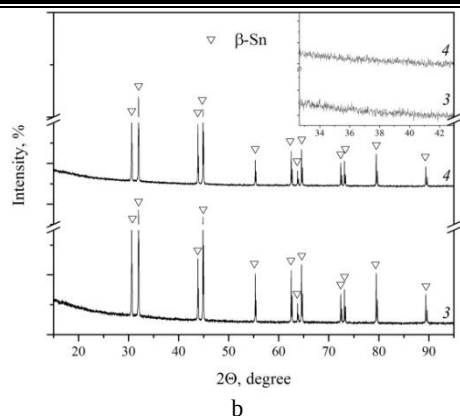


Figure 1. XRD-patterns of Sn–Ag-powders with Ag content 11.4 wt.% (a) and 6.3 wt.% (b) obtained from the cementation solutions with pH 0.5 and 4.0, accordingly. Duration of tin powder treatment was 2 min (curves 1, 3), 15 min (curves 2, 4)

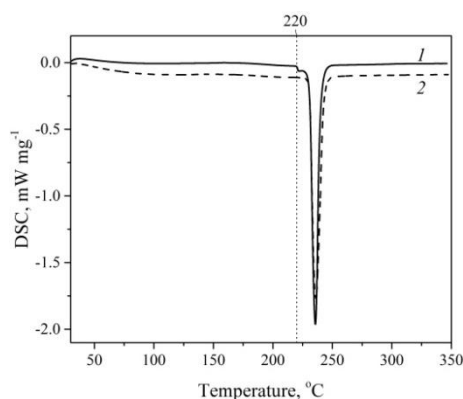


Figure 2. DSC-curves of Sn–Ag-powders with Ag content 11.4 wt.% (curve 1) and 6.3 wt.% (curve 2) obtained from the cementation solutions with pH 0.5 and 4.0

The results of DSC and phase analysis of Sn–Ag alloy powders with silver content 6.0–6.8 wt.%, indicate that there is no Ag_3Sn phase in the alloys obtained from solutions with pH 4.0 and they melt at tin melting point in spite of the fact that powder elemental composition is close to eutectic one. However, the alloy obtained from the solution with pH of 0.5, with nearly two-fold high silver content melts as eutectic one and consists of two crystalline phases distinguishing the eutectic. The presented results indicate the non-equilibrium compositions of the alloys synthesized in the result of cementation.

The authors of the work [11] showed that one of the reasons of non-equilibrium state of the alloy is related to particle size it forming. So, in case of eutectic Sn–Ag alloy formed with nanometer particles its melting point is not higher than 209 °C. SEM analysis was conducted for the comparison of the surface morphology of the particles making up the alloys obtained at different conditions in cementation solutions, Fig. 3. Sizes of the initial tin particles do not change (5–20 μm) during cementation regardless the solution pH, but the agglomerates of small grains with sizes 0.2–0.5 μm appear on the surface of each particle of the alloy powder, which are associated with Ag(I) reduction (Fig. 3, a and c). At the same time, the process of tin dissolution occurs with the formation of pores and loosening of the surface of initial particles. Quantity of the agglomerates on the initial particles surface slightly increases with the duration of cementation. A smaller number of grains, their agglomerates and pores on the surface of alloys obtained in a solution with pH 4.0, in comparison with a solution with pH 0.5, indicate a lower rate of cementation.

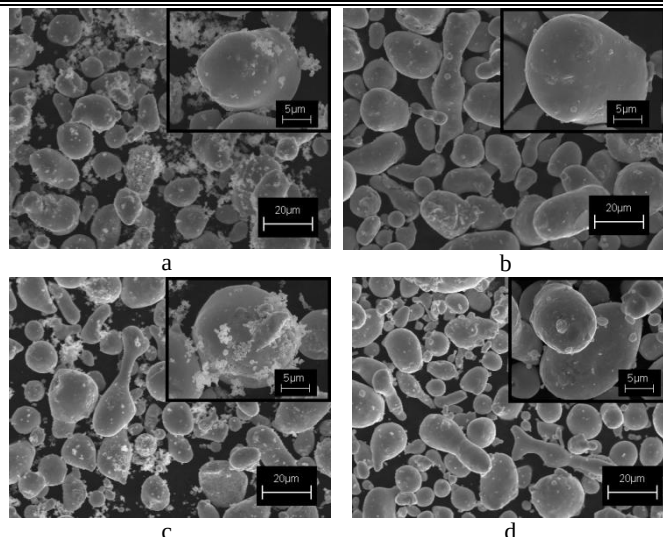
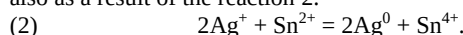
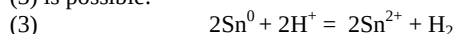


Figure 3. SEM photos of Sn–Ag-powders obtained from the cementation solutions with pH 0.5 (a, c) and 4.0 (b, d) for the samples treated for 2 min (a, b) and 15 min (c, d)

It was important to find out the reasons for the slowdown of the cementation process in solutions with pH 4.0. The reasons for the low rate of cementation can be the following: the formation on insoluble film of Sn(II, IV) oxides on tin particles surface; the adsorption on the surface of initial particles of oxy-hydroxy compounds of tin(II, IV), formed in the result of tin(II, IV) ions hydrolysis. Tin(II, IV) ions passed into the solution during cementation, at tin(II) oxidation by oxygen dissolved in water and also as a result of the reaction 2:



The hydrolysis of tin (II, IV) ions proceeded slightly in the solutions with pH 0.5, but tin dissolution according to the reaction (3) is possible:



Two special experiments were conducted in order to elucidate the role of side processes accompanying cementation and to explain the established fact of lower cementation rate in the solution with pH 4.0, the reasons for the higher melting temperature of powders with lower silver content. In the first experiment the transients of open circuit potential (OCP) of tin electrode from the duration of treatment in cementation solutions and in the solutions without Ag(I) ions (background solutions) were analyzed (Fig. 4). In the second experiment concentrations of Ag(I) and Sn (II, IV) ions were analyzed with XFS method after tin foil treatment in cementation solutions and in the background solutions (Fig. 5).

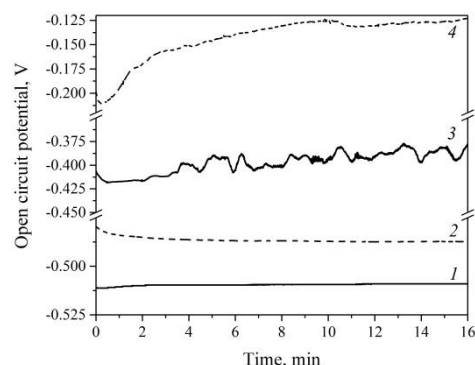
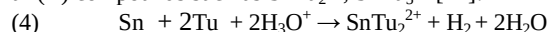


Figure 4. Transients of tin electrode OCP in the solutions with pH 0.5 (curves 1, 2) u 4.0 (curve 3, 4): background solutions – curves 1, 3, cementation solutions – curves 2, 4

Tin electrode OCP in the background solution with pH 0.5 increases by 0.003 V during the first 1.7 min and then does not change (Fig. 4, curve 1). The increase in potential is associated with the dissolution of tin. Passivation of tin surface due to the oxides formation leads to the potential stabilizing. Tin electrode OCP in

the background solution with pH 4.0 decreases during first 0.7 min by 0.010 V and then changes a little (Fig. 4, curve 3), but dependence does not reach a plateau, as in case of the solution with pH 0.5 and the potential varies up to ± 0.008 V. Probably the reason of potential decrease is the formation of thiourea complexes of tin(II) compounds such as SnTu_2^{2+} ; SnTu_5^{2+} [12]:



Thiourea complexes of tin(II) are not stable and Sn(II) ions hydrolysis with the formation of colloidal particles of oxy-hydroxy compounds is proceeded. Oxy-hydroxy compounds adsorbed and desorbed on the surface of tin changing its electrode potential within the specified limits.

In cementation solution with pH 0.5 tin electrode OCP decreases by 0.007 V in the first 2 min and then changes a little (Fig. 4, curve 2). It can be explained in the next way: in the first 2 min dissolution of tin is passed less effective than cementation process.

In case of cementation solution with pH 4.0 OCP decreases by 0.002 in the first 0.3 min, then increases by 0.08 V to 10 min, after that there is a slight drop in potential (Fig.4, curve 4). It is obvious that cementation efficiency is different at the indicated three stages in the solution with pH 4.0. At the first stage (up to 0.3 min), tin dissolves, probably due to the formation of thiourea complexes Sn(II) [12] and cementation process proceeded slowly. At the second stage (0.3–10 min), cementation process occurs mainly. At the third stage, the tin surface is passivated by hydrolysis products that impede the reaction 1.

In the result of cementation reaction (1) the molar ratio of reduced silver and oxidizes tin in the solutions should be 2 : 1. The comparison of the experimental results shows (Fig. 5, a, b, curves 1, 4) that the concentration of Ag(I) ions left the solution with pH 0.5 is greater than for the solution with pH 4.0 in 1.1 – 1.4 time and the increase in cementation duration leads to the growth of the difference in Ag(I) concentrations. Concentrations of tin ions experimentally determined and calculated (according to the reaction 1 and concentrations Ag(I)) in cementation solution with pH 0.5 are coincide up to the tin treatment time equal to 8 min. After this period of time, the experimentally determined concentration of Sn(II, IV) becomes 1.5 times lower than calculated one (for 16 min). The established fact indicates that the reduction of Ag(I) occurs according to reactions 1 and 2.

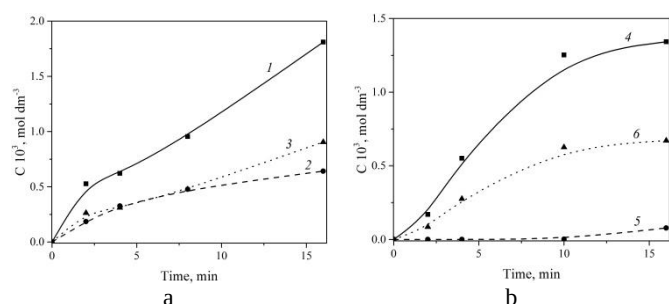


Figure 5. The dependences of metal ions concentrations in cementation solutions with pH 0.5 (a) and pH 4.0 (b) on treatment time: 1, 4 – cemented Ag(I); 2, 5 – Sn(II, IV) passed onto the solution; 3, 6 – Sn(II) calculated according to the reaction 1 and concentrations Ag(I). Tin foil with square 25 cm² was treated in 20 ml of the solutions

For the solution with pH 4.0, the experimental and calculated concentrations of tin ions at cementation duration from 2 to 16 min differ in ~4.5 times. The reason for such low concentration may be due to the fact that tin passing into the solution is easily hydrolyzed at pH 4.0 with formation of oxy-hydroxy compounds adsorbed on the surface of the tin and glass beaker in which the cementation process takes place, all these lead to underestimated results of tin concentration determination. So, it follows, that almost all Sn(II) ions passed into the solution through the reaction 1 participate in the reduction of Ag(I) by reaction 2 in the solution with the pH 4.0. To determine the quota of the reactions 3 and 4 in the total process of

tin dissolution, tin plates were kept in background solutions with pH 0.5 and 4.0 from 2 to 16 min. It was found that in the solution with pH 4.0, the concentration of Sn (II, IV) is below the level determined by XFS method. The absence of Sn(II, IV) in the cementation solution with pH 4.0 probably connected with the formation of insoluble oxy-hydroxy Sn(II, IV) compounds on tin plate surface. In case of the solution with pH 0.5 Sn(II, IV) concentration in the background solution is not more than 3% of the quantity determined after cementation. The slowdown of Ag(I) reduction by tin in cementation solution with pH 4.0 is caused by the formation of a SnO₂ film on the particles surface, which prevents diffusion of silver atoms into the tin crystal lattice as it was shown in [13], which explains the absence of the Ag₃Sn intermetallic compound in the obtained powder alloy. The absence of characteristic peaks of tin oxides on the X-ray powder diffraction patterns is probably due to the small thickness of oxide film. It is necessary to pick out that characteristic peaks of SnO₂ with low intensity are presented on the X-ray diffraction patterns obtained for tin plates after cementation.

4. Conclusion

The way of synthesis of Sn–Ag powder alloy with the eutectic phase composition (β -Sn, Ag₃Sn) and melting point (220.4 °C) based on the cementation reaction in the system Ag⁺/Sn⁰ in aqueous strongly acid (pH 0.5) solution contained thiourea was proposed.

It was found that cementation process in the system Ag⁺/Sn⁰ at pH 4.0 allow to receive alloy powder with elemental composition close to eutectic (6.0-6.3 wt.%) but included only one crystalline phase (β -Sn) and melted at tin melting point.

It was shown, that cementation in the solution with pH 4.0 is accompanied with tin surface oxidation, with Sn(II, IV) hydrolysis and formation of oxy- hydroxy- compounds adsorbed on the surface of tin. These side processes depressed Ag(I) reduction and formation of intermetallic Ag₃Sn.

5. Acknowledgements

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SIMULATION OF NANOCRATER FORMATION DURING LASER-INDUCED PHASE TRANSITIONS

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Abstract A theoretical study of the process destruction of a solid surface under the action of a powerful radiation impulse is carried out. The peculiarities of the dynamics surface destruction of the material and the features of the space-time dynamics of the gaseous phase were studied. This phase occurs as a result of local phase changes on the surface of the irradiated material. The differential equation to describe the dynamics of the corrosion crater formation on a solid surface was researched. This equation is analyzed together with equation of near-surface pressure dynamics. The asymptotic analysis for crater equation gives the basis to assert that mathematical interpretation of process of destruction corresponds to actual temporal dynamics of formation of a crater on the substance. The numerical simulation of the formation of a nanocrater with a model form of an active laser impulse is given. The test calculations correspond to experimental observation and theoretical ideas about the process of development of a corrosion crater under laser pulsed irradiation.

KEYWORDS: LOCAL PHASE CHANGES, POWERFUL RADIATION IMPULSE, CORROSION CRATER, PRESSURE

1. Introduction

Laser radiation (laser doping, annealing, heat treatment, coating, etc.) is used in many modern surface treatment (modification) technologies. Possibility of local influence on small surfaces, high speed heating, and manoeuvrability in laser beam controlling make laser methods of material modification more and more attractive. A lot of experimental and theoretical investigations are closely related to the problem of solid matter surface destruction by short high-power laser impulses. These technologies may, in particular, be useful in recording information, labeling and other technological applications.

Therefore development of theory of intense energy flow interaction with matter surface which takes into account local phase transformations during surface destruction is may be the most consecutive scientific approach.

2 Preconditions and means for resolving the problem

2.1 Experimental studies

Contemporary lasers and laser systems generate femtosecond impulses ($1 \text{ fs} = 10^{-15} \text{ s}$). Femtosecond laser systems with light impulse duration 10–1000 fs allow obtaining under focusing enormous light intensity over 10^{13} W/cm^2 . After falling on solid matter surface such high intensity impulses can, under some conditions, lead to considerable damages of this surface and are of special interest [1–10]. Examples of such a damage are shown on fig. 1

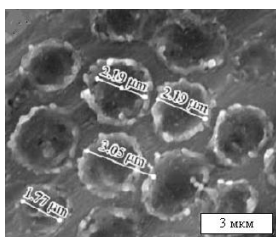


Fig.1 Microcraters obtained by femtosecond laser titanium irradiation [10]

The damages made by laser impulse are various on their form. The surface destruction may be accompanied by fusing as well as not fusing of crater edges. According to experimental estimations characteristic level of energy, from which active destruction of surface begins practically without formation of liquid phase exceeds $10 \div 100 \text{ MW/cm}^2$ depending on material. If the flow is substantially higher than this value, considerable part of energy of laser radiation is outlaid on a direct phase solid-gas

transition. A liquid phase in the area of treatment is practically absent in this case. Such streams represent the main interest of this research.

The formation of a corrosive crater on the surface of such a media depends on both the power flow parameters and the properties of the specific substance. This research is aimed at studying theoretically the dynamics of the crater formation and all the accompanying processes. In the case of destruction under real conditions the removal of a substance from the solid phase and its transfer into the gas one can occur not only directly from the surface in the form of individual atoms, but also through micro-clusters and micro-droplets which cannot but be formed in the gaseous phase.

2.2 Criterion for surface destruction in laser irradiation without crater melting

Flows that cause surface destruction without melting are of basic interest in this research. To define limit, which separates treatment with formation of the liquid state and treatment which is not accompanied with surface melting, we will consider the superficial layer of matter on an area with the size equal to the cross-section of laser impulse. To prevent liquid phase appearing on the solid surface, its temperature during impulse action has to amount, at least, critical value T_c , without going out the borders of the matter state phase surface which belongs exceptionally to the hard phase. Thus pressure in this near surface area of hard phase must also exceed some critical value P_c . As a laser impulse is considered, a necessary condition at which the system gets in the noted area is: $P_c < q_s(1+R)$ where q_s – power of electromagnetic wave falling on the matter surface, R – light reflectivity, c – light speed.

Taking into account, that on the critical isotherm of gas phase for arbitrary pressure P and volume V_T the state equation $PV_T = \nu R_T T_c$ is holding, where ν is a molar gas amount, it is possible to estimate the value of pressure P_c , which provides implementation of the above condition. This value can be estimated from the next considering. In order that a liquid phase did not appear, a hard phase after a phase transition must get on an isotherm which with a temperature not below than critical isotherm with a temperature T_c . Examining a critical isotherm, we will get the sought threshold value P_c for which gas state equation will acquire a kind $PV_T^{(c)} = \nu R_T T_c$. In this equation remains indefinite volume $V_T^{(c)}$ so far. For its estimation it is possible to take advantage of fact, that in the moment of phase state transition from solid to gas, the change of volume $V_T \rightarrow V_T$ is not so substantial comparing to the similar change for other points of isotherm T_c . (where this change is large). That is why a volume $V_T^{(c)}$ can be estimated counting it practically equal to the proper volume of hard phase $V_T^{(c)}$. As one mol volume of hard matter V_μ is determined by ratio: $V_\mu = \mu/\rho_0$, where μ is molecular mass, and ρ_0 is density, the volume of ν mols is obviously equal

to $V_T^{(c)} = v\mu/\rho_0$. Using this value of volume in state equation $P_c V_T^{(c)} = vR_T T_c$ in place of $V_T^{(c)}$ we will get an estimation: $P_c = \rho_0 R_T T_c / \mu$, and a sufficient condition for a flow q_s will look in this case like:

$$q_s > \frac{\rho_0 R_T T_c c}{\mu} \cdot \frac{1}{1+R}$$

In practice such estimation is interesting for an initial flow q , which is related to the flow q_s which passed in a solid by correlation $q_s = (1-R)q$. Then for the initial value of flow we get:

$$q > \frac{\rho_0 R_T T_c c}{\mu} \cdot \frac{1}{1-R^2}$$

After this formula estimations were made for concrete materials. They show that, for example, for aluminum the superficial value of stream must meet condition

$$q \geq \frac{6 \cdot 10^{13}}{1-R^2} \text{ W/cm}^2, \text{ for copper and chrome } q \geq \frac{9 \cdot 10^{13}}{1-R^2} \text{ W/cm}^2 \text{ for tungsten } q \geq \frac{1.5 \cdot 10^{14}}{1-R^2} \text{ W/cm}^2, \text{ for titan } q \geq \frac{7.6 \cdot 10^{13}}{1-R^2} \text{ W/cm}^2, \text{ for potassium } q \geq \frac{4 \cdot 10^{12}}{1-R^2} \text{ W/cm}^2.$$

As evidently, such estimations do not contradict experimental information [11]. Consequently, here we will name flows intensive, if they meet condition got before.

3 Solution of the problem

The model of the destructive process proposed in the paper was built on the basis of a system of inhomogeneous equations of mechanics of a continuous medium.

At action of irradiation on a surface there is a coexistence of the two, solid and gas, media due to local phase transitions. Using the three boundary conditions, namely [9]:

— the condition of a mass flux balance

$$(1) \quad \rho_s (\mathbf{v}_s \cdot \mathbf{n}) - \rho_s (\mathbf{v}_{0s} \cdot \mathbf{n}) = 0,$$

— the condition impulse flow balance

$$(2) \quad P_s n_i + \frac{1}{c} (n \cdot q_s) + \rho_s (n \cdot v_s) (v_s^i - v_{0s}^i) + P_{ij}^{0s} n_j = 0,$$

— condition of energy flow balance near the phase boundary:

$$(3) \quad (\mathbf{n} \cdot \mathbf{v}_s) \left(\rho_s H_s + \rho_s \frac{v_s^2}{2} \right) + L_0 (\mathbf{n} \cdot \mathbf{q}_s) - L \lambda_s (\mathbf{n} \cdot \text{grad} T)_s - (\mathbf{n} \cdot \mathbf{v}_s) \rho_s U_{0s} = 0.$$

has allowed us to formulate three equations which are characterized, in the main, by gas parameters and describe the dynamics of a crater formation – eq. (1), dynamics of a plasma plume formation – eq. (2) and dynamics of behavior of the basic macroscopic quantities of the process – eq. (3)

Here we designate by index "os" solid substance phase of and designate by index "s" gas. In the equations (1)–(3) U , ρ , v respectively intrinsic energy of the continuous medium mass unit, density of this medium, and a convection velocity vector, P pressure exerting, P_{ij}^{0s} – the surface value of a stress tensor, H_s – a heat Gibbs function (enthalpy) describing macroscopic system state in thermodynamic equilibrium when entropy and pressure are the main independent variables; U_{0s} is intrinsic energy of the condensed matter mass unity; $\mathbf{Q} = \mathbf{q}_s + \mathbf{q}_s^T$ – general energy flow in the medium, where q_s is an energy of a light flow and $\mathbf{q}_s^T = -\lambda_s (\text{grad} T)_s$ is an energy of a thermal flow L_0 is a light loss factor for the transition from gas to solid, L is a thermal loss factor for the transition gas-solid.

All boundary conditions are formulated in the local reference system, located on the boundary between the condensed media and the gas phase in the area of the impulse action. It is clear that when the solid surface does not destruct, the reference system will remain stationary relative to the observer. But when destruction occurs, then the chosen system in the area of this destruction is rigidly associated with a certain point of the surface

of the solid medium, and moves along with it. That is, such a system describes the events directly at each individual point of the surface. Therefore, there is a need to establish a connection between the local and laboratory coordinate systems. The laboratory coordinate system is stationary relative to the surface prior to its destruction.

The shape of the crater at each fixed time point is determined as follows $z(t) = S(t, x(t), y(t))$. Here $S(t, x(t), y(t))$ is the function of the shape of the surface of the formed crater (the crater shape function). For each moment of time, it determines a certain dependence z from x and y .

As a result of coordinate transformations from one system to another, ratios were obtained for velocities linking the two coordinate systems. The obtained ratios allow us to move from a local frame of reference, in which boundary conditions are formulated at the boundary of the separation of two phases to a laboratory frame of reference, in which the processes associated with destructive processing can be observed. At the expense of transformations, the equation of the dynamics of the crater formation relative to the laboratory frame of reference was obtained from the continuity condition. The feature of the equation is that the surface pressure that is included in the obtained equation is not constant. Therefore, the energy flow balance equation was used to determine the dynamics of the surface pressure.

A system of two differential equations was obtained. In dimensionless form:

— the crater dynamics equation

$$(4) \quad \frac{\partial \Sigma}{\partial \theta} = \Pi^\beta \sqrt{1 + \left(\frac{\partial \Sigma}{\partial x} \right)^2 + \left(\frac{\partial \Sigma}{\partial y} \right)^2} \equiv \Pi^\beta N,$$

— the equation of the dynamics of near-surface pressure:

$$(5) \quad \frac{\partial \Pi}{\partial \theta} = (-1 + \Lambda e_q \vartheta_\tau) \Pi^{\beta+\eta} - \Pi^{\beta+1} + \frac{e_q \vartheta_\tau \Pi^\eta}{\sqrt{1 + \left(\frac{\partial \Sigma}{\partial x} \right)^2 + \left(\frac{\partial \Sigma}{\partial y} \right)^2}} \equiv (-1 + \Lambda e_q \vartheta_\tau) \Pi^{\beta+\eta} - \Pi^{\beta+1} + \frac{e_q \vartheta_\tau \Pi^\eta}{N}$$

In the equation (4) the parameter e_q determines the ratio of the flow that enters the surface of the matter q_s to the output flow q_0 , i.e., in dimensionless units

$$e_q = \frac{q_s}{q_0} \equiv f(x, y) e^{-\Lambda M \Pi^{\beta+\eta} \Sigma},$$

where the function $f(x, y)$ – determines the transverse shape of the stimulating impulse and adds to (4) an additional dependence on x, y , Λ – parameter determining the degree of interaction of the evaporable matter with the incident radiation, M – dimensionless parameter determined by equality:

$$M = \frac{q_0 (\kappa - 1)^2 L^2}{2 \varphi_0^{3/2} \kappa^2 \rho_{0s} (\kappa + 1)^{1/2}}.$$

Here κ is polytropic index, φ_0 is specific heat of the condensate - gas phase transition, $\beta = (\kappa + 1)/(2\kappa)$, $\eta = 1/\kappa$. It is clear that in the presence of the destruction of the surface formed by the corrosion torch at the matter surface will significantly affect the factor e_q reducing it ($0 \leq e_q \leq 1$).

4. Results and discussion

4.1 Analysis of phase trajectories of pressure at crater formation

To fulfill asymptotic estimates of the "behavior" of the crater formation as a function of time it is convenient to analyze the phase dependence curves $\frac{\partial \Pi}{\partial \theta}$ from Π . Consider a situation where the width of the incident beam is much greater than the depth of the crater and the intensity is distributed evenly across its cross section.

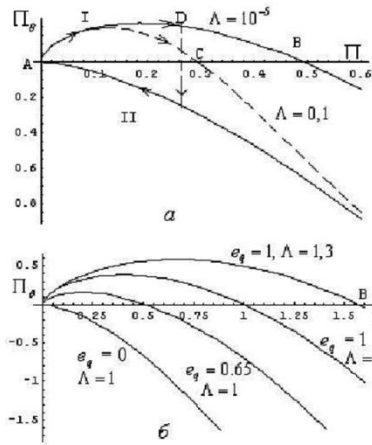


Fig.2 Phase trajectories of two periods: a) curve I corresponds to the time when the impulse is acting, curve II corresponds to the time when the impulse is ended. b) corresponds to the time when the impulse is acting for different values of parameter Λ and e_q . Here we use the approximation $\Sigma \sim 1$ and $N \sim 1$.

Arrows on fig. 2a designate the direction of the process movement of time pressure development indicate: the first stage (I) begins with point A, which is unstable for this stage (positive derivative $\frac{\partial \Pi}{\partial \theta}$), so the dependence change $\frac{\partial \Pi}{\partial \theta}$ from Π occurs along curve I to the moment of the impulse ending (indicated by D in the figure), or until the pressure reaches its maximum (Fig. 2a - points B or C). These points are stable - as soon as the curve crosses the axis Π the condition $\frac{\partial \Pi}{\partial \theta} < 0$ starts to be complied. This makes the process to return to point B (or C) again. At these points, the gas pressure remains constant until the impulse reached the end. As soon as the impulse is over, the transition to curve II occurs and the process begins to move along the curve until it reaches zero. In fig. 2a shows a dashed line that conventionally describes the dynamics of the process in the case of large ones Λ (an increase in this parameter physically means an increase in the interaction of radiation with the plasma-gas torch formed near the surface of matter). As can be seen from Fig. 2b, with $e_q \cong 1$ there are such values Λ , when in the point B, pressure value Π will be larger than unit. Also, for different values Λ at the similar e_q (on Fig. 2b are two curves that correspond $e_q \cong 1$) with increase Λ the value $\frac{\partial \Pi}{\partial \theta}$ increases in maximum.

4.2 Asymptotic study of the dynamics of the nanocrater formation

The dynamics of crater development on a solid surface under the action of a powerful laser impulse was investigated asymptotically (Fig. 3).

At the beginning of the formation of the crater the process has an explosive, power-law θ , character, and at reaching the maximum possible value of pressure (point B in Fig. 2a) - changes according to the linear law.

Upon completion of the impulse action, the crater formation is rapidly stopped, and when the situation is implemented under $\Lambda > 1$ the explosive (Fig. 3a) process is gradually transformed into logarithmic and only then becomes linear. As the degrees of freedom increase, the magnitude Σ responds more slowly to the external laser effect

The approximate qualitative dynamics crater formation in this sequence is presented in Fig. 4

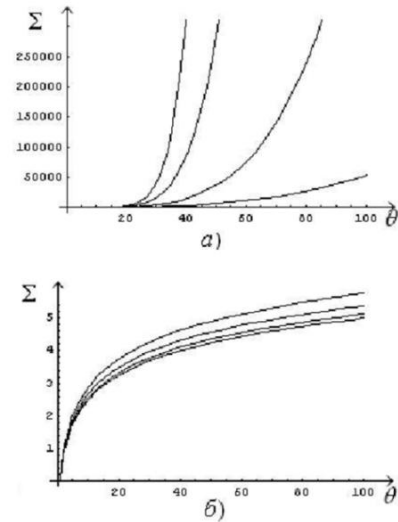


Fig. 3 Asymptotic behavior of the formation of a crater under the influence of a laser power impulse

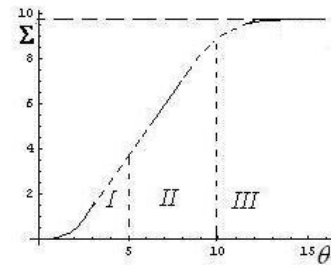


Fig. 4 Formation of a crater under the influence of laser radiation according to asymptotic analysis

Fig. 4 illustrates the formation of a crater in time. The first period (I) reproduces the formation of the crater at the beginning of the destruction of the surface. The second (II) is the dynamics of crater formation as the pressure approaches its maximum value. The last period (III) determines the change in the shape of the crater after the termination of the impulse, which is determined by asymptotic $\Sigma = \Pi_c^\beta \theta_\tau + \frac{25}{4\theta_\tau}$. Here Π_c is maximum value of pressure and θ_τ is dimensionless impulse length.

4.3 Numerical simulation of the dynamics of crater formation

A numerical simulation of the dynamics of crater formation was performed using the simplified formula

$$\frac{\partial S}{\partial t} = P \sqrt{1 + \left(\frac{\partial S}{\partial r}\right)^2}$$

The initial conditions for this equation are obvious:

$$S(0, r) = 0, S(t, \infty) = 0.$$

Specified typical model of pressure caused by laser impulse:

$$P = \frac{1 - \exp(-t^{10})}{1 + \exp(10(t - \tau))} \exp\left(\frac{r^2}{r_0^2}\right)$$

where τ is the laser impulse length, r_0 is beam width. The impulse lengths had femtosecond values at the values of the radiation flux $q \sim 10 \text{ TW/cm}^2$. The function of the crater shape $S(t, r)$ was calculated in nanometers.

In Fig. 5 shows the crater profiles for different time points. The origin coincides with the center of the laser impulse section.

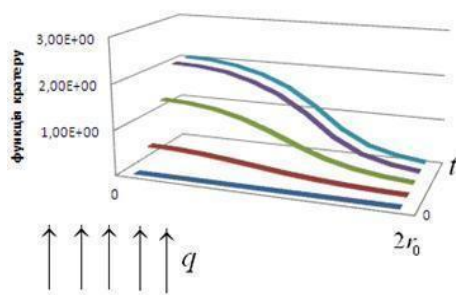


Fig. 5 Dynamics of crater development over time

5. Conclusion

The dynamics of the formation of corrosion crater on the surface of material subjected to destructive treatment is considered. The magnitudes of flows that lead to structural surface changes without surface melting were determined. They take values greater than 100 TW/cm^2 and depend on the properties of the irradiated material. Estimates were performed using phase diagrams, taking into account the local phase transformations of the solid surface under laser irradiation.

The phase diagrams of the equation of near surface pressure dynamics are analyzed. It is shown that the dynamics of the pressure, are significantly influenced by the parameters that determine the interaction of incident radiation with a plasma gas torch. Conformably these parameters define the process of forming a corrosion crater on the solid surface.

Asymptotic estimates of the dynamics of crater development have been performed. It is shown that the function of the shape of the crater surface is initially explosive and stabilizes in time after the ending of the affect impulse at arbitrary polytropic values. This indicates the internal consistency of the model.

The results of the numerical test calculations correspond to theoretical ideas about the process of a corrosion crater formation. Based on this, it can be argued that the constructed model theoretically describes the processes occurring on a solid surface under the influence of powerful femtosecond laser impulses.

The use of this model in the future may be useful for predicting changes on the surfaces of specific solid materials under the influence of high-power impulse radiation.

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ELASTIC AND STATIC CHARACTERISTICS OF INNOVATIVE CORUNDUM CERAMIC PRODUCTS

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Abstract: Using innovative technology, high alumina corundum ceramic products for ballistic protection have been produced and their elastic, physical and mechanical characteristics have been tested. The products are of different shape and thickness and are applied in the construction of the front layer of macro-dispersed ceramic-polymer modular systems for individual protection and for armoring of aircraft, of water and land mobile and stationary military objects, and the like.

Keywords: ELASTIC CHARACTERISTICS, BALLISTIC CORUNDUM CERAMICS, MACRO DISPERSARY MODULAR PROTECTION SYSTEMS

I. Introduction

Corundum ceramic has a tightly sintered polycrystalline structure. The starting material for its production is $\alpha\text{Al}_2\text{O}_3$ (corundum). The main requirement for the raw material is to be of high purity. The degree and permanence of impurities predetermines the purpose of the ceramics. Another important requirement is to provide a certain sediment composition (finely milled starting material) obtained without contamination during milling. The innovation in the development and application of the technology for the production of ballistic protection products lies in the modification of Al_2O_3 multipurpose powder with high dispersion and close particle sizes, as well as in the correct introduction of the plasticizer, a suitable compression mode and optimal regime of high temperature synthesis.

Over the last decade, high oxide corundum ceramic has found wide application for protection against high-velocity kinetic impacts, even though its density compared to that of boron carbide ceramic [1] is not in its favour. On the other hand, its price is many times lower. Density apart, the high alumina corundum ceramic constructive elements have an extremely wide range of elastic, physicochemical and mechanical properties, which makes them extremely useful not only for ballistic purposes but also in many other areas of technology.

Particular attention is paid to the improvement of the production method using isostatic pressing, Bulgaria is one of the countries where innovative production of high-oxide corundum ceramic parts is being carried out. A team including the company <https://tr.bivol.bg/view.php?eik=204283715> Techceramic Ltd, Mezdra, the MSETHC "Acad. A. Balevski" at the Bulgarian Academy of Sciences, and the Faculty of Physics at Sofia University "St. Kliment Ohridski" manufacture and conduct complex studies on the physico-mechanical and elastic characteristics of parts made of corundum and boron carbide ceramics and the ballistic characteristics of modular ceramic polymer systems for protection based on them [2].

The high temperature solid phase synthesis is carried out at optimum temperature and pressure.

II. Determination of the elastic properties of ceramic parts made of corundum ceramic

1. Subject of the study - square plates with thickness of 8 and 10 mm and 50 mm side length, a total of 40 pieces.

2. Investigation methods.

Two investigation methods have been applied to characterize the elastic properties of ceramic composite plates:

- Ultrasonic method;

- Vibration method.

2.1. Ultrasonic method for determining the elastic properties

The determination of the dynamic elastic material modules by ultrasound is based on the dependencies (1), (2) and (3) between the velocities of the longitudinal (C_L) and transverse (C_S) ultrasonic waves, the density (ρ), the linear deformation module (E), the shear modulus (G) and the Poisson coefficient (μ). The dependencies are derived from the equations for the propagation of a mechanical wave in isotropic medium [3,4]:

$$E = 4\rho C_S^2 \left(\frac{\frac{3}{4} - \left(\frac{C_S}{C_L}\right)^2}{1 - \left(\frac{C_S}{C_L}\right)^2} \right) \quad (1)$$

$$(2) \quad G = \rho C_S^2$$

$$(3) \quad \mu =$$

The ultrasound wave velocities are determined by measuring the propagation time of the waves. The ultrasonic wave velocity device consists of an ultrasonic apparatus and ultrasonic transducers for longitudinal and transverse waves. The measurements of longitudinal waves have been performed at a frequency of 10 MHz using an echo method. The transverse wave measurements have been made by transmission method at 3.5 MHz.

The relative errors in the determination of the propagation time and the ultrasound wave velocity in the reference sample are less than 1%. The accuracy of measurements is up to 2%. The measurements were made on the two preliminary polished plates from each type of material. The presented results are averaged on the 5 measurements and shown by type of plates in Table 1.

Table 1. Results from ultrasonic testing and elastic constants calculated by Eq.1-3 for plates with dimensions 50x50x8mm

No	kg/m ³	C_L , m/s	C_S , m/s	μ	G, Pa	E, Pa
8.1	3799	10004	5930	0.23	1.34E+11	3.28E+11
8.2	3804	10048	5927	0.23	1.34E+11	3.30E+11
8.3	3756	10034	5940	0.23	1.33E+11	3.26E+11
8.4	3763	10181	5936	0.24	1.33E+11	3.30E+11
8.5	3958	10136	6083	0.22	1.46E+11	3.57E+11
8.6	3793	10182	6079	0.22	1.40E+11	3.43E+11
8.7	3798	10183	6079	0.22	1.40E+11	3.43E+11
8.8	3764	10145	5936	0.24	1.33E+11	3.29E+11
8.9	3782	10155	6079	0.22	1.40E+11	3.41E+11

8.10	3822	10136	5930	0.24	1.34E+11	3.33E+11
8.11	3786	10152	6079	0.22	1.40E+11	3.42E+11
8.12	3784	10146	6079	0.22	1.40E+11	3.41E+11
8.13	3753	10172	5936	0.24	1.32E+11	3.28E+11
8.14	3780	10108	6083	0.22	1.40E+11	3.40E+11
8.15	3773	10124	6083	0.22	1.40E+11	3.40E+11
8.16	3754	10138	6083	0.22	1.39E+11	3.39E+11
8.17	3789	10134	6083	0.22	1.40E+11	3.42E+11
8.18	3812	10500	5936	0.23	1.34E+11	3.40E+11
8.19	3833	10185	6083	0.22	1.42E+11	3.47E+11
8.20	3804	10104	6083	0.22	1.41E+11	3.42E+11
Aver.	3795	10148	6022	0.22	1.38E+11	3.38E+11
StDev.	44	97	74	0.01	4.04E+09	7.75E+09

Table 2. Results from ultrasonic testing and elastic constants for plates with dimensions 50x50x10mm

No	ρ , kg/m ³	C_L , m/s	C_S , m/s	μ	G, Pa	E, Pa
10.1	3878	10293	5950	0.22	1.37E+11	3.43E+11
10.2	3838	10325	6059	0.23	1.41E+11	3.49E+11
10.3	3878	10169	6019	0.23	1.4E+11	3.46E+11
10.4	3855	10314	5979	0.23	1.38E+11	3.44E+11
10.5	3859	10325	6019	0.22	1.4E+11	3.47E+11
10.6	3885	10113	6019	0.23	1.41E+11	3.45E+11
10.7	3824	10165	5979	0.24	1.37E+11	3.38E+11
10.8	3830	10400	5890	0.23	1.33E+11	3.36E+11
10.9	3906	10214	5950	0.22	1.38E+11	3.44E+11
10.10	3814	10348	6019	0.24	1.38E+11	3.44E+11
10.11	3780	10323	6019	0.22	1.37E+11	3.40E+11
10.12	3896	10314	6019	0.24	1.41E+11	3.51E+11
10.13	3772	10381	6019	0.23	1.37E+11	3.41E+11
10.14	3830	10337	6019	0.24	1.39E+11	3.45E+11
10.15	3814	10153	6019	0.23	1.38E+11	3.40E+11
10.16	3873	10219	6019	0.23	1.4E+11	3.46E+11
10.17	3818	10326	6019	0.22	1.38E+11	3.44E+11
10.18	3795	10352	6019	0.22	1.37E+11	3.42E+11
10.19	3827	10347	6019	0.24	1.39E+11	3.45E+11
10.20	3859	10052	6019	0.22	1.4E+11	3.41E+11
Average	3842	10274	6004	0.22	1.38E+11	3.4E+11
StDev	38	98	37	0.008	2.0E+09	3.6E+09

2.2. Vibration method for the determination of elastic properties.

The impulse excitation method is a new technique for the determination of the dynamic elastic properties of materials. The applicability of the resonance method depends on the frequency equations relating the natural frequencies of the test specimens, dynamic elastic properties and density of the material. These relations are solutions of a differential equation, which depend on the boundary conditions and the shape of the specimen [5-7]. Procedures and recommendations for the elastic characterization of isotropic materials using free-edge test specimens like bars, rods, and circular plates are specified in ASTM Standards 1876.

In our work we use the following expression for estimating the natural frequencies of plates with freely supported boundary conditions [5,6]:

$$(4) \quad f = \frac{\lambda}{a^2}$$

Here f is the natural frequency in Hz, λ is a dimensionless natural frequency factor for freely supported plate [7,8], D is the plate flexural rigidity, ρ is the density, h and a are the thickness and the width of the square plate, E is the modulus of elasticity and μ is Poisson's ratio of the material of the plate. The frequency factors λ depend on the ratio of the length and the width of the plate as well as on Poisson's ratio, if one or more edges of the plate are free.

$$(5) \quad D = \frac{Eh^3}{12(1-\mu^2)}$$

Eqs. (4,5) allow the calculation of natural frequencies of plates having any combination of free, clamped, or simply supported edges, if the elastic constants are given, as well as the determination of the elastic modulus.

The values of the frequency factors λ are chosen from [7,8] for various values of Poisson's ratio, defined geometry of the plate and fixed values of the material density.

Experimental modal analysis

The test device for experimental modal analysis is shown in Fig. 1. The exciting impulse is produced by striking the plate with a suitable hammer. The pickup transducer is an acoustic microphone whose signals are transferred to a personal computer. After signal processing the values of the natural frequencies of vibration are obtained.

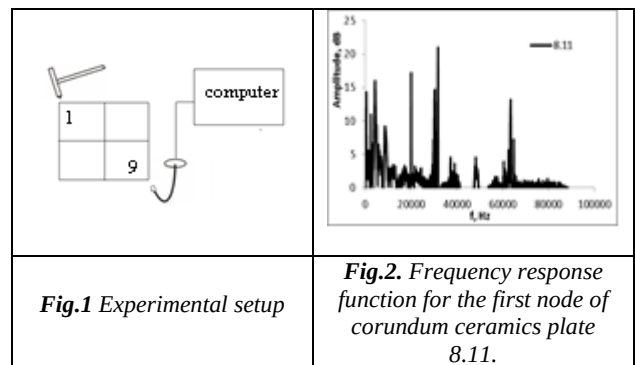
The specimens used in the experimental modal analysis are 20 plates with dimensions 50 mm x 50 mm x 8 mm and 20 plates with dimensions 50 mm x 50 mm x 10 mm. The reference sample is an aluminum square plate with the same dimensions.

The specimen is struck at position 1 and the microphone is located at position 9 (fig. 1). The frequency response function curve is plotted and natural frequencies are obtained. Fig. 2 shows the frequency response function for the first node of corundum ceramic plate No 8.11.

Young's modulus is derived using the formula (4)

$$(6) \quad E = \frac{48}{\pi^2} \left(\frac{f}{\lambda(\mu)} \right)^2 \frac{ma^2(1-\mu^2)}{h^3}$$

where f is the natural frequency, m is the mass of the specimen, a and h are the length and the thickness of the plate, and λ is a non-dimensional factor obtained from [8,9].



In the calculations were used the first and the second resonance frequencies. The relative errors between the analytical and the experimental frequencies of the freely supported plates can be calculated using the formula

$$(7) \quad \text{Error} = \frac{f_E - f_T}{f_E} \cdot 100\%$$

where f_E is the experimental natural frequency obtained through modal analysis; f_T is the theoretical natural frequency obtained by equation (4).

Comparisons between the experimental and theoretical natural frequencies, as well as the values of the elastic constants calculated by Eq.6 are presented in the Table 3 and 4.

Table 3. Comparisons between the experimental and the theoretical natural frequencies and values of the elastic constants for the studied plates with dimensions 50x50x8 mm

No	f1 teor., Hz	f2 teor., Hz	f1 exp., Hz	f2 exp., Hz	Error, %	E, Pa (Eq.6)
8.1	21125	31259	19910	30433.6	-6	3.12E+11
8.2	21249	31418	19863	31433.6	-7	3.3E+11
8.3	21195	31362	19910	31710.0	-6	3.33E+11
8.4	21395	31657	19933	31710.0	-7	3.37E+11
8.5	21586	31940	19910	31722.6	-8	3.79E+11

8.6	20778	30744	20109	30515.5	-3	3.07E+11
8.7	21541	31873	19910	30515.5	-8	3.3E+11
8.8	20931	30971	20003	30316.0	-5	3E+11
8.9	22254	32214	20039	30515.0	-11	3.06E+11
8.10	21502	31816	20015.6	31734.4	-7	3.4E+11
8.11	21600	31960	20003	31652.0	-8	3.27E+11
8.12	21834	32329	19957	30011.7	-9	2.94E+11
8.13	21640	32019	19839.8	30117.2	-9	2.91E+11
8.14	22293	32271	19980	30117.0	-12	2.96E+11
8.15	21829	32299	19898.4	30011.7	-10	2.94E+11
8.16	21757	32193	19910.2	30117.0	-9	2.96E+11
8.17	21752	32186	19839.8	30128.9	-10	3.07E+11
8.18	21634	32011	19945.3	30117.2	-8	3.01E+11
8.19	21557	31897	20167.9	30117.7	-7	3.09E+11
8.2	21460	31754	19933.6	30117.0	-8	3.08E+11
Average						3.15E+11
StDev						2.2E+10

Table 4. Comparisons between the experimental and theoretical first natural frequencies and values of the elastic modulus for plates with dimensions 50x50x10 mm

No	f1 teor., Hz	f2 teor., Hz	f1 exp, Hz	f2 exp, Hz	Error, %	E, Pa (Eq.6)
10.1	25807.6	33238.7	23777	30316.4	-9	3.4E+11
10.2	26135.8	33661.3	23637	31685.5	-11	3.4E+11
10.3	26071.6	33544.5	24000	30818	-9	3.1E+11
10.4	26107.5	33522.6	23789.0	31699.2	-10	3.5E+11
10.5	26388.5	33952.3	23847.6	31722.6	-11	3.6E+11
10.6	25607.6	32947.5	23578.1	31664.1	-9	2.9E+11
10.7	26543.6	34221.3	24011.7	31710.9	-11	3.4E+11
10.8	26140.4	33564.9	23753.9	31722.7	-10	3.2E+11
10.9	25789.9	33249.5	23859.4	31734.4	-8	2.9E+11
10.10	26237.0	33689.0	23601.6	31710.9	-11	3.6E+11
10.11	26385.8	33948.9	23484.3	31687.5	-12	2.7E+11
10.12	25700.0	33604.2	23847.6	31734.4	-8	2.9E+11
10.13	25329.3	32133.3	23484.4	31710.9	-8	3.0E+11
10.14	26041.9	33506.4	23542.9	31722.7	-11	3.7E+11
10.15	26102.3	33516.0	23683.6	31734.4	-10	2.8E+11
10.16	25736.8	33113.8	23496.1	31722.7	-10	2.8E+11
10.17	26793.3	34613.3	24000	31710.9	-12	3.5E+11
10.18	26263.5	33723.1	23718.7	31734.9	-11	3.6E+11
10.19	26363.7	33851.6	23753.9	31710.9	-11	3.6E+11
10.20	24000.0	33467.7	23812.5	31628.9	-1	3.4E+11
Average					-9	3.2E+11
StDev						3.E+10

Figure 3 shows good agreement between the values of the elastic modulus obtained by ultrasound and vibration method.

The obtained results show that the elastic modules of the corundum ceramic specimens obtained by the ultrasound method are approximately 340 GPa. The elastic modules obtained with the vibration method are 320 GPa, but the errors in the resonance frequencies are up to 12%.

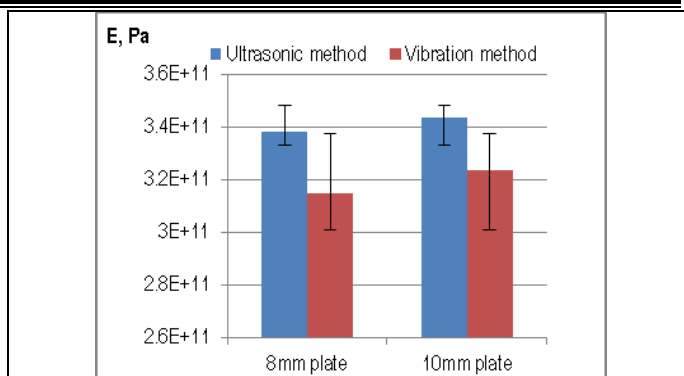


Fig.3. Elastic characteristics, obtained by ultrasonic and vibration methods

3. Measuring the Rockwell hardness number H_{Rc} of 50 x 50 x 8 mm corundum plates using Indentor w (a diamond cone).

Tab. 5. Results of the hardness measurement of 20 test specimens.

Spec. No	8.1	8.2	8.3	8.4	8.5	8.6	8.7	8.8	8.9	8.10
Value of HRC	88,5	90,0	86,5	89,5	92,0	87,3	89,2	91,4	88,7	89,7
Spec. No	8.11	8.12	8.13	8.14	8.15	8.16	8.17	8.18	8.19	8.20
Value of HRC	91,2	92,4	90,4	89,0	87,6	88,9	90,2	91,0	88,5	89,6

4. Measuring the Rockwell hardness number H_{Rc} of 50 x 50 x 10 mm corundum plates using Indentor w (a diamond cone).

Tab. 6. Results of the hardness measurement of 20 test specimens.

Spec. No	10.1	10.2	10.3	10.4	10.5	10.6	10.7	10.8	10.9	10.10
Value of HRC	92,0	91,3	90,6	91,5	90,0	91,5	91,0	89,5	90,2	89,6
Spec. No	10.11	10.12	10.13	10.14	10.15	10.16	10.17	10.18	10.19	10.20
Value of HRC	90,8	91,6	92,3	90,2	89,0	89,6	90,4	91,1	90,8	91,5

5. Examination of the compressive strength of corundum samples plates measuring 10x10x10 mm.

Tab. 7. Results of the hardness measurement of 10 test specimens.

Spec. No.	1	2	3	4	5	6	7
Value of σ , MPa	1792	1923	1398	1567	1600	1595	1423

6. The bending strength is 197 MPa on average.

III. Conclusion

A functional multilayer system for protection against high-speed kinetic impacts has been created based on the information obtained from the conducted tests, as well as on the results from the analysis of the created corundum ceramic compositions, the improved production conditions and the physical and physical-mechanical parameters of the tested batches of pates. The areal density of the armors meets NATO standards.

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