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Abstract: Mechanical or thermodynamic excitations in solid state physics – phonons, cause all fundamental physical properties of materials and always are present, regardless of what is the main carrier of transport properties and ordering (for example, in electroconductivity, it can be electrons / holes, ions, etc., and in magnetism – magnons). In particular, phonons play a different and more subtle role in low-dimensional nano-scale samples, because they, due to the confinement effects, influence the creation of completely unusual and altered characteristics in relation to large (bulk) samples of exactly the same material. Therefore, the possible phonon spectra and states in model of crystal nanostructures: ultrathin films, nano-wires and quantum dots were founded in the paper. The most noticeable phenomenon is the consequence of the dimensional quantization, but also the shape of the boundary surfaces, as well as the presence of the environment surrounding the nano-pattern. In addition to the analysis of the microscopic properties of the phonon subsystem, the calculation of the temperature dependence of the thermal capacity and entropy of these nano systems was also calculated and performed by comparisons with the same for bulk structure.

Keywords: PHONONS, GREEN’S FUNCTION, NANO-STRUCTURES, SPECTRA AND STATES, THERMODYNAMICS

1. Introduction

Over the last decade, we have been witness in rapid development of nanotechnology, i.e. production technologies of structures with nano-dimensions [1–3]. The trend of rapid development of nanotechnologies is not accidental since nanostructures possess physical characteristics that are substantially different from the physical characteristics of the structures, which are larger. Nanostructures have a number of qualitatively new effects. Superconductive, thermal insulating, acoustic and other features that characterize nanomaterials are better than in bulk structures. It is also expected that the usage of nanostructured elements may increase the instruments sensitivity for measuring, and that is leading to new experimental discoveries. All of the abovementioned leads to the conclusion that nanomaterials can be a good basis for further development of Physics [4–6]. In some way, nanostructure effects are connected to the effects in bulk structures, similarly to the relationship between quantum and classical effects. Therefore, further and even faster development of the science of nanostructure materials and nanotechnology is to be expected.

Application of nano-structures requires knowledge of their fundamental physical (mechanical, electro-magnetic, optical, etc.) characteristics. Thermodynamic properties associated with phonon displacements through the nano-samples are particularly interesting. Independent of the type of lattices, the thermodynamics of their subsystems (electrons, excitons, spin waves, etc.) is determined when the subsystem is in thermodynamic equilibrium with phonons. Phonons are quasiparticles that represent collective mechanical oscillations of molecules or atoms and they are the most important system of excitations [7–9]. Besides, the acoustical characteristics as well as conductive and superconductive properties etc. could not realistically being explained without knowing of phonons behavior. All quoted is well known and all applications of phonons in bulk structures have been intensively exploited for more than a century.

The fact, which must be especially pointed out, is that the role of phonons in nanostructures is much more impressive than in bulk structures. The main fact concerning phonon properties in nanostructures is the absence of the so-called acoustic phonons, i.e. phonons whose energy tends to zero when phonon momentum tends to zero. For the phonon excitation in nanostructures – activation energy different from zero is needed. These unexpected characteristics require revision of all conclusions obtained by bulk theories of phonons [10–12]. Therefore, the contribution of phonon subsystems to thermodynamic and energy transfer analysis is the first step in a research of nanostructure properties.

This paper describes a major aspect of the effort to understand nanostructures, namely the study of phonons and phonon-mediated effects in structures with nanoscale dimensional confinement in one or more spatial dimensions. During the last two decades, there has been a steady effort to understand the optical and acoustic phonons in nanostructures such as the superlattice, quantum wires, nanotubes and quantum dots. The central theme of this paper is the description of the acoustic phonons of the optical type in these nanostructures. Primarily, to describe the dispersion relations and mode structures for phonons in nanostructures, phonon amplitudes are quantized in terms of the harmonic oscillator approximation, and where anharmonic effects lead to phonon decay that is described in terms of the dominant phonon decay channels. These elastic and discontinuous models are applied to describe the deformation potential and interactions in a variety of nanostructures. Dependence of energy on the wave vector is highly nonlinear and linear approximations of the dispersion laws of phonons in small size nanostructures make no sense. Changing the phonon dispersion law due to the confinement severely affects the kinetic effects conditioned by the interaction of acoustic phonons with electrons, dotted defects and phonon-phonon interactions. Managing transport properties of acoustic phonons through the modification of their energy spectrum in nanostructures was named phonon engineering.

2. Research method and models

Since quantum low-dimensional structures are of the great interest in science, we have investigated and researched the basic microscopic behavior of phonon subsystem in following models of nano-structures: ultra-thin films (UTF), nano-rods (NR) and quantum dots (QD). The influence of the phonons in these structures is decisive on macroscopic properties, especially from the aspect of their possible usage in nanotechnology. This paper is based on research from our group of researchers gathered around Department for theoretical Physic of University of Novi Sad in the last decades [12–15]. In the opposite of the films which are quasi-2D structures, limited by two surfaces parallel to XY planes, nano-rods and quantum dots are quasi 1D and 0D crystal systems limited in two or three directions: y and z, or x, y and z respectively, (Fig. 1.). It should be mentioned that we will, in here presented calculations, take into account only so called “cut of” models, where we don’t consider influence of boundary parameters: (ε,γ,σ,φ) = 0, i.e. we wanted to explore only the influence of quantum size effects.
We have calculated dispersion law of the phonons using method of the Green’s function [9,16]. Let us observe two-time temperature dependent retarded Green’s function of displacement type:

\[ G_{\alpha\alpha}(t) = \left\{ a(t) \right\} = \left\{ -\frac{Q(t)}{\hbar} \right\} \left\{ a_0(0) \right\}, \]

(1)

where \( a_{\alpha} \) are displacement of atoms from the node \( \tilde{n} = (n_x,n_y,n_z) \) in the direction \( \alpha \in \{x,y,z\} \). Finding the second derivation we obtain equation of motion for the Green’s function:

\[ M \frac{d^2}{{dt}^2} G_{\alpha\alpha}(t) = -i \hbar \delta_{\alpha\alpha} \delta(t) + \frac{Q(t)}{\hbar} \left\{ \left[ p_\alpha', H(t) \right], a_{\alpha}^*(0) \right\}. \]

(2)

The Hamiltonian of the phonon subsystem in harmonic approximation and the approximation of the closest neighbor (with neglecting of the torsion constant \( C_{xx}^{\alpha\beta} \)) (see in [12–15]) is:

\[ H = \frac{1}{4} \sum_{\alpha x,y,z} \left\{ 2M_n \langle \delta_{\alpha x,y,z} \rangle \left[ \left( u_{\alpha x,y,z}^n - u_{\alpha x,y,z}^{n+1} \right)^2 + \left( u_{\alpha x,y,z}^{n+1} - u_{\alpha x,y,z}^{n-1} \right)^2 \right] + C_{xx}^{\alpha x,y,z} \left[ \left( u_{\alpha x,y,z}^n - u_{\alpha x,y,z}^{n+1} \right)^2 + \left( u_{\alpha x,y,z}^{n+1} - u_{\alpha x,y,z}^{n-1} \right)^2 \right] \right\}. \]

(3)

Using time Fourier transformation and when simplify (\( M_0 = M \) and \( C_{xx}^{\alpha x,y,z} = C_{xx}^{\alpha x} \)), and calculating of commutators \( \left\{ f_{\alpha x,y,z}^n, H \right\} \), equation of motion (2) turn into (see in [12–15]):

\[ M_0 \frac{d^2}{dt^2} G_{\alpha x,y,z}^{\alpha x,y,z,n,m}(\omega) = \frac{i \hbar}{2\pi} \delta_{\alpha x,y,z} \delta_{nm} \delta_{\omega} + \left[ C_{xx}^{\alpha x} \left\{ G_{\alpha x,y,z}^{\alpha x,y,z,n,m} - G_{\alpha x,y,z}^{\alpha x,y,z,n,m+1} \right\} \right] + \left[ C_{xx}^{\alpha y} \left\{ G_{\alpha x,y,z}^{\alpha x,y,z,n,m} - G_{\alpha x,y,z}^{\alpha x,y,z,n,m+1} \right\} \right] + \left[ C_{xx}^{\alpha z} \left\{ G_{\alpha x,y,z}^{\alpha x,y,z,n,m} - G_{\alpha x,y,z}^{\alpha x,y,z,n,m+1} \right\} \right]. \]

(4)

This equation has general character and it has the same form for all structures (as for the bulk too). To adjust equation to nanostructures it has to be modified to the spatial limitations of the observed systems:

\[ \nu_{\alpha x,y,z}^{\alpha x,y,z,n,m}(\omega) = 0 \quad (\alpha = x,y,z). \]

(5)

equations, respectively. Using partially spatial Fourier transformation (due to the brake of translational invariance along \( x \), \( y \) and \( z \)) axes, see in [12–15]), we obtain system of \( N_x \times (N_y + 1) \times (N_z + 1) \) or \( (N_x + 1) \times (N_y + 1) \times (N_z + 1) \) nonhomogeneous algebraic difference equations. The obtained Green’s function from the system we present as \( G_{\text{Poloidal}}(\omega) / D_{\text{Poloidal}} \), where \( D_{\text{Poloidal}} \) are determinants of the system from this equations, and \( D_{\text{Poloidal}}(\omega) \) – corresponding substitute determinants. As poles of the Green’s function define allowed energies of the phonons [16], this problem comes down to the finding the roots of the characteristic polynomials of these determinants.

### 3. Phonon spectra

Numerical and analytical results for phonon spectra in ideal ultra-thin films (UTF), nano-rods (NR) and quantum dots (QD) are already obtained in previous works [12–15]:

\[ E_{\nu_x,\nu_y,\nu_z} = \frac{\hbar}{\hbar \Omega} \left[ \sin \left( \frac{\nu_x}{2} \right) + \sin \left( \frac{\nu_y}{2} \right) \right] \left[ \sin \left( \frac{\nu_z}{2} \right) \left( N_x + 1 \right) \right] + \left[ \sin \left( \frac{\nu_x}{2} \right) + \sin \left( \frac{\nu_y}{2} \right) \right] \left[ \sin \left( \frac{\nu_z}{2} \right) \left( N_y + 1 \right) \right] \]

(6)

\[ E_{\nu_x,\nu_y,\nu_z} = \frac{\hbar}{\hbar \Omega} \left[ \sin \left( \frac{\nu_x}{2} \right) + \sin \left( \frac{\nu_y}{2} \right) \right] \left[ \sin \left( \frac{\nu_z}{2} \right) \left( N_z + 1 \right) \right] + \left[ \sin \left( \frac{\nu_x}{2} \right) + \sin \left( \frac{\nu_y}{2} \right) \right] \left[ \sin \left( \frac{\nu_z}{2} \right) \left( N_z + 1 \right) \right] \]

(7)

\[ E_{\nu_x,\nu_y,\nu_z} = \left[ \sin \left( \frac{\nu_x}{2} \right) \left( N_x + 1 \right) \right] + \left[ \sin \left( \frac{\nu_y}{2} \right) \left( N_y + 1 \right) \right] + \left[ \sin \left( \frac{\nu_z}{2} \right) \left( N_z + 1 \right) \right] \]

(8)

Quantum numbers \( \nu_{\alpha} \) (\( \alpha = x,y,z \)) in expressions (6-8) take values: \( \nu_{\alpha} \epsilon \{1, N_x + 1\} \). One can see that solutions have form of Pythagoras theorem and that discretization of the spectra along one direction is independent from discretization along other two directions.

Dispersion law (6-8) in thin films, quantum wires and quantum dots formally has the same form as for corresponding spatially unlimited crystalline structures. Significant difference is in appearing of discrete phonon energies along the direction of spatial confinement. We have numerically analyzed and calculated dispersion law for the 4-layered UTF (\( N = 4 \)) and quadratic surface NR with 5 crystalline planes (\( N = N_z = 4 \)), with the results showed on Fig. 2 (for the ideal infinity structures – with the dashed lines, between is continual and for the nanostructures – with the full lines, which is discrete one). Thereby, introduced are following labels: \( X = \sin \left( \alpha k_{\nu_x}/2 \right) \) and \( Y = \sin \left( \alpha k_{\nu_y}/2 \right) \). On the graphs are clearly visible gaps (\( E_{\text{min}} \) and \( E_{\text{max}} \)), as well as \( N_x = 1 \) (for UTF) and \( (N_x - 1) \times (N_y + 1) \times (N_z + 1) \) – for NR, allowed discrete values between the gaps.
ideal and unlimited structure, show that \( \omega_i^0 < \omega_{max}^0 \), i.e. Debye frequency has somewhat lower value in film (about 10%) in respect to the ideal bulk crystal. With the same procedure for NR and QD [18], follows: \( \omega_i^0 < \omega_{max}^0 < \omega_{max}^0 < \omega_{max}^0 \), and obtained is known as “softening of the nano-phonons”. With finding the ratio of the phonon states in bulk structures [7–9]) and UTF, but exactly on Debye frequencies, follows:

\[
\frac{D_i(\omega)}{D_i(\omega_{max})} = 6 \frac{N_i}{\sqrt{6\pi}} N_{max} + 1
\]  

(11)

therefore, we obtain that population of phonons in film is smaller, i.e. \( D_i(\omega_i^0) < D_i(\omega_{max}^0) \). With the same procedure applied on NR and QD (as in [18]), finally follows:

\[
D_i(\omega_i^0) < D_i(\omega_{max}^0) < D_i(\omega_{max}^0) < D_i(\omega_{max}^0)
\]

5. Phonon thermodynamics

Regarding the fact that the properties of anisotropic structures are conditioned with the change of dispersion law, it is needed to observe behavior of some thermodynamic values in order to get complete picture of these properties. Accordingly, we will analyze heat capacity of the observed models of nanostructures, but before we need to calculate internal energy of this system, starting from standard form [7–9]:

\[
U = 3 \sum_{k,i} E(\tilde{k}) \left[ e^{(\varepsilon(\tilde{k})/\theta)} - 1 \right]^{-1}; \quad \theta = k_B T.
\]

Taking into account that when \( k \rightarrow 0 \) (in long wave approximation) energies of all three phonon branches stay different from zero, we can use dispersion relation (6) is somewhat simplified form: \( E_{\omega}(\tilde{k}) = \sqrt{\alpha^2 + \tilde{k}_x^2 + \tilde{k}_y^2 + \tilde{k}_z^2} \); \( \tilde{k}_x = \tilde{k} \); \( \tilde{k}_y = \tilde{k} \); \( \tilde{k}_z = \tilde{k} \); \( \tilde{k}_z = 0 \), \( \Delta = \Delta_{nano} = \omega_{max}^0 E_0 \); \( E_0 = k_B \Omega \) and \( \varepsilon = \sqrt{1 + (E_0/\Delta)^2} \). We will execute this calculation with transition from summation to integration (more detailed in [12–15]), and after doing this, we obtain:

\[
U_{nano} = \frac{3N_{nano}}{2\pi} \left[ \frac{\Delta}{E_0} \right] \theta^{3/2} \left[ Z_i \left( \frac{\Delta}{\theta} \right) - e^{\varepsilon} Z_i \left( \frac{\varepsilon}{\theta} \right) + 2 \left( \frac{\theta}{\varepsilon} \right)^{3/2} \left[ Z_i \left( \frac{\theta}{\varepsilon} \right) - Z_i \left( \frac{\varepsilon}{\theta} \right) \right] \right],
\]

(12)

where \( Z_i(X) = \sum_{j} j e^{-jX} \) represents Dyson function. To obtain expression for the heat capacity per elementary cell (here, per atom), we start from standard form [7–9]:

\[
C = \frac{1}{N} \frac{\partial U}{\partial T} = \frac{k_B}{N} \frac{\partial U}{\partial \theta}
\]

and after that we obtain:
that is shown on Fig. 3, where we temperature dependence of entropy of the crystalline film, we

\[ C_{\text{bulk}} = \frac{3k_b}{2\pi} \left( \frac{\Delta}{E_c} \right)^2 \int \frac{\Delta}{\theta} \left[ \frac{a}{e^{\Delta/\theta} - 1} - e^{\Delta/\theta} \frac{a}{e^{\Delta/\theta} - 1} \right] + 3Z \left( \frac{\Delta}{\theta} \right) - e^{\Delta/\theta} Z \left( \frac{\Delta}{\theta} \right) + 6 \left( \frac{\Delta}{\theta} \right)^2 \right]. \] (13)

With analysis of this expression, we could observe that it contain two essential terms. The first one has inverse exponential dependence from the reciprocal temperature: \( e^{\Delta/\theta} - 1 \), and that term is responsible for the heat capacity behavior on extreme temperatures (very low and very high temperatures). The second term, expressed over Dyson function \( Z_c(\Delta/\theta) \) and \( Z(\Delta/\theta) \), show the heat capacity behavior in the region of medium temperatures (significant lower from the faze transition temperature). This term represent linear dependence of the heat capacity from temperature.

Along with the internal energy and heat capacity, it could be observed temperature behavior of the free energy and entropy. Based on the definition of free energy [7–9]:

\[ F = \theta \sum_a \ln \left[ 1 - e^{-\epsilon_a/(k_B T)} \right], \]

and with the same procedure as just has been explained, for the case of observed nanostructures upper expression comes down to:

\[ F_{\text{w/d}} = -3N_0k_b \left( \frac{\Delta}{E_c} \right)^2 \theta \left[ \ln (1-e^{-\Delta/\theta}) - e^{-\Delta/\theta} \ln (1-e^{-\Delta/\theta}) \right] - \frac{1}{2} U_{\text{w/d}}. \] (16)

Using standard defined form [7–9]:

\[ S = -\frac{1}{N} \frac{\partial F}{\partial T} = -k_B \frac{\partial F}{\partial \theta}, \]

for the phonon contribution to the entropy of the crystalline film, we obtain next expression:

\[ S_{\text{w/d}} = 3N_0k_b \left( \frac{\Delta}{E_c} \right)^2 \left[ \ln (1-e^{-\Delta/\theta}) - e^{-\Delta/\theta} \ln (1-e^{-\Delta/\theta}) \right] + 3Z \left( \frac{\Delta}{\theta} \right) - e^{\Delta/\theta} Z \left( \frac{\Delta}{\theta} \right) + 6 \left( \frac{\Delta}{\theta} \right)^2 \right]. \] (17)

In entropy expression we could notice that, similar to specific heat, exist two fundamental terms. The first one has logarithm dependence from reciprocal temperature and it determines entropy behavior on low and high temperatures. The second term is defined with Dyson functions and determines entropy behavior on medium temperatures.

Graphic representation of the low-temperature dependence of the heat capacity and entropy is shown on Fig. 3, where we introduce next labels: \( i,f \) for indices ideal (bulk) and finite modeled nanostructures, respectively, as well as \( x = \theta / \Delta = k_B T / \Delta. \) It is clearly visible that specific heat of nanostructures below values for the bulk, but with entropy is opposite situation.

![Fig. 3](image-url)  
**Fig. 3** Temperature behavior of phonon participation in heat capacities (left) and entropies (right) bulk and nanostructures

### 6. Conclusion

On relatively low temperatures the heat capacity and entropy of massive samples is changing with temperature as \( T^4 \), while in nanostructures that dependence is: \( T^{-1} \exp(\text{const}/T) \). Until some temperature \( T^* \), the heat capacity in nanostructures has lower values in than in massive samples. Until that temperature \( T^* \), it has to load more energy (per volume) to heat up nanostructure, which is in agreement with the fact that energy of phonon excitation is bigger in nanostructures than in massive (bulk) samples.

Until temperature \( T^* \), entropy in nanostructures has higher values than in bulk structures, which implies that nanostructures are more unordered structures than bulk, up to \( T^* \), and closer to equilibrium. This corresponds to the fact that in nanostructures is better achieved phonon collectivization and that they have longer-range influence onto physical properties of materials. Regarding that dominant part in these differences between bulk and nanostructures is existence and magnitude of gaps, it is not hard to conclude that these differences will be most evident with QD (\( ~3 \) times bigger than corresponding UTF), than with NR (\( ~2 \) times bigger).

As we know that, on Debye frequencies, phonons are responsible for electric and heat transport properties of materials, follows that nanostructures will be weaker electric \( (\sigma_{\text{w/d}} < \sigma_b) \) and heat \( (C_{\text{w/d}} < C_b) \) conductor in comparison to corresponding bulk structures, so far as between them there are no chemical or crystallographic differences. That mean that phonon excitation in nanostructures occur more difficult. Certainly, this effect is most evident in QD, than in NR and only then in UTF.

All these results are in agreement with the fact that superconducting samples (in form of quantum nanostructures) has better superconductive properties and higher critical temperatures than corresponding massive samples [19]. It is very interest to mention that high-temperature superconductors are distinctly fine grained structures [20] and that quantum dots could connect with the Josephson tunnel junctions.

### Acknowledgements

This work was partially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants: ON-171039 and TR-34019) and by the Secretariat for
Higher Education and Scientific-Research Activities of the Autonomous Province of Vojvodina (Grant: 142-451-2413/2018-03) as well as by the Ministry for Scientific and Technological Development, Higher Education and Information Society of the Republic of Srpska, B&H (Grants: 19/6-020/961-21/18 and 19/6-020/961-35/18).

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STIMULATION OF THE CRYSTALLIZATION PROCESSES OF CASTS OF
PETRURGICAL MATERIALS OBTAINED BY THE GAS COUNTER-PRESSURE
CASTING METHOD

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Abstract: Test recipes of petrurgical materials, based on basalt raw materials and technological additives were developed. The influence of the additives used, their quantities and the mode of thermal treatment on the crystallization processes in the experimental samples was investigated. Products with microcrystalline structure and predominant crystalline phase of augite were obtained. By applying the gas counter-pressure casting method and a set of precision casting molds, products with a variety of mechanical and physicochemical characteristics were obtained. The optimal technological conditions for the production of petrurgical materials, suitable for the making of technical equipment with application in different industries, were established experimentally.

Keywords: STIMULATED CRYSTALLIZATION, BASALT RAW MATERIALS

1. Introduction

The gas counter-pressure casting method makes it possible to improve the mechanical and operational properties of the casted products at high efficiency [1, 2]. It is a unique method for the production of materials with optimal structure, well-reproduced shape configuration, hard surfaces and absence of external and internal defects. This method allows filling the casting molds with a dense laminar flow of melt as a result of which after crystallization castings that meet the preset technical requirements [2] are obtained. The difference between the pressure and the counter-pressure can be controlled and regulated within wide margins. It is possible to choose a suitable difference between these pressures not only for each individual casting but also for the filling and shaping of the individual parts of a casting. Crystallization occurs at high pressure (about 2 MPa), which prevents the gases dissolved in the melt from being released as gas bubbles. The value of the pressure can be controlled precisely at all stages of the process and thanks to this it is possible to fill the casting mold uniformly. This results in high-quality, dense and pore-free castings.

The processes of glass formation, the structure of the glassy state and the crystallization of glassy materials have been investigated by a number of authors [3-11]. The obtained samples with amorphous structure can be subjected to heat treatment for secondary crystallization. It is slower than primary crystallization, but the structure that is formed is finer and homogeneous, as a result of which the physicochemical characteristics of the materials improve. At the same time, the introduction of some additional components (elements and compounds) into the primary compositions stimulates the crystallization process [3].

Basalt is one of the most widespread magma rocks and is a preferred raw material for petrurgy. It is suitable as feedstock for the production of a variety of cast stone products due to its relatively low melting temperature, suitable linear properties, and high crystallizing ability. The obtained products can be exploited under different conditions [12] and are characterized by a variety of properties [13-15].

The purpose of the present paper is to study the stimulation of the crystallization processes of casts made of petrurgical materials using the gas counter-pressure casting method and to explore the possibilities of obtaining products with microcrystalline structure.

2. Experimental procedures

The starting materials were prepared using a set of KERN laboratory scales, a 50 liter porcelain mill with milling bodies, a set of standard sieves, etc. A prototype two-chamber autoclave installation for the casting of silicate melts by the gas counter-pressure method was used (Fig. 1). In the lower chamber was placed the melt to be cast, and in the upper chamber was installed the casting mold.

Fig. 1. Casting installation using the gas counter-pressure method.

The melt is pushed to the mold under the pressure in the lower chamber, overcoming the counter-pressure of the gas in the mold.

The installation was designed as a standard vertical pneumatic machine with a working pressure of 10 kg/cm², with the possibility of creating a difference between the pressures in the two chambers. The filling of the mold was monitored and, when necessary, was accelerated in order to improve the feeding in the areas of the casting where there was a risk of voids. The pressure was maintained until the crystallization was completed by adjusting the desired pressure difference between the two chambers.
The working gases used were nitrogen or argon, depending on the composition of the melt. The installation was able to function both under pressure and in vacuum. The melting chamber is a cylinder with a bottom and a top cover that has a hole and ends with a flange for attaching the casting chamber. Inside the melting chamber is installed an inductor powered by a 25 kW, 8 kHz generator. Melting is carried out in a quartz glass ceramic crucible placed in a heating sleeve made of high-density graphite. The bottom cover has nozzles for filling with gas and for vacuuming, as well as mounting holes for the power supply cable of the inductor and for a thermocouple. The casting chamber consists of a cylindrical part with two connecting flanges and a cover. There is a guide bushing and a fixing bolt at the upper part of the camera. The casting parameters were: pressure of 5 kg/cm², mold temperature of 250°C and casting time of 10 seconds.

The experiments were conducted using basalt frit (with dimensions of less than 5 mm) obtained from a deposit near the village of Voneshta Voda – Veliko Tarnovo District and the town of Tsarevo – Burgas District.

X-ray analysis was performed with an automatic X-ray powder diffractometer Bruker D8 Advance with CuKα radiation (Ni filter) and registration by a LynxEye solid state detector. Qualitative phase analysis was performed using the PDF-2/2009 database of the International Centre for Diffraction Data (ICDD). Differential Thermal Analysis (DTA) was performed using a STA PT1600 TG-DTA/DS (Germany) apparatus. The experiments were done in an inert gas medium at a temperature range from 20 to 1300°C at a heating rate of 10°C/min.

A microscopic examination was performed on laboratory prepared sections, which were micrographed using a Stemi 2000-C binocular microscope and a Amplival Pol D laboratory polarizing microscope with installed ProgRes CT3 Jenoptic (Germany) camera.

The obtained samples were examined using a SEM Philips 525 U scanning electron microscope with an EDAX 9900 analytical system.

### 3. Results and discussion

In the study of the crystallization process of the amorphous samples it was found that despite the well-defined peak of crystallization in the obtained DTA curves, the time for the formation of the crystalline structure (about 9 hours) was unsatisfactory.

Different quantities of initiators were used to stimulate the crystallization processes of castings made of petrological materials (Table 1).

<table>
<thead>
<tr>
<th>Initiator</th>
<th>CaF₂</th>
<th>TiO₂</th>
<th>Cr₂O₃</th>
<th>SiC</th>
<th>MoSi₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity, %</td>
<td>2 ÷ 4</td>
<td>5 ÷ 8</td>
<td>2 ÷ 4</td>
<td>1,5</td>
<td>1 ÷ 4</td>
</tr>
</tbody>
</table>

It was found that when using CaF₂ as an initiator, at a concentration of 2-3% the samples began to opalesce after 5 hours, and at a concentration of 4% – after 1 hour when kept at the temperature of maximum crystallization rate. The observed opalescence is considered a consequence of the presence of small amounts of residual CaF₂ (due to its strong volatility) and of the prolonged retention during melting. On the other hand, the presence of CaF₂ in larger quantities disturbs the CaO:MgO oxide ratio and adversely affects the physicochemical characteristics of the final product. On this basis, the introduction of CaF₂ in the compositions was determined to be technologically inappropriate.

Upon adding 5 to 8% of TiO₂ as an initiator of crystallization, a surface crystallization was observed after keeping the samples at a temperature of 900°C for 6 hours, which suggests that upon prolongation of the retention time (over 6 h), the crystallization will spread into the volume of the samples. From a technological point of view, this retention time is unjustifiably long.

Upon the addition of 2 to 4% Cr₂O₃ during melting (at about 1350°C), a sustainable fluidized bed was observed, indicating that Cr₂O₃ is not absorbed by the melt, and the crystallization centers are unevenly distributed, resulting in a non-uniform structure of the final product.

When SiC was introduced in varying amounts, satisfactory results were obtained, but at temperatures above 1400°C was observed an increase of the gas phase (when monitored under a microscope, small bubbles could be seen). This is probably due to the thermal decomposition of SiC and the oxidation of C to CO₂.

When introducing MoSi₂, no such phenomenon was observed and therefore this stimulator has been considered the most appropriate one for the purposes of the study.

Basalt frit was mixed with finely ground (below 0.063 mm) MoSi₂ at concentrations of 1, 2, 3 and 4%. The melting was carried out at 1350°C for 2 hours. Crystallization was recorded at 820-840°C using DTA analysis. The petrographic analysis of the obtained samples showed that the structure is microcrystalline, grainy, with prism-needle transitions. The resulting petrosilicates were mainly formed from pyroxene (about 80-85%), which was in the form of grain germs of 2-10 μm. In some regions it was present in the form of developed individuals with a prismatic-needle, partially-skeleton shape, grouped into cirrus or pseudo-spheroid aggregates. The crystal sizes range from 15 to 30 μm and in rare cases, up to 40 μm. The performed X-ray analysis confirmed the petrographic one, with the crystalline phase of augite being identified (Fig. 2), and the resulting sillitic structure was characterized by the presence of augite mineral composition.

![Fig. 2. X-ray diffractogram of a sample of marlstone from a deposit near the village of Svetlen, Targovishte District.](image_url)

Using basalt raw material from a deposit near the village of Voneshta Voda, with the addition of 2% MoSi₂, specimens of an amorphous structure were prepared using the method of gas counter-pressure casting and were subsequently subjected to secondary crystallization.
The study of the physicomechanical properties of these samples gave the following results:

- relative weight – 2.99 g/cm³;
- acid resistance to H₂SO₄ – 99.04%;
- acid resistance to HCl – 97.12%;
- water absorption - no more than 0.13%;
- compressive strength – 623.2 MN/m²;
- flexural strength – 97.8 MN/m².

The developed materials can be used for the production and assembly of different aggregates, equipment and systems involved in metallurgical and chemical industrial technology: installations for pneumatic transport of fluxes and other bulk materials, hydraulic transport of aggressive liquid reagents to and from reaction vessels (electrolysis baths, etc.), construction of supporting tubular fittings, lining of reaction vessels and of appliances supplying coke to blast furnaces, equipment for cyclones for capturing powder fractions in agglomeration plants, etc.

Using the gas counter-pressure casting method, various articles were produced by the research team: stop valves; thin-walled pipes (with diameter below 80 mm) suitable for pumping equipment for acids; stirrers resistant to aggressive substances (various liquids, suspensions), etc.

4. Conclusion

The processes of stimulated crystallization of samples obtained from basaltic raw materials using crystallization promoters/stimulators were investigated. When incorporating some additives (TiO₂, CaF₂, Cr₂O₃ and SiC), the desired technological results were not obtained. By introducing up to 3% MoS₂ as a crystallization stimulator, materials with a suitable microcrystalline structure and a predominant crystalline phase of augite were obtained.

The physicochemical and mechanical properties of the products obtained by the gas counter-pressure casting method are superior to the performance characteristics of the products obtained by the conventional casting methods. The optimal technological conditions for obtaining technical products applicable in chemically aggressive and abrasive environments have been established. The obtained products can be used to manufacture industrial equipment for various technological processes: transportation of bulk raw materials and aggressive liquid reagents to and from reaction vessels, tubular fittings, lining of reaction vessels and of appliances supplying coke to blast furnaces, etc.

5. Acknowledgement

The authors wish to thank the National Science Fund at the Bulgarian Ministry of Education and Science for financing their research project, (Contract No. KII-06-OIP03/4 from 14.12.2018), which won a grant in the Competition for financing fundamental scientific research on social challenges - 2018.

6. Literature

SEMI-AUTOMATIC MAG WELDING OF ALLOYED MACHINE-BUILDING STEELS

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2Technical University of Varna, Department Thermal Engineering, 9010 Varna, Bulgaria

Abstract. The present study explores the possibility of semi-automatic MAG welding of three steels with carbon equivalents of 0.40%, 0.50% and 0.60%. The impact of the welding speed on the crack formation is determined by a structural analysis of the TIZ (Thermal Impact Zone). A three-factor experiment was conducted to determine the impact of the factors on the obtained hardness in the TIZ. The regression equation was obtained and the isolines were outlined showing the impact of these factors.

1 Introduction
The task of the present study is to determine, by means of a full factorial experiment, by metallographic analysis of the structural changes in the welding compound in semi-automatic MAG welding of different types of steels with carbon equivalents in the range of (0,40 ÷ 0,60) %. The study is necessitated as a result of the introduction into the industry of low carbon low alloyed steel with enhanced strength (Re to 1300 MPa), table 1. These steels have a carbon equivalent of up to 0,60 % and a large proportion of them are used in the construction of pipelines and metal structures operating under harsh conditions. The idea is to determine the structural changes in TIZ of these steels and the change in Vickers’ hardness [1, 2, 3].

2 Semi-automatic Mag Welding of Alloed Machine building Steels
Three steels listed in Table 1 were selected for the experiments. The carbon equivalent is defined by formula (1), [4, 5].

\[ C_{eq.} = C, \% + \frac{\text{Mn, } \%}{6} + \frac{(\text{Cr } + \text{ Mo } + V), \%}{5} \]

\[ + \frac{(\text{Ni } + \text{ Cu}), \%}{15} \]

(1)

The selected experimental steels and their mechanical properties are shown in Table 2 [1, 2].

Table 1. Chemical composition and carbon equivalent of low-carbon low-alloyed steels

<table>
<thead>
<tr>
<th>Item</th>
<th>Steel grade</th>
<th>Chemical elements, %</th>
<th>Carbon equivalent, Ceq, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>X60</td>
<td>C 0.14, Si 0.29, Mn 1.42, Cr 0.01, Ni 0.03</td>
<td>0.40</td>
</tr>
<tr>
<td>2.</td>
<td>S460N</td>
<td>C 0.15, Si 0.33, Mn 1.34, Cr 0.031, Ni 0.053</td>
<td>0.50</td>
</tr>
<tr>
<td>3.</td>
<td>S960QL</td>
<td>C 0.15, Si 0.33, Mn 1.34, Cr 0.031, Ni 0.053</td>
<td>0.60</td>
</tr>
</tbody>
</table>

According to reference [4], with respect to the values of the carbon equivalents of the steels under study, the latter can be classified as hardly temperable and temperable steels.

The welding was carried out by semi-automatic arc welding in a carbon dioxide protective atmosphere (C1 DIN EN439) under the following conditions:
- parent metal, 180x140x12 mm;
- type of welding current - DC+;
- distance between the protective gas nozzle and the parent metal- 5 mm;
- stick-out of the electrode wire-12 mm;
- electrode wire feed rate- \( V_f = 5,5÷5,7 \) m/min;
- consumption of protective gas- \( Q = 15÷18 \) dm³/min;
- diameter of the protective nozzle- d=12 mm;
- welding speed- \( V_s = 10 \) m/h;
- voltage- \( U = 18÷35 \) V;
- welding current- \( I = 12÷220 \) A

Welding of the three grades of steel was carried out with an electrode wire of the brand OK AutRod 12.51 (EN ISO14341-A- G3Si1; AWSA5.18ER70S-6). The metal of the joint is of the type: EN440 G38 2C G3Si1 or G42 3M G3Si1. Table 3 shows the mechanical characteristics of the metal at the joint, with the following chemical composition of the electrode wire: C=0,09%; Si=0,90%; Mn=1,50% [5].

Table 3. Mechanical characteristics of the metal at the joint, %

<table>
<thead>
<tr>
<th>Test</th>
<th>Condition</th>
<th>Protective gas</th>
<th>Yield limit, Re [MPa]</th>
<th>Tensile strength, Rm [MPa]</th>
<th>Relative elongation, As [%]</th>
<th>Impact strength, KCU [J/°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>+20 +20 +20 +20 +20</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-20 -20 -20 -20 -20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-40 -40 -40 -40 -40</td>
</tr>
<tr>
<td>AWS</td>
<td>TZ0</td>
<td>C1</td>
<td>&gt;400</td>
<td>&gt;480</td>
<td>&gt;22</td>
<td>-</td>
</tr>
<tr>
<td>EN</td>
<td>TZ0</td>
<td>C1</td>
<td>440</td>
<td>540</td>
<td>25</td>
<td>110 70</td>
</tr>
</tbody>
</table>

The levels of hardness in the different zones of the welding joint are determined according to the requirements of the standard: TGL RGW 470-77, Germany [6].

3 Statistical processing of results
The experiments were carried out according to Hartley-Rechtshafner’s plans [3]. In the specific case, a three-factor plan is chosen with a parameter of optimization - micro-hardness in the depth of the sample determined by the Vickers method according to BDS EN 23878; 2000 and BDS EN ISO 6507-1; 2006 [6, 7].

For variables, the following factors were selected:
- \( x_1 \) - carbon equivalent, \( C_{eq} \) [%];
- \( x_2 \) - welding speed, \( V \) [m/h];
After processing the experimental results using the software Microsoft Excel, we obtained a regression equation of the type:

\[ y = 465.16 + 75.24x_1 + 83.74x_3 + 18.99x_1 + 13.79x_1x_2 + 14.54x_2x_3 - 4.91x_2x_3 + 12.03x_1^2 - 
\frac{36.47x_2^2 + 16.28x_3^2}{3} \]  \hspace{1cm} (2)

On the basis of the developed mathematical model, diagrams were obtained with isolines of the variables \( f(x_1, x_2, x_3) \) with variability of the factors (Fig. 1, 2 and 6).

From Fig. 1 ÷ 6 it can be seen that the welding speed directly affects the instantaneous cooling rate and hence the alteration in hardness in the TIZ. With the decrease of the carbon equivalent, the hardness also decreases.

Figures 7 ÷ 9 show the TIZ micro sections for the three steels at a welding speed of 5 m/h and 10 m/h [8, 9].

From the macro-and microstructural analysis thus made (Fig. 7b, Fig. 8b and Fig. 9b) [10, 11, 12] it is seen that at welding speeds of 10 m/h, in the TIZ is observed formation of cracks in steel S460N and S960QL.
With X60 steel, at a welding speed of 10 m/h, no cracks are formed in the TIZ.

At a welding speed of 5m/h, no cracks are formed in the TIZ with all the three grades of steel.

The structural transformations at this welding speed (5m/h) for individual steels are as follows:

- Steel X60: The structure in the TIZ of this steel (Fig.7 (a)) is unbalanced. It is basically mosaic-martensite, going deep into martensite plus bainite. There are no micro defects. The boundary of alloying consists of dispersed troostite and perlite. The metal of the joint has an unbalanced ferrite-pearlite needle-like structure.

- Steel S460N: The structure in TIZ (Fig.8a)) is martensitic bainite, with a predominant amount of martensite. At the boundary of alloying there is a dispersed troostite - pearlitic structure, with martensite and fine ferrite;

- Steel S960QL: The structure in TIZ (Fig.9 (a)) has a large amount of martensite and bainite. At the boundary of alloying, an upper bainite, martensite with a mosaic structure and great hardness are observed. The metal at the joint has a dendritic ferrite-pearlite structure.

**Conclusions:**

1. With semi-automatic welding in carbon dioxide environments with the increase of the carbon equivalent (0.40%≤C_{eq}≤0.60%) at welding speeds ~10m/h, formation of cracks in the thermal impact zone is observed;

2. With semi-automatic MAG welding of steel: X60, S460N and S960QL, at welding speeds of less than or equal to 5 m/h, no cracks in the thermal impact zone are formed;

3. With semi-automatic MAG welding of steels with C_{eq}≥0.40% for determination of welding modes, it is necessary to use the thermo-kinetic diagrams of the respective steels.

**References**


11. D. Spasova, Production of moulded metal composites (MMCs) with fiber reinforcing phase of the "in vitro" type, *Month of Science – Varna., (2017)*

DETERMINATION OF THE TRIBOLOGICAL CHARACTERISTICS OF HEAVY LOADED FRICTION PAIRS BASED ON DENSITY MODIFICATIONS OF BORON NITRIDE

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Abstract: In this work the constructive solution of the friction node is proposed, which provides the possibility to obtain reliable information about the tribological characteristics of the materials for work in heavy loaded slip supports. The method of determining the expediency of application in friction pairs of different materials is considered, which is based on certain shapes and sizes of the contact spot and the state of the friction track on the counter bodies. The efficiency of polycrystalline superhard materials application based on the wurtzite boron nitride in heavy loaded friction pairs due to an increase in the antifriction characteristics of the pair by the formation of graphitelike boron nitride on the surface of a thin film $B_2O_3$ as a result of the reverse phase transformation of dense phases ($cBN + wBN$) $\rightarrow$ $gBN$ is shown.

KEYWORDS: FRICTION NODE, SAMPLE OF POLYCRYSTALLINE SUPERHARD MATERIAL, COUNTERBODY, CONTACT SPOT, WEAR INTENSITY.

1. Introduction

For efficient functioning of heavy-duty friction pairs of machines and mechanisms, complex technological and design solutions are used to create nodes and aggregates that are operated under the influence of severe adverse factors: corrosive environments, abrasive components, temperature difference, etc.

In most cases, the given adverse factors act simultaneously, resulting in a reduction in working capacity and warranty resource for the operation of machines, mechanisms, transport systems, mining equipment.

In working junctions and nodes of machines and mechanisms, heavy-loaded friction pairs are subject to intense wear in the process of operation, especially in conditions of limited lubrication.

Such objects include shaft bits, which are widely used in boring, in the minerals exploration, during boring operations for oil and gas, as well as for the continuous boring of wells for various purposes in the mining industry and construction with the sludge cleaning by washing with liquid or using compressed air.

The resource of the bit is determined by many factors, the most important of which are mining-geological conditions (hardness, abrasiveness and rock blockage, the degree of rock mass homogeneity, its watering, etc.), and the associated conditions of operation (load on the chisel, rotation frequency, lubricating and cooling medium).

The efficiency analysis of the chisel bit in conditions of operation of the ore mining and processing plants showed that mainly the failure of the bit is observed due to the failure of the support sliding bearing (60 ... 70%), therefore, the work aimed at increasing the service life of the parts of the friction pairs of the bearings with the use of functional materials based on composite superhard materials are an effective means of reducing the efficiency of operating factors, mainly corrosion-mechanical.

2. Problem status.

Investigation of frictional characteristics and possibilities of composite material usage of the «wBN-diamond» system in heavy loaded nodes operating under axial load conditions.

The friction pair of the axial slide bearing is the tip of the pin 1 on the foot of the chassis body 2 and the support washer 3, pressed into the cavity of the shaft 4 body, located at the top of its cone (Fig 1). During the bit operation, its support is subject to significant dynamic loads that are accompanied by heat release. To reduce the temperature in the contact area of the friction pair, a five-point purge hole is forged in a pinion with a support or solid lubricant.

Consideration of the wear process of the contacting friction pair indicates its complex nature, which includes such phenomena as interaction in the relative displacement of friction surfaces, changes occurring in the surface layer of materials, the destruction of surfaces.

In this case, the mechanical interaction of surfaces is expressed in the mutual penetration and involvement of microinhomogeneity in combination with their collision in the case of high level of micro-rigidity, so the state of the surface of the friction pair is of great importance, and the molecular interaction is manifested in the form of adhesion and seizure. It should be noted that gripping is characteristic only of metal surfaces and differs from adhesion with more strong bonds. Changes in the friction surfaces are due to plastic deformation, temperature rise and chemical interaction with environment.

Plastic deformations lead to a change in the structure of the surface layer of the material, which at a temperature below the temperature of recrystallization, will lead to defamation and its strengthening to some depth, however, the microhardness is unchanged at the very surface.

The temperature exceeding the recrystallization threshold contributes to increased plasticity, and in some local areas, under high load conditions, the formation of tempered structures. Plastic deformations, possible high temperature gradients and structural changes cause tension in the material of the friction pair, which can affect its wear resistance. Therefore, the materials of the friction pair of bitumen are subject to high requirements. They should have high strength, hardness, heat resistance, wear resistance.

Fig. 1. Shaft bearing design with sliding bearing: 1 - pin; 2 – bit chassis; 3 - support puck; 4 - shafters housing
Selection of the most suitable materials for slip friction pairs can be made on a case-by-case basis only by carefully comparing the working conditions of the contacting parts, the initial properties of the materials and those changes taking place on the surfaces of friction, and also taking into account other essential circumstances.

According to, there are some following rules for the selection of friction pair materials, in accordance to which it is necessary:
- to combine hard metal with solid: such friction pairs have a high wear resistance due to the small mutual penetration of their surfaces;
- application in hard-to-reach for lubrication of structures of antifriction materials;
- application of the selective transfer mode by the selection of friction pair materials and antifriction additives.

The application of coatings to the spin improves the reliability of the pairs in the most dangerous period - at the initial stage of work, while high precision of manufacturing and assembly, considerable rigidity of construction, thorough tuning, and improved lubrication conditions significantly increase the service life of the friction pair of solid materials. This is confirmed by the use as a material of the support washer of a solid alloy BH-20, which allowed to increase the resource of friction pair in 1.5 .. 1.8 times.

3. Experimental part.

In this paper, the possibility of using in a friction pair of an axial slide bearing of a roller bit of a composite on the basis of dense modifications of boron nitride and diamond was studied.

Based on the recommendations of the friction pair selection, which has the maximum wear resistance for the material of the basic bit washer, composite polycrystalline superhard material (PCSM) on the basis of dense modifications of boron nitride obtained by sintering a powder of wurtzite-like boron nitride and diamonds of static or dynamic synthesis under high pressure and temperature conditions has been investigated. It can be both in a single-phase state in the form of sphalerite boron nitride (cBN), and contain wurtzite and graphite-like components.

For tribotechnical studies, a developed universal friction node was used to test materials for heavy-duty friction pairs and to perform oil or grease selection, air-emulsion environment or lubricating fluid, etc., since at this time the selection of materials for sliding pillars of roller shutters was carried out only with bench and field tests, which are relatively labor-intensive and expensive.

The use of the proposed friction unit, which provides the conditions for obtaining reliable information about the tribotechnical characteristics of materials in heavy loaded sliding supports, makes it possible to select new materials used for operation in these mechanisms. The design of the universal friction node is shown in Fig. 2.

The dimensions of the friction unit are selected so that it can dissipate a thermal power of about 100 watts at a temperature in the friction zone of not more than 120 °C.

The dimensions of the counterbody and the samples were determined experimentally and had dimensions - a disk (counterbody) with a diameter of $20_{a,5}$ mm, a height of $7_{a,5}$ mm, samples in the form of a disk of the same size with a counterbody, and those in the form of a cylinder of dimensions: diameter $10_{a,1}$ mm and height $20_{a,5}$ mm

Surface roughness of samples and counterbody after lapping by steel washer with boron carbide 50 micron grain powder was $R_a \approx 0.63 ... 0.32$.

Friction node consists of housing (cup) 1, which is executed with step cavity, the lower part accommodates the sample holder, and the top part is designed for lubrication and moving grip with counterbody. The sample 4 is set in the grip 2 and tightened with a clamping screw (clamp) 7. After filling the shell with the oil, it is installed in the centering slot, fixed by the shpanizers on the desk of the table drill machine.

The chuck of the machine fix a clamp with a counterbody, which has the ability to move by the machine spindle, and make it contact with the sample. In this case, the contact area "counterbody-sample" with a clamp 8 is immersed in oil by 3...4 mm. On the handle of the spindle tare weight is hanged and machine is started. At the end of a given test time the machine turns off and the friction node is getting disassembled in reverse order.

For the study of the tribotechnical properties of the pair «counterbody WC10-PCSM» (counterbody WC10, a sample of composite PCSM) the following conditions of friction were adopted: a rotational speed of 1410 rpm; average slip speed of 1 m/s; lubricating oil industrial I20; duration of tests not less than 35 min; load - 50 kg.

After the tests, the shape and dimensions of contact spot on the specimens, the condition of the friction track on the counterbodies were determined. Also, calculations of the coefficient of friction, intensity of wear $I_w$ and the contour pressure $A_k$ were also performed.

To find out the effectiveness of the application of PCSM in friction pairs, comparative tests of different materials were conducted under the same conditions.

Figure 3 shows the wear and tear on the counterpart and the test specimen from a composite PCSM based on wurtzite boron nitride and diamond.

**Figure 3. The nature of the wear of the friction pair "solid alloy-PCSM" × 3: 1 - counterbody of solid alloy; 2 - sample of composite PCSM; 3- wear spots.**

Abrasion wear spot after the test has a mirror surface whose roughness is at $R_a \approx 0.16 ... 0.08$ μm.

The bearing capacity of the resulting oil film in the friction pair "solid alloy - composite PCSM" reaches 1000 kg/cm², and the coefficient of friction is characterized by the smallest value, which in our opinion is due to the following. Composite PCSM based on wurtzite-like boron nitride is a heterogeneous high density material with a homogeneous, fine-crystalline structure having a grain size of 0.1 ... 0.3 μm.
High compressive strength (up to 4 GPa), modulus of elasticity, hardness and thermal conductivity in combination with high values of crack resistance (Table) can provide resistance to fracture at high critical loads, as indicated in the work.

Table. Tribotechnical characteristics of friction pairs

<table>
<thead>
<tr>
<th>Materials of friction pair counterbody-sample</th>
<th>Slip friction coefficient</th>
<th>Wear intensity of the sample, ( I_w ) μm/kN·m</th>
<th>Contour pressure ( \sigma_c ), kg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC10-WC10</td>
<td>0.058</td>
<td>1,8×10⁻⁸</td>
<td>570</td>
</tr>
<tr>
<td>WC10-WC10*</td>
<td>0.05</td>
<td>1,7×10⁻⁸</td>
<td>600</td>
</tr>
<tr>
<td>WC10-PCSM</td>
<td>0.04</td>
<td>2,5×10⁻⁸</td>
<td>800</td>
</tr>
</tbody>
</table>

* Counterbody with bronze coating

The increase of the antifriction characteristics of the friction pair “solid alloy - composite PCSM” is likely to occur both through the formation of a stable oil film and by the formation on the surface of a thin film \( \text{B}_2\text{O}_3 \) or graphite boron nitride (gBN) arising during the reverse phase transformation of dense phases \((\text{cBN}+\text{wBN})\rightarrow\text{gBN}\) in microobjects, when contacting surfaces are interacting, when short-range flashes \((10^{-7}...10^{-6})\) occur in the microcontact zone with a significant energy release and a decrease in the coefficient of friction due to the presence in the composite of a high proportion of solid BNC solution and high thermophysical characteristics.

Figure 4 shows the construction of the proposed composite solid-alloy bearing equipped with composite elements with PCSM based on wurtzite boron nitride with increasing antifriction characteristics.

The research carried out by the method of electronic OZE - spectroscopy of steel samples treated with cutting with the presence of shock loads, showed the presence of oxygen, as well as boron and nitrogen on their surface, which was confirmed in, where the frictional properties of materials are considered on the basis of dense modifications of boron nitride, which gives reason to assume the possibility of formation of thin antifriction films on test samples.

4. Conclusion.

The possibility of using in a friction pair of an axial slide bearing of a shale bit of a composite based on dense modifications of boron nitride and diamond is considered.

The method of evaluation of tribological characteristics of heavy loaded friction pairs and the design of the device for realization when selecting the most efficient materials pair is developed.

Literature

Abstract. In several metal forming processes, relation between stress and effective strain of the material must be known for obtaining important forming parameters such as forces and work, required for metal forming processes. Dependence of the flow stress on the effective strain is called the flow curve and is influenced by strain rate and temperature. In order to reach high quality and full functionality of the product, the characteristics of formed material must be determined as precisely as possible and flow stress is one of the main characteristics of the metal materials. In general, flow curves are determined by experiments such as tensile test, upsetting test and torsion test. The proper choice of testing method depends on the metal forming process to be simulated.

In this paper we present the experimental measurements of flow stress for stainless steel at elevated temperatures by using torsion test. In the experimental work a torque, temperature and number of twists of test pieces were measured. Also, the influence of forming parameters such as strain, strain rate and temperature on flow stress was analysed. Experimental results are presented in form of tables and diagrams. Finally, from experimental data the regression model was obtained for successful prediction of flow stress of stainless steel at elevated temperatures. The method of regression analysis allows with relatively small number of experiments the accurate information about the influence to mathematical model of the process.

Keywords: FLOW STRESS, STRESS-STRAIN CURVE, STAINLESS STEEL, TORQUE, HIGH TEMPERATURES, REGRESSION MODELLING.

1. Introduction

For obtaining high quality metal forming processes and full functionality of the product, the characteristics of formed material must be determined very precisely. The flow stress is one of the main characteristics of the metal materials and provides a full description of the workability of the material. Also, for obtaining the forces that are required in forming processes, it is necessary to know the dependence of flow curves on different parameters. These curves are influenced by two factors substantially [1]:

- factors, which relate to the material, e.g. chemical composition, metallurgical structures etc.
- factors, which are function of the metal forming process, e.g. temperature, strain rate, heat pre- treatment etc.

For a metal forming processes, it is important to obtain loads and forming energies necessary to accomplish the necessary plastic deformation. The flow stress is directly connected to the instantaneous value of load, which is needed to continue the yielding and flow of the material at any point during the metal forming process. The main parameters that influence the flow stress are strain, strain rate and forming temperature. In hot forming, for example, the influence of strain rate is significant while the influence of strain is insignificant; this is possible when the forming temperature is below the temperature of recrystallization [2]. On the other hand, in cold forming, the influence of strain rate is negligible and the effect of strain prevails. The dependency of flow curves on temperature varies considerably for different material.

In general, flow curves are determined by experiments such as tensile test, the upsetting test, bending test and torsion test. The proper choice of testing method depends on the metal forming process to be simulated. Many papers describe different techniques of torsion testing in sheet [3, 4, 5] and bulk metal forming [6, 7, 8]. In the paper [9] the authors used axial and torsion test to develop multiaxial state of deformation kinematics and stresses in bulk metal forming processes and evaluation of workability. A high temperature torsion testing system was developed for obtaining the workability of various materials under temperatures up to 1300 °C. Some failure criterions in dynamic torsion tests of cylindrical specimens were described in papers [10, 11, 12, 13].

In order to reduce the cost of the experiment and of the computer computations, several modeling methods predicting the dependent output variables have been developed so far. In most conventional deterministic modeling methods, such as regression method described in papers [14, 15] a prediction model is determined in advance. These modelling methods have one common feature: all of them optimize a given model of a problem. Many authors have also used in their investigations [16, 17] combination of regression and some non-deterministic methods, such as neural network or evolutionary computation methods for modelling and predicting flow curves and other properties of formed material.

2. Torsion test for obtaining flow curves

To test the material in torsion the proper test procedure is needed. It involves mounting a specimen on the testing machine. The torque is applied incrementally and both the applied torque and the corresponding angle of twist are measured. Using the appropriate formulae, relationships and the measured dimensions, shear stress and shear strain can be determined [7]. Then, plot the torque vs. angle of twist, and shear stress vs. shear strain curve. In torsion test the specimen is mounted between the two heads of a testing machine and twisted for a certain angle (Fig. 1).

Fig. 1 Torsion test
Successful applications of torsion test are: the determination of flow curves for high strains; the determination of multiple cyclic flow curves with only one specimen in one test and the characterization of the forming limit [2]. The specimens can be made of solid bars or thin-walled tubes. Torsion tests have the following advantages [1]:

- simple loading condition
- long loading time
- uniform stress state
- good measurement of signals of stress and strain data.

Also, the test specimen does not present significant shape changes during deformation as long as the gage section is restrained to a fixed length. The disadvantage of the torsion test is the fact that is characterized by non-uniform distribution of deformation over the length and cross-section of specimen.

The stress and strain are equal to zero at the center and maximum at the surface of the test specimen. Due to a large material reorientation, the deformation in the torsion test is not an accurate simulation of metalworking processes [2]. The output of the torsion test is represented by torque versus twist angle, that must be converted into the stress and strain.

The relation between torque and shear stress is given by [1]:

\[ M = \frac{2\pi R^3}{\gamma} \int \gamma^2 d\gamma \]  

(1)

The shear strain at distance \( \gamma \) from the axis along test piece at a twisting angle \( \alpha \) is given by:

\[ \gamma = \frac{r}{R} \cdot \alpha \]  

(2)

Torque \( M \) depends on shear strain \( \gamma \) and after differentiation of Eq. (3), the equation for shear stress is [1]:

\[ \tau = \tau(\gamma) = \frac{1}{2\pi R^3} \left( 3M + \gamma \frac{dM}{d\gamma} \right) \]  

(3)

When shear strain rate is added in Eq. (4), then this equation can be written as:

\[ \tau = \tau(\gamma, \dot{\gamma}) = \frac{1}{2\pi R^3} \left( 3M + \gamma \frac{dM}{d\gamma} + \gamma \frac{d\gamma}{d\tau} \right) \]  

(4)

Relation between torque and shear strain rate is given by:

\[ M = M_0 \cdot \gamma^m \]  

(5)

and relation between torque and shear strain is written:

\[ M = 10^{(a_0 + 2a_2 \log_2 \gamma)} \cdot \gamma^{a_1} \]  

(6)

\( m, \log \gamma, a_0 \) and \( a_2 \) are empirical coefficients which take into account strain rate and strain \( \varepsilon_c \).

By inserting (6) and Eq. (7) in the Eq. (5), equation for shear stress is:

\[ \tau(\gamma, \dot{\gamma}) = \frac{M}{2\pi R^3} (3+m+p) \]  

(7)

Empirical coefficient \( p = a_1 + a_2 \).

Because of low influence of deformation to torque by high temperature and low strain rate, and according to Tresca yield criterion, the relation between flow stress \( k_\tau \) and torque \( M \) is [1]:

\[ k_\tau = 2\tau_{\text{max}} = \frac{M}{\pi R^3} (3+m) \]  

(8)

3. Experimental measurements

For the experimental work the dependence of flow stress for stainless steel X22CrNi17 on three different parameters was analysed by using torsion test. The chemical composition of this stainless steel is presented in Table 1.

Table 1: Chemical composition in percentage [%].

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>P</th>
<th>Mn</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15 - 0.25</td>
<td>0.8</td>
<td>0.04</td>
<td>0.9</td>
<td>0.02</td>
<td>15 - 18</td>
<td>1.5 - 2.5</td>
</tr>
</tbody>
</table>

The value for the tensile strength of the steel X22CrNi17 varies from 800 N/mm\(^2\) to 980 N/mm\(^2\), yield strength is from 590 N/mm\(^2\) to 680 N/mm\(^2\) and elongation \( \varepsilon \) varies from 11 % to 18 %. This stainless steel is used as tool steel for the glass industry to high temperature glass molds and tools. Other applications are blow moulds for plastic production, ship and machine building industry, automotive industry, pump parts, shafts, etc.

Torsion tests were provided and measured by using special torsion testing equipment. The temperature of test specimens during torsion test of steel WNi.l.4057 (X22CrNi17) was changed with electric-inductive heater from 900\(^\circ\)C and up to 1300\(^\circ\)C. Inductive heater is a part of torsion test equipment. It was also possible to change the number of rounds per minute stepwise from 2 min\(^{-1}\) to 1500 min\(^{-1}\). During the experiment a torque, temperature and number of twists of test specimens were measured. The dimension of test specimens was \( \Phi 6 \times 60 \) mm.

Three parameters were changed during our experiments: first parameter (temperature \( T \)) was changed in the range from 900\(^\circ\)C to 1300\(^\circ\)C, second parameter (strain \( \varepsilon_c \)) was changed from 0.1 to 1 and third parameter (strain rate \( \dot{\varepsilon}_c \)) was changed between 0.2 s\(^{-1}\) and 4 s\(^{-1}\). Table 2 shows all obtained experimental results of torsion tests.

Table 2: Experimental results.

<table>
<thead>
<tr>
<th>Exper.</th>
<th>( \dot{\varepsilon}_c ) [s(^{-1})]</th>
<th>( \varepsilon_c )</th>
<th>( T ) [(^\circ)C]</th>
<th>( k_\tau ) [N/mm(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>0.1</td>
<td>900</td>
<td>150</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.55</td>
<td>900</td>
<td>149</td>
</tr>
<tr>
<td>3</td>
<td>2.1</td>
<td>0.55</td>
<td>900</td>
<td>160</td>
</tr>
<tr>
<td>4</td>
<td>0.2</td>
<td>1.0</td>
<td>900</td>
<td>142</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>0.1</td>
<td>900</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>4.0</td>
<td>1.0</td>
<td>900</td>
<td>175</td>
</tr>
<tr>
<td>7</td>
<td>4.0</td>
<td>0.1</td>
<td>1100</td>
<td>127</td>
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<tr>
<td>8</td>
<td>2.1</td>
<td>0.55</td>
<td>1100</td>
<td>110</td>
</tr>
<tr>
<td>9</td>
<td>4.0</td>
<td>0.55</td>
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<tr>
<td>15</td>
<td>2.1</td>
<td>0.1</td>
<td>1300</td>
<td>70</td>
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</tbody>
</table>
4. Results and discussion

Experimental measurements have shown different influence of three parameters on flow stress of investigated stainless steel. The greatest influence is that of temperature. At lower temperature values of obtained flow stress was higher the values obtained at highest temperature 1300 °C. Other two parameters also have smaller impact on flow stress.

Many different methods for obtaining the most suitable models for prediction of flow stress are known. We decided to choose multiple regression analysis method, due to a quite simple model. A mathematical model for regression method was chosen according to [18]:

\[ y(x) = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{j=1}^{n-1} \sum_{k=j+1}^{n} b_{ij} x_i x_j + \sum_{i=1}^{n} \sum_{j=1}^{n} b_{ij} x_i^2 \]

(9)

In equation (9) \( y \) is dependent variable, \( x_i, x_j \) are independent variables (in our case there are three) and coefficients \( b_0, b_i \) and \( b_{ij} \) are coefficients which have to be obtained by using regression analysis. In the investigation dependent variable was flow stress \( k_f \) and independent variables were strain \( \epsilon_e \), strain rate \( \epsilon_f \) and temperature. Regression analysis was performed by using SPSS modeling program. Significance of independent parameters was determined by dispersion analysis and because of very low significance of some parts in equation (9) those parts were left out from final regression model for flow stress. By inserting real values for each independent parameter in the equation (9) the final regression model for flow stress can be written as:

\[ k_f = 322,5 - 0,19 \cdot T - 6,1 \cdot \epsilon_e + 15,56 \cdot \epsilon_f + 1,77 \cdot \epsilon_e^2 - 0,016 \cdot T \cdot \epsilon_e \]

(10)

Equation (10) shows a mathematical model for the impact of temperature, strain and strain rate on flow stress for chosen material in given experimental area. It has the average percentage deviation of 2,1 %. Deviation means the difference between measured flow stress and predicted flow stress by using (10). Deviations in single experimental points are in the range from 1,1 % to 3,5 %.

The obtained regression model was used to analyse the influence of all three independent parameters on flow stress.

In Fig. 2 the influence of effective strain and strain rate on flow stress is presented. The values of flow stress decreases with increasing effective strain. At the strain rate \( \epsilon_f = 2,1 \text{ s}^{-1} \) the highest value of nearly 160 N/mm² for flow stress was reached. These values then decrease and reach 154 N/mm² at highest effective strain. Almost identically happened when lower strain rate was applied.

Fig. 3 shows the influence of temperature \( T \) and effective strain \( \epsilon_e \) on flow stress at constant strain rate. The value of strain rate in this case was the highest possible (\( \epsilon_f = 4 \text{ s}^{-1} \)).

Fig. 3 Influence of temperature \( T \) and effective strain \( \epsilon_e \) on flow stress \( k_f \) at constant strain rate \( \epsilon_f = 4 \text{ s}^{-1} \).

If we compare the results for flow stress \( k_f \) calculated at two different values of effective strain very interesting thing can be observed. The influence of effective strain on flow stress is quite low comparing with that of the temperature. There is only a few percentage difference between flow stress at lowest temperature \( (T = 900 \text{ °C}) \) when highest and lowest values of effective strains are used. Then, with increasing temperature the values of flow stress fall very steeply.

From the shape of the curve in Fig. 3 it can be observed that dependence between flow stress and temperature is linear in both cases. And because the slope of the line in diagram is very steep we can see that the influence of temperature on the flow stress is huge. The difference between highest (at lower temperature) and lowest (at high temperature) calculated values for flow stress is almost 55 %. If higher temperatures would be used the decrease of flow stress would be even bigger.

Influence of strain rate \( \epsilon_f \) and temperature \( T \) on the flow stress \( k_f \) at constant effective strain \( \epsilon_e = 1,0 \) is presented in Fig. 4. Three different temperatures (1000 °C, 1100 °C and 1300 °C) were used to observe the influence on flow stress. At lowest temperature it is obviously that flow stress is increasing constantly with increasing strain rates. The same influence can be observed when second lowest temperature (\( T =1100 \text{ °C} \)) was used. The shape of these two curves are almost identical. But when the temperature \( T = 1300 \text{ °C} \) was applied the dependence between strain rate and flow stress is different especially at lower values for strain rate.

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Strain rate values from 0,2 s\(^{-1}\) and up to 1,6 s\(^{-1}\) causes decrease of flow stress, but from 1,6 s\(^{-1}\) and to highest value of 4 s\(^{-1}\) the flow stress persistently but slowly increases.
5. Conclusion

The goal of this paper was to determine the influence of different parameters on flow stress of stainless steel by using torsion test. The flow stress is one of the main characteristics of the metal materials and provides a full description of the workability of the material. The main parameters that influence the flow stress are strain, strain rate and forming temperature. The experimental measurements were used to determine the plastic behaviour of investigated steel, combined with the methodology applied to flow curve modelling.

For mathematical processing of obtained experimental results, multi-regression analysis method was used. With this method it is possible to get very accurate mathematical models of the influence of temperature, strain and strain rate on flow curve.

With obtained regression models very accurate prediction of flow stress is possible for every value of three applied process parameters inside experimental range and also optimal values of parameters for desired flow stress can be obtained. The regression model presented in the paper is quite simple and is very accurate. The multi-regression method of modelling, described in our paper can also be used for mathematical modelling of other parameters in metal forming. In the future work we intend to use evolutionary computation methods for modelling not only flow stress but also other important material characteristics.

References

HIGH PERFORMANCE METAL-MATRIX COMPOSITE COATINGS

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Abstract: The effect of the initial structure of the fillers on the structure formation of the dissolution-and-diffusion type interfaces in macroheterogeneous composite coatings with a metal binder has been investigated. It has been shown that by combining phases in the filler structure, which differ in resistance to molten binder during infiltration, it is possible to attain an increased resistance of composite coatings to dry friction, abrasive, gas abrasive, and corrosion wear. The compositions of composite coatings to strengthen the surface of the parts of machine-building industry have been recommended.

Keywords: COMPOSITES, INFILTRATION, BINDER, FILLER, INTERFACES, PERFORMANCE CHARACTERISTICS

1. Introduction

Macroheterogeneous composites produced by a furnace infiltration find the wide application as coatings to protect and restore the quick-worn parts of the machine-building and metallurgical equipment. The widest use has found a coating, whose composition consists of the W–C (relit eutectic alloy or related alloys (WC–6Co, WC–8Co, etc.) as a filler and MNMs 20–20 manganese melkhiur (Cr20–20Ni–20Mg alloy) as a metal binder. This composite material was designed for facing charging equipment of blast furnaces of metallurgical plants, which work under the conditions of gas-abrasive wear. The use of the coating made it possible to solve the problem of this type parts durability increasing their operating life by a factor of 3–15.

To expand the applications of this class of composite coatings, further studies were conducted in two main directions. The first direction was associated with the use of a more wear-resistant than manganese melkhiur binder. The operating characteristics of composite coatings were increased by a factor of 1.5–2 in the case of the infiltration by iron-based binders. However, the main disadvantage of these coatings is the intensive interaction of tungsten carbide with molten iron alloys in the course of the infiltration at a sufficiently high melting temperature of the latter. With the aim to reduce the filler dissolution rate on the average by 15–20%, it was proposed to use filler particles of a spherical form produced by thermocentrifugal atomization of a rotating bar. The result attained was related to a decrease of the area of spherical granules that contact with a molten binder, but no attention was paid to changes in the granules structure with increase of their cooling rate up to $10^7$ K/s.

The second direction covers studies conducted with the aim to replace the expensive filler based on tungsten carbides by a cheaper high-melting alloy and maintain basic operational characteristics of composite coatings. For example, alloys containing carbides of chromium, titanium, boron, etc. are proposed. Nitrides of titanium, aluminum, zirconium, etc. are also promising fillers of composite coatings. Borides of metals occupy a special place among filler alloys designed for reinforcing metal binders. Borides have a higher hardness and lower brittleness as compared with those of corresponding carbides and nitrides. The best known is the filler of composition 80 wt. % TiB2 and 20 wt. % CrB2. As a binder of composite coatings reinforced by (Ti, Cr)B2 filler, the manganese melkhiur with additions of Mo, Si, and other components that inhibit the boron diffusion into the metal binder is used.

In many publications on the development of the novel composite coatings, a special attention is given to the investigation of the processes of wetting and contact interaction at the interfaces between the hard filler and molten binder during the infiltration. Such an approach is justified, since the structure and properties of these boundaries in the long run are responsible for the performance of composite coatings. However, it should be noted that inadequate attention is given to the prognosis of the contact interaction kinetics with regard to the initial structure of the fillers, though one may efficiently control these processes, e.g., by combining phases of different stabilities in the filler structure. Therefore, in this study we investigated the effect of the filler phases having crystalline, microcrystalline, and quasicrystalline structures on the formation of the interfaces in composite coatings designed for operation under the conditions of the dry friction, abrasive, gas-abrasive, and corrosion wears.

2. Experimental Procedure

Samples of composite coatings were prepared in three stages: i) preparation of the filler; ii) preparation of the binder; iii) production of composite coating by a furnace infiltration. The fillers were prepared from W–C, Fe–B–C, Cr–Ti–C, Al–Co–Cu, Al–Ni–Co alloys by mechanical crushing ($v_{cool} = 10–20$ K/s) or thermocentrifugal atomization of a rotating bar ($v_{cool} = 10^3–10^4$ K/s). In the first case the filler particles were of irregular shape, in the second case they were spherical. The particle sizes varied from 0.2 to 2.5 mm. Alloys on an iron, copper, or aluminum base were used as binders. The furnace infiltration was performed for 15–60 min at a temperature, which exceeded the binder melting point by 50–100 K. The filler content of a finished composite coating was 50–70 vol %.

The structure of the alloys and composite coatings was studied by quantitative metallographic and X-ray analyses as well as X-ray energy dispersive spectrometry and scanning electron microscopy using standard procedures. The corrosion resistance of composite coatings was assessed by the gravimetric method in HCl aqueous solution at room temperature for 4 hours. The corrosion rates were measured every hour. The resistance of composite coatings to abrasive wear was studied on an NKM plant and to gas-abrasive wear on an OBB76 device. The tribological characteristics were defined by the shaft–plug scheme at the dry friction on the grade 45 steel at a sliding rate of 20 m/s and load of 4 MPa.

3. Results and Discussion

The composite coatings studied may be divided into three groups:

– coatings based on iron alloys reinforced by crystalline and microcrystalline tungsten carbides or crystalline chromium–titanium carbides;

– coatings based on copper alloys reinforced by crystalline and microcrystalline iron borides;

– coatings based on copper or aluminum alloys reinforced by quasicrystalline Al–Co–Cu or Al–Co–Ni fillers.

During the infiltration, the formation of the filler–binder interfaces in the above composite coatings occurs by the solution- and-diffusion mechanism. This allows one to control the properties by varying the contact interaction intensity at the interfaces, which is regulated by the choice of the filler and binder compositions. The Fe–3.5B–0.2C binder (in wt. %) is for the infiltration of the filler particles made of W–C eutectic alloy ($v_{cool} = 10–20$ K/s). The choice is justified by the boron positive effect on technological
characteristics of iron binders like relatively low melting temperature, fluidity, oxidation resistance, etc. Before the infiltration, this alloy has a hypoeutectic structure consisting of primary crystals of boron-doped ferrite and Fe–Fe₃(B,C) eutectics. The contact interaction of the molten Fe–B–C binder with the W–C filler during the infiltration is accompanied by dominating dissolution of W₃C carbide. The second WC carbide is dissolved to a much lower degree and is observed from the filler side as inclusions into a solid ring of the Fe₃W₃C phase (Fig. 1a).

![Image](image1.png)

**Fig. 1** Microstructure of composite material with the Fe–B–C binder reinforced by the W–C filler cooled at a rate of 10⁻⁴ (a) and 10⁻⁸ (b) K/s.

On the side of the hardened binder in the tungsten doped Fe–Fe₃(B,C) eutectics, there are numerous inclusions of the Fe₃W₃C phase as well. A change of the binder structure near the interface is caused by the enrichment of the melt, whose composition corresponds to the composition of the Fe–Fe₃(B,C) initial eutectics, with tungsten and carbon from the dissolving filler. For the same reason during the consequent recrystallization forms the Fe₃W₃C phase in the contact interaction zone between the filler and binder. This phase is responsible for the impairment of corrosion, abrasive, and gas abrasive wear resistances of composite coatings.

In the structure of composite coatings reinforced by rapidly cooled spherical granules of the W–C filler (\(v_{\text{cool}} = 10^{-4} - 10^{4}\) K/s), the width of contact interaction zones at the interfaces decreases by a factor of 10–15 (Fig. 1b) and is 15–20 μm. This points to a decrease of the dissolution rate of the filler eutectic phases in the molten iron binder during the infiltration. The result obtained may be attributed to an increase of the uniformity of the W₃C–WC fine-differentiated eutectic structure of the filler and difficulty of the penetration of the Fe–B–C molten binder deep into the filler along the interfaces of eutectic phases and boundaries of eutectic colonies during wetting. Because of this, the Fe₃W₃C phase is virtually absent in the structure of the contact interaction zones. Thanks to this, the composite coatings of the above composition exhibit higher wear resistance in abrasive and gas abrasive media (Table 1).

![Image](image2.png)

**Fig. 2** Microstructure of composite coatings with the Fe–B–C binder reinforced by the Cr–Ti–C filler (a) and zones of contact interaction between the filler and binder (b).

The width of contact interaction zones attains 250 μm. Since the increase of the dissolution rate of crystalline phases of the Cr–Ti–C filler does not bring about the undesirable phases in the structure of interfaces, their formation ensures a strong adhesion of the filler and binder. Because of this, under the conditions of abrasive and gas abrasive wear, a high stability of the composite material with the iron binder reinforced by Cr–Ti–C filler is attained. This material is of a considerable promise for strengthening and restoration of parts of metallurgical and mining equipment. The revealed features of dissolution of eutectic and peritectic fillers in iron binders are observed in the case of the infiltration by copper binder as well.

Of interest are composite coatings based on MNMts 20–20–manganous melkhior reinforced by iron borides. In the structure of fillers of compositions 9.0–12.0 B, 0.01–0.17 C, the rest being Fe (all wt. %) there are primary crystals of Fe(B,C) iron monoboride and crystals of Fe₃(B,C) iron hemiboride. The latter are formed both by the peritectic reaction and crystallize directly from the liquid because the stoichiometric composition of this phase is close to the composition of the peritectic point (Fig. 3a).
However, as the cooling rate increases up to $10^3$–$10^4$ K/s in producing the boride filler by thermocentrifugal atomization, it acquires a microcrystalline structure. Depending on the granules diameter, the size of $\text{Fe}_2(\text{B},\text{C})$ crystals ranges from 1.0 to 4.5 μm. In addition, the $\text{Fe}–\text{Fe}_2(\text{B},\text{C})$ metastable eutectics appears along the $\text{Fe}_2(\text{B},\text{C})$ phase boundaries. As a result, in infiltration the molten binder penetrates along the $\text{Fe}_2(\text{B},\text{C})$ grain boundaries over the whole volume of granules of the rapidly cooled filler (Fig. 3b) and the so called “through” infiltration is observed. Therefore, despite the retardation of the dissolution of $\text{Fe}(\text{B},\text{C})$ and $\text{Fe}_2(\text{B},\text{C})$ microcrystalline phases in molten melkhior by a factor of 5–7 as compared with crystalline phases, the strong adhesion of the filler with a hardened binder is attained. As a result, the gas abrasive wear resistance of composite coatings reinforced by microcrystalline filler increases. In the same time coatings reinforced by boride crystalline filler are characterized by a higher resistance to abrasive wear thanks to the optimal combination of the filler hardness and plasticity. In addition, the reliable adhesion with the binder is assured due to more intensive dissolution of crystalline phases during the infiltration. After the binder solidification, the contact interaction zones up to 50 μm in width form at the interfaces, which contain no brittle phases. Thus, the wear resistance of composite coatings reinforced by iron borides in abrasive and gas abrasive media increases with increasing rate of the fillers dissolution in the molten melkhior. This is brought about by the presence of metastable or crystalline phases in the filler’s structure. The set of operation characteristics of these composite coatings makes it possible to increase the service lives of various parts of metallurgical equipment.

By varying the amount of phases in the filler’s structure which differ in stability under effect of molten metal binder, one may ensure the formation of defect-free interfaces in macroheterogeneous composite coatings reinforced by quasicrystalline fillers. Quasicrystalline phases that have unique physical, mechanical, and operational properties are characterized by a low surface tension. This impedes the wetting of these phases by infiltrating metals. Therefore, the basic methods to obtain composite coatings reinforced by quasicrystals are extrusion, cold and hot pressing, static and dynamic compacting of mechanically activated powders, directed crystallization, etc. Though it is possible to achieve the adhesion at the interfaces of composite coatings by choosing the optimal amount of crystalline and quasicrystalline phases in the filler structure. Our studies have shown that the promising quasicrystalline fillers for composite coatings are $\text{Al–Co–Cu}$ and $\text{Al–Co–Ni}$ alloys in combination with binders on a copper or aluminum base. The decagonal quasicrystalline D-phase stable up to 1000°C forms in the above alloys. In the case that the content of this phase is no less than 80–85% of the filler volume, it remains in the structures of composite coatings after the thermal cycle of infiltration (Fig. 4).

In the contact with the molten binders the filler crystalline phases like $\text{Al}$_{(\text{Co,Cu})}_3$, $\text{Al}(_{\text{Cu}},\text{Cu})$, $\text{Al}$_{(\text{Co,Cu})}_2$, $\text{Al}$_{(\text{Co,Ni})}_3$, $\text{Al}$_{(\text{Co,Ni})}_2$ dissolve to a higher degree than the quasicrystalline D-phase. The strong adhesion of the filler and copper-based binder is also achieved due to the “through” infiltration (Fig. 4).

The tests of composite coatings reinforced by quasicrystalline fillers show a decrease of the friction coefficient and wear intensity (see Table 2). Besides, these coatings are characterized by a high resistance to acid media. This result correlates with the above conclusion that to achieve corrosion stability, one should decrease the dissolution rate of phases of a filler in a molten binder. These composite coatings may be used to strengthen parts of the automobile transport and rocket-and-space equipment.

### 4. Conclusions

The character of the contact interaction processes occurring at the interfaces between the filler and the molten binder during the infiltration of macroheterogeneous composites of the dissolution-diffusion type may be predicted by considering the initial structure of fillers. In wetting hard fillers of eutectic type, one of the eutectic phases has been dissolved in the molten binder at a higher rate, with binder penetrating deep into the filler along the interfaces and eutectic grain boundaries. Peritectic filler has been dissolved mainly where grain boundaries of peritectic phase are located. The dissolution rate of the phases of the filler in a molten binder during the infiltration of the composites depends on their structure and decreases in the following order: crystalline $\rightarrow$ microcrystalline $\rightarrow$ quasicrystalline phases. The intensity of interfacial reactions may also be controlled by combining phases of various stabilities in the structure of the filler. This approach makes it possible to predict performance characteristics and enhance their level due to strict control of interfacial reactions during infiltration.

The lower friction coefficients and wear intensity at dry friction have been shown by composites reinforced by the fillers containing in the structure no less than 80–85 vol. % of stable quasicrystalline phase. The resistance to abrasive and gas abrasive wear has been ensured by the presence of crystalline phases in the filler structure provided that an increase of their dissolution rate in the molten binder during the infiltration does not give rise to brittle phases formation in the contact interaction zones at the interfaces between the filler and the binder. To attain high stability of composite coatings in acid media, the fillers should contain microcrystalline or quasicrystalline phases.

So, developed metal-matrix macroheterogeneous composite coatings obtained by furnace infiltration feature high performance characteristics. Technology of furnace infiltration allows fabricating one-layer or multilayer composite coatings for various applications. Layers of the composites may differ in the filler or the matrix compositions or structure type. They can be utilized for excellent abrasive or corrosive resistance.

Fig. 3 Microstructure of composite coatings with the MNMts 20–20 binder reinforced by $\text{Fe–B–C}$ filler cooled at a rate of 10 (a) and 10$^3$–10$^4$ (b) K/s.

Fig. 4 Microstructure of composite coatings with the L62 brass binder reinforced by the Al–Co–Cu (a) and Al–Co–Ni (b) fillers.
INVESTIGATION OF THE STRUCTURE AND SOME OF PHASE TRANSFORMATIONS IN WEAR-RESISTANT CAST ALLOYS

ИЗСЛЕДВАНЕ НА СТРУКТУРАТА И НЯКОИ ФАЗОВИ ПРЕВРЪЩАНИЯ В ИЗНОСОУСТОЙЧИВИ ЛЕТИ СПЛАВИ

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Abstract: The study of phase transformation processes in wear-resistant alloys from Fe-Cr, Fe-Ni-Cr, Fe-Cr-Mn base systems has not only a fundamental, but also a practical significance, especially with regard to alloys with a chemical composition with difference from the conventional one - this is an interesting scientific and applied direction. The importance of this type of researches is motivated by fact, that in the available literature there is insufficient data on the structure and properties of non-standard iron-based materials, with variation amount of alloying elements (as well as additional alloying or modification) not only in the cast state, but also after thermal or plastic treatment. That’s why, the aim of the present study is to obtain data on alloys with the most mass application that have increased carbon and reduced chromium content relative to stainless deformable steels.

Keywords: WEAR-RESISTANT CAST ALLOYS, STRUCTURE TRANSFORMATIONS

1. Introduction

The choice of materials is motivated by their most extensive application for body parts and components in responsible constructions or apparatuses [1, 2, 5, 6] operating under special conditions - their working environment is loaded with abrasive wear, aggressive corrosive environments, cavitation, impact loads, etc.

Chemical compositions of the examined alloys are shown in Table 1. From each alloy, 11 samples were obtained and further processed.

Table 1. Chemical compositions of the alloys

<table>
<thead>
<tr>
<th>Alloys composition</th>
<th>C, %</th>
<th>Mn, %</th>
<th>Si, %</th>
<th>Cr, %</th>
<th>S, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (406)</td>
<td>0.43</td>
<td>14.17</td>
<td>0.32</td>
<td>5.48</td>
<td>0.011</td>
</tr>
<tr>
<td>2 (408)</td>
<td>0.92</td>
<td>14.85</td>
<td>0.21</td>
<td>6.12</td>
<td>0.011</td>
</tr>
<tr>
<td>3 (410)</td>
<td>1.48</td>
<td>15.05</td>
<td>0.23</td>
<td>5.8</td>
<td>0.011</td>
</tr>
<tr>
<td>4 (412)</td>
<td>1.98</td>
<td>14.43</td>
<td>0.21</td>
<td>5.8</td>
<td>0.012</td>
</tr>
<tr>
<td>5 (414)</td>
<td>2.35</td>
<td>15.05</td>
<td>0.28</td>
<td>5.72</td>
<td>0.012</td>
</tr>
</tbody>
</table>

2. Experiment

Experimental tasks are carried out in the following order:

2.1. Heat treatment under different modes
- The heat treatment of the samples was carried out in two stages in a laboratory furnace.
- Homogenization for austenitization at 1150°C, retention time of 2 hours and quench hardening of the samples in water are provided, to be fixed the high temperature state and probably the most higher rate of carbon uptake from the decomposed carbide phases, [2-4, 7, 8].

The specimens are treated to heating regimes shown in Table 2.

Table 2. Regimes of heat treatment

<table>
<thead>
<tr>
<th>Heat treatment regimes</th>
<th>Alloys composition</th>
<th>Temperature, [°C]</th>
<th>Time, [h]</th>
<th>Cooling conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (406)</td>
<td></td>
<td>1150</td>
<td>2</td>
<td>H₂O</td>
</tr>
<tr>
<td>2 (408)</td>
<td></td>
<td>350</td>
<td>5, 10, 20</td>
<td>H₂O</td>
</tr>
<tr>
<td>3 (410)</td>
<td></td>
<td>550</td>
<td>5, 10</td>
<td></td>
</tr>
<tr>
<td>4 (412)</td>
<td></td>
<td>750</td>
<td>5, 10</td>
<td></td>
</tr>
</tbody>
</table>

2.2. Rockwell hardness testing

Each stage of the heat treatment to the samples is accompanied by a measurement of changes in their macrohardness according to a standard Rockwell method (HP-250 combined hardness meter, penetration depth 1Rc=0.002mm), [3, 5]. The obtained results are averaged from all testing specimens. They are shown at Fig.1.

Fig.1. Data for macrohardness of the alloys

2.3. X-ray structural analysis

The phase composition of the alloys is determined from the interplanar distance data, which gives different lines on X-rays. The results are compared with literature data on the basic carbide phase lines and the solid solutions in the matrix of the alloys [1, 4, 7].

The anode of the X-ray tube is the lightest element of the
system under study - Cr-radiation with wavelength $\alpha = 2.29092 \ \text{Å}$ is used. To achieve accuracy, unfiltered radiation is applied, i.e. the characteristic X-ray spectrum of chromium consists four lines $(\alpha_1, \alpha_2, \beta_1, \beta_2)$. Strong alpha lines have a very near wavelength and count as a single line. The intensity of the $\beta_2$ line is very weak and absent from the X-rays. The data for $\alpha_1$ and $\beta_1$ are taken from tables [4]. Some of the X-rays diffraction patterns are shown in Fig. 2a and 2b (Alloy 3, homogenized and after $550^\circ C/10$ h). Results of analysis of the examined alloys are shown in Table 3.

### 2.3. Metallographic examination

The preparation of specimens is standard - mechanical grinding and polishing. Surfaces are etching with nital (1.5% solution of HNO$_3$ in ethyl alcohol) and ammonium persulfate (10% solution of (NH$_4$)$_2$S$_2$O$_8$) in water [3]. The micro-photographs are taken at a 300x magnification with a camera, attached to the Epigraph-2 metallographic microscope. Some of important transformations, seems on the spesimen’s structures are shown in Fig. 4, (see the next page).

### 2.4. Microhardness testing

Microhardness testing carried out using a Neophot-2 metallographic microscope equipped with a additional equipment. For calculation it was found that 20 divisions of the micro-scale corresponded to a load equal to 46.95 grams. The calculations are made according to the formula:

$$H = 1.8544 \frac{P}{d^2} \text{ [MPa]}$$

where $P$ is load size of kg; $d$ is the arithmetic mean of the length of the two diagonals, resulting from the penetration of hardness indenter, [6]. Measurements are performed at different locations in the main solid solution. The results, as measurement values are presented in Table 3. Graphically, the changes of microhardness as a result of heat treatment for all examined alloys are shown at Fig. 3.
3. Results and Discussion

After austenization all compositions of the alloys have an austenitic matrix structure, with the exception of the 0.43%C composition, that containing ferrite. According to the carbon content of the alloys, an increase in the volume of the second phase and the coalescence of the carbides start at lower temperatures. At a temperature range between 550 to above 700°C, the decomposition of the solid solution proceeds with separation, formed from pearlite-like colonies.

As separations at 750°C are maximum for all investigated alloys, with a longer retention time at this temperature, for example 10 hours, starts the process of re-dissolving the second phase in the austenitic matrix [9]. This trend is most pronounced in alloys with 1.98 and 2.35% carbon. With defined carbon content of 1.48 and 1.98%, a needle-like phase formation in the temperature range of 550-750°C is observed.

By increasing the retention time, Rockwell hardness (HRC) increases. The highest values are fixed at 10 hours for a temperature of 550°C. With temperatures up to 750°C, a hardness reduction was observed for all tested compositions with 0.92 to 2.35% carbon. Studies show that hardness increases due to different mechanisms:

- After austeniation and rapid cooling, the hardness increase is due to the dissolved carbon and the residual carbide phases in the matrix.
- The increased hardness as a result of the additional heat treatment is probably due to the presence of residual carbide phases of type $\text{Me}_3\text{C}$ and $\text{Me}_2\text{3C}_6$, as well as to the formation of new phases with specific quantity and morphology.

4. Conclusion

The received results will be useful in future researches and projects, related to the stages of structure formation, separations of strengthening phases in state of time of the thermal processes, mechanical and exploitation properties, and application of this type of metal materials.

5. References

VIBRO-AcouSTIC APPROACH FOR REGISTRATION AND EVALUATION OF TECHNICAL DEVIATIONS IN ALUMINUM CASTINGS

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Abstract: Superficially masked internal discontinuities in the aluminium casting during the manufacturing process occurs often. As a result of dynamic loads in the process of operation, it is possible the occurrence of leakage in the machine. The application of classical methods of non-destructive testing of internal discontinuities in parts with relatively complex geometric dimensions requires a significant resource or is not always possible.

A vibro-acoustic study for express diagnosis of internal discontinuities in aluminium castings is shown in the work.

The resonance behaviour of a part depends on its specific shape and material properties of the elastic medium. This allows diagnostic approaches for registration of different technical deviations, estimating an equivalent size of internal discontinuities, to be created.

Classical theory of resonance is used for scientific justification of study. It is suitable in spatial parts of complex shape the theoretical results to be obtained for each particular construction by means of the constructive model in CAD environment. The possible technical deviations are created in the geometric model by software. The model is divided into elementary parts and a detailed description of their properties and the elastic connections are described by the Finite Element Method (FEA). This allows diagnostic models for registration of discontinuities, incl. for assessing its equivalent size in a particular section of the casting to be created rapidly.

A study of an aluminium part by a universal acoustic apparatus is shown in this work. The samples are separated into factory conditions of „suitable“ and „unsuitable“ after machining of the joining dimensions. Typical areas of occurrence of discontinuities in the casting process are defined. The „suitable“ samples are divided according to the specific elastic characteristics of the material used. Insignificant scattering (2-6 Hz) of resonant frequencies in the range 20 Hz to 20 kHz is measured. Discontinuities in the typical areas of registration in the real parts are formed successively in the CAD model. The resonances are calculated in FEA. Diagnostic signs for registration and evaluation of an equivalent size of discontinuity according to its disposal are created. Discontinuities of irregular shape are created in part of the „suitable“ samples and the resonances are registered again; the changes of resonances are determined. The principle consistency between theory and experiment is assessed. A good compliance is obtained.

The work may be used to assess the technical condition of castings by manufacturers of such parts.

Keywords: ALUMINUM CASTING, INTERNAL I DISCONTINUITIES REGISTRATION AND SIZE EVALUATION

1. Introduction

As a result of technological deviations in the process of aluminium parts casting superficially masked internal discontinuities occurs often[1]. The problem with internal discontinuities is significant for thin-walled details, from which both mechanical strength and tightness are required. As a result of internal discontinuities accidents of product leakage after a certain period of dynamic load during the operation are possible.

Internal discontinuities can be recorded by well established non-destructive methods. For each method a scientifically justified sensitivity threshold is defined, i.e. the minimum amount of discontinuities that can be registered. There are also specific requirements for the shape of the parts in order to realize the study.

In parts with relatively complex geometric shapes nonconformities with different locations are possible. For their registration, technical devices have been developed to explore the subject from different sides and make 3D computer images. This makes the application of classical methods for non-destructive testing of internal discontinuities to require a significant resource or is not always applicable.

The resonance behavior of a part depends on its particular shape and material properties of the elastic medium [2]. An opportunity to assess the technical condition, incl. the registration of internal discontinuities in aluminium castings gives the analysis of some characteristic resonant frequencies, excited in the parts. The vibrations are recorded quickly by means universal acoustic equipment and no highly qualified personnel is needed to determine resonant frequencies [3]. The vibro-acoustic method is not universal in terms of diagnostics of machine elements. This defines it as a highly effective method for controlling the technical condition of concrete parts after a specialized procedure to demonstrate its application.

The aim of the work is to show a vibro-acoustic express diagnostic approach of internal discontinuities in aluminum castings.

2. Stages of the study

To clarify the resonance phenomenon in theory, mathematical dependencies are usually presented for simple bodies. For example, the basic (first) critical angular velocity of one shaft is given by the dependence [2]:

\[ \omega = \sqrt{\frac{k}{m}} \]  

(1)

Here \( k \) is stiffness on the shaft, \( m \) - mass. For each body, resonant modes of a specific nature exist; they are determined by the major deformation in the material, such as: transverse, longitudinal, twisting, etc. In complicated parts, consisting of simple interconnected bodies, there are conditions for the simultaneous stimulation of more resonances. In fact these are systems of elements with elastic connections between them, which make their theoretical description difficult. The shape of complex details is easily described using engineering CAD and strength analysis (FEA) software, widespread in engineering. Once created, the geometric model of a part in a CAD is used for technological purposes, and can also be used for vibro-acoustic control of the productions. In a CAD environment, it is appropriate to work on the model to create some technical deviations that are found experimentally. After translating into FEA environment, the revised geometric variants are separated to elements by software, and the elastic properties of the material are set. Depending on the complexity of the model and the level of computer equipment, the time for calculating the resonant frequencies is 2 - 60 minutes, followed by an analysis of the results obtained with respect to the change of frequencies compared to those of the model without technical deviations.
One of the frequent reasons for changing the resonant frequencies in serially produced parts is the permissible deviation of the elastic characteristics of the metal. These deviations are difficult to record by non-destructive methods, such as an ultrasonic method, but they change the resonant frequencies of the part. It is appropriate for the “elastic medium” factor to be read in advance so as to achieve a good recognition of unacceptable technical deviations.

The theoretical results are evidenced by comparing theoretical results with experiments with details with artificial discontinuities, which repeat the CAD deviations, as well as with details with proven discontinuities. Difficulties in proving the theoretical results create the possibility in a part with the recognized discontinuities by leakage to exist other inconsistencies/deviations.

2.1. Preparation for Vibro-Acoustic Control:
- Demonstration of the metrological accuracy of finished products in one series - this activity is performed by comparing the deviation of resonant frequencies in a series;
- Analysis of typical sections with a discontinuity in the parts;
- Modeling of the dependence between the resonance frequency deviation and an equivalent degree of discontinuities in the way $\Delta f_i = f - f_{\text{def}}$; i - the number of the resonance, $\Delta f_i$ - its frequency deviation from the technical variance; or reverse function $- \Delta = f_i (\Delta f_i)$;
- Creating samples with artificial discontinuities and verifying the theoretical results;
- Setting standards to control for registration and diagnosis of inconsistencies.

2.2. Control procedure
- Distribution of parts in batches, e.g. by mass measurement or reference resonance frequencies;
- Recording resonance frequencies and analysis by comparing with selected standards for recording inconsistencies in typical sections;
- In case of suspected frequency deviations, conclusions are drawn about the location and the extent of the discontinuities.

This sequence helps to quickly create diagnostic signs for registration of technical deviations, such as geometric deviations, deviations in product density.

3. Example of illustrating the approach

An example of a study of an aluminum piece shown in Fig. 1 a) with a universal vibration-acoustic apparatus is shown in this paper. In factory conditions the samples are processed to the exact size, after which they were tested for leakage. The typical areas of discontinuities in the casting process are selected [5]. The good samples are separated into groups according to the specific elastic characteristics of the material used. Insignificant scattering (2-6 Hz) of resonant frequencies in the range 20 Hz to 20 kHz is determined and higher resonances have greater scatter. In addition, higher-frequency resonances require extra attention on excitation and analysis.

The mass of samples was examined and a change of 2.8% was found.

3.1. Preparation of the test sample

In the constructive model of the sample are formed consecutive irregularities in the typical areas of registration in real details. Part of the sample models are modified by irregularities in the sections established by practical studies, established by practical research and changes $\Delta f$ of some resonance frequencies are registered $\Delta f = f - f_{\text{def}}$; $f$ - frequency of sample with normal quality, $f_{\text{def}}$ - frequency of sample with discontinuities. Frequency variation $\Delta f$ depends on the equivalent depth $\delta$ of discontinuities and on the particular disposition of the discontinuities. For the specific detail, four sections are found [5]. They are shown in Fig. 1 b). In the first section the possibility of double-sided leakage, indicated as I and I', is established. When the depth of discontinuities ranges from 0 to 3 (6) mm, some resonant frequencies change significantly (above 10 Hz). They are shown in Table 1. It is appropriate to use them as informative it is appropriate to use them as informative features for registration of discontinuity and for determine its equivalent depth.

![Fig. 1. 3D model of research example (a) and typical sections with discontinuity in the real samples (b).](image)

Resonance 4 changes insignificantly (up to 10 Hz) in case of discontinuities in section IV, and otherwise does not change and is suitable to be selected as a benchmark for assessing the quality of the parts.

| Tab. 1. List of resonant frequencies up to 10 kHz which changes in case of discontinuity according to the section. |
|---|---|---|
| Section № | Significant change in the resonant frequencies, № | Minor change in resonant frequencies, № |
| I | 1, 3, 10, 11, 12 | 5 |
| II | 26*, 37* | - |
| III | 2, 7, 8 | 3, 5, 12 |
| IV | 2, 3, 5 – 10, 12, 13 | 1, 4, 11 |

Note: * Resonances specified are only informative and are outside the frequency range.

A statistical analysis of the frequency of occurrence of discontinuities in the different sections of the sample is done. The most common cases of leakage (about 60%) are recorded in section I. Sections I and IV are used here as examples of creating
diagnostic signs for registration and evaluation of equivalent discontinuity dept.

Theoretical results for the frequency variation $\Delta f$ of resonances with conditional serial number (№) in sections I (a) and IV (b) depending on their serial number are shown in Fig. 2.

![Fig. 2. Results for variation of $\Delta f$ in section I (a) and IV (b) depending on the serial number (No) of the resonant frequency.](image)

Diagnostic signs for registration and assessment of an equivalent depth $\delta$ of discontinuity according to its location were created on the so-called nomograms as follows:

For section I

$$\Delta f = -0.1288 \delta^4 + 0.8485 \delta^3 - 0.2947 \delta^2 + 0.026 \delta + 6 \times 10^{-11}$$

for resonance № 1

$$\Delta f = -1.1666 \delta^3 + 9.9951 \delta^2 - 22.643 \delta + 19.138 \delta + 2.1 \times 10^{-10}$$

for resonance № 27

For section IV

$$\Delta f = 2 \delta^2 - 2.6667 \delta + 6 \times 10^{-14}$$

- for resonance № 2

$$\Delta f = 2.6667 \delta^2 - 3.6667 \delta + 6 \times 10^{-14}$$

- for resonance № 5

Here $\Delta f$ is in Hz, and $\delta$ - in mm. These equations are processed to the following:

For section I

$$\delta = 0.002 \Delta f^3 - 0.0649 \Delta f^2 + 0.735 \Delta f + 0.1$$

- for resonance № 1

For section IV

$$\delta = -0.0042 \Delta f^2 - 0.3419 \Delta f + 3 \times 10^{-14}$$

- for resonance № 2

The main criteria for selection of informative resonance frequencies are:

- Target sensitivity of the analysis, which determines the minimum recognizable value of $\Delta f$ and is related to the scattering of the results for one batch of parts;

- Recognition of resonance; this problem is typical for close-to-order resonances for which overlapping is possible. In this case, the inspection body may make a wrong conclusion. The results of processing multiple experiments show that lower frequency resonances are easier to analyze. For example, the resonance change № 27 of depth incoherence $\delta$ in section I shown in Fig. 2 (a) has a theoretical meaning due to difficulties with its registration.

The main factors of scattering for a batch are related to:

- Variations in geometric dimensions of the parts due to technological reasons;

- Non-metal inclusions and porosity of the material (in case the study does not have a purpose for their registration).

3.2. Experimental results

The experimental results were obtained by universal acoustic equipment and were realized in a soundproofed room. Audio signals are recorded in the 20 Hz - 20 kHz range and they are entered and saved on a computer via a USB. The samples are suspended on a perfectly flexible and unstretchable thread and are dynamically excited by impulse. Attention is paid to the relatively uniform amplitude excitation of resonant frequencies over a wide frequency range. Registration and frequency analysis of signals is done in digital form by software for a recording time range 0.5 s.

In Fig. 3, a typical experimental result of the resonance recording is shown. By software the exact measured values of the resonant frequencies are determined and the values of $\Delta f$ are determined according to the depth of discontinuities.

![Fig. 3. A typical result obtained by experimental study of resonant frequencies.](image)
Fig. 4. Stages of the study; a) - to determine the frequency resonance change, b) - to confirm the theoretical results.

A comparison of the resonance frequencies № 1 and № 2 obtained for detail without deviation (used as etalon) and for detail with discontinuity 2.5 mm depth in section I is shown in Fig. 4 (a). The figure is shown for illustrative purposes and it is obtained by overlaying screen images of recorded signals and formatted for the same frequency range (2440 to 2780 Hz). It is noted that for the part with discontinuity the first resonance is lower (13 Hz is reading) from the etalon and for the second resonance the both frequencies are equal. Basically, these results correspond to the theoretical values shown in FIG. 2 (a).

A quantitative comparison between theoretical and experimental results in case of discontinuities in section I is made. For this purpose discontinuities with different depth $\delta$ are formed in the section of a series part and the frequency difference $\Delta f$ for each modified part has been measured. The results of the comparison of resonance frequencies № 1 and № 3 are shown in Fig. 4 (b). Principal coincidence between theoretical and experimental results is observed. This allows resonances 1 and 3 to be used for registration and determination of equivalent depth of discontinuities in section I.

4. Conclusion

The approach described above for vibro-acoustic assessment of internal incompleteness in aluminum castings is illustrative and object-oriented. For its application, no specialized knowledge and further continuing training in non-destructive testing is required. The approach is based on general engineering fundamental knowledge in the field of defectology and software products widely used in engineering. It can be applied using affordable acoustic equipment. The assessment of the technical condition of the products is made by comparing the reference resonance frequencies of the studied parts with those obtained for good quality products.

The approach is not universal and requires considerable theoretical and experimental work to demonstrate its validity. But it provides an opportunity for an express assessment of the technical condition of the parts and is cost-effective.

The work may be used for self-assessment by manufacturers of technical condition of cast parts.

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Abstract: This paper proposes the idea of a "small volume" in which to consider complicated processes to create structures in phase transitions of first and second order in the foundry. The small volume is chosen based on the classical theory of crystallization and its use for quantum mechanics. A numerical solution of Stefan-Schwarz's task was presented by obtaining the temperature field of solidification of a composite cast in a squeeze casting. This little volume we proposed for a good possibility in the direction for a theoretical possibility of hybridization of production and technology.

Keywords: "LITTLE VOLUME", SOLIDIFICATION COMPOSITE, 3D PRINTING, ADDITIVE, MICROSTRUCTURE

1. Introduction – science

The phase transition from the first order is an irreversible process and flows into an open thermodynamic system (OTS). The dynamic state of the particles in it is represented by the generalized entropy function [22]:

\[ S = k \ln \pi, \]  
(1)

where, k is Boltzmann constant. We applied [8] the second low of thermodynamics in the form of the extend of I. Prigogine [11]

\[ \frac{dS}{dt} = \frac{dS_{ex}}{dt} + \frac{dS_{int}}{dt}, \]  
(2)

At the interphase surface (front) is the limited the change of properties and the thermodynamic state is introduce by Gibbs-Lengmure isotherm

\[ d\sigma/d\mu_i = - \frac{(RT\mu_i \alpha_i)}{(1 + K'_i \alpha_i)} \]  
(3)

where \( \sigma \) - surface tension; \( K'_i \alpha_i \) is chemical activity of \( i \)-component; \( I'_i \) is maximum concentration at the front. The measure of metastability of phases is the different (\( \Delta \mu \)) between chemicals potentials (call driving force) while the change is local equilibrium from anisotropy of surface energy with relation to isotropic is being determined by Gibbs-Thomson equation:

\[ \Delta \mu = \mu_1 - \mu_5 = \alpha \mu_5 (R_1^2 + R_5^2) \]  
(4)

where \( \mu_1, \mu_5 \) – are chemical potentials of phases on both sides of surface front; \( R_1, R_5 \) – curve radii on surface for location; \( \alpha \mu_5 \) – specific value of (one molecule) of crystals phase; \( \alpha \) - surface energy [8]. Theory of Kossel-Stransky-Folmer-Kaishev molecular-kinetic theory. The solution of thermodynamic of equation of Gibbs-Thomson

\[ \ln \left( \frac{P_{eq}}{P_{cr}} \right) = \left( \varphi_{1/2} - \overline{\varphi}_{3/4} \right) / kT, \]  
(5)

where \( P_{eq}, P_{cr} \) – the pressure of the surface of the crystal and environment; \( \varphi_{1/2}, \overline{\varphi}_{3/4} \) – the energy for separation (incorporation) of a particle from semi-crystal state; \( \overline{\varphi}_{3/4} \) – the average energy used for a particle. The equation much more general [8]. The functional relation between kinetic motion and velocity of crystallization \( V_{crys} \) is driving force of crystallization \( \Delta T_k \) at three growth mechanisms:

1. 2D nucleus formation \( V_{crys} \sim \Delta T_k \); 2. through screw dislocation \( V_{crys} \sim \Delta T_k \); 3. Continuous growth \( V_{crys} \sim \Delta T_k \). Character macro- and micro-scales on the base of [11] in [8 and 9] is obtained:

\[ \Delta v_{corr} = v_{corr}^{-1} = D \Delta v^{-1/d} \]  
(6)

where \( \Delta v_{corr}, v_{corr} \) are correlations scales and local characteristics volume and time \( \tau_{ch} \) d is growth directions; and from [2] we accept

\[ \tau_{ch} = \tau_j \sim \Delta k^2/d \]  
(7)

where D, \( \Delta T_k \), \( V_j \) are coefficient of diffusion, locals temperature gradient and velocity of solidification.

The aim of this work we present through paragraphs 1.1 additivity, and 1.2 Synergic.

2.1 Additive – know how

Additive It is known that in a production cycle we have a compulsory sequence of technologies shown in Fig. 1

![Fig. 1 Know How – Technological additive on the basis of the two basic processes of material science, casting and heat treatment, where 1 (2) are two real technological circuits, and various well-known combinations of technologies can be made.](image-url)

From Fig.1 we add the technology 3D printer.
3.2 Synergic – unification of sciences and technologies

If Material-science is understood full knowledge we introduced on Fig.2: by the through the concepts of science, materials,

**STRUCTURE-PROPERTIES-PRODUCT**

- METALS, ALLOYS, CERAMICS, PLASTICS, COMPOSITES.

**TECHNOLOGIES**

- CLASSICAL PHYSICS
- QUANTUM MECHANICS

- ENTRANCE

**MARKET AND LIFE OF PRODUCT**

- END OF PRODUCT

**PROCESSING OF MATERIAL**

**Fig.2** Synergic the least knowledge of the material science needed for the participation of a family or large foundry company in a circular economy. Material science is unification of sciences: classical physics; mathematics; mathematical physics; theoretical physics, quantum mechanics. Integration of casting technology to produce an article whose material has a particular structure and working properties for the longest possible life of the product. Integration of Foundry Technologies we consider as hybrid technology - a combination of foundry machines and 3D printers [1].

4. Materials science in foundry – sciences and technologies

Composite technologies allow new materials to be obtained whose working properties are generally represented by the definition on the base of well-known results [1, 2, 3, 4] and [5, 6, 7] is:

Each composite material is non-homogeneous on a micro scale because it consists of two or more components of different chemical composition and a clear boundary between them but is homogeneous (in properties) on a macro scale. (WPC)

Bridge to unite science and technology in materials science is the basic process - the phase transition of the first order. That is the fundamental task at foundry Stefan-Schwarz problem (St-Sch). The mathematical model of foundry in 3D case is

- equation of heat conductivity

\[
\frac{\partial \mathbf{T}}{\partial t} = \mathbf{A} \cdot \frac{\partial \mathbf{V}}{\partial t} + \mathbf{B} \cdot \frac{\partial \mathbf{V}}{\partial z} \quad \text{in } V_{OTS} \equiv \begin{cases} V_{C} \cup V_{E} \cup V_{M} & \text{or} \\ V_{C} \cup V_{E} \cup V_{M} & \text{SS, 1} \end{cases}
\]

- initial conditions at \( t = 0 \):

\[
T_C(x, y, z, t = 0) = \text{const}_3 \text{ and } T_M(x, y, z, t = 0) = \text{const}_2 \quad \text{SS, 2}
\]

- boundary conditions at \( t \geq 0 \):

\[
\begin{align*}
\left[ -\lambda_p \rho H \right] & = \alpha [T_C(x, y, z, t) - T_{\text{Environment}}] \\
\left[ -\lambda_p \rho V \right] & = \alpha [T_M(x, y, z, t) - T_{\text{Environment}}] \\
\frac{\partial T}{\partial H} & = \sigma [T_C(x, y, z, t) - T_{\text{Environment}}] \\
\frac{\partial T}{\partial H} & = \sigma [T_M(x, y, z, t) - T_{\text{Environment}}]
\end{align*}
\]

\[
\begin{align*}
& \text{at } T_C: \left. \frac{\partial T}{\partial H} \right|_{H = 0} = \alpha \left[ T_C(x, y, z, t) - T_{\text{Environment}} \right] \\
& \text{at } T_M: \left. \frac{\partial T}{\partial H} \right|_{H = 0} = \alpha \left[ T_M(x, y, z, t) - T_{\text{Environment}} \right] \\
& \text{at } W_5: \left. \frac{\partial T}{\partial H} \right|_{H = 0} = \sigma \left[ T_C(x, y, z, t) - T_{\text{Environment}} \right]
\end{align*}
\]

\[
\begin{align*}
\frac{1}{\rho_1} \rho_1 \mathbf{c}_1 \cdot \frac{\partial T}{\partial \tau} & = -\lambda_0 \mathbf{u} \cdot \nabla T + \frac{\partial T}{\partial \tau} \quad \text{SS, 1} \\
\frac{1}{\rho_1} \rho_1 \mathbf{c}_1 \cdot \frac{\partial T}{\partial \tau} & = -\lambda_0 \mathbf{u} \cdot \nabla T + \frac{\partial T}{\partial \tau} \quad \text{SS, 3}
\end{align*}
\]

\[
\begin{align*}
& \text{for } T_{EL}(\tau) \leq T_m + \Delta T \\
& \text{for } T_{EL}(\tau) \geq T_m + \Delta T \\
& \text{for } T_{EL}(\tau) = T_m + \Delta T \\
& \text{for } T_{EL}(\tau) = T_m + \Delta T 
\end{align*}
\]

from the time of application of pressure to solidification of the composite casting

\[
\begin{align*}
\frac{1}{\rho_1} \rho_1 \mathbf{c}_1 \cdot \frac{\partial T}{\partial \tau} & = -\lambda_0 \mathbf{u} \cdot \nabla T + \frac{\partial T}{\partial \tau} \quad \text{SS, 1} \\
\frac{1}{\rho_1} \rho_1 \mathbf{c}_1 \cdot \frac{\partial T}{\partial \tau} & = -\lambda_0 \mathbf{u} \cdot \nabla T + \frac{\partial T}{\partial \tau} \quad \text{SS, 3}
\end{align*}
\]

\[
\begin{align*}
& \text{for } T_{EL}(\tau) \leq T_m + \Delta T \\
& \text{for } T_{EL}(\tau) \geq T_m + \Delta T \\
& \text{for } T_{EL}(\tau) = T_m + \Delta T \\
& \text{for } T_{EL}(\tau) = T_m + \Delta T 
\end{align*}
\]

the function of the heat source is approximated by \( \delta \)-type function
The following symbols are used in this model: thermophysical coefficients $\lambda, \rho, c$ - thermal conductivity, density and thermal capacity for the individual parts of the OTS according to the indices used $M$ - mold, $2$ - preform (corundum), $L$ and $S$ - melt and solid phase of pure Al, lower index $C$ - casting, upper index $C$ - composite area; lower index $EL$ - final element; $k_{SD}, k_2$ - percentage of pure Al and corundum fibers in the composite area; $x, y, z$ - coordinates of OTS; heat transfer coefficients $\alpha_{WS}$ and $\alpha_{M}$ - at working and external surfaces of the $Q_F$ - heat of phase conversion; $T_m$ - phase transition temperature, the same for the composite and Al-casting areas; $\Delta T$ - temperature range of $T_m$; $D$ - dispersion of the $S_F$ function; $T_{AR.M.}$ - ambient temperature; $V_2$ - volume of preform (carbodurnum) which after filling with Al melt is the volume of the composite area, - volume of pure Al; $V_M$ - mold volume; $W_S$ and $\Gamma$ - working and external surfaces of the mold.

On Fig. 2 we present General Scheme of the experiment for production of composite casts by squeeze casting; and Fig. 3 present solidification of composite at squeeze casting technology:

![Composite Casting Diagram](image)

**SQUEEZE CASTING**

**COMPOSITE ALUMINUM - CARBORUNDUM THREADS**

**MATERIALS SCIENCE. NON-EQUILIBRIUM PHASE TRANSFORMATIONS. Issue 2/2019**

And important Methodology for connection crystallization and quantum mechanics is in the frame of [16] - work $\varphi$ two charges $q_1, q_2$ should be kept at a minimum distance $r$ (metal chemical connection MCC) only coulomb forces. According to a classical methodological principle, is only for ionic crystals [16]:

$$\varphi = \frac{(q_1 q_2)}{(4 \pi \varepsilon_0 r)}$$  

(MCC)

Work to bring one positive charge to the end of a chain of alternating (+) and (-) charges of equal distance $r$ is the coming expression:

$$\varphi_{/2} = (e^2 /4\pi \varepsilon_0 r) (-e/1 + e/2 - e/3 - ...) = (e^2 /4\pi \varepsilon_0) \ln 2$$ or $$\varphi_{1/2} = (-e^2 /4\pi \varepsilon_0 r) \Phi$$  

(MCC2, 3)
where $\Phi$ corresponds of $ln2 \Rightarrow$ for work to build a grid of large numbers of particles N (or energy of lattice) is

$$E_{\text{particles}} = (-e^{-n}/4\pi\Phi^2) \Phi$$

and for energy 3D lattice, $E_{\text{particle}} = E_{\text{Lattice}}$ and $\Phi$ is constant of Madelung [16, 3]. To describe the chemical bond, quantum mechanics must be used [3, 16, and 17]. In an electronic approach, the Vigner-Geitz cell method is used for solution Schrödinger equation (SEQ) in character volume $\Delta V_{corr}$ and time eq.(6 and 7) are the connection Classical physic and Quantum mechanics.

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(r) + V(r) \Psi(r) = E \Psi(r)$$

and conditions of (SEQ1)

$$\Psi(r) = \exp(ikr)u_k(r)$$

(SEQ2)

$$u_k(r) = u_k(r + T_p)$$

(SEQ3)

where $n$ is the electron mass; $\hbar$ – Planck constant; $V$ is the periodic potential of the interaction electron/all other electrons); $\Psi$ is a wave function, a solution to equation; $k$ is a vector defined of the crystal Brave lattice $T_{n_{1}n_{2}n_{3}} = n_{1}t_{1} + n_{2}t_{2} + n_{3}t_{3}$ is $T_p$, $n$ is numbers $(n_1, n_2, n_3)$; $u_k$ is a periodic function with the period of $V$.

Composite materials [5, 6 and 7] obtained by casting have great development potential. For example, heat-physical coefficients eq.(SSS). The machines and technologies created in our institute allow create of new composites.

The characteristic volume $\Delta V_{corr}$ and time eq.(6 and 7) is a model of consideration for mathematical and theoretical consideration of processes to create structures in phase transitions. This approach allows the conditions of structuring in foundry machines and technologies. In [21] are tied to a 3D printer. Important moment in additive manufacturing is combination between new [21] software and traditional production (for our institute foundry machines and technologies). In [21] is called „hybrid production“ and „hybrid machines“.

At work [23] it is emphasized the need to describe structures by quantum mechanics in a "small volume". For us, this is a clear emphasis on "knowledge transfer" or the most difficult work with "full knowledge" and "prognosis". Concentration of research is precisely the "drop" model chosen by us ($\Delta V_{corr}$ and time eq. (6 and 7)).

3. Conclusions

A characteristic volume on the consolidation front was obtained to calculate the microstructure using quantum mechanics software.

It is obtain the numerical result of solidification composite material at squeeze casting.

3D Printer is additive through its drop and the characteristic volume for storing the solidification conditions in foundry and creating hybrid technologies.

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INFLUENCE OF EB RADIATION ON THE MECHANICAL PROPERTIES OF ORGANIC BENTONITES-HIPS NANOCOMPOSITES

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Abstract. The effect of EB radiation on the mechanical properties of HIPS matrix nanocomposites is discussed in this paper. Two different types of clays were used (calcite Cuban and sodic Brazilian bentonites) as reinforcement material, in 5 and 7% additions regarding the weight of the material. All clays used were subjected to organic modification. Composite material pellets were prepared in a hot extrusion process adding the clays aided by a vibrating dispenser. Mechanical test samples for tensile and impact tests, according to ASTM standards, were elaborated in an injection molding machine. Half of the samples were irradiated at 600KgY and seven days later, they were tested. The rest of the specimens were tested from their direct injection state. It was shown that an addition of up to 5% of clay as reinforcement in a matrix of HIPS achieved increases in tensile strength over 30% compared with the unreinforced polymer. Additions of higher amounts of clay (7%) represented a decrease on mechanical strength, compared with the 5% addition. Electron beam irradiated samples showed a considerable increase in the tensile strength with respect to this strength in pure material. Increases between 48 and 56% were achieved. In all cases elongation and impact strength decreased with the aforementioned increase in tensile strength.

1 Introduction
High Impact Polystyrene (HIPS) is a two phase blend polymer [1] with a broad field of applications. Due to its excellent toughness, good electric insulation, processability and low cost, it has been widely used for toys, disposable packages, furniture accessories, electrical-electronic goods, medical equipment, etc. Nowadays the automotive industry and modern manufacturing processes as 3D printing have also benefited from the use of this material. Several studies have been carried out to improve the mechanical properties of this polymer, most of them, by controlling rubber domain size and distribution, and changing the morphology of salami rubber particles [1-5] or by designing a novel polymer injection process [6]. The use of ionizing radiation is known to be a powerful tool for crosslinking elastomers, with the subsequent enhancement of mechanical properties when the proper dose is used, [7]. The usage of radiation on HIPS for improving its mechanical properties has been scarcely studied to our knowledge. This has been limited to the use of gamma radiation [7] and although high doses of electron radiation have been employed [8] we did not find references to the use of this ionizing radiation source aimed at achieving the purpose above.

Another way of increasing mechanical properties in this kind of polymer is the creation of composite materials. Particles of organic clays are widely used as reinforcement for polymers, and HIPS has been employed as matrix [9]. The addition of up to 10% of clay can modify effectively the properties of the material [10, 11] due to the large surface contact area between the clay and the polymer. The particle size and distribution play an important role on the reinforcement effectivity, the smaller and better distributed the better the reinforcement properties [9]. Two different types of organic clays were used to prepare HIPS nanocomposites. The resultant nanocomposites were subjected to electron beam (EB) radiation for further improvement and the mechanical properties were evaluated.

Table 1. Reinforcement type and amount of addition for each sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bentonite Type</th>
<th>Modification Process</th>
<th>Load %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cuban (C)</td>
<td>Small scale (SS)</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>SS</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>Large Scale (LS)</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>LS</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>Brazilian (B)</td>
<td>SS</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>B</td>
<td>SS</td>
<td>7</td>
</tr>
<tr>
<td>7</td>
<td>B</td>
<td>LS (Industrial Process)</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>B</td>
<td>LS (Industrial Process)</td>
<td>7</td>
</tr>
</tbody>
</table>

2 Experiments
2.1. Sample preparation
Two different types of bentonites, a Cuban calcite and a Brazilian sodic bentonite, were subjected to an organic modification process. Both clays were modified with the use of organic quaternary ammonium salts and sodium carbonate. The modified bentonites showed an increase of the swelling capability in organic solvents according to Foster swellability test with slightly higher values for the Cuban bentonite (for example, swellability values in gasoline ranged 15-16 ml/g and 11-12 ml/g for Cuban and Brazilian bentonites respectively). The modification process was carried out in small and large scales according to the amount of treated clay for the Cuban bentonite. An industrially modified sample from the Brazilian sodic bentonite was also used. The clay particles size was in the nanometer range according to the results of the organoclays X ray diffraction [12]. Composite material pellets were prepared in a hot extrusion process adding the nanoclay particles with the aid of a vibrating dispenser. Two levels of loads (5 and 7%) were used for each group of samples. Table I presents the characteristics of each composite material studied with the kind and amount of reinforcement, besides the scale of the process employed for the modification. The small-scale process refers to the modification process with a 40g sample of clay, and the large-scale process refers to a 240g clay sample.

2.2 Electron Beam Radiation Procedure
A Dynamitron DPC2000-JOB 307 was used for the radiation process. Pellets of 3 representative samples were irradiated with 200, 400 and 600KgY respectively; to determine the optimal radiation dose, according to machine characteristics. The reticulation was evaluated according to ASTM D 2765-11, being the better results associated with the higher radiation dose. None of the samples showed signs of degradation; therefore, the 600 Kgy dose was selected for all the samples. Half of the mechanical test samples were subjected to a total dose of 600Kgy with a rate of 22.39Kgys/s and energy of 1.288 MeV. The irradiated samples were mechanically tested 7 days after the application of the radiation. This ensured the structure stability.

2.3 Material characterization and Mechanical Property tests
Tensile strength and Charpy tests were performed to the irradiated and non-irradiated samples. The ASTM standards D638 and D6110 were respectively followed. A deformation speed of 5mm/min was selected. Portions of the tensile test samples were used to perform X ray analysis and the fractured zone of the Charpy samples were prepared for SEM analysis.

3 Results and discussion
Figure 1 shows the effects of the amount of clay addition on tensile strength. For all the samples studied, the higher values of yield strength were obtained for the samples with 5% of addition. The
increase up to 7% of addition resulted in a decrease of this mechanical property. Slightly higher values were displayed by Cuban bentonite. This result could be associated to the modification process effectiveness, with lower swellability values for the Brazilian bentonite. The pure HIPS showed a yield strength of 20 MPa; therefore, all the composites tested showed an effective reinforcement within 8 and 20% increment on tensile strength for a 5% organoclay addition.

A comparison of the yield strength obtained after EB radiation with the ones prior to the EB process showed that the reticulation process due to radiation increases the tensile strength. All the irradiated samples showed higher yield strength than the non-irradiated ones (Figure 3). The increase ranged between 31 and 36% above the value from the non-irradiated sample, but comparing it with the pure HIPS the increase was bigger, ranging from 46 to 55% above the yield strength of the pure material. Similar behaviors were found regarding Young modulus, and tensile strength.

The impact resistance decreased with the irradiation process (Table II), although the fracture zone displayed in figure 2 shows a fibrous surface consistent with a ductile fracture for both irradiated samples.

<table>
<thead>
<tr>
<th>Sample No</th>
<th>( a_k ) (J/m)</th>
<th>( a_k ) (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75</td>
<td>33.3</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>33.3</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>33.3</td>
</tr>
<tr>
<td>4</td>
<td>62.5</td>
<td>33.3</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>33.3</td>
</tr>
<tr>
<td>7</td>
<td>62.5</td>
<td>43.3</td>
</tr>
<tr>
<td>8</td>
<td>58.3</td>
<td>43.3</td>
</tr>
</tbody>
</table>

4 Conclusions

Composite materials reinforced with two types of organic bentonites and HIPS matrices were obtained and EB irradiated with a 600 kGy dose. The yield strength achieved increases above 30% regarding the non-irradiated samples, which is significant. No degradation was observed in the material, it indicates a feasible way of enhancing mechanical properties. The use of Cuban and Brazilian organoclays in a 5% load of the composite weight showed an efficient mode of strengthening HIPS.

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