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TRIBOLOGICAL STUDIES FOR COMMERCIALLY PURE GRADE 4 TITANIUM WITH DIFFERENT MICROSTRUCTURES, WITH AND WITHOUT COATING

ТРИБОЛОГИЧЕСКИЕ ИССЛЕДОВАНИЯ НА ТЕХНИЧЕСКИ ЧИСТОМ ТИТАНЕ GRADE 4 С РАЗЛИЧНОЙ МИКРОСТРУКТУРОЙ С ПОКРЫТИЕМ И БЕЗ ПОКРЫТИЯ

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Abstract. The paper presents experimental data on the tribological properties of commercially pure titanium with different microstructures with and without coating. As a result of the conducted experiments, it was established that the integral value of the friction coefficient, as well as its adhesion component, are structurally sensitive parameters. It is noted that the ultrafine-grained structure, obtained as a result of intense plastic deformation, contributes to the reduction of the coefficient of friction, as well as to the increase of the load-bearing capacity of tribo-conjugation.

KEY WORDS: COEFFICIENT OF FRICTION; SHEAR STRENGTH OF ADHESION BONDS, HARDNESS, INTENSE PLASTIC DEFORMATION, MICROARC OXIDATION, ION-PLASMA SPRAYING.

Introduction

According to the expert assessment, the use of strain-hardened commercially pure titanium in the field of medicine (as implants, tools, fasteners, etc.) is promising [1]. This is largely due to the fact that commercially pure titanium has a high biocompatibility, bioinertness, hypoallergenicity and is also non-toxic [2 - 5]. The applied deformation processing technologies make it possible to achieve a high-strength state due to the formation of ultrafine-grained (UFG) microstructure, which contributes to a significant increase in mechanical and functional properties [6, 7].

There are known works on the production of semi-products from commercially pure titanium for medical use with ultrafine-grained (UFG) structure, produced by high pressure torsion (HPT) [8 - 10], with subsequent application of a coating from titanium nitride [8, 9] and diamond-like carbon with zirconium [10]. At the same time, high strength of the material with improved tribological properties is achieved, but the samples have very small dimensions – a diameter of up to 5 - 8 mm and a thickness of less than 1 mm - which create significant limitations for their widespread use. In addition, it is difficult to conduct tribological tests on such samples.

Thus, for engineering applications, of great interest are technologies that make it possible to produce bulk (large-sized) nanostructured materials with unique physico-mechanical, performance and functional properties [1, 2, 11 - 14]. These technologies are based on the methods of equal-channel angular pressing (ECAP) [11, 14, 15], in particular, the ECAP-Conform process for the formation of UFG structures in large-sized long-length metallic materials (the principle is shown in Fig. 1).

![Fig. 1 Principle of the ECAP-Conform process for producing long-length semi-finished products with ultrafine-grained structure](image)

For large-sized samples, many aspects related to the study of functional properties, in particular tribological ones, remain open, depending on the structural state of commercially pure titanium. In addition, comparative tribological studies of the material with different microstructures with and without coatings are of practical interest.

1.1. Methods to evaluate the integral quantity of the friction coefficient and its adhesive component

For tribological studies, the two schemes are shown in Fig. 2.

![Fig. 2. Reciprocal test scheme: a) 1 - spherical indenter; 2 - the test sample; b) 1 - spherical indenter; 2 and 3 are test samples](image)

The first scheme for reciprocating motion (Fig. 2a) was used to estimate the friction coefficient in pairs "commercially pure titanium Grade 4 - chromium steel of composition Fe-1.5Cr-1.0C". This scheme was implemented on the tribometer “Nanovea TRB-1” (Fig. 3).

![Fig. 3. Tribometer “Nanovea TRB-1”](image)

For the tests we used samples in the form of a parallelepiped with a length of 25 mm and a section of 9.5 x 9.5 mm. For the indenter, we used bearing steel of composition Fe-1.5Cr-1.0C with a spherical contact surface with a diameter of 3 mm. The test conditions are as follows: temperature – room temperature; the displacement amplitude at a normal load of 5 N was 20 mm at 5000 cycles. Speed of movement was 30 cycles per min.
The second scheme (Fig. 2, b) was used to evaluate the shear strength of adhesive bonds and the molecular component of the friction coefficient. The test samples were made in the form of parallelepipeds with a section of 9.5 x 9.5 mm and a thickness of 5 mm, a spherical indenter with a sphere radius of 2.5 mm - from high-speed tool steel of composition Fe-6W-5Mo. Tests to determine the shear strength of adhesion bonds were carried out on a one-ball adhesion tester by the scheme shown in Fig. 2, b. In Fig. 4 shows a general view of the equipment for evaluating the strength of adhesion bonds.

The tests were carried out at a temperature of 20 °C on a one-ball adhesion tester [16]. This method is based on the physical model, which in the first approximation reflects the actual conditions of friction at the local contact.

According to this model, the spherical indenter 1 (simulating a single asperity of the contact spot of rubbing solid bodies), compressed by two plane-parallel samples 2 and 3 (with high accuracy and cleanliness of the contacting surfaces) rotates under load around its own axis. The force F expended on the rotation of the indenter is mainly due to the shear strength of the adhesion bonds.

The initial roughness of the contact surfaces of the test samples and indenter in both test schemes was \(0.06-0.16\) \(\mu\)m on the Ra scale. The test samples used for both schemes had a coarse-grained (CG) and ultrafine-grained (UFG) structure, obtained in the first case after annealing at 600 °C for 1.5 hours and, in the second case, after six cycles of severe plastic deformation (SPD) processing by ECAP-Conform.

For comparative tests via both schemes, one group of samples was without surface treatment (without coating), TiC coating was applied by ion-plasma spraying (IPS) to the surface of the other group of samples, and the surface of the third group of samples was treated by micro-arc oxidation (MAO) to producing of titanium oxide TiO₂.

The shear strength of adhesive bonds (MPa) was determined from the relationship:

\[
\tau_s = 0.75 \frac{M}{\pi \left( \frac{d_{1.2}}{2} \right)^2},
\]

where \(d_{1.2}\) are the diameters of indents on the tested samples, \(\text{mm}\); \(M\) is the moment of the indenter’s rotation, \(\text{Nm}\).

The adhesive (molecular) component of the friction coefficient was determined as:

\[
f_M = \frac{\tau_s}{p_r},
\]

where \(p_r\) – is the normal pressure, MPa

\[
p_r = \frac{p}{\pi \left( \frac{d_{1.2}}{2} \right)}
\]

where \(p\) is the force of sample compression, \(N\).

The high sensitivity of measurements is ensured by the absence of additional supports of the upper and lower samples. The standard values of the radius \((r=2.5\ \text{mm})\) of the spherical specimen (indenter) and the compressive force ensure that the conditions \(0.02 \leq \frac{h}{r} \leq 0.2\) (where \(h\) is the penetration depth), which mainly covers the range of the ratio of the microasperity depth to the radius at the vertex, characteristic for external friction. In this case, the pressure at the contact site can be considered as uniformly distributed (with an error of no more than 10%). The deformation of a spherical specimen that is harder than a plane sample is neglected.

### 1.2. Determinations of the friction coefficient under elastic contact conditions

The results of tribological tests according to the first scheme (Fig. 2, a) in the following friction pairs: "commercially pure Grade 4 titanium without coating - chromium steel of composition Fe-1.5Cr-1.0C"; "Commercially pure Grade 4 titanium with IPS coating - chromium steel of composition Fe-1.5Cr-1.0C"; "Commercially pure titanium Grade 4 coated with MAO - chromium steel of composition Fe-1.5Cr-1.0C" in Fig. 5. The material under investigation was of different microstructure: coarse (CG) after annealing and ultrafine-grained (UFG) after six cycles of severe plastic deformation by the method of equal-channel angular pressing (ECAP) combined with Conform (ECAP-Conform).

As it can be seen from the presented graph, the values of the friction coefficient obtained for annealed samples, both coated and uncoated, are higher (curves 1, 2 and 3) than for samples after 6 cycles of SPD processing by ECAP-Conform (Curves 1 ’, 2’ and 3 ’). And it is noted that the greatest effect, in terms of reducing the friction coefficient from the deformation-induced increase in strength, is observed on uncoated samples (curves 1 - 1 ’). For the sample with a CG microstructure, after 5000 cycles of action on the surface of the test specimen during reciprocating motion according to the scheme shown in Fig. 2, a, the friction coefficient is about 0.6, while for the UFG sample after 6 cycles of the SPD processing it decreases, approximately, to 0.4, which is an important indicator.

For samples with different microstructures with applied coatings, the effect of a sharp decrease in the friction coefficient is not observed (curves 2 - 2 ’ and 3 - 3 ’). But, nevertheless, we can see some decrease. Most probably, this is due to the fact that the coating itself has a greater effect on the tribological properties of commercially pure titanium, rather than the changes in the rheological properties of the substrate on which it is applied. It was noted that the TiO₂ coating formed on the surface of commercially pure titanium by its treatment with MAO technology is most preferable from the point of view of reducing the friction coefficient (curves 3 - 3 ’). In addition, it should be noted that in
the case of using this coating, a much shorter run-in area is observed, especially on a material with a UFG microstructure. This property, due to the high tribological properties of the MAO coating, is very important and attractive for medical implants that are in frictional contact.

Fig. 6 shows the friction paths after testing samples with different surface preparation.

The lowest values of the friction coefficient, as already noted above, are observed on a sample whose surface is treated with MAO technology to form titanium oxide TiO₂.

From the analysis of Fig. 6 it can be seen that the similarity of the friction paths on samples from commercially pure titanium Grade 4 without coating (a) and with ion-plasma coating (TiC) (b) is observed. Apparently, this is due to the fact that under the accepted conditions of the physical experiment, intensive abrasion of the coating and baring of the substrate material (commercially pure titanium Grade 4) occurs. The friction path shown in Fig. 6, c and formed on a sample with TiO coating, obtained by MAO technology, is a smooth trace without any breaks. This indicates the preservation of the integrity of the investigated coating and its high strength.

The visual analysis of the friction paths during tribological tests on samples with a UFG microstructure and an applied coating (see Figure 6, d, e, f) provided approximately the same results as we can observe on samples with a CG microstructure (see Figure 6, b, c). The friction paths on the samples with CG and UFG microstructures without coating are somewhat different. Thus, on a sample with a UFG microstructure (Fig. 6d), the trace is more "blurred" in comparison with the friction track on a sample with a CG microstructure (Fig. 6a). Most probably, the "blurring" of the friction path on the UFG sample is associated with a higher strength obtained as a result of SPD processing by ECAP-Conform.

Thus, from the point of view of tribological efficiency, the most interesting is the TiO₂ coating obtained by the microarc oxidation method, as well as the material (in this case, commercially pure titanium Grade 4) with a UFG microstructure.

1.3. Evaluation of the strength of adhesive bonds and determination of the adhesive component of the friction coefficient

Of great interest is the study of the shear strength of adhesion bonds as a function of pressure. Knowing the results of these studies, it is possible to calculate the adhesion component of the friction coefficient by formula (2). Figures 7 and 8 show the results of the evaluation of the shear strength of adhesive bonds of the material under study in the annealed state with CG and UFG microstructures, with different surface preparation.

The full-scale experiment was carried out on samples from commercially pure titanium with different microstructures and different types of surface preparation. For the indenter, we used tool steel of composition Fe-6W-5Mo. Samples with a CG microstructure were prepared by annealing at 600 °C for 1 hour. The UFG microstructure was obtained as a result of the 6-cycle SPD processing by ECAP-Conform via route Bc with a rotation by 90 ° around the longitudinal axis of the workpiece after each processing cycle. The average grain size was about 300 nm.

In addition, samples with CG and UFG microstructures were coated with a TiC coating by ion-plasma spraying (IPS) and oxide TiO₂ obtained using micro arc oxidation (MAO) technology. The tests were carried out at room temperature without lubricants.

Fig. 7 shows the imprints after exposure to the indenter on the samples.

From the figures shown, it is seen that in the indentation craters on the surface of the sample without coating (a), exposed surfaces are observed due to the formation of adhesive bridges with the indenter material. On the surface of the sample with TiC coating deposited by ion-plasma spraying, (b) there can also be seen exposed areas (light fragments in the photo) caused by the adhesive interaction of the materials of the sample and indenter. The most even and clean impression was obtained on a sample with TiO coating (c) obtained by MAO technology. For samples with a UFG microstructure (see Fig. 7, d, e, f), under the same surface treatment of commercially pure titanium approximately the same effects are observed, as for samples with a CG structure. The main difference between these samples is only the smaller diameters of the craters under the same normal load, which is due to the greater hardness of the material under study after SPD processing by ECAP. As a consequence, a higher hardness determines the greater load-bearing capacity of the tribocoupling.

As a result of the tribological tests and processing of the obtained data using formulae (1) and (3), the shear strength of adhesion bonds was plotted versus normal pressure, as shown in Fig. 8.
Table 1 presents the results of a comparative evaluation of the tribological characteristics in the friction contact "steel indenter from tool steel of composition Fe-6W-5Mo - commercially pure titanium" with different microstructure and surface preparation.

**Table 1. Influence of the structural state of commercially pure titanium and coatings on the tribological characteristics under extreme loading conditions**

<table>
<thead>
<tr>
<th>Structural state and surface treatment type</th>
<th>Tribological characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$p_{\text{max}}$ (MPa)</td>
</tr>
<tr>
<td>1. CG microstructure (without coating)</td>
<td>1605</td>
</tr>
<tr>
<td>2. UFG microstructure (without coating)</td>
<td>1988</td>
</tr>
<tr>
<td>3. CG microstructure with TiC</td>
<td>2158</td>
</tr>
<tr>
<td>4. UFG microstructure with TiC</td>
<td>2311</td>
</tr>
<tr>
<td>5. CG microstructure with TiO$_2$</td>
<td>2480</td>
</tr>
<tr>
<td>6. UFG microstructure with TiO$_2$</td>
<td>2937</td>
</tr>
</tbody>
</table>

where $\beta$ is the coefficient of molecular bond strengthening under the action of compressive stresses, $\tau_0$ is the shear strength of adhesive bonds in the absence of normal load.

Analyzing the tabular values and graphical dependences shown in Fig. 8, it was established that the lowest shear strength of adhesion bonds is observed on samples with both CG and UFG structures coated with titanium oxide using MAO technology. In this case, the bearing capacity of the UFG material is higher than that of the material with a CG microstructure (see Fig. 8, curves 5 and 6). As it can be seen from the presented results, the greatest shear strength of adhesion bonds is observed on a coarse-grained material without coating (curve 1). The TiC coating on the substrate with a CG structure (curve 3) demonstrates slightly lower shear strength of adhesive bonds and a higher load-bearing capacity.

Under the considered conditions, the lowest shear strength of adhesive bonds is in the contact pair "steel indenter from tool steel of composition Fe-6W-5Mo - commercially pure titanium Grade 4" with oxidized surface using MAO technology" (curves 5 and 6).

Moreover, in all variants of the test samples, a high load-bearing capacity is observed for a material with a UFG structure (curves 2, 4 and 6) compared to a similar surface treatment on samples with a CG microstructure (curves 1, 3, and 5). This observation is associated with the deformation-induced increase in the strength of the material under study - commercially pure titanium Grade 4.

Correlating results were obtained both in the determination of the integral value of the friction coefficient and in the evaluation of the adhesion component of the friction coefficient.

Thus, it can be stated that, from the considered options, the most acceptable type of surface treatment for commercially pure titanium, from the point of view of obtaining high tribological properties with relatively low shear strengths of adhesive bonds and high load-bearing capacity of the tribocoupling, is TiO$_2$ oxide coating deposited by microarc oxidation in combination with severe plastic deformation by ECAP-Conform.

**CONCLUSIONS:**

1. The coating itself has a greater effect on the tribological properties of commercially pure titanium, and not the change in the rheological properties of the substrate on which it is applied. It was noted that the TiO$_2$ coating formed on the surface of commercially pure titanium by its treatment with MAO technology is the most preferable from the point of view of reducing the friction coefficient. It is established that in the case of using this coating, a much shorter run-in area is observed, especially on a material with a UFG microstructure. This property, conditioned by the high tribological properties of the MAO coating, is very important and attractive for medical implants that are in frictional contact;

2. The friction path formed on a TiO$_2$-coated sample obtained using MAO technology is a smooth trace without any breaks. This indicates the preservation of the integrity of the investigated coating and its high strength;

3. The most acceptable type of surface treatment of commercially pure titanium Grade 4, from the point of view of obtaining high tribological properties with relatively low values of shear strength of adhesive bonds and high load-bearing capacity of tribocoupling, is TiO$_2$ oxide coating deposited by microarc oxidation in combination with severe plastic deformation by ECAP-Conform;

4. The correlation dependence between the values of the complex parameter of plastic frictional contact and the strength of adhesive bonds is established for the friction pairs "material under study - tool steel of composition Fe-6W-5Mo", which is described by a single dependence in a temperature range of 20-450 °C.

5. The temperature range of frictional interaction is defined for a number of investigated materials;

6. A regression formula is obtained, reflecting the analytical dependence of the experimentally obtained results;

7. The dependence between the adhesion component of the friction coefficient and the structural state of the deformed material in friction pairs "commercially pure titanium - steel of composition Fe-6W-5Mo" in plastic contact is established. From this dependence, it follows that the strength of adhesion bonds and the molecular component of the friction coefficient are structurally sensitive characteristics.

**ACKNOWLEDGEMENTS**

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TRANSFORMATION OF HETEROPHASE NON-METALLIC INCLUSIONS “PHASES ARE BESIDE” IN STEELS UNDER LASER ACTION

ТРАСФОРМАЦИЯ ГЕТЕРОФАЗНЫХ НЕМЕТАЛЛИЧЕСКИХ ВКЛЮЧЕНИЙ «ФАЗЫ РЯДОМ» В СТАЛЯХ ПРИ ЛАЗЕРНОМ ВОЗДЕЙСТВИИ

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Abstract. Melting and crystallization of heterophase non-metallic inclusions “phases are beside” was investigated. It was shown that under laser action the initial structure of inclusion-steel matrix boundaries transits into unstable equilibrium high-energy condition that cause development of the dissipation processes connecting with aspiration of system inclusion-matrix to the state with minimum of the free energy. In the result of the system heterophase inclusion-matrix transits to the state of unstable equilibrium which determines structure and properties of laser-quenched interphase boundary. Processes of melting, fusion and dissolution of non-metallic inclusions “phases are beside” and also of the melting of steel matrix play the great role in transformation of interphase inclusion-matrix boundaries under laser action.

KEYWORDS: HETEROPHASE NON-METALLIC INCLUSIONS “PHASES ARE BESIDE”, STEEL, STRENGTHENING, LASER TREATMENT

1. Introduction.
In steels, heterophase type inclusions are often present, where the phases seem to exist side by side - these are the inclusions of the “phases are beside” ph1 and ph2 (Fig. 1) [1-3]. Respectively, the interphase boundaries of the inclusion-matrix can be designated ph1↔m and ph2↔m. These type of heterophase inclusions is associated with the appearance of the first phase ph1 serving as a substrate for the crystallization of the second phase ph2; however, here ph2 is not a shell or a matrix of inclusions, but exists next to the ph1 phase. There is not necessarily a great difference in the melting points of the phases, they can be quite comparable. Often there are such variants as, for example, Al2O3 + MnO · Al2O3, TiN + TiCN, TiC + FeO · TiO2, FeO · Al2O3 + MnO · Al2O3, MgS + MnS and others.

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

Specimens made of wheel steel R7, 08Yu, 08T, 08Kp, 08Ch18N10T, ShCh15, NB-57, 12GS, E3 were irradiated by laser in GOS-30M installation with an excitation voltage of 2,5кV and pulse energy of 10, 18, 25 and 30J at heating rate of 10⁵ °C/s and cooling rate of 10⁶ °C/s with action time of (1,0, 2,5, 3,6, 4,2 и 6,0) 10⁻³ s. heterophase non-metallic inclusions “phases are beside” were identified by metallographic, X-ray microspectral and petrographic methods, see [1]. Distribution of elements and nanohardness of steel matrix near inclusions were determined.

3. Results and discussion.
Both phases of inclusions “phases are beside” in the moment of laser action are fully or partly melted. If the both phases are high-melting they are fused or partly melted (Fig. 2, a, b). Liquid phases are mixed under convective flows in micrometallurgical bath that is accompanied with interaction of components of both phases of inclusion and steel matrix across both interphase inclusion-matrix boundaries ph1↔m and ph2↔m and also across interphase boundaries inside inclusions ph1↔ph2. If the both phases are low-melting they are fully melted in the moment of laser action (Fig. 2, c). Liquid phases are mixed and supersaturated liquid solutions are formed then they are crystallized with high speed and zones of liqutation are formed too. If the phases of inclusion have very different temperatures of melting they show different behavior in the moment of laser action. Analysis discovered mutual mass transfer between each phase of inclusions and steel matrix and between both phases of inclusions “phases are beside”. Change of chemical composition on the surfaces of both phases of inclusions “phases are beside” and achievement limit of solubility of elements creates the conditions in each phase for transition of surface layer to liquid state with minimum expenditures of energy on the break of interatomic bonds.

Figure 1. Heterophase non-metallic inclusions “phases are beside” before laser action; х600

Figure 2. a) Heterophase non-metallic inclusions “phases are beside” after laser action; х600
Besides that interphase bound ary \( \phi_1 \leftrightarrow \phi_2 \) in the moment of \( \phi_1 \leftrightarrow \phi_2 \) and also breaks equilibrium shape of that boundary. Inclusion cause change of surface tension of interphase boundary inclusion-matrix boundary. In turn action of melted the phases of both phases of inclusion that breaks equilibrium shape of interphase inclusion-matrix boundaries \( \phi_1 \leftrightarrow m \) and \( \phi_2 \leftrightarrow m \) and also on the interphase boundary inside inclusion \( \phi_1 \leftrightarrow \phi_2 \) is increased considerably. Inner stresses in surface layers of both phases of inclusion control the development of melting process which happens in limited volume owing to preservation of contact between phases of inclusion and also between each phase of inclusion and steel matrix. Elementary act of the stresses relaxation causes activation and drawing in considerable number of atoms of both phases of inclusion to the process of disordered similar melting. In the moment of laser melting of inclusions “phases are beside” origin high degree of nonequilibrium of liquid phases (both phases of inclusion and steel matrix) and bifurcation instability of melt. This ensures gradient of vibration pressure on both interphase inclusion-matrix boundaries \( \phi_1 \leftrightarrow m \) and \( \phi_2 \leftrightarrow m \) and also on the interphase boundary inside inclusions \( \phi_1 \leftrightarrow \phi_2 \) (fully or partly liquid) which checks convective and abnormal flows of mass transfer. Considerable stresses appearing in thin surface layers of both phases of inclusion and steel matrix in the result of local heat flashes of laser radiation together with action of reactive forces of recoil by ejection from zone of treatment of liquid allows to high-temperature deformation of liquid interlayers continuing under crystallization during rapid cooling.

After high-speed melting of inclusions “phases are beside” happens the hyper-nonequilibrium crystallization connecting with formation of heavy supersaturated solid solutions with liquational zones (including liquation connecting with separation of liquid solutions) and also with microphases, nanophases and sometimes with amorphous phases of inclusions. Zones with ultrasmall grains, columnar shape of grains and liquation and also with mixed amorphous-nanocrystalline structures are formed in both phases of inclusions (Fig. 2, a - d). Evidently silicate compositions have tendency for amorphization mostly display but amorphization of another phases of inclusions was observed too. Besides that “satellite” particles in steel matrix near different phases of inclusion (Fig. 2, c) and new phases with different chemical compositions on interphase boundaries \( \phi_1 \leftrightarrow \phi_2 \) inside inclusions were observed (Fig. 2, f).

Sequence of heavy distortion areas on the surfaces of both phases \( \phi_1 \) and \( \phi_2 \) of inclusion “phases are beside” and also the movement of both parts of interphase boundary inclusion-steel matrix \( \phi_1 \leftrightarrow m \) and \( \phi_2 \leftrightarrow m \) and interphase boundary inside inclusion \( \phi_1 \leftrightarrow \phi_2 \) in the process of melting one can present with next image (Fig. 3). On the surfaces of both phases of inclusion saturating with elements of steel matrix the heavy disordered areas (the areas of melting) are formed (Fig. 3, a). The whole these areas pass into liquid steel matrix and are dissolved saturating it with elements of phases of inclusion. Character of saturating of steel matrix is different near various phases of inclusion. Position of the inclusion-steel matrix boundary is changed owing to melting in dependence on character of mass transfer between each phase of inclusion and steel matrix (Fig. 3, b, c).

Evidently one of phases of inclusion is melted scarcely earlier than other and its nucleuses of melting promote disordering and melting of interphase boundary inside inclusion. That promotes the melting of other phase of inclusion and its nucleuses of melting wholly pass to liquid zone on the interphase boundary inside inclusion (Fig. 3, c). Grain boundaries of the both phases of inclusion contacting with liquid steel matrix are melted more quickly than body of grains. It is possible the speed melting along grain boundaries of both phases of inclusion and their separation or “fracture” on the isolated grains is happened (Fig. 3, d, e). That will causes the transition of complexes of former grains (micrograins, nanograins) of both phases of inclusion into liquid state. These complexes of phases 1 and 2 are become the component of structure of liquid steel matrix and liquid layer on the boundary of phases of inclusion containing both complexes of phase of inclusion has complicated structure.
Figure 3. Schemes of laser melting of inclusions “phases are beside”: $\sigma_{b,1}$ – stresses on boundary between hard heavy distortion area of inclusion and liquid steel matrix, $\sigma_{b,disor}$ - stresses on boundary between disordered area and hard inclusion or liquid steel matrix, 1 – inclusion-matrix boundary, 2 – zone of steel matrix saturation with elements of inclusion, 3 – zone of phase 1 of inclusion saturation with elements of steel matrix, 4 – zone of phase 2 of inclusion saturation with elements of steel matrix, 5 – initial position of inclusion-matrix boundary, 6 – interphase boundary inside inclusion, 7 – zone of saturation of phase 1 with elements of phase 2 of inclusion, 8 – zone of saturation of phase 2 with elements of phase 1 of inclusion, 9 – initial position of interphase boundary inside inclusion.

Process of melting of the inclusions “phases are beside” is corresponded with the change of distribution of the forces near heavy disordered areas in the surface layers in both phases (Fig. 3, f, g). Action of liquid steel matrix causes the change of surface tension of both phases of inclusion ph1 and ph2 and that breaks equilibrium shape of both parts of interphase boundary ph1↔m and ph2↔m. Action of liquid phase 1 or liquid phase 2 of inclusion causes the change of surface tension of both phases and that breaks equilibrium shape of the boundary ph1↔ph2.

Previous studies have shown that in the process of pulsed laser action between nonmetallic inclusion and steel matrix, a high-speed exchange of atoms across the interface occurs under anomalously high mobility of atoms that does not meet the conditions of classical diffusion (anomalous mass transfer) [1,4,5]. The driving force of such an exchange in the case of heterophase inclusions is the drop in the chemical potentials of the elements contained in the various phases of inclusions in contact with the metal matrix and in the surrounding steel matrix. It is known that an important role in this process is played by the fact that the diffusion coefficients of the interstitial and replacement atoms that make up the matrix and the phases of inclusions in the conditions of laser action exceed the equilibrium value by an order of magnitude or more [1,4,5]. In addition, the factors of mass transfer are influenced by such factors and processes as the possibility of ionizing the atoms of steel components and inclusions under irradiation, heating to high temperatures and the movement of defects in the crystalline structure arising from thermal shock, melting and convective mixing, electronic and electromagnetic interaction of the phases of the inclusions and matrices, formation in the surface areas of inclusions of zones with an increased density of dislocations. Obviously, under nonequilibrium conditions of laser action, the directed mass transfer of elements across the boundaries of a two-phase inclusion-matrix is a complex quantity that depends on the level and inhomogeneity of the temperatures, stresses, chemical potentials of the inclusion phase elements and other factors. For heterophase inclusions of the “phases are beside” type, where both phases $\text{ph}_1$ and $\text{ph}_2$ of the inclusion are in contact with the metal matrix, the mass transfer rates of the element through the boundaries $\text{ph}_1 \leftrightarrow m$ and $\text{ph}_2 \leftrightarrow m$ will be different and each of them contributes to the total mass transfer rate of the element.

Peculiarities of the structure of saturated zones in steel matrix near heterophase non-metallic inclusions depends on their type. All heterophase non-metallic inclusions promote the heterogeneous strengthening of steel matrix. That connects with its microalloying from inner sources – the different phases of non-metallic inclusions and also with the origin of thermal
stresses, big density of crystalline defects and localization of relaxation processes having high-speed character. The interaction between phases of non-metallic inclusions and steel matrix promote the formation of complicated composite zones in the areas of saturating. Such zones consist of microstructural, nanostructural and amorphous elements.

Near inclusions “phases are beside” formation of saturated zones is controlled with both phases ph1 and ph2 of inclusions which are the sources of alloying of steel matrix. In the results near these inclusions the composite liquidation zones of a few types are formed: the cascade type with structure of layer composite; “spot” type with heterogeneous distribution of elements of phases ph1 and ph2 of inclusion and steel matrix; dispersed type with “satellite” particles; mixed layer-dispersed composite with cascade distribution of chemical elements of phases ph1 and ph2 of inclusion. Characteristic sign of saturated zones is various structures near different phases of inclusions having different behavior and abilities of their elements for the speed mass transfer to steel matrix in the moment of laser action.

The analysis of the sections of the steel matrix adjacent to the two-phase inclusions of the “phases are beside” type, where both phases ph1 and ph2 of the inclusion are contacted with the matrix, showed that their structure is non-uniform not only near each phase, but also near different phases of the same inclusion. Various variants of their structure are possible, revealed by thermal etching in the course of laser action. Near each of the two inclusion phases, this can be one, two, three saturation zones of the metal matrix (Figure 4).

The sections of the steel matrix adjacent to the inclusion are distinguished by the distribution of the chemical elements, which is established by microroentgen spectral analysis of the saturation zones (Fig. 5).

The results of a study of the distribution of nanohardness in the zones of saturation of the metal matrix adjacent to the phases of ph1 and ph2 inclusions of the “phases are beside” type showed that the nanohardness is much higher than its average value for the matrix far from the inclusions (Table 1). Of course, the level of nanohardness of each zone of the metal matrix is determined by the type of steel, since the degree of hardening in the process of laser action depends on its composition and structure. In the first saturation zone, the values of \( H^* \) at a pulse energy of 25 J and an exposure time of 3.6 \( 10^{-3} \) s at 1.35 ... 1.75 times higher than in the steel matrix far from the inclusion. In the second and third saturation zones, the values of the nanohardness of the steel matrix are lower than in the first zone, but exceed the values of \( H^* \) for the matrix far from the inclusions, respectively, in 1.35 ... 1.75 and 1.1 ... 1.3 times at a pulse energy of 25 J and exposure time 3.6. 10-3 sec. Obviously, a cascade distribution of the values of the nanohardness of the metallic matrix is observed at a distance from the phases \( \phi 1 \) and \( \phi 2 \) of the inclusion.
Figure 4. Distribution of elements near inclusions of the " phases are beside " type

Table 1.

Nanohardness values of the saturation zones of the steel matrix near the phases inclusions of the "phases are beside " type \( H_{sw} \) and far from them, \( H_{sw} \), as well as the coefficient (\( K_i \)) at a pulse energy of 25 J and an exposure time of 3.6. 10-3 s

<table>
<thead>
<tr>
<th>Inclusion ph1+ph2, steel, ( H_{sw} \times 10, \text{MPa} )</th>
<th>Phases of inclusion</th>
<th>Condition of phases under laser action*</th>
<th>( H_{sw} \times 10, \text{MPa} ) and (( K_i )) in zones</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiCN+TiO2, 08H18N10T, 340</td>
<td>TiCN solid/melted</td>
<td>liquid</td>
<td>459(1,35)/516(1,52) 408(1,2)/469(1,38) 418(1,23)</td>
</tr>
<tr>
<td>TiO2 liquid</td>
<td>TiO2 liquid</td>
<td>liquid</td>
<td>595 (1,75) 561 (1,65) 442 (1,3)</td>
</tr>
<tr>
<td>MnO - AlO3+ (Fe,Mn)S, 08Uy, 290</td>
<td>MnO - AlO3 solid/melted solid/liquid</td>
<td>392(1,35)/424(1,46) - / 377 (1,3) - / -</td>
<td></td>
</tr>
<tr>
<td>MnO - SiO2 liquid</td>
<td>MnO - SiO2 liquid</td>
<td>liquid</td>
<td>364 (1,4) 338 (1,3) 304 (1,17)</td>
</tr>
<tr>
<td>(Fe,Mn)O liquid</td>
<td>(Fe,Mn)O liquid</td>
<td>liquid</td>
<td>386 (1,33)/446 (1,54) 351 (1,21)/367 (1,27) - / -</td>
</tr>
<tr>
<td>MnO - AlO3 Solid/Melted Liquid</td>
<td>MnO - AlO3 solid/melted liquid</td>
<td>438 (1,51) 396 (1,37) -</td>
<td></td>
</tr>
</tbody>
</table>

The main factor for strengthening the phase-adjacent type of "phases are beside" the metal matrix is its microalloying from internal sources, which are the phases of ph1 and ph2 of nonmetallic inclusion. In this case, by forming local liquation zones near each inclusion phase, saturation zones of a cascade-type steel matrix are created, which are layered composite regions near the phase differences of nonmetallic inclusions.


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

5. Literature.

Abstract: Effects of additions of 0.0039, 0.01, 0.019 and 0.029 wt.% Sb on austenite transformation and the metallic matrix structure in the wall thicknesses of 3, 12, 25, 38, 75 and 100 mm of ductile iron casting containing 2.11 wt.% Si and a low amount of Cu, Sn and Mn were analyzed in this paper. In the examined ductile iron casting without the addition of Sb, the share of pearlite in the metal matrix was decreased and the share of ferrite was increased with increasing wall thickness. The share of pearlite was low. Additions of Sb increased the share of pearlite in all the walls. Increase of Sb content resulted in increasing the share of pearlite. Almost the same high share of pearlite in the wall thicknesses of 12, 25, 38, 75 and 100 mm was obtained by addition of 0.029 wt. % Sb (varied from 96.00 to 97.61 %). The additions of 0.01, 0.019 and 0.029 wt.% Sb were resulted in a fully pearlitic metallic matrix in the wall thickness of 3 mm. Iron carbides were found in the wall thickness of 3 mm when Sb was added.

Keywords: DUCTILE IRON CASTING, AUSTENITE TRANSFORMATION, METALLIC MATRIX STRUCTURE, ANTIMONY, MICROSTRUCTURE

1. Introduction

Ductile iron belongs to the family of cast irons containing graphite particles in the microstructure. These particles have a spheroidal (nodular) shape in a ductile iron and are not interconnected. This enables significantly better utilization of the mechanical properties of the metallic matrix than in the case of flake or vermicular shape of graphite particles. Due to these facts, ductile iron has significantly greater mechanical properties than other graphitic cast irons.

Metal matrix greatly influences the mechanical properties of ductile iron [1 - 4]. Another important factor is the graphite morphology [5 - 8]. In most cases, the metallic matrix is composed of ferrite or pearlite or ferrite + pearlite. Elongation and toughness of ductile iron increase with increasing the share of ferrite. On the other hand, an increase in the share of pearlite results in an increase in tensile strength and yield strength.

Chemical composition, the number and distribution of graphite nodules, and the cooling rate are the most important factors that affect the transformation of austenite and the structure of the metallic matrix of ductile iron [1, 2, 9, 10]. Sn, Cu, Mn, Ni, Cr, etc. are pearlite promoting elements. On the other hand, Si is a ferrite promoter. The share of ferrite in the metallic matrix generally increases with increasing the number of graphite nodules. Increasing the cooling rate increases the share of pearlite and decreases the share of ferrite.

Sb is pearlite promoting element [1, 2, 11 - 13]. Pearlite promoting effect of Sb can be seen from the pearlitic influence factor \( P_x \) [14, 15]:

\[
P_x = 3.0 \text{(wt.\% Mn)} - 2.65 \text{(wt.\% Si - 2.0)} + 7.75 \text{(wt.\% Cu)} + 90 \text{(wt.\% Sn) + 357 (wt.\% Pb) + 333 (wt.\% Bi) + 20.1 (wt.\% As) + 9.60 (wt.\% Cr) + 71.7 (wt.\% Sb)}
\]

Equation 1 shows that the Sb is considerably more powerful pearlite promoting element than Cu, which is most commonly used for increasing the share of pearlite in ductile iron. During solidification Sb is adsorbed on the surface of graphite nodules and forms a barrier that prevents the diffusion of carbon atoms from austenite to nodules during the cooling after solidification [1, 11, 16]. The high content of carbon remains in austenite. This results in the transformation of austenite to pearlite.

When we use Sb in ductile iron, we have to consider that it also affects the graphite morphology. The Sb content above 0.004 wt.% hinders the formation of spheroidal graphite, particularly in the thick walls [2]. It segregates to the intercellular regions where promotes the formation of very harmful intercellular flake graphite [1, 2, 17, 18]. Studies have shown that the detrimental effect of Sb on the graphite morphology can be neutralized by adding appropriate amount of RE elements [14, 18 - 20].

Real castings in most cases do not have a uniform thickness. The cooling rates of certain segments of casting vary due to differences in thickness. In this case the casting will not have a uniform structure of the metallic matrix. This means that the casting will not have the same properties in all areas. Uniform pearlitic metallic matrix is difficult to achieve in the ductile iron casting containing a thin, medium-thick and thick walls. The thick walls often contain a higher share of ferrite. It would be useful to investigate whether Sb can reduce variations in the structure of the metallic matrix in such castings. This paper deals with the influence of various Sb contents on austenite transformation and the structure of the metallic matrix in low-silicon ductile iron casting containing a thin, medium-thick and thick walls.

2. Experimental

Special low-manganese pig iron (50 wt.%), steel scrap (20 wt.%) and ductile iron returns (30 wt.%) were used for the production of the base iron. Melting was performed in a medium-frequency coreless induction furnace. Preconditioning of the base iron was carried out using commercial preconditioner containing 63 to 69 wt. % Si, 3 to 5 wt. % Al, 0.6 to 1.9 wt. % Ca, and 3 to 5 wt. % Zr. The addition of preconditioner was 0.1 wt. %. The Si content in the base iron was adjusted to achieve Si content between 2.0 and 2.2 wt.% in ductile iron melt.

FeSiMg treatment alloy containing 29 wt.% Mg, 42 wt.% Si, 1.4 wt.% Ca, 0.9 wt.% Al, 0.2 wt.% La and 0.5 wt.% Ce was used for graphite spheroidization, i.e., nodularization in the Cored wire process. The first step of inoculation was performed at the same time by the addition of the commercial inoculant containing 67 to 72 wt. % Si, 1.5 wt. % Ca, 1.9 wt. % Al, and 2.2 wt. % Ba. The addition of inoculant was 0.5 wt. %.

The step wedge test block (SWTB) consisted of seven walls with the following thicknesses: 3, 12, 25, 38, 50, 75 and 100 mm (Fig. 1). Five step wedge test blocks were casted in green sand molds. The second step of inoculation was performed during the pouring of the ductile iron melt into the molds. Commercial inoculant containing 70 to 76 wt. % Si, 0.75 to 1.25 wt. % Ca, 0.75 to 1.25 wt. % Al and 1.5 to 2 wt. % Ce was added to the melt stream in the amount of 0.2 wt.%. The first SWTB was casted without the addition of Sb. Pure Sb (99.99 wt.%) was added in second, third, fourth and fifth SWTB along with inoculant. Targeted Sb contents are shown in Tab. 1.

Samples for determining the contents of C, Si, Mn, P, S, Cr, Mo, Ni, Cu, V, W and Mg were taken immediately before pouring.
the ductile iron melt into molds. The contents of these elements were determined by optical emission spectrometry (OES). Samples for determining the contents of Sb, Ce, La, Nd, Pr, Gd, Sm, Y, Sn, Ti, Cd, Bi, Zr, Nb, Ca, Co, As, Pb and Al were cut from the step wedge test blocks. The contents of these elements were determined by inductively coupled plasma mass spectroscopy (ICP-MS).

Fig. 1 Schematic show of the step wedge test blocks and places where samples for metallographic analysis were taken.

Table 1: Additions of inoculant in melt stream during pouring into the mold and the targeted Sb contents.

<table>
<thead>
<tr>
<th>Step wedge test block (SWTB)</th>
<th>Additions of inoculant in melt stream, wt. %</th>
<th>Targeted Sb contents, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWTB 1</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>SWTB 2</td>
<td>0.2</td>
<td>0.005</td>
</tr>
<tr>
<td>SWTB 3</td>
<td>0.2</td>
<td>0.01</td>
</tr>
<tr>
<td>SWTB 4</td>
<td>0.2</td>
<td>0.02</td>
</tr>
<tr>
<td>SWTB 5</td>
<td>0.2</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Fig. 1 shows places where samples for metallographic analysis were taken. Light metallographic microscope with a digital camera and the image analysis system was used for the analysis of microstructure of samples.

3. Results and discussion

The chemical compositions of step wedge test blocks are shown in Tab. 2.

Table 2: Chemical composition of examined step wedge test blocks (\( P_x \) - pearlitic influence factor (defined by the Eq. (1)).

<table>
<thead>
<tr>
<th>Step wedge test block (SWTB)</th>
<th>Chemical composition, wt.%</th>
<th>( P_x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWTB 1</td>
<td>C-3.55; Sr-2.11; Mn-0.098; P-0.035; S-0.012; Mg-0.048; Cu-0.0025; Al-0.002; Sb-0.0042</td>
<td>1.14</td>
</tr>
<tr>
<td>SWTB 2</td>
<td>0.018; Cr-0.029; Mo-0.002; Ni-0.016; V-0.01; W-0.005; Sn-0.005; La-0.0045; Pr-0.00000038; Nd-0.000012; Sm-0.0000017; Gd-0.0000003; Bi-0.000011; Ph-0.00052; As-0.00015; Ti-0.0169; Nb-0.0039; Zr-0.00029; V-0.000014; Ca-0.0048; Co-0.016; Cd-0.000017</td>
<td>2.47</td>
</tr>
<tr>
<td>SWTB 3</td>
<td>0.0034; 0.016; 0.019</td>
<td>3.19</td>
</tr>
</tbody>
</table>

It can be seen that the targeted Sb contents and targeted Si content were achieved. Yield of Sb was varied from 69.6 to 95.8 %. Low Si content was chosen because it adversely affects the graphite morphology in the thick walls and promotes the formation of ferrite. RE elements (Ce and La) were added through the inoculant and FeSiMg treatment alloy because these elements neutralize the harmful (antinodularizing) effect of Sb on the morphology of graphite. In addition, these elements increase the nodule count in thin walls, which is important for preventing the formation of carbides in these walls. The data in Tab. 2 show that the content of carbide promoting elements was low. With the exception of Sb, the content of other pearlite promoting elements was low. Pearlitic influence factor \( P_x \) (defined by the Eq. (1)) significantly increases with increasing Sb content.

The obtained results of metallographic analysis indicate that the wall thickness and the Sb content have a very significant effect on the structure of the metallic matrix in ductile iron castings (Figs. 2 and 3). In SWTB 1, where Sb was not added, the share of ferrite in the metallic matrix increases, and the share of pearlite decreases with increasing wall thickness due to decrease in the cooling rate. The share of pearlite is low (varies from 11.92 % (in the wall thickness of 100 mm) to 32.95 % (in the wall thickness of 3mm)). Addition of Sb increased the share of pearlite in all the walls (SWTB 2 – 5). The share of pearlite increases with increasing Sb content.

Fig. 2 Optical micrographs of the central part of the wall thicknesses of 3, 12, 25, 38, 50, 75 and 100 mm at various Sb contents (etched in Nital).

Fig. 3 Effect of Sb addition on the share of pearlite in the metallic matrix of the wall thickness of 3, 12, 23, 38, 50, 75 and 100 mm.
Addition of only 0.0039 wt.% Sb in SWTB 2 increased the share of pearlite in all the walls compared to SWTB 1 (Figs. 2 and 3). The effect is more pronounced in the wall thicknesses of 3, 12, 25, 38 and 50 mm. The share of pearlite is not significantly increased in the wall thicknesses of 75 and 100 mm. It is obvious that the thicker walls require a higher Sb addition due to very slow cooling. Iron carbides are present in the wall thickness of 3 mm. Since the wall thickness of 3 mm in SWTB 1 does not contain carbides, obtained results indicate that Sb promotes the formation of iron carbides in very thin walls when the Si content is low because it lowers the stable and metastable eutectic temperatures.

Increase of Sb content to 0.01 wt.% (SWTB 3) resulted in a further increase in the share of pearlite in all the walls (Figs. 2 and 3). The variations in the share of pearlite between the walls are significantly lower than in SWTB 1 and SWTB 2. Fully pearlitic-metallic matrix is obtained in the wall thickness of 3 mm. The share of pearlite in the wall thicknesses of 25, 38, 50, 75 and 100 mm is greater than 80 % (varies from 83.67 % to 91.59 % depending on the wall thickness and nodule count). Nodule count increased with decreasing wall thickness and influenced the formation of pearlite. Increasing the share of pearlite is slightly lower in the wall thickness of 12 mm due to the high nodule count. It is obvious that a high nodule count facilitates the formation of ferrite and hinders the formation of pearlite. Therefore, required addition of Sb for obtaining pearlitic-metallic matrix increases with an increase in the nodule count. The share of iron carbides is greater than in SWTB 2 due to higher Sb content.

The share of pearlite greater than 90 % was obtained in the wall thicknesses of 12, 25, 38, 50 and 75 mm in SWTB 4 by the addition of 0.019 wt.% Sb (Figs. 2 and 3). In the wall thickness of 100 mm, the share of pearlite is slightly lower than in the other walls. Fully pearlitic-metallic matrix is obtained in the wall thickness of 3 mm. The variations in the share of pearlite between the walls are further decreased. The share of iron carbides in the wall thickness of 3 mm is further increased due to increase in Sb content.

Very uniform pearlitic-metallic matrix was obtained in SWTB 5 containing 0.029 wt.% Sb (Figs. 2 and 3). Fully pearlitic-metallic matrix is obtained in the wall thickness of 3 mm. Almost the same share of pearlite was obtained in the wall thicknesses of 12, 25, 38, 50, 75 and 100 mm (varies from 96.00 to 97.61 %). Ferrite is present only in a narrow area around the nodules. It is obvious that sufficiently high Sb content eliminates the influence of the cooling rate and the nodule count on the share of ferrite in the metallic matrix. Due to higher Sb content, share of iron carbides in the wall thickness of 3 mm is further increased.

Fig. 2 shows that all Sb additions had a positive effect on the graphite morphology, except in the wall thickness of 3 mm. The effect is more pronounced in the thick walls. Nodularity and nodule count were significantly increased in the wall thicknesses of 50, 75 and 100 mm. This indicates that the content of RE elements (Ce + La) was sufficient considering the added amounts of Sb (wt.% Ce + wt.% La was varied from 0.00325 to 0.00385 wt.%). RE elements react with Sb and neutralize its harmful effect on the graphite morphology [18, 21, 22]. Nucleation potential of the melt is improved at the same time, because formed intermetallic compounds act as nucleation sites for graphite [18, 21, 22].

4. Conclusions

Obtained results show that the Sb is a very effective element for increasing the share of pearlite in the metallic matrix of thin, medium-thick and thick walls of ductile iron castings. Required addition of Sb for obtaining pearlitic-metallic matrix increases with increasing wall thickness and nodule count. Sb reduces variations in the structure of the metallic matrix of ductile iron castings. It allows to obtain a uniform pearlitic-metallic matrix in ductile iron castings containing a thin, medium-thick and thick walls. This reduces the variations in mechanical properties in the casting. RE elements (Ce and La) neutralize the deleterious effect of Sb on the graphite morphology in ductile iron castings. Moreover, when Sb is added together with the appropriate amount of RE elements, it increases the nodule count and nodularity in medium thick and thick walls. This positive effect of Sb on the graphite morphology is significantly more pronounced in the thick walls.

In addition to the identified positive effects of Sb, one negative effect was also found. Already very low Sb content promotes the formation of iron carbides in a very thin wall (3 mm) when the Si content is low.

5. References

STRUCTURAL FORMATION OF HIGH-HEAT-CONDUCTING POLYMER MICRO- AND NANOCOMPOSITES IN THE PROCESSES OF THEIR CRYSTALLIZATION

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Abstract: The results of experimental and theoretical studies of the crystallization regularities of polymer micro- and nanocomposite materials based on polyethylene, polypropylene and polycarbonate filled with high-heat-conducting fillers - carbon nanotubes, microparticles of aluminum or copper are presented. The mechanisms of structure formation at the stage of the formation of individual ordered structures in the material and the formation of such subregions in the entire volume of the polymer composite were established based on the analysis of the crystallization exotherms obtained within the scope of the nucleation equation and Kolmogorov-Avrami.

Key words: POLYMER MICRO- AND NANOCOMPOSITES, MECHANISMS OF STRUCTURE FORMATION, HIGH-HEAT-CONDUCTING COMPOSITES.

1. Introduction

The effectiveness of the use of polymer micro- and nanocomposite materials in engineering practice is largely due to their characteristics, such as a wide range of heat-conducting properties, increased corrosion resistance, low specific weight, etc. [1-10]. Thus, the high heat-conducting properties of these materials determine the prospects of their use for the manufacture of heat exchange surfaces for various purposes, elements of electronic equipment, etc. Increased corrosion resistance of polymer composites allows their operation in various aggressive environments. A relatively small specific weight makes it possible to create from these materials details and nodes of different equipment with low mass size parameters, etc.

One of the important trends in expanding the fields of application of polymer micro- and nanocomposite materials is the use of their high-heat-conducting modifications. The tasks of developing such materials require in-depth investigations aimed at studying the features of their structure formation in the crystallization processes, which to a large extent determines the properties of the resulting materials.

This article is devoted to experimental and theoretical studies of the regularities of the structure formation of a wide class of high-heat-conducting polymer micro- and nanocomposite materials.

2. Prerequisites and means for solving the problem

The research task included the establishment of mechanisms of structure formation during cooling of polymer composites from the melt. These mechanisms were subject to consideration at the stage of nucleation of individual structurally ordered subregions (nucleation stage) and at the stage of formation of such subregions in the entire volume of the composite (the crystallization stage in the volume of the material as a whole). The studies were carried out for polymer composites based on polyethylene (PE), polypropylene (PP) and polycarbonate (PC) filled with carbon nanotubes (CNTs) or microparticles of aluminum or copper with a change in their mass fraction from 0.2 to 4% and varying the cooling velocity of the composite from 0.0083 K/s (0.5 K/min) to 0.333 K/s (20 K/min).

The experimental-theoretical technique used to establish the mechanisms of structure formation involved two stages, the first of which consisted in the experimental determination of the solidification exotherms of the composite when it was cooled from the melt at a given constant velocity. Here, the specific heat flux \( Q \) removed from the composite was determined in a dry nitrogen atmosphere by differential scanning calorimetry method on a Perkin Elmer DSC-2 unit with modified IFA Gmb, Ulm software. In this case, the sample placed in the cell was heated to a temperature exceeding the melting point of the matrix by approximately 50 K, held at this temperature for 180 s and then cooled to a temperature of 400 K at a fixed cooling velocity \( V_c \). Samples were prepared by the method of hot pressing the composition obtained as a result of mixing in magnetic stirrer its components that are in a dry state.

The second stage of the applied technique consisted in the theoretical determination, based on the experimental data obtained, of the structure formation characteristics at the stage of formation of separate ordered structures (the nucleation stage) in the material and in determining the formation parameters of such structures at the stage of their formation in the entire volume of the composite. At the initial stage, the corresponding analysis was carried out using the nucleation equation.

\[
\ln \left[ V \left( (m+1)T_n - T_0 \right) \right] / T_n^2 (\Delta T)^m = \ln \left[ K_n(a_n - a_0) / T_n (\Delta T) \right] + \ln \left[ (m+1) / T_n^2 \right] / T_n (\Delta T)
\]

where \( m \) - is the dimensionless parameter of the form; \( T_n \) - temperature of the beginning of crystallization; \( \Delta T \) - temperature range of crystallization; \( T_m \) - is the melt temperature corresponding to the maximum value of the heat flux \( Q \) on the crystallization exotherm; \( K_n \) - reduced transport barrier; \( a_m \) is the reduced nucleation parameter.

At the stage of crystallization in the entire volume of the composite as a whole, the determination of the parameters of the structure formation was carried out on the basis of the standard and modified Kolmogorov-Avrami equation

\[
\alpha(t) = 1 - \exp(-K_n t^\mu)
\]

Here \( \alpha(t) \) - is the relative volume fraction of the crystalline phase; \( t \) - is the reduced time, \( t = V_c / t \); where \( t \) - is time; \( f \) - is the relative fraction of the crystallization mechanism associated with crystallization on polymer density fluctuations; \( K_n \) - is the effective velocity constant; \( n \) - is the pseudo-parameter of the form; \( n' \) - are the values of \( n \) corresponding to the crystallization on density fluctuations of the polymer and the filler particles, respectively.

The fillers used in the polymer composite materials studied corresponded to the following geometric characteristics. For CNTs obtained by the chemical vapor deposition method, their outer diameter is 20 nm, the length is from 1 to 5 \( \mu \)m, the wall thickness is 5 nm, and the specific surface area is 190 m\(^2\)/g. Dimensions of microparticles of aluminum and copper were in the range 0.5 ... 1 \( \mu \)m. They were obtained from the corresponding sawdust by grinding in a ball mill.

Results and discussion

An analysis of the results of the experimental studies carried out to determine the exotherm of crystallization showed that for all the composites under consideration there is a generally similar pattern of change of these exotherms as a function of the cooling velocity \( V_c \) and the mass fraction \( \alpha \) of the filler. In Fig. 1 and Table 1 as an example, the corresponding data for a polycarbonate filled with aluminum microparticles are given. Here, first of all, a very significant decrease in the maximum of the specific heat flux \( Q_{max} \) taken from the composite with an increase in the cooling velocity \( V_c \).
is noticeable, with a shift of this maximum position on the curve \( Q = f(T) \) to lower temperatures. Thus, for a microcomposite containing 0.2% aluminum, the value \( Q_{\text{max}} = 1.84 \text{ W/kg at } V_i = 0.0083 \text{ K/s and decreases to } 1.02 \text{ W/kg at } V_i = 0.333 \text{ K/s.} \) As for the temperature \( T_N \) corresponding to the heat flux \( Q_{\text{max}} \), for the indicated velocities \( V_i \), it is 463.5 K and 448.9 K, respectively.

An increase in the cooling velocity \( V_i \) of the composite also leads to a decrease in the temperatures of the beginning of the \( T_N \) and the end of the \( T_K \) crystallization. In this case, the temperature range of the crystallization \( \Delta T \) (\( \Delta T = T_N - T_K \)) is markedly increased. For example, for a composite based on polycarbonate containing 4% aluminum microparticles, this \( \Delta T \) interval is 7.7 K at \( V_i = 0.0083 \text{ K/s and reaches 17.2 K at } V_i = 0.333 \text{ K/s.} \)

![Figure 1](image)

**Figure 1.** Crystallization exotherms for polymer composite materials based on polycarbonate filled with aluminum microparticles with filler content \( \omega = 0.2\% \) (a), 1.0 \( \% \) (b) and 4.0\% (c) at different cooling velocity of the composite from melt: 1 - \( V_i = 0.0083 \text{ K/s; 2 - 0.0333 K/s; 3 - 0.0833 K/s; 4 - 0.333 K/s.} \)

<table>
<thead>
<tr>
<th>( \omega, % )</th>
<th>( T_{Nc}, K )</th>
<th>( T_{c}, K )</th>
<th>( T_{f}, K )</th>
<th>( \Delta T, K )</th>
<th>( Q_{\text{max}}, \text{ W/kg} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>467.5</td>
<td>460.0</td>
<td>460.0</td>
<td>7.5</td>
<td>1.79</td>
</tr>
<tr>
<td>0.2</td>
<td>468.0</td>
<td>463.5</td>
<td>460.6</td>
<td>7.4</td>
<td>1.84</td>
</tr>
<tr>
<td>1</td>
<td>468.7</td>
<td>463.8</td>
<td>460.5</td>
<td>8.2</td>
<td>1.81</td>
</tr>
<tr>
<td>4</td>
<td>468.5</td>
<td>464.4</td>
<td>463.7</td>
<td>7.7</td>
<td>1.75</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( V_i )</th>
<th>( V_i = 0.0083 \text{ K/s} )</th>
<th>( V_i = 0.0333 \text{ K/s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>465.2</td>
<td>460.0</td>
</tr>
<tr>
<td>0.2</td>
<td>465.7</td>
<td>460.5</td>
</tr>
<tr>
<td>1</td>
<td>466.3</td>
<td>460.8</td>
</tr>
<tr>
<td>4</td>
<td>466.2</td>
<td>460.4</td>
</tr>
</tbody>
</table>

As can be seen from the data presented in Fig. 1 and in Table 1, with an increase in the mass fraction of the filler from 0.2 to 4.0\%, for all values of the cooling velocity \( V_i \), a certain decrease in the value \( Q_{\text{max}} \) occurs. In this case, there is a transformation of the monodalous type on the curve \( Q = f(T) \) to the bimodal one.

On the basis of the experimental data on the crystallization kinetics of composite materials for the initial stage of crystallization - the nucleation stage, the crystal formation dimension \( m \) was determined from the results of solving the nucleation equation (1). The obtained data showed that for all the composites studied, there are two mechanisms of structure formation: two-dimensional, planar, \( (m = 1) \) and three-dimensional, volumetric \( (m = 2) \) in the investigated mass fraction of the filler. In this case, the three-dimensional mechanism predominates over the planar one.

As for the second stage of crystallization (crystallization throughout the volume of the composite), experimental crystallization exotherms were considered under the assumption of present of two mechanisms of crystal formation, the first of which is associated with the crystallization of the polymer matrix (which is realized on polymer density fluctuations) and the second of which with crystallization in which the filler particles play the role of its centers. Accordingly, the results of experiments on the kinetics of crystallization were analyzed according to the Kolgomorov-Avrami equations (2) and its modified version (3). The data obtained (Table 2) indicate that for composites based on the polyethylene, both mechanisms are volumetric \( (n \approx 3) \) for all fillers in the entire range of variation of \( \omega \). For composites based on PP and PC, crystallization on density fluctuations of a polymer occurs by the mechanism of a strained matrix. Regarding the mechanism of crystallization on the filler particles, for these polymers, when they are filled with copper microparticles, it is the same as for the polymer matrix. The same mechanism is also preserved for PP-based composites filled with aluminum microparticles.
Table 2. Parameters of the structure formation (n', n'') in the crystallization stage in the volume of polymer composites based on polyethylene, polypropylene and polycarbonate for different filler content  \( \omega \) of fillers (CNTs, microparticles of copper or aluminium) for different cooling velocity \( V_e \), K/min.

<table>
<thead>
<tr>
<th>( V_e ), K/min.</th>
<th>Matrix PE</th>
<th>Fillers</th>
<th>CNTs</th>
<th>Copper</th>
<th>Aluminum</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1.0</td>
<td>4.0</td>
<td>0.2</td>
<td>1.0</td>
<td>4.0</td>
</tr>
<tr>
<td>( \frac{n^*}{n''} )</td>
<td>( \frac{n^*}{n''} )</td>
<td>( \frac{n^*}{n''} )</td>
<td>( \frac{n^*}{n''} )</td>
<td>( \frac{n^*}{n''} )</td>
<td>( \frac{n^*}{n''} )</td>
</tr>
<tr>
<td>0.5</td>
<td>0.32</td>
<td>0.31</td>
<td>0.32</td>
<td>0.29</td>
<td>0.31</td>
</tr>
<tr>
<td>2</td>
<td>3.3</td>
<td>3.0</td>
<td>3.2</td>
<td>2.8</td>
<td>3.1</td>
</tr>
<tr>
<td>5</td>
<td>3.2</td>
<td>3.1</td>
<td>3.1</td>
<td>3.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Conclusions

For polymer micro- and nanocomposite materials based on polyethylene, polypropylene and polycarbonate filled with high-heat-conducting fillers (carbon nanotubes or aluminium or copper microparticles) using exotherm crystallization obtained crystallization mechanisms are established for two stages of structure formation in the range of changes in the mass fraction of the filler from 0.2 to 4% and the cooling velocity of composites from the melt in range from 0.5 to 20 K/min. Wherein:

1. At the initial stage of crystallization, based on the results of the solution of the nucleation equation, the presence of two mechanisms of structure formation, planar and volumetric, is shown, with a certain predominance of the latter for all investigated composites.

2. In the second stage of crystallization (the stage of crystallization in the entire volume of the composite), the investigations were performed assuming the presence of two crystal formation mechanisms, the first of which is associated with the crystallization of the polymer matrix proper, the second with crystallization, in which the microparticles of the filler play the role of its centers. According to the results of the analysis performed using the modified Kolmogorov-Avrami equation, it was shown that at this stage the crystallization mechanisms can depend substantially on the type of polymer matrix and filler, its mass fraction and the cooling velocity of the composite from the melt.

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DEVELOPMENT OF NEW NANOSIZED SOL GEL COATINGS ON STEEL WITH ENHANCED CORROSION RESISTANCE

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Abstract: Sol gel method is a simple a low cost technique, which gives possibility to deposit coatings with definitely chemical and phase composition at low temperatures. Here we report an application of sol gel method by dip coating technique to prepare a several type of nanosized coatings: (a) one-component coatings such as TiO₂ and Nd doped TiO₂; (b) two types of bi-component layers, which contain as underlayer SiO₂ and upper layer TiO₂ or CeO₂. The coatings were characterized by XRD, SEM and AFM analyses. The XRD data revealed good candidates due their excellent chemical stability. There are several methods of corrosion control: inhibitors, cathodic procedures (dipping-drying) were repeated and then the deposits were treated at 500° C for 1 hour. These steps are repeated two times. For SiO₂/CeO₂ (SC) samples on silica sol gel under-layer 3 CeO₂ layers were deposited using Ce(NO₃)₃⋅6H₂O ethanolic solution, then was dried sequentially at 300°C. These steps were repeated two times. For SiO₂/TiO₂ (ST) samples on SiO₂ under-layers 3 CeO₂ layers were deposited using Ce(NO₃)₃⋅6H₂O ethanolic solution, then was dried sequentially at 300°C. These steps are repeated 3 times, ending finally with calcination at 500°C. The same procedure was applied for the preparation of SiO₂/TiO₂ (ST) samples, using as precursor titanium tetraisopropoxide (TTIP); Ti(OC₃H₇)₄.

Keywords: Sol gel method, nanomaterials, nanosized coatings

1. Introduction

It is well known that the majority of metals and alloys even stainless steel are susceptible to corrosion attack in medium which contains halide ions. In order to overcome this problem, several barrier oxide coatings could be deposited on the metals. Among them, the most widely studied are CeO₂, TiO₂, ZrO₂, SiO₂ etc [1-3] The method for deposition of these coatings could be physical or chemical. Contrary to the physical deposition methods, the sol-gel method has the advantages of high chemical homogeneity, low cost, effectiveness and feasibility for mass production. During the last years a new approach is applied-deposition of coatings composed by 2 or 3 types of oxides, which deposited over the other. The new multilayer materials blend the advantages of the individual component oxides. It was proved by Alat et al. that the multicomponent coatings exhibit higher anticorrosion resistance than one component. [4] The aim of this study is to compare the corrosion properties of one-component TiO₂ coatings and bi-component CeO₂ or TiO₂ coatings, on silica sol gel underlayer, which are prepared by dip coating technique.

2. Prerequisites and means for solving the problem

The stainless steel are widely used in all world infrastructures, but due to the electrochemical reactions in the environment the corrosion process of steels proceeds spontaneously and can not measure or control it. In this The efforts of researchers is to provide more effective corrosion protection of steel. This can be overcome by using of protective inorganic layers deposited on the steel. There are several methods of corrosion control: inhibitors, cathodic protection and applying of protective organic or inorganic coatings. The ceramic nanosized oxide coatings are potential good candidates due their excellent chemical stability.

3. Solution of the examined problem

Taking into account the excellent pysicochemical properties of CeO₂ and TiO₂ (chemical stability, high corrosion resistance, thermal and mechanical properties etc.), we have chosen these oxides in order to apply them as protective films against corrosion. As the bi-component coatings combines the advantages of the both constituents we have examined and compare the barrier properties against the corrosion of one component TiO₂ coatings coatings and bicomponent CeO₂ or TiO₂ coatings, deposited over silica sol gel underlayer.

3.1. Experimental procedure for one component oxide coatings

Titanium isopropoxide (TTIP); Ti(O(C₂H₅)₃)₄, 98% purity, (Acrros) and AcAc were dissolved in 2-propanol under vigorous stirring. (sol A) The molar ratio of components is TTIP: iPrOH: H₂O: AcAc = 1: 30: 1: 1. The resulting sample was denoted as TP. For doped TiO₂ coatings, definite quantity of Nd₂O₃ was dissolved in 2 ml of nitric acid and isopropanol and was added to sol A to obtain TiO₂ doped with 1at% Nd. (Sample TP-1). After cleaning the steel substrates in acetone, they were dipped into each of the precursor solutions and held for 10 seconds, then withdrawn (velocity 30 mm/min). After each deposition, the samples were air-dried in two stages: first at 100°C, after which the temperature is raised to 300°C for 1 hour. These procedures (dipping-drying) were repeated and then the deposits were treated at 500°C for 1 hour.

3.2. Experimental procedure for bi-component oxide coatings

The SiO₂ under-layers were applied from a solution of tetraethylorthosilane (TEOS) in a mixture of ethanol, water and hydrochloric acid as a catalyst. The molar ratio H₂O: TEOS is 3.7. The solution undergoes aging for 7 days. The metal substrates are immersed into the solution and withdrawn at a constant rate of 3 cm / min and then dried at 60°C and at 90°C and finally treated at 300°C. These steps are repeated two times. For SiO₂/CeO₂ (SC) samples on SiO₂ under-layers 3 CeO₂ layers were deposited using Ce(NO₃)₃⋅6H₂O ethanolic solution, then was dried sequentially at 300°C. These steps are repeated 3 times, ending finally with calcination at 500°C. The same procedure was applied for the preparation of SiO₂/TiO₂ (ST) samples, using as precursor titanium tetraisopropoxide (TTIP); Ti(OC₃H₇)₄.
3.3. Characterization

The phase compositions of the samples were studied by X-ray diffraction (XRD) with CuKα-radiation (Philips PW 1050 apparatus). The surface topography was studied by means of Atomic Force microscope (AFM) (NanoScopeV system, Bruker Inc.) operating in tapping mode in air. The scanning rate was set at 1 Hz. Subsequently, all the images were flattened by means of the Nanoscope software. The AFM images are calculated. The roughness analysis gives the value Rₐ, which is an arithmetic average of the absolute values Zₗ of the surface height deviations measured from the mean plane, while the image Rₜ is the root mean square average of height deviations taken from the mean image data plane. A scanning electron microscope (SEM) Philips 515 was used for morphology observations of the films.

3.4. Corrosion test

The chemical corrosion resistance of the investigated samples and uncoated stainless steel (reference sample) were studied using salty corrosive solution of 3.5% NaCl at 25°C (EN ISO10289/2006. The temperature of solution and the air temperature were controlled by calibrated thermometers. The mass weight loss was estimated after 200 hours of corrosion attack.

4. Results and discussion

X-ray diffraction analyses data showed that a nanocrystalline phase of the anatase was formed after isothermal heating, of non-doped TiO₂ coatings (PDF78-2486), (Fig. 1). The XRD patterns of neodymium doped TiO₂ coatings show a decrease in the (101) peak intensity of the anatase phase, i.e. neodymium dopant suppresses the crystallization process. The sizes of the crystallites also slightly decreased: for the TP sample the sizes of the crystallites is 10 nm, while for Nd doped sample is 7 nm, respectively. Xiao et al. have demonstrated that the introduction of lanthanide dopant in TiO₂ results in a reduction in the size of the crystallites, which is attributed to the segregation of doping cations at the grains inter-phase boundaries, thus suppressing the growth of nanocrystallites [5].

Figure 2 presents the XRD pattern of SC coating, which indicates the presence of cubic CeO₂ (crystallites size 6 nm) and SiO₂ crystallographic phases. The X-ray diffraction patterns of sample ST do not indicate the presence of a crystalline phase of TiO₂, so the sample has amorphous structure (it is not shown). The same result was obtained by Cheng and co-authors for sol-gel SiO₂ doped titanium dioxide films [6]. They have proved that the peaks intensity of the anatase phase is weakening with an increase in silica concentration and the films doped with 20% SiO₂ is amorphous.

Figure 3 shows the topography of a TiO₂ coatings obtained from titanium isopropoxide fresh and after corrosion attack. The surface is relatively dense with numerous nano-sized crystallites. After the corrosion test the surface becomes rougher and pits are observable. The doping of titania coatings with neodimium leads to formation of much rougher surface than those of non-doped sample (Fig 4a). It consists of many crystalline aggregates. Corrosion process induces insignificant alteration of the surface morphology of doped samples (Fig. 4b). There are no visible pores and pits, which proved the corrosion resistance of the Nd doped TiO₂ samples. The same results were proved by the SEM analyses of the coatings (not shown here). Scanning electron microscopy of SiO₂/CeO₂ coatings reveals surface with many fine nanocrystals (Fig 5a) and the corrosion process does not lead to significant changes in the surface - cracks are not observable, which proves the high corrosion stability of this multilayer (Fig. 5b). Titania coatings are relatively dense and consist of larger superficial nanocrystals (Fig. 5c). The immersion in corrosive NaCl medium does not affects appreciably the nature of the surface – there are not any visible cracks; the roughness increases slightly (Fig. 5d).
Fig. 5 SEM photographs of SC -freshly prepared SC (a), SC -after corrosion test (b); ST- freshly prepared (c) and ST after corrosion test (d).

Fig. 6 Weight losses of SiO2/TiO2, SiO2/CeO2 multilayer and TiO2 nondoped and Nd doped TiO2 after corrosion attack.

The corrosion resistances of SiO2/TiO2, SiO2/CeO2 nondoped and Nd doped TiO2 coatings after 200 hours corrosion attack, estimated by the weight losses are shown in Figure 6. Zero weight loss was registered for titania deposited on SiO2 after 200 hours in corrosive medium, while for the ceria/silica coatings weight loss of 4.10^-4 g/m². The possible reasons for the anticorrosion action of Nd in TiO2 can be explained by (i) the low degree of crystallinity of the titania coatings. According to the ref. [7] the improved barrier properties of TiO2–CeO2 composite is due to the presence of amorphous structure, which deteriorates the ion and electron conduction of the films (ii) the presence of rare-earth elements suppresses the cathodic oxygen reduction reaction as have been proved by et al. Fahrenholtz [8]. The CeO2 and TiO2 on SiO2 layers exhibit much better corrosion resistance in comparison with one-component TiO2 coatings. The possible reason for this behaviour is the low degree of crystallinity of the titania coatings, which improves their anti-corrosion properties. The obtained new bi-component coatings are promising with the view to increase the corrosion resistance of the steel, which gives the reason to extend the scope of the future experiments.

5. Conclusions

Several types of of nanosized coatings were prepared by sol gel methos: (a) one-component coatings -TiO2 (b)Nd doped TiO2 (c) bi-component layers, which consist of TiO2 over SiO2 (d) bi-component layers, which consist of CeO2 over SiO2 The XRD data revealed anatase phase for TiO2 and Nd doped TiO2 coatings. Ceria deposited on silica underlayer revealed well crystallized CeO2 cubic phase, while TiO2 deposited on SiO2 has amorphous structure. The SEM and AFM studies show that the CeO2 on SiO2 bicomponent coatings have relatively dense surface. The TiO2 coatings possess many surface nanosized crystallites. The corrosion resistance of the one-component and bi-component oxide coatings were evaluated by the weight loss after immersion in corrosive medium. The CeO2 and TiO2 coatings on SiO2 exhibit better protective properties than the non-doped and Nd doped TiO2 coatings as well as uncoated steel. The corrosion attack induces insignificant alteration of the surface morphology of both Nd doped TiO2 samples and multilayer barrier coatings. The morphological and corrosion investigations proved that the bi-component oxide coatings on the base of titanium dioxide and cerium dioxide deposited on silica underlayer have perspective anticorrosion properties for various applications in industry.

Acknowledgements

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References

MEASUREMENT OF THE VELOCITY PROPAGATION OF ULTRASONIC WAVES IN CASTINGS

ИЗМЕРЕНИЕ РАСПРОСТРАНЕНИЯ СКОРОСТИ УЛЬТРАЗВУКОВЫХ ВОЛН В ОТЛИВКАХ

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Abstract: Ultrasonic testing (UT) of castings is common foundry practice. For the correct calibration of UT, it is necessary to measure the velocity propagation of the ultrasound waves in the castings. It is inverse ultrasonic problem. A method for velocity measurement, according to ASTM E 494: 2015, with one-sided access to the casting, is being considered.

In this article the equations for determined of transversal and longitudinal velocities propagation - \( V_T^X \) and \( V_L^X \), through measurement: distance between transducers (source-reflector) - \( 2W^X \) and the time of propagation - \( t_T^X \) are obtained.

KEY WORDS: ULTRASONIC WAVES, CASTING

1. Introduction

Ultrasonic testing (UT) of castings is common foundry practice [1,2,5]. For the correct calibration of UT, it is necessary to measure the velocity propagation of the longitudinal and transversal ultrasound waves in the castings. It is inverse ultrasonic problem. A method for velocity measurement, according to ASTM E 494:2015, with one-sided access to the casting, is being considered.

2. Evaluation of the velocity \( V_T \)

The measurement of the velocity of transverse ultrasound wave propagation - \( V_T^X \) in castings at one-sided access to the casting is been considered, The velocity \( V_T^X \) by Snellius’s law, \[1\], fig.1. is calculated i.e.

\[
\frac{V_T^X}{V_1} = \frac{W^X}{\sin^2 \varphi_{1b}}
\]

where \( V_1 \) - ultrasonic velocity of the protector in the transducer, \( \varphi_{1b} \) - incidence angle, \( W^X \) - distance between transducers (source-reflector), \( t_T^X \) is time of propagation of transversal ultrasonic wave. The value \( 2W^X \) is calculated through expression \( 2W^X = W_F + W_L + W_R \), where \( W_F \) is distance between foreheads of transducers, \( W_L \) and \( W_R \) are distances between centers of left and right transducers respectively.

The Snellius’s law, \( 1 \), in pitch and catch ultrasonic technique, fig.1, is transformed to

\[
\varphi(p;V_T^X) - W^X / (p\cdot t_T^X) = 0
\]

where \( \varphi(p;V_T^X) = \frac{(pV_T^X)^2}{\sqrt{1 - (pV_T^X)^2}} \), \( p = \frac{\sin \varphi_{1b}}{V_1} \) - beam parameter.

3. Calibration at UT of castings

The basic parameter of the UT calibration, for ultrasonic flaw detector, is the velocity of ultrasonic propagation \( V_T^X \equiv (MTL VEL) \), fig.2. The values of \( W^X \) and \( t_T^X \) in (2) are measured [3].

The value of \( V_T^X \) in (2) by means the Newton’s method [4] in \( 2000 \div 5000 \) m/s is looking for.

The algorithm ZEROIN [4], is used .This algorithm is fast approaching and robust .

The velocity \( V_L^X \) of propagation of longitudinal ultrasonic wave is calculated by equation \[3\].

\[
\frac{V_T^X}{V_L^X} = \sqrt{\frac{1 - 2\nu}{2 - 2\nu}}
\]

where \( \nu \) - Poisson’s ratio. For most castings, the reference values for \( \nu \) may be adopted \( \nu \in (0.23 \div 0.28) \) [1]. In this case the equation \( 3 \) is reduced to

\[
\frac{V_T^X}{V_L^X} \approx (0.592 \div 0.553) \cdot V_T^X
\]

Therefore

\[
V_L^X \approx (1.689 \div 1.808) \cdot V_T^X
\]
The other calibration parameters at UT: (dB, RANGE, D-DELAY, P-DELAY), Fig.2 are clear.

4. UT of castings

The main task at UT of casting, the reflected area of unknown discontinuity - $S_X$ is evaluated. The result from the analysis of acoustical tract [2] is the equation (6) for $S_X$.

$$q(x) \cdot S_X - \tilde{p}_S(x) = 0,$$

where $q(x) = \frac{D_J \cdot S_{pp} \cdot \cos \beta}{(V_X^T / f)^2 \cdot (R(x) + r_{pp})^2}$.

In (6) the parameters are two groups:

A/ Assignment parameters: $D_J$ - energy transmission factor, $S_{pp}$ - area of piezo ceramic plate, $\beta$ - angle of refraction, $f$ - frequency.

B/ Evaluated parameters: $V_X^T$ - the evaluated value for velocity of transversal ultrasonic wave in the casting for calibration, $(R(x) + r_{pp})$ - distance “source – reflector”.

The ratio of acoustical pressure - $\tilde{p}_S(x)$ by the amplification $N, dB = -20 \log(\tilde{p}_S(x))$ is evaluated.

The solution of (6) is $S_X$, where $q(x)$ and $\tilde{p}_S(x)$ are known.

The equation (6) is inverse problem at UT for sensitivity [2,5].

5. Sizing error at UT of castings

If done incorrect calibration, there is error of sizing. The relationship between error of refracted area - $\Delta S_X, \%$ and error of ultrasonic velocity - $\Delta V, \%$ is

$$\Delta S_X, \% = (\Delta V, \%)^2 + 2(\Delta V, \%)(\Delta V, \%) = \left(\frac{S_X^{(m)} - S_X}{S_X^{(n)}}\right) \cdot 100\%,$$

$$\Delta V, \% = \left(\frac{V_T^m - V_T^n}{V_T^n}\right) \cdot 100\%.$$

$S_X^{(m)}, S_X^{(n)}$ are respectively measurement and used area of reflectors, $V_T^m, V_T^n$ are respectively measurement and used velocity of transversal ultrasonic waves.

For example:

A/ If take it $\Delta V, \% = (1-2) \%$ (which is acceptable accuracy for velocity $V_T^m$ measurement), then, according (7), $\Delta S_X, \% \approx (3-8) \%,$ which is a good result.

B/ If take it $\Delta V, \% > (3-5) \%$ (which is not acceptable accuracy for velocity $V_T^m$ measurement), then, according (7), $\Delta S_X, \% > (15-35) \%,$ which is a bad result.

6. Conclusion

The calibration condition at UT of castings was obtained. The main parameter of calibration is velocity of ultrasonic propagation $V_T^X$. An equation (6) for determining $V_T^X$ is obtain. The velocity of propagation $V_T^X$ is measured through the time of propagation - $T_T^X$ of transversal ultrasonic wave and distance between transducers (source – reflector) - $W^X$. The sizing of unknown discontinuity - $S_X$ is evaluated by (6) after correct calibration at known velocity $V_T^X$.

By its very nature, the calibration process at UT of castings is essentially the inverse ultrasonic problem [5].

7. Literature

3. ASTM E 494:2015, Standard Practice for Measuring Ultrasonic Velocity in Materials
INTENSITY OF SOLIDIFICATION

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Abstract: The identification of the heat exchange intensity at the work surface of the mold is defined by the base information of the type and movement of the solidification front. Parameters and their influence are shown on the type and movement of the solidification front: initial melt temperature; initial temperature of the mold; the ceramic coating on the work surface of the mold; distribution of the mass of the mold. The methodological link of these parameters is shown in the creation of each casting technology.

Keywords: Heat transfer intensity identification, parameters, methodology, technological regime of solidification.

1. Introduction

At work [1] an experimental indirect method for estimating the thermo-resistance and thickness of the ceramic coating of the working surface cast/(metal mold) in a cyclic casting process according to the following methodology: 1. Recorded with thermocouples non-stationary temperature field in the formation of cylindrical castings; 2. A 1D thermo-elastic model [2] is used to describe the non-stationary temperature field of solidification; 3. Time-temperature curves in the mold are used to estimate the thermo-resistive casting/(metal form); 4. Very important information is also the type of structures at the surface of the casting. On Fig. 1 these structures are presented [1]:

![Fig. 1 Структури при повърхност на цилиндрична отливка [1] и идентифицирани коефициенти на топлопредаване при граничната отливка-(метална форма) в началния момент от време t=0 sec: a) – без керамично покритие $\alpha(0) = 4932 \text{ w/m}^2 \text{ K}$; b) – със свежо керамично покритие на работната повърхност на металната форма $\alpha(0) = 2174 \text{ w/m}^2 \text{ K}$; c) – износено керамично покритие $\alpha(0) = 3164 \text{ w/m}^2 \text{ K}$.

On the basis of the methodology [1 and 2], modern software can be used to solve the non-stationary temperature field in the case of solidification by Stefan-Schwarz 3D task. In our institute, non-commercial software products have been created.

Here is used a software product was created and developed by M. Dimitrov and S. Bushev for numerical solution of Stefan-Schwarz's 3D task by Finite Elements Method (FEM). The methodology of [1 and 2] is developed by numerical representation of the solidification process – a first-order phase transition as follows: 1. The numerical 3D task of Stefan-Schwarz in cylindrical geometry is solved; 2. The most important is the representation of the movement of the solidification front; 3. The heat transfer coefficients identified at the boundary casting/(metallic form) of [1] (see Fig. 1) are used; 4. A technological regime of motion of the hardening front is created.

The aim of this work is to obtain a technological mode of consolidation through the influence of: 1. the initial thermo-resistance of the work surface casting/(metal mold); 2. The initial temperature field of the metal mold; 3. Initial temperature of the metal melt; 4. Distribution of the mold mass.
2. Receive technological regime of phase transition from the first order in casting.

3.1 Comparative analysis of the solidification process at different initial thermal-resistances at the border casting - metal form.

In Fig. 2 is a comparative analysis of the solidification with a heat transfer coefficient without ceramic coating $\alpha_{CM(0)} = 4932 \text{ w/m}^2 \text{ K}$ and with a fresh ceramic coating on the work surface of the metal mold $\alpha_{CM(0)} = 2174 \text{ w/m}^2 \text{ K}$ (see Fig. 1).

The numerical experiment does not account of the fill process. The cast is of pure aluminum with thermal coefficients of cast – melt (m) heat conduction $\lambda_m = 209 \text{ w/m K}$, heat capacity $c_m = 1149 \text{ J/kg}$, density $\rho_m = 2380 \text{ kg/m}^3$ and solid phase (s) $\lambda_s = 228 \text{ w/m K}$, $\rho_s = 2500 \text{ kg/m}^3$, $c_s = 1279$; steel mold $\lambda_{mold} = 54.28 \text{ w/m K}$, $\rho_{mold} = 7900 \text{ kg/m}^3$, $c_{mold} = 486 \text{ J/kg}$. Temperature melting point of pure Al is $T_m = 660.1 \text{ °C}$ and latent heat of melting is $Q_L = 408020 \text{ J/m}^3$. The initial temperature of melt is $T_C = 720 \text{ °C}$ and the temperature of mold is $T_M = 218 \text{ °C}$. The thermal coefficients of heat transfer at boundary cast/mold are shown above.

It is well known that the thermal resistance of the cast/mold boundary in during the actual casting process. We choose constant thermal resistance i.e. constant heat transfer coefficient for numerical experiments.

![Fig.2 Geometry view of thermodynamics system.](image)

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**Fig. 2** Geometry view of thermodynamics system. Comparative analysis in free regime of solidification with different coefficients of thermal-resistances $\alpha_{CM(0)} = 4932 \text{ w/m}^2 \text{ K}$ and $\alpha_{CM(0)} = 2174 \text{ w/m}^2 \text{ K}$ at the work surface cast/(metal mold). Contact temperatures of cast $T_C^*$ and mold $T_M^*$ at the cast/(metal mold) boundary. Regions 1 and 2 are important interest – Impact of boundary conditions of the mold.

The temperature field of the thermodynamic system at successive moments of time are as follows: at thermal-resistance $\alpha_{CM(0)} = 4932 \text{ w/m}^2 \text{ K}$

- $t = 0.0296 \text{ s}$ is the temperature field of the whole cast/mold system;
- $t = 1 \text{ s}$ obtaining closed isotherm lines;
- $t = 3 \text{ s}$ open solidification front;
- $t = 7 \text{ s}$ obtaining of closed melt metal liquid area;
- $t = 14 \text{ s}$ end of the solidification process;

- at thermal-resistance $\alpha_{CM(0)} = 2174 \text{ w/m}^2 \text{ K}$

- $t = 7 \text{ s}$ closing time and formation of a closed melt metal liquid area;
- $t = 10.9927 \text{ s}$ closed area and naturally non-filling with liquid metal;
- $t = 14.999 \text{ s}$ solidification of the melt in the closed area;
- $t = 14 \text{ s}$ end of the solidification process in the closed zone;

The heat transfer coefficient of the form surface 4932 w/m² K is a real value because the shape surface of the form is not processed for a higher heat transfer coefficient. The value 4932 w/m² K is much lower than the maximum possible values of 40,000 for the theoretically possible value of 56,000 [5]. The coefficient of thermal conductivity of the coating used in work [1] is obtained in the range of 0.22-0.25 w/m K. A ceramic coating with this thermal conductivity coefficient defines a value of 2174 w/m K by the ratio $\lambda_{ceramic coat}/\delta$, where $\delta$ is where $\delta$ is the thickness of the ceramic coating.

In the free solidification regime, closed melt zones are always formed, creating macro and micro-structural defects. It is not possible to supply these areas with liquid metal.

Filling the shape cavity is from the bottom (see Fig. 2). This is the only place to enter the fresh melt, i.e. the end of the metal pipe is also in the role of the "dead head". It follows that the solidification regime to be "technological" is necessary in such cases to be opened to the melt inlet. On Fig. 3 we present a technological regime of solidification by: Different constant coefficients of heat transfer on the cast/(metal mold) boundary; different initial temperature; mass distributed of the mold.
Fig. 3 Technological regime of solidification by: 1. Different coefficients of heat transfer at the cast/(metal mold) boundary $\alpha_C = 4932 \text{ w/m}^2\text{ K}$ $\alpha_C = 500 \text{ w/m}^2\text{ K}$ and at mold/environment boundary $\alpha_E = 4932 \text{ w/m}^2\text{ K}$ $\alpha_E = 0 \text{ w/m}^2\text{ K}$; 2. Initial temperature of metal melt is $T = 777^\circ\text{C}$. Three different initial temperature of the mold $570^\circ\text{C}$, $257^\circ\text{C}$, $70^\circ\text{C}$; 3. Mass distributions of the mold. The solidification process we introduced by solidification zone $[663.6, 660.1, 656.6]$. Technological solidification regime is obtained. Up to a point in time of 9.99555 sec, the hardening zone is open to the hottest part of the thermodynamic system. At a time of 13.9934 sec, the isotherm line $T = 663.6^\circ\text{C}$ closes, but the remainder of the hardening zone remains open to the hot end. It is important to note that the solidification zone until the end of the numerical experiment is kept open (see the next Fig.4).
Figure 4 shows the end of our numerical experiment.


It is well known that the heat exchange rate influences the local conditions of polycrystalline structure formation by the local solidification time (LST) along with the local crystallization time (LCT). It is assumed that \( \text{LST} \sim \text{LCT} \). The ultimate casting structure is most often obtained after heat treatment [3 and 5]. DAS and SDAS analyzes determine scales that work: SDAS \( \rightarrow 40,17 \mu \text{m} \) and

\[
\text{LST} \sim \text{LCT} = (\text{SDAS}/10)^3 \text{sec.} \quad \text{(SDAS)}
\]

In Fig. 5 is a specific microstructure of casting after curing for which \( \text{LCT} = (\text{SDAS}/10)^3 \text{sec} = (40,17/10)^3 = (4,017)^3 = 64,819,472,913 \text{sec} \). This value is decisive for the type of heat exchange intensity in the foundry process. The presented methodology in this article specifies precisely separate stages for estimation of important foundry parameters of the phase transitions of first and second order i.e. the macro-level micro level relationship or the relation micro-structure \( \rightarrow \) properties [3, 4, 5, 6].

The idea of scale from this point of view is in Fig. 5.

4. Conclusions

The presented methodology shows: The identification of the intensity of the heat exchange during casting is a constructive stage in the creation of each casting technology. The type and movement of the solidification front is basic information and control design.

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CASTING OF CARE WHEELS LOW PRESSURE OF A1Si7Mg MICRO-FOUNDRY – INTEGRAL PRESENTATION OF THE TECHNOLOGICAL CYCLE

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Abstract: An integral representation of technological parameters of low pressure casting for the production of a car wheel is made. An algorithm and methodology for communication between micro-foundry and material science induced by the change Industry 4.0.

KEYWORDS: ALGORITHM OF INTEGRAL REPRESENTATION OF LOW PRESSURE CASTING TECHNOLOGY; GENERAL METHODOLOGY.

1. Introduction – cast care wheels technology.

Full description in material science imposed by [1] and is on the base of principles [9]:

Processing→Structure→Properties→Performance. (PSPP)

Mechanical properties of the care wheel are shown in Table 1

<table>
<thead>
<tr>
<th>Zone</th>
<th>Rp0.2 [MPa]</th>
<th>Rm [MPa]</th>
<th>A5 %</th>
<th>HBW</th>
<th>DAS μm</th>
<th>LST s</th>
<th>Hμ -</th>
</tr>
</thead>
<tbody>
<tr>
<td>Center</td>
<td>169.0</td>
<td>236.6</td>
<td>3.2</td>
<td>93.6</td>
<td>43.53</td>
<td>82.31</td>
<td>91.5</td>
</tr>
<tr>
<td>Ribs</td>
<td>156.0</td>
<td>246.0</td>
<td>5.8</td>
<td>91.2</td>
<td>44.10</td>
<td>85.77</td>
<td>81.3</td>
</tr>
<tr>
<td>Bed/Board</td>
<td>175.5</td>
<td>266.0</td>
<td>8.0</td>
<td>91.4</td>
<td>24.38</td>
<td>14.53</td>
<td>83.5</td>
</tr>
</tbody>
</table>

where: Rp0.2 – yield limit; Rm – tensile strength; A5 – relative elongation; HBW – Brinell hardness; DAS – grain size; LST – local crystallization time; Hμ – micro-hardness.

The open thermodynamics system (OTS) is shown on Fig.1:

Fig. 1 Mold for low pressure casting of care wheels with control sensors – thermocouples T1 and T6.

Technological parameters measured at the casting of 20 automobile wheels are on Fig.2:

The quality cast according to (PSPP) the final structure of the care wheel is obtained after heat treatment:

- Homogenization – (535 ± 3 °C)/(6 hours), quenching in water (up to 45 ÷ 50 °C) not later of 10 sec after removing from the furnace;
- Aging at room temperature for 10 ÷ 12 hours;
- Artificial aging of (160 ± 3 °C)/(4 hours), cooling at room temperature;

but each of the two technologies of casting and heat-treating itself is subject to the principles (PSPP).
Aim of this paper is integral introduction of technological information to micro-foundry and scientific support in large and small scales.

2. Integral representation – basic information.

Integral representation of the baseline information through the parameters in the previous paragraph: Gas cycle times - $P$ with temperature control of the mold by the temperatures $T_1$ and $T_2$, which provides maximum communication with a fast response capability. The integral representation of the low pressure casting of a car wheel from an AlSi7Mg alloy is shown in the following Fig. 3:

![Fig. 3 Integral representation of the basic information of low pressure casting of wheel AlSi7Mg on machine CPC-1000: The gas cycle – $t_0$, $t_1$, $t_2$, $t_3$, $t_4$ [s] and $\Delta P_1$, $\Delta P_2$ [bar]; the cooling circuits; the control by temperature with thermocouples $T_{6\text{start}} = 350 \, ^\circ\text{C}$ and $[350 \div 740 \, ^\circ\text{C}]$, $T_{1\text{start}} = 350 \, ^\circ\text{C}$ and $[400 \div 511 \, ^\circ\text{C}]$.](image)

To estimate tolerances of the above parameters (see Fig. 3), we select the following data for one cycle as follows: 1. Temperature of the molten metal in the furnace of the machine; 2. one machine gas cycle; 3. Temperature upper mold; 4. Temperature of lower mold.

Figure 4 shows two parameters $6\text{Melt-}T_{2m}$ [$^\circ\text{C}$] and $P$ [bar]:

![Fig. 4 Furnace of the Low pressure casting machine: Temperature $6\text{Melt-}T_{2m}$ [$^\circ\text{C}$]; the pressure $P$ change of the gas for the production of one casting.](image)

On Fig. 5 are shown the date thermocouples $T_6$ and $T_1$ [$^\circ\text{C}$]:

![Fig. 5 Time-temperatures curves in mold: $T_6$, t.m. and $T_2$, b.m. [$^\circ\text{C}$]. The base information is: ($6\text{Melt-}T_{2m}$ [$^\circ\text{C}$], $P$ [bar] + $T_6$, t.m. and $T_2$, b.m. see above). The data shown (Figures 4 and 5) is a](image)
swirl of an optimized Low pressure casting of care wheel 7JX15H2 in machine CPC–1000.

Optimal casting process we understand casting without defects and with a structure giving the best working properties of each casting. In principle (PSPP), it follows that the ultimate performance requirement is the market and the maximum life of the vehicle here. The aggregate information in Figure 3 suggests that it integrates into a well-understood scheme as an idea of the basic standard of micro-foundry communication for assessing the fundamental results of material science. Such a scheme is proposed in Fig. 6:

![Diagram of mechanical properties and process]

**Fig. 6** Standard scheme for communication between micro-foundry and fundamental scientific results and fundamental results of material science. This scheme is a computational algorithm for assessing necessary (new and old) knowledge such as mathematics, mathematical physics; the need to assess future market requirements for castings. Estimates of future requirements are a probabilistic answer to the questions: What structures and working properties are needed for casting materials? Are secondary alloys used without / (or minimal) losses?
3. Materials science in Industry 4.0.

The properties of materials are determined by their structures. A. Balevski’s definitions of alloys in article [2] are:

A. Balevski’s definitions of alloys in article [2] are: 

Such a combination of mechanical and technological (and in some cases, physical and chemical) properties, which no pure metal possesses, whatever mechanical and thermal treatment it is subjected to;

(A, 1)

Such a combination of mechanical and technological (and in some cases physical and chemical) properties, which does not have any cast of pure metal, regardless of the mechanical and thermal treatments it undergoes.

(A, 2)

The structure of metals and alloys is: an ideal crystal lattice, but defects are polycrystalline (grains - diameter, orientation) and carry the working properties (A, 1, 2).

(A, 3)

In addition to the phase transitions of first and second order, the processes of hot and turbid elastic and plastic deformation also affect the structure. [2]. S. Vodenicharov makes an important development of the toughness assessment [5]:

**Toughness** – the ability of the metal structure to resist under impact conditions in the presence of one or several acute overcuts causing stress concentration; **Measure** - the amount of energy needed to destroy a sample body at a given temperature; **Two types**: toughness with cut and toughness against destruction of the monolithic body. A physical model and calculation algorithm for the process of destroying metal structures for very short time intervals is develop in [5].

The material properties will be obtained through design with new knowledge and technology. For this reason, we offer a general methodological approach to phase transitions technology in Material science of Industry 4.0 on Fig. 7:

**Fig. 7 General methodology to approach the phase transition of first and second order in Material science of Industry 4.0 [1].**

Industry 4.0 is great change [1], which is connected with the need for very intensive scientific development of material science and new technologies [12]. The principles of material handling [8] may change (robots), but general principles remain [9]. Electron microscopy is intensively developing [6 and 7]. Metal science [2] developed with the research of the theory of solidification and crystallization of metals and alloys [4]. The description of phase transitions requires the use of quantum mechanics, for example, the methodological connection between works [2] and work [3]. To day the application of quantum mechanics in material science is essential for understanding and describing the structure and properties of materials [9]. To create a casting technology, it is necessary to assess the controllability of solidification and crystallization processes [11].

The use of secondary alloys [10] is essential. The use of secondary alloys is likely to become a “metal and alloy circle” based on known and new technologies.

4. Conclusions

The results of technological experiments and the optimal technology for obtaining a cast wheel type are presented. For communication micro-foundry and material science are proposed: a general algorithm for creating a casting technology for low-pressure casting; and a methodology for a common approach to industrial change caused by Industry 4.0.

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INFLUENCE OF THE QUANTITY OF CARBIDE PHASE AND THE TYPE OF HEAT TREATMENT ON THE MECHANICAL PROPERTIES OF CARBIDE-BAINITE DUCTILE IRONS

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Abstract: The purpose of this research work is to determine the influence of the carbide phase and the austempering temperature on the mechanical properties of carbide-bainite ductile irons. Two groups of irons have been investigated: austempered at 300°C, with a lower bainite structure, and at 400°C, with an upper bainite structure. Tensile strength, yield strength, elongation, impact strength and hardness have been tested.

Keywords: Carbidic Austempered Ductile Iron, Mechanical Properties, Heat Treatment.

1. Introduction

The combination of excellent casting properties and a set of high mechanical characteristics maintains increasing interest in spheroidal graphite irons [SGI] [1].

With the introduction of austempered ductile irons (ADI) in practice values for the strength complex, that successfully compete with greater part of forged- carbon and low-alloyed steels, have been obtained [2]. The optimum combination of high-carbon austenite and bainite ferrite ensures excellent mechanical properties of this kind of irons.

Another variant of bainite ductile irons is the so called “Carbide Austempered Ductile Iron –CADI. The final structure of CADI is formed as a result of austempering in the bainite area of SGI containing a cast carbide phase. A bainite-austenitic metal matrix containing a certain quantity of carbide phase and spheroidal graphite inclusions is fixed. Unlike ADI those irons have high wear resistance at the expense of their lower elongation and toughness [2, 3, 4].

Research in CADI field shows that the final set of properties is strongly influenced by the structure changing factors: austempering temperature, holding time at that temperature and carbide phase quantity [5, 6].

The purpose of the present study is to investigate the influence of carbide phase quantity and austempering temperature on the set of CADI mechanical properties.

2. Presentation

In order to investigate the influence of the quantity of carbide phase and the austempering conditions on the mechanical properties of carbide- bainite ductile irons four compositions of irons were cast. The content of carbide phase varied from 0 to 27 %. Tests on standard test samples were carried out (Fig.1). The following strength characteristics were tested: tensile strength – Rm, yield strength – Rp0,2, hardness – HV, elongation – AS and impact strength–KCV.

Figure 1. Dimensions of test samples for tensile test – a) and impact test – b)

The investigation was carried out for both isotherms of austempering - at 300°C with holding time of 90 min and at 400°C with holding time of 60 min thus providing two groups of bainite ductile irons - irons with upper bainite and lower bainite structure of the metal matrix.

The structure obtained after austempering of SGI at 300°C is lower bainite. Within this temperature range irons have high strength indices at the expense of lower ductile ones. This isotherm is characterized with the fact that the bainite ferrite is considerably more carbon-saturated than the balance content that provides the spheroidal graphite iron with high strength and hardness and relatively low elongation and toughness. Elongation reaches up to 5 % for the carbide-free structure. The presence of a carbide phase in the structure of the bainite spheroidal graphite iron leads to a significant change in the strength complex.

The investigation shows that stress decreases approximately two times as the quantity of carbide phase increases at the expense of an increase in hardness. The latter increases from 433 HV to 574 HV for structures with 27 % carbide phase – Table 5. The reduction of elongation is more sensitive: from 4,5 % for carbide-free structures to 0,8 % for structures with 27 % carbides. The change of impact strength for both structures is from 100J/cm² to 5 J/cm² – Table 4.

The investigation results are shown in Tables 1-5 and in Figures 2-6.

Table 1. Influence of the quantity of carbide phase on the tensile strength of CADI austempered at 300°C

<table>
<thead>
<tr>
<th>T aust., °C</th>
<th>Structure No</th>
<th>Carbide phase, %</th>
<th>Tensile strength, Rm, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1</td>
<td>0</td>
<td>1430</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9</td>
<td>930</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>18</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>27</td>
<td>690</td>
</tr>
</tbody>
</table>

Table 2. Influence of the quantity of carbide phase on the yield strength of CADI austempered at 300°C

<table>
<thead>
<tr>
<th>T aust., °C</th>
<th>Structure No</th>
<th>Carbide phase, %</th>
<th>Yield strength, Rp0,2, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1</td>
<td>0</td>
<td>1265</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9</td>
<td>780</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>18</td>
<td>726</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>27</td>
<td>680</td>
</tr>
</tbody>
</table>

Table 3. Influence of the quantity of carbide phase on the elongation of CADI austempered at 300°C

<table>
<thead>
<tr>
<th>T aust., °C</th>
<th>Structure No</th>
<th>Carbide phase, %</th>
<th>Elongation, AS, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1</td>
<td>0</td>
<td>4,5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>18</td>
<td>1,3</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>27</td>
<td>0,8</td>
</tr>
</tbody>
</table>
Spheroidal graphite irons austempered in the upper bainite temperature range of 400°C are characterized with high toughness. The elongation of materials within this group reaches up to 10–15%. This complex is obtained from a bainite-austenitic metal matrix free of carbides and brittle phases.

The presence of a carbide phase, which the carbide-bainite spheroidal graphite irons (CADI) possess, abruptly changes the strength complex. In this respect the ductile characteristics – elongation and hardness - are especially sensitive.

The results of the influence of the carbide phase quantity on the mechanical characteristics of CADI austempered at 400°C are shown in Tables 6-10 and Figures 2–6.
3. Conclusions

The influence of the quantity of carbide phase up to 27 % on the strength complex of carbide-bainite spheroidal graphite irons at two austempering temperatures: 300°C and 400°C have been identified.

As carbide phase quantity changes, CADI strength properties considerably change as well. When its percentage content increases, the whole strength complex decreases. Tensile strength, yield strength, elongation and impact strength decrease whereas hardness increases. Elongation and toughness appear especially sensitive to the presence of a carbide phase.

The changes of both isotherms are as follows:

- At austempering temperature of 400°C:
  Strength decreases from 969MPa for the carbide phase-free structure to 590 MPa for 27 % carbide phase. The change of ductile characteristics such as impact strength and elongation is more sensitive. Elongation decreases from about 12% to 2.6% for the initial structure while impact strength from 152 J/cm² to 9.6 J/cm² for the structure with 27% carbides.

- At austempering temperature of 300°C:
  Strength decreases from 1430 MPa for the carbide phase-free structure to 696 Mpa for 27 % carbide phase. Elongation decreases from 4.5% to 0.8% and impact strength from about 100 J/cm² to 5.25 J/cm².

4. Bibliography


I. Introduction

Nowadays, polymeric materials are applied practically in all areas of human activity and replace the increasingly used traditional metals and alloys from the modern fields of engineering, machine building, etc.

A particular place in the polymeric materials is elastomers. This is related to their unique mechanical properties, one of which is the presence of high values of the reversible deformation, which is based on their ability to be in their working high elastic state.

The dynamic development of nanotechnology with the processing of elastomers determines the great importance of studying the structure of the elastomeric material.

One of the important components of the composite material (CM) - the elastomeric mixture (EM) is the fillers. The importance of fillers is related to the production of materials with specified properties necessary for certain branches of the economy, research, medicine, etc.

II. Explanation

Concerning nanotechnologies and fillers for elastomeric mixtures, the influence of nanodiamonds (ND) as an element of the nanoparticles on the elastomeric mixtures before the formation of the supramolecular structure of the mixture and in the vulcanization process preceding the manufacture of the rubber article is inevitably studied.

The influence of ND on the EM should be directed to the interfacial processes and superficial phenomena of the boundary elastomer - filler, because precisely the changes occurring in them determine the emergence of a new complex of properties of CM.

As the first stage of this study, physicochemical properties of ND should be determined.

The diamond modification of carbon has the highest values of free surface energy [1], which leads to a high activity of nanoparticles in the modified material but is found in a powdery state in air. ND tends to agglomeration, leading to a reduction in excess surface energy - deactivation.

On the other hand, [2] the introduction of DB (diamond batch) in the ready-mixed mixture with a formed supramolecular structure (rubber-filler), they play the role of a solid lubricant rather than an active filler, thereby increasing the elasticity, the relative elongation at break, but a decrease in the contingent tension at 100 and 300% was observed.

It follows that it is expedient, from the point of view of the modifying effect, the introduction of ND before the formation of the supramolecular structure, i.e., to examine their impact on its formation.

In order to increase the ND's modifying effect on the EM, in order to preserve the values of free surface energy, the ND should be introduced together with the inert storage medium by retaining the activity of the elastomer mixture. There are two problems in the reasoning here, namely:

- Influence of fat and olefin based ingredients on surface activity of ND.
- The influence of the inert environment in which ND is stored on the characteristics of the vulcanized EM.

If an analogy between ND and diamond batch (DB) is made as the raw product of the blast, the authors [3, 4] have found that DB has a modifying effect on all types of rubber mixtures tested, regardless of type and type of rubber, the main effect of the modifying effect was the degree of filling and the means and variants for introducing the components into the mixture and, to a lesser extent, the type and activity of the filler. As proof of the claim, the following experiments can be presented:

- For example, according to [5] the cohesive strength of oil-filled blends depends to a large extent on the mode of introduction of DB, if they are introduced into a composition with the oil, the cohesive strength falls, and if introduced together with the soot and then the oil increases.

- It is also found [2] that the modifying activity of DB depends on the presence of plasticizers (oil) in the composition of the EM and on the mode of incorporation of DB into the mixture.

In addition, the introduction of ND along with the stearic acid [6], besides wetting the filler particles, in this case ND, the polar acid residue is oriented towards the particles of the filler by covering them with a monomolecular layer, thus deactivated.

So far, we can conclude that if we want to preserve free surface energy values of ND in the EM (formulations), fat and olein-based ingredients should be excluded from the composition, irrespective of their importance in the formation of the necessary physical-mechanical and vulcanization characteristics.

On the question of the inert environment in which NDs are stored.

In general, the inert environment falling into the mixture would have to evaporate, react with the components of the mixture, or remain in the mixture without adversely affecting the formation of the actual vulcanisation agent (AAV).

When introducing ND along with accelerators, more than one accelerator can be used to model the properties of vulcanisates in the process of forming the AAB.

According to [4], dual accelerator systems, the impact they exert on the properties of vulcanisates can be divided into:

- Systems with mutual activation of accelerators (dibenzo[ghi]disulfide (Altax) and diphenyldisulfide (DPG)).
- Systems with activation of one accelerator (cyclohexylbenzothiazole sulfenamide (CZ) and DPG).
- Systems with additive action of accelerators (sulfenamide and tetramethyl thuram monosulfide (TMTM)).

If a system with activation of one accelerator is considered (CZ and DPG), the DPG substitution lowers the tear resistance and reduces the modulus to mixtures with CZ only [7]. In the present case, according to [6] there is activation of DPG with CZ.

An explanation of the process can be given in the following way:

- In the initial stage, the accelerators interact with one another to form a less active complex with respect to the addition of sulfur to the elastomer mixture;
- In the next stages of the process, the complex decomposes to radicals initiating the interaction of sulfur with rubber and other structuring processes.
Historical data were obtained [6] in studying the mechanism of action of DPG in sulfur vulcanization. DPG heated in an inert environment disintegrates with the formation of ammonia, aniline, tetraphenylamines, triphenyl di uramide. With the method of infrared and ultraviolet spectroscopy in the products of interaction of DPG and sulfur, linear polysulfides containing from two to five atoms of sulfur are found. Also, thio ketones and amonia have been found along with the polysulphides.

\[ \text{(C}_6\text{H}_5\text{N}_2\text{)}_2\text{C}=\text{NH} + \text{H}_2\text{S} \rightarrow \text{(C}_6\text{H}_5\text{N}_2\text{)}_2\text{C}=\text{S} + \text{NH}_3 \]

Sulfur vulcanization in the presence of amines may be described by an ionic mechanism:

\[ \text{RNH}_2 + \text{S} \rightarrow \text{H}^+ + \text{RNH} - \text{S}^- + \text{H}_2\text{O} \]

\[ \text{H}^+ + \text{RNH}_2 \rightarrow \text{RNH}_3^+ \]

\[ \text{RNH}_2 + 2\text{S} \rightarrow \text{RNH} - \text{S}^- \rightarrow \text{RN} - \text{S}^- \rightarrow \text{RN} - \text{S}^2^- \rightarrow \text{RN} - \text{S}^3^- \rightarrow \text{(vulcanize).} \]

According to [6] with the DTMA method the influence of DPG on the vulcanization process was investigated. It has been found that DPG is not only an accelerator, but also acts as a water regulator on the vulcanization process. In turn, the released water is a catalyst for the oxidation reaction of the SH groups.

The basis of the mechanism of action of accelerators containing no sulfur is the following factors [8]:

- Sulfur-containing amine-containing accelerators participate in oxidation-reduction processes and produce the formation of free radicals causing rubber to be structured.

### Table 2 Strengths of pre-aging vulcanizates.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>C-1</th>
<th>C-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tension at 100% deformation M\text{100,MPa}</td>
<td>1.8</td>
<td>0.88</td>
</tr>
<tr>
<td>Tension at 300% deformation M\text{300,MPa}</td>
<td>5.7</td>
<td>2.65</td>
</tr>
<tr>
<td>(\sigma), MPa</td>
<td>20</td>
<td>3.5</td>
</tr>
<tr>
<td>(\epsilon_0), %</td>
<td>590</td>
<td>310</td>
</tr>
<tr>
<td>(\epsilon_\text{rel}), %</td>
<td>(\times 6)</td>
<td>15</td>
</tr>
<tr>
<td>Hardness Shore A, ref. a.</td>
<td>50</td>
<td>52</td>
</tr>
</tbody>
</table>

The results of the physico-mechanical tests of the above-mentioned elastomeric mixtures are shown in Table 2:

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>C-1</th>
<th>C-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tension at 100% deformation M\text{100,MPa}</td>
<td>1.4</td>
<td>0.8</td>
</tr>
<tr>
<td>Tension at 300% deformation M\text{300,MPa}</td>
<td>4.8</td>
<td>-</td>
</tr>
<tr>
<td>(\sigma), MPa</td>
<td>18.8</td>
<td>-</td>
</tr>
<tr>
<td>(\epsilon_0), %</td>
<td>550</td>
<td>-</td>
</tr>
<tr>
<td>(\epsilon_\text{rel}), %</td>
<td>(\times 6)</td>
<td>-</td>
</tr>
<tr>
<td>Hardness Shore A, ref. a.</td>
<td>50</td>
<td>52</td>
</tr>
</tbody>
</table>

The C-1 mixture retains its strength and mechanical performance while decreasing slightly, while C-2 (without ND) does
not withstand 300% deformation by stretching and does not retain its strength-mechanical performance.

In the study of the degree of swelling of the investigated vulcanizates, the following results are shown in Table 4.

Table 4 Degree of swelling in toluol

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>C-1</th>
<th>C-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of swelling in toluol for 24 hours in%</td>
<td>308</td>
<td>310</td>
</tr>
</tbody>
</table>

In the case study it is evident that the equilibrium degree of swelling of the individual vulcanizates is commensurate. This shows that the density of the vulcanization network in the studied composites is almost the same.

III.Conclusion

By using the above-mentioned composition and method of introducing ND into the elastomer mixture, the formation of its own hierarchy of supramolecular structures is achieved by:

- averaging the packing density of the macromolecule chains over the entire polymer matrix volume;
- uniform distribution of ND in the polymer mixture;
- enhancing the modifying effect of ND with a significant increase in the strength, mechanical and vulcanization characteristics of the elastomer mixture.

The amplification of the ND modifying effect is achieved by:

- exclusion of fat and olein-based ingredients from the composition of the mixture, maintenance of ND in active state allowing the use of the dispersion effect of the intermolecular interaction (London composition);
- the use of water as a catalyst for the oxidation reaction of the SH groups;
- the use of suitable accelerators for the vulcanization process.

IV. References:

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