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GREEN CHEMISTRY: CARBON-BEARING MINERALS AS A SOURCE OF NANOCARBONS

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Abstract: Natural abundant, cheap and widely used raw materials like calcite, magnesite and dolomite contain elemental carbon up to several wt percent. Such rocks have been chemically processed here using combustion synthesis route to yield novel nanocarbons including two-dimensional graphene-like structures. The fast and efficient reduction of powdered minerals with strong reducer (Mg) produces, after chemical wet purification, carbon nanomaterial which was analyzed using different techniques like XRD and SEM. This combustion process was followed on-line to evaluate reaction duration (usually within 1 sec).

Keywords: COMBUSTION SYNTHESIS, CARBON-BEARING MINERALS, NANOCARBONS

1. Introduction

Carbon is one of the most important elements in the world as it builds both organic and inorganic matter. Till XX century only two allotropes of carbon were known, graphite and diamond (in addition to amorphous carbon, i.e. soot or carbon black). Recent decades brought into a daylight, however, new nanocarbon allotropes. In 1985 the fullerenes were discovered, with the importance of the discovery honored with a Nobel Price (1996). Soon later, carbon nanotubes (even called the ‘black diamonds of XX century’) were shown to the world (1991). The very beginning of the XXI century brought one, even more important discovery of next new carbon allotrope – graphene. Graphene and graphene-related nanomaterials are indeed a revolutionary materials. They have many applications replacing conventional materials as well as the ability to support applications previously not possible before the advent of two-dimensional materials. The applications of graphene are truly endless and many are yet to be conceived.

Essentially, the nanomaterials are synthesized using either ‘top-down’ (miniaturation) or ‘bottom-up’ approach. The latter one makes the use of the smallest ‘building blocks’ (atoms, ions and molecules) which form nanostructures via coalescence and coagulation during quench. Those starting promoters are usually produced via high-energy activation of a bulk material (i.e. plasma, laser or high-temperature activation). Dyjak et al. synthesized an intriguing carbon nitride C₃N₄ via high-temperature pyrolysis of melamine. In a search for novel nanocarbons, Manning et al. prepared the exfoliated graphite (in minuscule, however, amounts) from fluorinated graphite already in 1999 using inductively coupled Ar plasma. High energy consumption is, however, a drawback of the listed routes.

Here we propose a SHS (Self-propagating High-temperature Synthesis) approach for the formation of nanocarbons. SHS also termed combustion synthesis (CS) is a strong high-temperature, exothermic and autothermic, and fast redox reaction that leads to the formation of new thermodynamically stable nanomaterials with structures often not obtained under conventional conditions. We reported earlier that silicon carbide nanowires were efficiently synthesized via silicon-polytetrafluoroethylene thermolysis. Later on, the solid carbon nanomaterials were successfully obtained using the reduction of different carbon-bearing compounds. Thus, Dąbrowska et al. atomized different carbonates by using strong reducers to obtain novel nanomaterials. Such research was later continued towards the heterogeneous autothermic reduction of CO₂ and CO to elements using the following reducers: Li, Mg, Ca, B, Ti, Zr, and Al. The solid product contained the layered graphite and nanocaricides. Novel carbon nanostructures were also obtained by Huczko et al. from the mixtures of strong metal reducers and strong oxidizers (fluorinated graphite, TEFLON®, PTFE and PVC). Few-layered graphene was also produced via reduction of graphite oxide and fluorinated graphite using different reducers. Recently, Dyjak et al. prepared porous graphenic nanomaterials through a self-sustaining magnoisothermic reduction of oxalic acid.

Here, we’ve extended such research into a field of ‘Green Chemistry’ – processing of cheap and abundant minerals (which contain elemental carbon) via combustion synthesis. Specifically, the minerals (natural carbonates) of Polish and Nepal origin were chosen as oxidents with a relatively high content of elemental carbon. A phthalic acid, as a pure carbon-bearing reference reactant, was also reduced with magnesium.

2. Experimental

The reduction of carbon-bearing compounds was carried out in the stainless-steel high-pressure vessel (volume 375 cm³, Fig. 1) following the protocol outlined earlier. The reactor (a modified bomb calorimeter) is resistant to extreme process parameters (very high temperature, pressure gradients, and chemically aggressive reaction environment) and was pre-tested at the pressure up to 10 MPa.

![Fig. 1. Modified bomb calorimeter as a CS reactor](image)

A stoichiometric mixture of the reactants (Mg powder/carbon-bearing oxidant) was powdered and loaded into the quartz crucible under the pre-planned atmosphere (Ar) and pressure. The reaction was started by the resistive heating of the crucible with the igniter (carbon thread). After combustion and cooling down the system the solid raw product was collected. The product was later purified (leaching of Mg/MgO compounds using hot 3M HCl). The final sample contained mostly carbon (its content was analyzed using the elemental analysis). Both raw and purified products were examined using SEM (morphology) and XRD (phase composition) analyses.
3. Results and Discussion

3.1. System Mg/C6H4(COOH)2

The combustion of minerals was pre-tested (2 runs) with the magnesiothermic decomposition of the phthalic acid, a carbon-rich (58 wt% of C) commodity chemical produced on a large scale, following the reaction scheme

\[ 4 \text{Mg} + \text{C}_6\text{H}_4(\text{COOH})_2 = 8 \text{C} + 4 \text{MgO} + 3 \text{H}_2 \]

For a better conversion, 2-fold excess of a reducer (Mg powder, below 40 µm) was used. The operating parameters of combustions are shown in Table 1.

Table 1. Combustion of Mg/C6H4(COOH)2 mixture

<table>
<thead>
<tr>
<th>Run #</th>
<th>1 – 1</th>
<th>1 – 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion atmosphere/Starting pressure, MPa</td>
<td>Ar, 0.1</td>
<td>Ar, 1.0</td>
</tr>
<tr>
<td>Peak pressure, MPa</td>
<td>1.1</td>
<td>3.2</td>
</tr>
<tr>
<td>Starting mass of reactants, g</td>
<td>6.55</td>
<td>7.21</td>
</tr>
<tr>
<td>Mass of solid product, g</td>
<td>6.08</td>
<td>6.57</td>
</tr>
<tr>
<td>Mass decrease, %</td>
<td>7.2</td>
<td>8.9</td>
</tr>
<tr>
<td>Starting mass of raw product, g</td>
<td>6.04</td>
<td>6.2</td>
</tr>
<tr>
<td>Mass of purified product, g</td>
<td>2.31</td>
<td>2.45</td>
</tr>
<tr>
<td>Mass decrease, %</td>
<td>61.8</td>
<td>60.5</td>
</tr>
</tbody>
</table>

The combustion was easily initiated and strongly exothermic reaction was accompanied by a distinct pressure increase. The mass decrease of reactants was relatively low (below 10%) thus confirming the desirable reaction scheme. Puffy, greyish/blackish product was collected and leached with HCl. Up to 40 wt% of the raw product was recovered as an insoluble blackish residue (carbon-containing phase). The change of the starting pressure does not seem to influence the process. Fig. 2 and 3 present the representative images (SEM observation) of the raw and purified products.

![Fig. 2. Run # 1-1. SEM images of raw (A-B) and purified (C-D) product](image)

The results of those reference combustions showed that magnesium effectively reduces oxygen-containing organic matter yielding the final nanopowder composed mostly of C (60-70 wt%). This nanocarbon material dominates the purified product which, however, still contains MgO nanocrystallites encapsulated in a carbon shell.

3.2. System Mg/magnesite MgCO3 (Szkłary, Poland)

The composition of magnesite (mostly nanometric powder, Fig. 4) was analyzed with EDX technique (the spectra not shown here). The results (C, Mg, O and Si content 7.7, 21.3, 49.8, and 20.3 wt %, respectively) confirmed that it is mostly composed of MgCO3 with some silica/silicates admixtures, as expected for a mineral.

![Fig. 4. Fine-grinded magnesite (Szkłary, Poland)](image)

The mineral was reduced with magnesium (Mg powder, below 40 µm) following the reaction scheme

\[ 2 \text{Mg} + \text{MgCO}_3 = \text{C} + 3 \text{MgO} \]
This reaction can be, however, accompanied by the parallel thermal decomposition of magnesium carbonate with the evolution of carbon dioxide carrying away the carbon from the solid products:

\[ \text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2 \]

Thus, the final composition of the solid product is governed by the kinetics of both competing reactions. The operating parameters of all combustions (stoichiometric composition of reactants) are shown in Table 3. In runs 2-2 and 2-4 the starting mixture was additionally ball-milled (2 h) in hexane.

Table 3. Combustion of Mg/magnesite mixture

<table>
<thead>
<tr>
<th>Run #</th>
<th>2 – 1</th>
<th>2 – 2</th>
<th>2 – 3</th>
<th>2 – 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion atmosphere/Starting pressure, MPa</td>
<td>Ar, 0.1</td>
<td>Ar, 0.1</td>
<td>Ar, 1.0</td>
<td>Ar, 1.0</td>
</tr>
<tr>
<td>Peak pressure, MPa</td>
<td>0.4</td>
<td>0.3</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Starting mass of reactants, g</td>
<td>5.47</td>
<td>3.46</td>
<td>6.91</td>
<td>3.38</td>
</tr>
<tr>
<td>Mass of solid product, g</td>
<td>5.24</td>
<td>3.16</td>
<td>6.07</td>
<td>3.16</td>
</tr>
<tr>
<td>Mass decrease, %</td>
<td>4.2</td>
<td>8.7</td>
<td>12.2</td>
<td>6.5</td>
</tr>
<tr>
<td>Starting mass of raw product, g</td>
<td>4.77</td>
<td>2.7</td>
<td>5.19</td>
<td>2.54</td>
</tr>
<tr>
<td>Mass of purified product, g</td>
<td>0.94</td>
<td>0.51</td>
<td>0.82</td>
<td>0.42</td>
</tr>
<tr>
<td>Mass decrease, %</td>
<td>80.3</td>
<td>81.1</td>
<td>84.2</td>
<td>83.5</td>
</tr>
<tr>
<td>Combustion duration, sec</td>
<td>2.52</td>
<td>3.34</td>
<td>1.3</td>
<td>2.27</td>
</tr>
</tbody>
</table>

The reaction mixture was easily and effectively combusted with a pressure jump caused by a heat-up of reactants and the evolution of hot gaseous by-products. The mass decrease of starting mixture was found to be within ca 10.0 wt%. Thus, one can conclude that the thermal pyrolysis of a carbonate (directly into MgO and CO₂) is responsible for the loss of only below 20 wt % of starting carbonate while its almost total conversion is dominated by a fast (well below 5 sec, Table 3) direct magnesiothermic reduction following the main reaction scheme. This conclusion was confirmed by the elemental analysis (C content) of reactants. Puffy, greyish/blackish product was collected and leached with HCl. The mass of purified product was monitored and compared to that of raw material. In agreement with the reduction stoichiometry up to 20 wt% of the raw product was insoluble (carbon phase). Neither the change of the starting pressure nor the prolonged milling in hexane influenced the process. Fig. 5 presents the representative images (SEM observation) of the reactants.

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The starting reactants (A-B) are inhomogeneous mixture of micron-sized particles which, during the combustion, form mostly the conglomerates of nanosized MgO crystallites. Those are essentially removed during the acid leaching but the nanostructure of the solid residue (mostly carbon material) is still preserved. New structures are, however, also spotted in a purified product, i.e. nanowires (probably SiC₈) and layered graphene-related nanomaterial. XRD spectra of selected samples are shown in Fig. 6.

Fig. 5. Run # 2-4. SEM images of starting mixture (A-B), raw (C-D) and purified (E-F) product

Fig. 6. XRD spectra (run # 2-2) of selected samples: A – starting mixture; B – raw product; C – purified product

Mg and MgCO₃ are the main components of starting mixture (A) with some silica/silicates as the minor impurity of a magnesite. The XRD spectrum of the raw product (B) is completely different thus confirming the deep transformation of the magnesite during the reduction. MgO dominates the product with some traces of un-reacted Mg. Carbon phase is also present while silicon elemental phase presence is the result of either silica/silicates or crucible material magnesiothermic reduction. Carbon phase dominates the purified product (C) while SiO₂, Si, MgO, and SiC are the side admixtures still present in the sample. The composition of the purified product confirms that alkaline components have not been removed during the acid leaching while SiC was formed from elemental silicon and carbon which dominates the reactants.
The EDX analyses of a purified product fully confirmed that finding with the following content of the main elements: C – 51.7, Mg – 0.9, O – 16.5, and Si – 30.9 wt %.

3.3. System Mg/dolomite (Kavre, Nepal)

Powdered dolomite (calcium magnesium carbonate) was also reduced with Mg metal via combustion synthesis following the reaction scheme

\[ 4 \text{Mg} + \text{CaMg(CO}_3\text{)}_2 \rightarrow 2 \text{C} + \text{CaO} + 5 \text{MgO} \]

Again, the parallel high-temperature thermal decomposition of this complex carbonate is also possible. All combustions were easily initiated and greyish/blackish fine powder was collected for the purification and the following analyses. The operational parameters of those combustions are shown in Table 4.

<table>
<thead>
<tr>
<th>Table 4. Combustion of Mg/dolomite mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run #</td>
</tr>
<tr>
<td>Combustion atmosphere/Starting pressure, MPa</td>
</tr>
<tr>
<td>Peak pressure, MPa</td>
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<td>Mass of solid product, g</td>
</tr>
<tr>
<td>Mass decrease, %</td>
</tr>
<tr>
<td>Starting mass of raw product, g</td>
</tr>
<tr>
<td>Mass of purified product, g</td>
</tr>
<tr>
<td>Mass decrease, %</td>
</tr>
</tbody>
</table>

The very low mass decrease (ca 1 wt%) of solid reactants during combustion confirms practically the only reaction channel as shown in the desired scheme above. Above 10 % of the solid product (nanocarbon phase) was recovered after the purification stage. The change of the starting combustion pressure thus not seem to influence the process confirming its course entirely in solid-liquid phase. The representative SEM images of the selected products are shown in Fig. 7.

Fig. 7. Run # 3-2. SEM images of raw (A-B) and purified (C-D) product

The raw product (A-B) is an inhomogeneous mixture of un-reacted micron-sized Mg particles and agglomerates of nanostructured matter (mostly MgO). The purified blackish product (C-D) contains mostly MgO nanocrystallites covered with a thin carbon layer. Some intriguing one-dimensional and layered structures (nanocarbons?) can also be spotted in the product.

The non-linear course of combustion synthesis allows to obtain a nanomaterial, which may be impossible to obtain by conventional methods. The SHS processes, however, are susceptible to changing initial conditions and phase transformations of reactants disturbing heat and mass transport in the system. The consequence of such phenomena causes a difficulty in process modeling, which makes it impossible to predict the final synthesis product. The attempt to optimize the process involves time-consuming parametric studies, which makes the calculations of equilibrium thermodynamics often too much simplified. Lack of sufficient information on transient compounds prevents the modeling of process kinetics for higher orders of reaction. In the answers to these limitations the methods arose that investigate processes based on propagation combustion wave, using fractal analysis or identification of compounds at their stage follow-up reactions using time-variable analysis of the light signal on based on registered images.

In the combustion synthesis process, the heated reactants emit the radiation that is responsible for variable light signal. Optical and/or spectral registration of such a signal can be used in the process diagnostics to measure the duration of the flash or other parameters accompanying combustion.

The flash sequences for the synthesis # 2-1 and # 2-3 were photographically recorded by means of a Pentax digital camera with HD resolution of 1920x1800 and speed of 30 frames per second (duration of one frame is about 0.03s). Based on divided and selected frames, combustion maps have been made for each test from photos arranged in the process sequence (from left to right). On the basis of these data it was possible to determine the flash time, maxima, qualitative mileage and occurrence of follow-up reactions. Fig. 8 and Fig. 9 present representative combustion maps for those synthesis with an initial pressure of 0.1 MPa and 1.0 MPa.

Fig. 8. Combustion map for run # 2 –

For the run # 2-1 the flash lasted about 3.34s and the maximum reached after 0.81s. The observed extended flash-out times were slower and the passage of the combustion wave was smoother than in run # 2-3. For the run # 2-3 the flash lasted about 1.30s and the maximum reached after 0.97s. A rapid flash was observed and a greater scattering of the solid product was found within the reactor.

4. Conclusions

Carbon-bearing synthetic (phthalic acid) compound and natural minerals (magnesite of Polish and dolomite of Nepal origin) were processed via fast magiesiothermic and autothermic reduction. The resulting solid product was chemically (wet chemistry) purified to yield mostly carbon-containing nanomaterial. The presence of silica/silicates in a purified product calls for the improvement of the purification protocol. Thus, the raw product should be leached not...
only with HCl but also with NaOH. The produced nanosized carbon material should present the prospective applications, i.e. as an adsorbent, substrate for catalyst, and a component of electrodes in electrochemistry (lithium ion batteries and fuel cells).

5. References

INCREASE IN STRENGTH PROPERTIES OF LOW-CARBON STEELS DUE TO STRUCTURAL TRANSFORMATIONS AT DEFORMATION BY ROTARY SWAGING

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Abstract: Mechanical properties of low-carbon St.20 and 07G2MFB steels after rotary swaging (RS) were studied. It was established that an increase in strain ratio and decrease in temperature increase strength but decrease plasticity. The ultimate tensile strength of 867-927 MPa was obtained in both steels after deformation at temperature of 400 °C with a true strain ratio of 2.3 at good ductility of 15-17%.

Keywords: LOW-CARBON STEEL, ROTARY SWAGING, ULTRAFINE-GRAINED (UFG) STRUCTURE, THERMAL STABILITY OF STRENGTHENING, MECHANICAL PROPERTIES

1. Introduction

It is well known that methods of severe plastic deformation (SPD) such as high-pressure torsion and equal-channel angular pressing lead to significantly refinement of structure and improve the strength and service properties of low-carbon steels [1,2]. But at the present time, SPD methods are difficult to embed into the industrial production. Therefore, it is important to obtain low-carbon alloys with ultrafine grained (UFG) structure by industrial deformation methods, such as rotary swaging [3].

The purpose of this research is to establish a possibility of producing ultrafine-grained (nano- and submicrocrystalline) structures of low-carbon steels by rotary swaging and to study of its mechanical behavior.

2. Materials and experiment

The deformation of St.20 (0.19%C, 0.49%Si, 0.21%Mn, 0.03%Ni, 0.25%Cr, 0.19%Cu, 0.05%A, and Fe as a balance in wt.%) and 07G2MFB (0.073%C, 0.252%Si, 1.58%Mn, 0.242%Ni, 0.007%P, 0.005%S, 0.151%Cr, 0.22%Cu, 0.037%Al, 0.018%V, 0.195%Mn, 0.015%Ti, 0.02%W, 0.08%Nb, 0.0029%, and Fe as a balance in wt.%) low carbon steels was carried out by rotary swaging (Fig.1). St.20 was subjected to quenching in water from a temperature of 880°C (1 hour) and high-temperature tempering at 680°C (1 hour).

The initial structure of both steels was similar. It was a polyhedral (globular) ferrite with pearlitic colonies, and also oriented products of quenching (Fig. 2). Transmission electron microscopy (TEM) revealed that the quenching products are acicular ferrite and tempered martensite.

Rotary swaging of 07G2MFB steel was carried out in two modes with a decrease in the deformation temperature: 650°C (true strain ratio – 0.6) – 575°C (total true strain ratio – 1.2) – 500°C (total true strain ratio – 2.3) and 600°C – 500°C – 400°C with the same strain ratio. Rotary swaging of St.20 was carried out according to the second mode. The limited facilities of equipment and size of specimens did not allow an increase in the strain ratio during RS.

The microstructure was investigated using an Olympus PME 3 optical microscope and a JEM- 1400 transmission electron microscope operated at 120 keV. Static tensile tests were performed using an INSTRON 3380 tensile testing machine with a load capacity of 100 kN. Measurements of microhardness were taken by means 402 MVD Wolpert Wilson with loading 1N.

3. Results and discussion

The structure of 07G2MFB steel after rotary swaging (RS) was studied in two modes with a decrease in the temperature of deformation: 650 °C - 575 °C - 500 °C and 600 °C - 500 °C - 400 °C. The structure after RS at 650 °C with a true strain ratio of 0.6 does not practically differ from the structure of this steel after quenching and tempering (Fig.2, 3a). Decreasing the temperature of RS to 575 °C and increasing the strain ratio to 1.2 led to the orientation of the initial grain structure (Fig. 3b). The final stage of
the RS at 500 °C with a total true strain ratio of 2.3 led to the formation of considerably oriented initial structure judging by the metallographic analysis (Fig. 3c). The TEM analysis revealed the formation of a submicrocrystalline structure with an average grain size of 343 nm inside this highly oriented initial structure. The metallographic analysis of 07G2MFB steel after RS by the mode of 600 °C - 500 °C - 400 °C with a total true strain of 2.3 revealed an even more oriented structure due to a decrease in the strain temperature (Fig. 4).

Fig. 3. The structure of 07G2MFB steel after rotary swaging with a decrease in temperature of deformation: 650 °C (true strain ratio - 0.6) (a) - 575 °C (1.2) (b) - 500 °C (2.3) (c) (optical microscopy)

It can even metallographically observed the substructure inside highly elongated initial grains (Fig.4b). In this case, the TEM analysis revealed a submicrocrystalline structure with a smaller average grain size of 312 nm (Fig. 5).

Fig. 4 The structure of 07G2MFB steel after rotary swaging with a decrease in temperature of deformation: 600 °C (true strain ratio - 0.6) - 575 °C (1.2) - 500 °C (2.3) (optical microscopy).

The metallographic analysis of St.20 after RS by the 600 °C - 500 °C - 400 °C mode (true strain ratio - 2.3) also revealed a highly oriented initial structure (Fig.6a). The TEM analysis revealed a submicrocrystalline structure with an average grain size of 285 nm (Fig.6b).

Fig. 5 The structure of 07G2MFB steel after rotary swaging with a decrease in the temperature of deformation: 600 °C - 500 °C - 400 °C (true strain ratio - 2.3); (a) bright-field; (b) dark-field image obtained in [110]_αFe.

Thus, the selected modes of rotary swaging of St.20 and 07G2MFB steels made it possible to obtain a predominantly submicrocrystalline structure with grain sizes ranging from 285 to 375 nm in these steels.

Fig. 6 The structure of St.20 after rotary swaging with a decrease in deformation temperature: 600 °C - 500 °C - 400 °C (true degree of deformation - 2.3); (a) - optical microscopy; (b) - TEM

The thermal stability of strengthening of St.20 and 07G2MFB steels after RS was studied according to the microhardness vs. annealing temperature. The values of microhardness increase with decreasing temperature of RS and increasing strain ratio (Fig. 7 and 8). After RS, the microhardness of 07G2MFB steel as compared with St.20 steel is higher (Fig.8).

Fig. 7 The thermal stability of strengthening of 07G2MFB steel after quenching and tempering and RS by mode of 650 °C - 575 °C - 500 °C

The thermal stability for these steels of both treatments is about the same, but lower than that after quenching and tempering, despite a significantly higher level of strengthening.

For example, the thermal stability of the strengthening of 07G2MFB steel after the final stage of the RS at 400 °C is 400-450 °C, and after quenching and tempering it is 700 °C, but the microhardness level is 2.9 and 2.2 GPa, respectively (Fig.8a).

The mechanical properties of low-carbon St.20 and 07G2MFB steels after rotary swaging were studied. With a decrease in temperature and an increase in the strain ratio, the strength properties increased, and plasticity declined only slightly, which is observed both on 07G2MFB steel (Fig. 9 a, b, Table 1), and on St.20 (Fig. 9c, Table 1).

Acknowledgements

The work was carried out within the governmental task 075-00746-19-00 and supported by RFBR (grant 18-08-00321-a).
Comparing the ultimate tensile strength both of steels, deformed by the second mode of 600 °С – 500 °С – 400 °С, it can be seen that swaging at 600 °С with a true strain ratio of 0.6 leads to a slightly greater tensile strength in 07G2MFB steel, and swaging at 400 °С with a true strain ratio of 2.3 - in St.20. But it should be noted in this case rather close values of the ultimate strength. Therefore, it can be argued that the ultimate tensile strength of 867-927 MPa was obtained for both steels at the final stage of the RS at 400 °С and with a true strain ratio of 2.3 at good ductility of EL = 16-17%.

### Table 1: Mechanical properties of low-carbon 07G2MFB and St.20 (c) steels

<table>
<thead>
<tr>
<th>Treatment /Ta/°C,</th>
<th>Ultimate Tensile Strength σUTS, MPa</th>
<th>Yield Stress σYS, MPa</th>
<th>EL, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>07G2MFB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quenching at 920°C (1h) → high-temperature tempering at 680°C (1h)</td>
<td>594</td>
<td>481</td>
<td>27</td>
</tr>
<tr>
<td>RS / T=600°C</td>
<td>654</td>
<td>604</td>
<td>28</td>
</tr>
<tr>
<td>RS / T=600°C—500 °C</td>
<td>690</td>
<td>654</td>
<td>22</td>
</tr>
<tr>
<td>St.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quenching at 880°C (1h) → high-temperature tempering at 600°C (1h)</td>
<td>600</td>
<td>460</td>
<td>21</td>
</tr>
<tr>
<td>RS / T=600°C</td>
<td>565</td>
<td>505</td>
<td>27</td>
</tr>
<tr>
<td>RS / T=600°C—500 °C</td>
<td>673</td>
<td>664</td>
<td>17</td>
</tr>
<tr>
<td>RS / T=600°C—500 °C—400 °C</td>
<td>927</td>
<td>923</td>
<td>15</td>
</tr>
</tbody>
</table>

### 4. Conclusions

1. Rotary swaging of 07G2MFB steel was carried out by two modes with a decrease in the deformation temperature: 650 °C (true strain ratio - 0.6) - 575 °C (1.2) - 500 °C (2.3) and 600 °C - 500 °С – 400 °С with the same strain ratio. Rotary swaging of St.20 was carried out according to the second mode.

2. Rotary swaging of low-carbon St.20 and 07G2MFB steels at the final stage of the RS at 400 °С with a true strain ratio of 2.3 leads to the formation of an ultrafine-grained (UFG) structure with a size of structural elements 285-312 nm.

3. The ultimate tensile strength in the range from 867 to 927 MPa with a true strain ratio of 2.3 and with good ductility EL = 16-17% was obtained in both steels at the final stage of the RS at 400 °С.

### 5. References


FEATURES OF STRUCTURE FORMATION AND MECHANICAL BEHAVIOR OF METALLIC MATERIALS UNDER CONDITIONS OF APPLICATION OF GRADIENT DEFORMATIONS

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Abstract. The study of technological methods of plastic structure formation is an urgent task. Taking into account that structure formation depends on many factors and, first of all, on the deformed state, studies of the deformed state and structural studies involving TEM were carried out in the work. It is known that reliable data of the structural state allows predicting the mechanical and operational properties of the obtained semi-finished products and products. In this regard, the analysis of the effect of the processing route (C, Bc) on the structural changes after high-cycle active bending was carried out. A numerical simulation of the active bending process was also carried out, and the accumulated strain values were determined for 8 processing cycles. Established patterns of structure formation, depending on the level of accumulated deformation and processing route.

KEYWORDS: PLASTIC STRUCTURE FORMATION, ACTIVE BENDING, MODELING.

1. Introduction

In the context of expanding industrial production, the need for new materials and for improving the physico-mechanical properties of known materials increases. Researches in this direction are conducted by many scientific centers all over the world. Great efforts are aimed at studying the features of the structural states of materials and their connection with the stress-strain state and other factors [1,2]. In this regard, there is an increasing need for the creation of promising industrial methods that allow to achieve improved properties of materials [3-5].

One of them is the method of active bending, which makes it possible to act on the initial structure under conditions of a strain gradient. In this regard, the aim of the work was to study the effect of the deformed state and other factors on the microstructure of copper after active bending.

2. Concept of process

A schematic diagram of the active bending used in research is presented in Figure 1. The proposed development is based on the well-known ECAP- ‘Conform’ scheme, while in the deformation process, the workpiece 3 is pushed into the stationary bending matrix consisting of two elements of the matrix 1 and 2. The method allows to combine the high-performance process “Conform” with bending deformation, which leads to an intensification of the hardening process of the deformable material due to the formation of a gradient structure. Active friction forces ensure process continuity.

For the simulation, the Deform 3D program was used to analyze the three-dimensional (3D) behavior of the metal during pressure treatment. This made it possible to obtain important information about the nature of the material flow in the forming tool, as well as about the stress-strain state and the temperature distribution during the deformation process.

When modeling the bend according to the “Conform” scheme at an angle of 90°, a square section sample with a size of 10x10 mm and a length of more than 150 mm was used for the first deformation cycle, a bend radius of 10 mm. For the subsequent cycles, a sample obtained by modeling on the previous cycle was used in order to obtain generalized data after passing through four sample processing cycles.

3. Results and discussion

Description of the structure of copper (M1) after bending on a horizontal installation ECAP-Conform

After 8 passes of active bending along the Bc route, a fragmented, close to equiaxed microstructure with misoriented fragments with sizes of ~ 0.3-0.5 μm was formed in the alloy. In the body and the boundaries of a significant part of the fragments, dislocation clusters with a scalar dislocation density $\rho_d$ are observed, reaching values $\rho_d$ in individual fragments of ~ $10^{11}$ cm$^{-2}$. With a further increase in the number of passes (degree of deformation), the dislocation density practically does not increase, i.e., it reaches saturation after 8 passes.

The estimate of the dislocation density, determined from the results of X-ray structural analysis, corresponds to the maximum value of $\rho_d$ obtained by electron microscopic studies of thin foils.

Analysis of microdiffraction patterns obtained on thin foils from deformed flexible materials, as well as EBSD analysis, indicates a significant disorientation of the fragments after four passes. In general, these studies showed that in the process of bending along the V-route, medium- (5–15 °) and high-angle (~ 15 °) boundaries of deformation type are formed in copper.

At the same time, eight passes, which are flexible along route C, lead to the formation of a microstructure with lengths stretching in the direction of ~ 35–45 ° to the rod axis with sizes of ~ 1–3 μm in length and 0.2–0.6 μm in thickness. In many elongated fragments and boundaries between them there are clusters of dislocations with a scalar density $\rho_d$ exceeding $10^{11}$ cm$^{-2}$. EBSD analysis showed the presence of a whole ensemble of fragment boundaries with different misorientations, among which medium- and high-angle deformation boundaries predominate.

The definition of microhardness in cross section of samples after bending is shown in Fig. 2 and 4. The magnitude of microhardness in the cross section varies in accordance with the character of the formed gradient structure, the features of which are higher HV values in the central rod area and a decrease in the HV value in near-surface areas for both bending paths (Fig. 2 and 4).
Obviously, such a dependence of the microhardness variation is due to the heating of the rods in the process of bending and the possible redistribution of dislocations and a decrease in their density in the near-surface region of the rods.

\[\text{Figure 2. 8 passes are flexible: } a \text{ - route Bc; } b \text{ - route C; } c, d \text{ – the dependence of the microhardness HV on the distance along the diameter of the rod, respectively, for routes Bc and C} \]

4. Conclusion

1. Using numerical simulation, it is established that active bending provides, after 8 processing cycles, the level of accumulated deformation \(e = 4.2\) in the middle region and \(e = 5.0\) in the near-surface cross-sectional area of the workpiece.

2. It has been established that when using the method of active bending along the Bc route, a grain-subgrain equiaxial structure with an average grain size of \(\sim 0.3-0.5\) µm is formed in a deformed copper sample; a cross section of \(\sim 0.2-0.6\) µm and a length of \(\sim 1-3\) µm. UMP range.

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5. References

THE INFLUENCE OF HEAT TREATMENT ON PROPERTIES OF STEEL FOR CEMENTATION

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Abstract: During the injection molding procedure of plastics, the gear pumps in their work are exposed to the effect of elevated pressure and temperature. On one of these pumps there has been frequent downtime due to breakage of the driven gear. Gears which were installed as standard spare parts had stood out in operation for three months. On a sample of a broken gear were performed laboratory examinations (metallographic examinations, hardness control on cross-section and surface of the fracture was examined). Conclusion was that it was high quench hardening of a steel of which a part is made, the most likely cause of the fracture of a standard gear. In order to extend the useful life, two test gear are made from steel for cementation 20MnCr5. By applying the appropriate parameters of thermal chemical treatment useful life of the gear is significantly extended, after which the test gears have worked for nine months from the moment of installation.

Keywords: HEAT TREATMENT, STEEL 20MnCr5, MICROSTRUCTURES, HARDNESSES

1. Introduction

Machines for injection molding of plastics are used for making a great array of parts in the automotive industry, for making plastic parts of household appliances and making simple plastic elements [1]. Plastics are polymers which can be added various additives. Given the behavior of the application and processing, are divided into two categories, plastomers and duromers. Duromers are at the beginning of the process soft but during heating at an elevated temperature they irreversibly become a solid material. Further heating results in their thermodegradation. Plastomers are polymeric materials with linear and branched structure. They are soluble in the solvents and fusible. Heating to softening temperatures do not change their structure and therefore their processing includes reversible changes. At these temperatures they can be formed into desired shapes. The structure of plastomers can be amorphous or crystalline [1]. One of the most common methods of processing plastomers is injection molding. This is a procedure of fast injection of molded plastomer into tempered mold and solidification in the workpiece. There is a possibility of process automation that makes it suitable for mass production. Important components of these machines for injection molding are plastic pumps which allow the circulation of heated raw material. They are at work exposed to elevated pressures and temperatures. Gear pumps with external gear, especially a spiral, are often used because they are silent in operation. Tight tolerances in the bearings and shafts mounted on either side of the gear are enabling the achievement of operating pressures above 200 bar. The bearings with narrow tolerances of pumps are not suitable for high temperature application in the presence of abrasive media. Figure 1 shows schematically how gear pumps work. In the initial stage of operation, the gears on the inlet side of the pump affect the media and tend to stand by in the holes on the side of the pump housing. The media is traveling between the gear and the inside of the housing in the moving pockets without passing between gears. Gears displace the affected medium, through the outlet opening, under pressure.

2. The properties of steel 20MnCr5

Steel 20MnCr5 belongs to a group of steel for cementation. These steels represent a structural steels which after machining by particle separation are carburizing on the edge of the layer. After carburizing of the edge layer, by hardening is achieved high resistance to wear of the edge layers and the increased toughness of the non-carburized core [2]. Steels for cementation mainly contain from 0,1 to 0,2 % carbon before carburizing, and may be a non-alloyed or low-alloyed. The edge layer after process of carburizing contain from 0,8 to 0,9 % carbon, and with hardening is achieved hardness from 61 to 64 HRC. After the process of cementation carburized core remains a ferrite-perlite structure, if the material is not hardenability. In the case of hardenability the low-carbon martensite is formed. Both of these microstructures are characterized by high toughness with high wear resistance. After the process of cementation the surface layers contain high-carbon martensite. The most common application of steel 20MnCr5 is in the production of gears, shafts and axles of machines, camshafts etc. [3]. Declared mechanical properties of steel 20MnCr5 are shown in Table 1 [4].

Table 1: Mechanical properties of steel 20MnCr5.

<table>
<thead>
<tr>
<th>Steel mark</th>
<th>Hardness, HB</th>
<th>$R_{p0.2}$, MPa</th>
<th>$R_{m}$, MPa</th>
<th>$A_s$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20MnCr5</td>
<td>152 ÷ 201</td>
<td>685</td>
<td>980 ÷ 1280</td>
<td>7</td>
</tr>
</tbody>
</table>

3. Condition recording

Following the cancellation of the gear pump for transportation of liquid polymer material, damaged driven gear, shown in Figure 2 was submitted to the Laboratory of the Institute of Engineering Materials, Mechanical Engineering Faculty in Slavonski Brod. A few of these gears, the drive and driven are exposed to the operating temperature of about 210 °C. Their task is to manage the rotation and provide transportation of liquid material formed by heating the secondary polymer granules. Part of the gear, on gear pump shown on side „B” was broken after ≈ 3 months of work. This was one of the failures which have generally occurred every 3 months after installing new, standard driven gear. Objective is that after completion of appropriate tests, based on the analysis of the results is noting the potential causes of the breakage. After that, taking into consideration the estimated cause of damage, it is possible to set the guidelines for the preparation of test driven gears.
Recording of the situation showed that on machines equipped with this type of pump usually comes to a breakage of driven gear of gear pumps in the area of step-change from diameter of the shaft to diameter of the gear. Bearing of the gear is steel on steel with very tight tolerances and it is unfavorable in terms of wear [5]. One possible approach to extending the life of the gear is testing which steel with appropriate parameters of cementation can can satisfy the required conditions without breaking.

**Figure 2** Review of broken standard driven gear of the gear pumps.

### 4. Selection of materials and parameters of heat treatment

The main requirement of the cementation process is to obtaining the materials of hard surface and tough core. After the carburizing of surface the hardening was performed. After hardening the core must remain tough [6]. The cemented layer was characterized by a martensitic structure in which maximum hardness can reach up to values 65 HRC [7]. In addition, the HV1 hardness flow rate is determined on the cross-section, by Vickers method with a load of 10 N. The received results can serve to determine the effective depth of the cemented layer according to the criterion $E_{dc} = 550\ \text{HV1}$ [8]. From CrMo steel for cementing, 20MnCr5, is made one test driven gear. That gear is built in to the pump gear and condition was recorded. After 9 months in exploitation there was a fracture of that test gear. The plan for the experiment is to provide same tests on test sample of the gear and on samples of the broken standard gear.

### 5. Experimental part

On broken parts of the gear pump, visual control is performed for the insight of the current condition. Particular attention was paid to the control of the surface fracture on the side „B”, as shown in Figure 2. Then, using MC-80 cutter, pattern was cut out for continue testing. In order to preserve the existing situation material cutting is performed with intensive water cooling, Figure 3.

**Figure 3** Device for the samples cutting.

Samples are prepared for determination of the chemical composition of the material using an optical spectrometer type Belec, Figure 4. This device allows the selective testing of the sample surface. In this way, with appropriate sample preparation, testing can be carried out both in the core and in the surface of the layer. Metallographic examinations were performed on the cross-section of the sample under different magnifications. Corrosion is performed with nital and microstructure of the core and edge of the samples was photographed by camera of the microscope.

**Figure 4** Device for the chemical analysis.

### 6. Analysis of the results

Breaking surface of the standard gear is shown in Figure 5.a. The characteristic appearance of the fracture surface indicates the presence of brittle fracture due to material fatigue. Place of origin of the initial break is not expressed. All over the outside diameter of the surface fracture can be seen zone formed by merging of multiple tiny breaks around the same size. These cracks have created a unique breakout area of annular shape. Look is characteristic for the first phase of breaks with the elements that are in operation torsionally burdened. The border between growth zone of the fracture and final fracture zone is not expressed. Breaking surface of the shaft of gear is shown in Figure 5.b. The characteristic appearance of the fracture surface indicates the presence of ductile fracture due to material fatigue. Place of origin of the initial breaks is expressed and indicated by an arrow. Similar to the previous sample, around the outside diameter of the fracture surface zone formed by merging of multiple tiny breaks around the same size (I) can be seen. The breaks of the formation zone (I) are converted into the border between growth zone (II) of the fracture and final fracture zone is clearly expressed (III).

**Figure 5** Review of fracture surface.

a) standard gear;  
b) test gear

Chemical analysis of the material was performed out on samples of one standard and one test gear. Test results are showed in Table 2.

**Table 2:** Chemical composition of the gear after cementation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measuring position</th>
<th>Percentage, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard gear</td>
<td>Core</td>
<td>C  0.219</td>
</tr>
<tr>
<td></td>
<td>Surface</td>
<td>C  0.639</td>
</tr>
<tr>
<td>Test gear</td>
<td>Core</td>
<td>C  0.197</td>
</tr>
<tr>
<td></td>
<td>Surface</td>
<td>C  1.064</td>
</tr>
</tbody>
</table>
The results indicate that the standard gear is made of steel 15CrNi6, while test gear is made of steel 20MnCr5. There is an increased content of carbon in the surface layer of samples. It has emerged as a result of the cementation. Hardness values were measured on the surface of broken part of standard and test gear, on side „B“. Measured by HRC. Standard gear hardness values range between 57 to 59 HRC and in the trial between 56 to 58 HRC. Hardness values measured on the cross-section of the sample were determined using the method HV1. Results are shown in Figure 6. Results determined the effective depth of cemented layers, $E_{dc}$. For a standard gear, $E_{dc}$ is approximately 2,4 mm and for test gear is 1,6 mm. The values obtained are within the limits expected for the observed steel. The course of hardness measured on cross-section of standard and test gear confirmed assumptions about the properties of the material from which they are made.

![Figure 6](image1)  
*Figure 6 A diagrammatic representation of hardness values on cross-section of broken gear.*

Recording the characteristic microstructures of the standard and test gear was performed on a light microscope Leica DM 2500 M, Figure 7.

![Figure 7](image2)  
*Figure 7 The light microscope Leica DM 2500 M.*

Characteristic appearance of microstructure of broken part of the standard gear is shown in Figure 8. Martensitic layer is noticed with some retained austenite.

![Figure 8](image3)  
*Figure 8 Microstructure of standard gear (nital etched 3 %).  
a) edge layer, 100:1;  
b) transition zone, 100:1;  
c) transition zone, 500:1*

Characteristic appearance of microstructure of broken part of the test gear is shown in Figure 9. For it is noticed that the structure of the hardened layer in addition to martensite and bainite has some retained austenite.

![Figure 9](image4)  
*Figure 9 Microstructure of test gear (nital etched 3 %).  
a) edge layer, 100:1;  
b) transition zone, 100:1;  
c) transition zone, 500:1*

7. Conclusion

The analysis of the test results have found that the standard gears are made of steel 15CrNi6 which are thermochemically processed. Due to its characteristics, and taking into consideration the operating conditions in which pumps are installed, it was proposed to use less hardened steel 20MnCr5. The tests performed on the samples of the standard and the test gear, it was shown that steel 20MnCr5 after thermochemical treatment has a significantly different course of hardness of steel 15CrNi6, diagrams in Figure 6. Despite a slightly lower hardness of the surface layer and less effective depth of the layers, because of the less hardened of the core, parts made of steel 20MnCr5 in the same operating conditions lasted 9 months. That is three times longer than standard gear life. Based on the control of working conditions of observed pump problems in the cancellation of the work may be connected with the manner of handling. At the (cold) start, solidified media should be previously warmed in the pump which remained after the previous stop.

8. References


CORROSION STABILITY IN SALT MEDIUM OF STAINLESS STEEL AND CARBON STEEL, USING DIFFERENT OXIDE SOL GEL COATINGS

1. Introduction

The family of stainless steels is widely used in various industries as well as in the biomedical sectors due to its tailorability, mechanical, etc properties and biocompatibility [1]. However, in the presence of halide ions, corrosion proceeds in stainless steels [2]. Carbon steels are the most commonly used pipeline materials in petroleum industry, but they are prone to corrosion in environmental containing CO2 [3]. In order to overcome this problem various oxide films (SiO2, ZrO2, Al2O3 and TiO2) can be deposited on the metals to improve their barrier properties [4,5]. Among them titania and ceria coatings are the most widely used barrier properties of the steels. Pinzon et al have successfully obtained thermally sprayed alumina-titania anticorrosion coatings on carbon steel/DIN 1.0065 USSt37-1/ [6]. The preparation and properties of TiO2-CeO2 coatings by the sol-gel dip-coating process, using cerium chloride and various titanium alkoxides, and the effect of catalysts were studied. Gelation time of the coating solution became longer with an increase in the molecular weight of titanium alkoxide. The transmittance, thickness, chromaticity and acidic durability of the coating films were measured as a function of aging time of the coating solution. The most transparent and acidic durable coating film was obtained by using a solution just before gelation. In the case of using a alcohol based sol-gel route via the spin coating technique using mixed inorganic-organic [CeCl3.7H2O and Ti(OrPr)4] precursors. Ion storage capacity for films obtained from aged sols was studied. Enhanced titanium oxide content improved the insertion complex formed. The complex formation reaction is exothermic. After vigorous stirring at room temperature, a mixed solution of distilled water and i-propanol was added dropwise to the above solution under continuous stirring. The molar ratio of components is TiOP: H2O:AcAc=1:30:1:1. The resulting solution was denoted as 1. Then the deposition-drying procedures and final treatment followed the scheme described deposition of CeO2 coatings. The samples were denoted as T1 (on stainless steel) and T3 (on carbon steel). For the composite coatings were used solution mixture of titanium and cerium precursors in atomic ratio 30/70. Then the deposition-drying procedures and final treatment followed the scheme described deposition of CeO2 coatings. The corresponding samples were denoted as CT1 (on stainless steel) and CT3 (on carbon steel)

2. Experimental procedures

2.1. Deposition procedures

Two types of substrates were used for the deposition of anticorrosion coatings: stainless steel AISI 316 and carbon steel/DIN 1.0065 USSt37-1/. The substrates were cleaned ultrasonically in hot ethanol and acetone, after that were dried in air at 100oC. Three types of samples were prepared: cerium oxide, titanium dioxide and titanium -cerium composite oxide. Cerium nitrate (Ce(NO3)3.6H2O) dissolved in isopropanol was used as precursor solution. The substrates were immersed in the solution and holding for 10 seconds, after that withdrawn at a speed of 30 mm/min. Then, the samples were dried in air first at 100°C for 1 hour, after which the temperature rises to 300°C for 1 hour. After fifth dipping-drying cycles the samples were treated at 400°C and were denoted as C1 (on stainless steel) and C3 (on carbon steel/DIN 1.0065 USSt37-1/). Titanium isopropoxide (TTIP) were used to obtain the TiO2 deposition solution. Acetylace tone (AcAc) is used as a stabilizing agent. Titanium isopropoxide (TTIP); Ti(OC4H9)4, 98% purity, (Acros) and AcAc are dissolved in 2-propanol. The resulting solution is transparent and orange in color, which is typical of the chelated complex formed. The complex formation reaction is exothermic. After vigorous stirring at room temperature, a mixed solution of distilled water and i-propanol was added dropwise to the above solution under continuous stirring. The molar ratio of components is TiIP: iPrOH: H2O:AcAc=1:30:1:1. The resulting solution was denoted as 1. Then the deposition-drying procedures and final treatment followed the scheme described deposition of CeO2 coatings. The samples were denoted as T1 (on stainless steel) and T3 (on carbon steel). For the composite coatings were used solution mixture of titanium and cerium precursors in atomic ratio 30/70. Then the deposition-drying procedures and final treatment followed the scheme described deposition of CeO2 coatings. The corresponding samples were denoted as CT1 (on stainless steel) and CT3 (on carbon steel)

2.2. Analyses

The phase compositions of the samples were studied by X-ray diffraction (XRD) with CuKα-radiation (Philips PW 1050 apparatus). A scanning electron microscope (SEM) Philips 515 was used for morphology observations of the films.

2.3. Evaluation of the corrosion resistance of the coatings.

The corrosion resistance of the samples was evaluated weight loss method, using salty corrosive solution of 3.5% NaCl at 25°C (EN ISO10289/2006). The corrosion resistance of the investigated samples and uncoated stainless steel (reference sample). The temperature of the solution and the air temperature were calibrated by controlled thermometers. The mass weight loss was determined after 1200 hours of corrosion attack.
3. Results and discussion

From the XRD analyses of the both C and CT samples confirm the presence of pure cubic CeO\(_2\) phase according to JCPDS card 43-1002 with polycrystalline nature. It has to be note that in the composite CT1 and CT3 coatings (i) no peaks corresponding to anatase phase were detected; (ii) peak broadening was observed in comparison to the pure ceria coatings (Fig. 1a,b). X-ray diffraction pattern of T1 and T3 coatings revealed pure anatase phase without any peaks of rutile or brookite phase. The average crystalline size of CeO\(_2\) coatings is 7 nm, while the composite materials have lower crystalline size - 4 nm. This may be due to the formation of Ce–O–Ti bonds, which inhibited the crystallite growth of TiO\(_2\). The TiO\(_2\) crystallite size was calculated from the highest intensity plane (101) and found to be around 13 nm.

Fig. 1-a

![XRD pattern of CeO\(_2\) (a)](image)

Fig. 1-b

![XRD pattern of CeO\(_2\)-TiO\(_2\) (b)](image)

Fig. 1-c

![XRD pattern of TiO\(_2\) (c)](image)

Fig. 1. XRD patterns of CeO\(_2\) (a), CeO\(_2\)-TiO\(_2\) (b) and TiO\(_2\) (c) coatings on stainless steel AISI 316

Figure 2 shows the SEM images on the surface of the samples before and after the corrosion test. Sample C2 is relatively dense and smooth. After the corrosion test, the surface retains its characteristics and holes, pits and other characteristic signs of corrosion are not observable (Fig 2b).

Fig. 2. Morphology of freshly prepared CeO\(_2\) (C1) - (left) and after corrosion test (right)

Fig. 3. Morphology of freshly prepared TiO\(_2\) (T1) - (left) and after corrosion test (right) at higher magnification (20 000).

Fig. 3 shows the morphology of the TiO\(_2\) coating, obtained from the titanium isopropoxide sol on stainless steel substrates. The surface is continuous, but microcracks are visible, which could be due to the small residual compressive stresses [9]. During the drying, crystallization and densification processes the coatings were subjected to fracture and macro cracking due to the intrinsic film stresses, caused by chemical reactions during drying, difference in thermal expansion coefficients between substrate and the TiO\(_2\) film, grain interaction and grain size of the TiO\(_2\) film [10]. Also the stainless steel substrate has a higher coefficient (17×10\(^{-6}\)\(^\circ\)C) of linear thermal expansion than the TiO\(_2\) film (2.1–2.8×10\(^{-6}\)\(^\circ\)C) [11]. On cooling, the stainless steel substrate shrinks more than the TiO\(_2\) film leading to the formation of small microcracks.

As can be seen the coating C3 has a relatively dense, but rough surface with several microcracks. After the corrosion attack the morphology changes, and visible signs of corrosion are visible (Fig 4-c,d).

Fig. 4-a

![SEM image of C3] (image)

Fig. 4-b

![SEM image of C3 after corrosion] (image)

Fig. 4-c

![SEM image of TiO\(_2\)] (image)

Fig. 4-d

Fig. 4. Morphology of freshly prepared CeO\(_2\) on carbon steel/DIN 1.0065 USt37-1/ (C3) - (a,b) and after corrosion test (c,d).

It has to be note that the surface morphology of TiO\(_2\) coating is a relatively dense without cracks. (Fig. 5) It is obvious numerous small crystallites on the surface. After the immersion in corrosive salt medium the surface of titania coating remains almost unchanged even
such long period of time. This result proves the good barrier properties of TiO$_2$ coatings deposited on carbon steel/DIN 1.0065 US37-1/

Fig. 5. Morphology of freshly prepared TiO$_2$ coatings on carbon steel/DIN 1.0065 US37-1/ (T3) - (left) and after corrosion test (right).

Fig. 6. Morphology of freshly prepared CeO$_2$–TiO$_2$ coatings on carbon steel/DIN 1.0065 US37-1/ (CT3) - (left) and after corrosion test (right).

It has to note that the corrosion attack influences significantly the surface features of the composite CT coatings. The SEM pictures revealed deep craters and even sections, where the coating has begun to be removed from the substrate.

<table>
<thead>
<tr>
<th>Table 1. Corrosion rate for all tested coatings after 50 and 1200 hours corrosion attack.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Code</td>
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<tr>
<td>CT 1</td>
</tr>
<tr>
<td>CT3</td>
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<tr>
<td>C 1</td>
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<td>C 3</td>
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<tr>
<td>T 1</td>
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<td>T3</td>
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</table>

The analysis of the results of the corrosive test is as follows. For CT samples the corrosion rate K is the lowest for CT1 (after the first fifty hours it is zero) and the highest for CT3. In the Ce series in the Ce1 sample there is no corrosion process during the first fifty hours, and in the second run (1200 hours) the weight loss is negligible and the value of K is equal to zero. These results refer to both test periods. In the TiO$_2$ coatings, T1 corrosion rates K are zero for both test periods due to minor weight changes. In T3, the corrosion rate is higher than that of T1 in both periods.

The weight loss of CT coatings deposited on stainless steel after corrosion attack is $7 \times 10^{-5}$ g/m$^2$, while for T1 and C1 zero weight loss was observed (Fig. 7). The corrosion resistance of the all investigated coatings on stainless steel is higher, than those on carbon steel/DIN 1.0065 US37-1/. The results presented on Figures 6 and 7 confirm that TiO$_2$ coatings exhibit increased ability to protect both the stainless and carbon steels, in comparison to that of C and CT coatings. This result probably is due to the less pronounced crystallization of titanium dioxide (Fig. 1-c) and suitable surface features.

Fig. 7. Weight loss for all tested coatings after 50 and 1200 hours corrosion attack.

4. Conclusion

The anticorrosion resistance of stainless steel and carbon steel coated with several coatings: TiO$_2$, CeO$_2$ and TiO$_2$/CeO$_2$ by sol gel method were investigated. The coatings on stainless steel are relatively dense. After the corrosion attack the morphology of cerium dioxide coatings changes, and visible signs of corrosion are visible. It is obvious numerous small crystallities on the surface. The composite TiO$_2$/CeO$_2$ samples possess deep cracks which evidently favor the attacks in corrosion medium. Titania coatings exhibit good barrier properties both on stainless steel and carbon steel: the surface of titania coating remains almost unchanged even at such long period of corrosion attack. Ceria and titania coatings deposited on stainless steel have zero weight loss in corrosive medium. The TiO$_2$ coatings could also effective protect carbon steel, while the TiO$_2$/CeO$_2$ and CeO$_2$ coatings exhibited lower corrosion resistance. This results could be due to the less pronounced crystallization and suitable surface morphology of the titania coatings.

Acknowledgement: The authors are grateful to the financial support of Bulgarian National Science Fund at the Ministry of Education and Science, Contract No DN07/2 14.12.2016.

5. Literature

COMPARATIVE TRIBOLOGICAL PROPERTIES OF AZ91D MAGNESIUM ALLOY AFTER STRENGTHENING BY SiC POWDER AND AFTER SEVERE PLASTIC DEFORMATION

Abstract. The paper presents the results of studies of tribological properties of the contact of the tool steel composition Fe-18W-4Cr-1,2V with the magnesium alloy AZ91D strengthened by submicron powder filling out of SiC and severe plastic deformation (SPD), namely equal-channel angular pressing (ECAP). It is stated that introduction of SiC powder filling to the magnesium alloy the friction coefficient on the moving frictional contact increases, the wear rate reduces. These tribotechnical characteristics are influenced by the size and volume of the particles of powder filling, normal loading force and slip rate. SPD of the initial material results in reduction of the adhesion constituent of the friction coefficient.

KEYWORDS: MAGNESIUM ALLOY; METALLIC COMPOSITE MATERIAL; POWDER FILLING; SEVERE PLASTIC DEFORMATION; EQUAL-CHANNEL ANGULAR PRESSING; SILICICUM CARBIDE; FRICTION COEFFICIENT; ADHESIVE BOND SHEAR STRENGTH; WEAR RATE.

Introduction

In modern mechanical engineering, in particular in friction knots, one of the ways to reduce the weight of cars is to apply light alloys with enhanced mechanical properties. Magnesium is attractive to be applied as structural material due to attractive strength-to-weight ratio that exceeds the one for aluminum and other light metals and alloys [1-3]. High damping capacity of magnesium alloys allows using them effectively to manufacture automobile and aircraft wheels, various components for motor- and tractor and aerospace engineering, rollers for cargo conveyors [6, 7] etc. The strength of magnesium could be enhanced without significant change in the strength due to addition of small amount of submicron powder filling of SiC [3-5]. Besides, severe plastic deformation is known to effectively increase the strength of bulk metals due to fabrication of ultrafine-grained structure [8, 9]. SPD techniques can be considered as alternative techniques to dispersion strengthening of composite materials. However, tribological behavior of these materials is studied insufficiently for application in friction knots [10, 11].

In this paper the results of definition of wear rate of the magnesium alloy, the friction coefficient and its molecular constituent depending on the content of the powder filling are given. Comparative evaluation of the adhesive bond strength and molecular constituent of the friction coefficient of the magnesium alloy AZ91D strengthened by ECAP in the slipping tribological contact with the tool steel composition Fe-18W-4Cr-1,2V is presented.

Experimental procedure and materials

Magnesium alloy AZ91D (89.89%Mg-9.0%Al-0.68%Zn-0.13%Mn) was used as material for study. In comparative tests there were employed matrix composite materials, containing submicron powder filling out of SiC, and the magnesium alloy AZ91D after 2 ECAP passes.

The variants of investigated composite materials differing in dispersity and amount of added powder of SiC and strain-hardened magnesium alloy of the initial state are the following: AZ91D in the initial state; AZ91D + 3% SiC with an average particle size of 5 μm; AZ91D + 3% SiC with an average particle size of 11 μm; AZ91D + 6% SiC with an average particle size of 11 μm; AZ91D + 3% SiC with an average particle size of 15 μm; AZ91D after 2 ECAP passes.

Tribological tests of the initial alloy and dispersion-strengthened composite materials were carried out on the friction machine “Timken”. Fig. 1 presents the set and the processing scheme.

Fig. 1. Machine of friction “Timken” (a) and testing scheme (b): 1 – tested sample; 2 – rotating steel disk.

Testing of the initial and dispersion-strengthened materials was conducted under normal loading of 10N and 50N and a disk rotation speed of 250 min⁻¹ and 1000 min⁻¹, the slip distance was 1650 m in all the tests.

Friction force (F), loss of sample mass (Q) and geometric area of the contact (S) were recorded during tests. The wear rate (Jw) value was defined with the help of the mentioned parameters.

The diameter of the disk out of tool steel composition Fe-18W-4Cr-1,2V was 70 mm, the thickness was 20 mm. The wear of the disk quenched to the hardness of HRC58...65 was neglected due to its low value as compared to the wear of the tested samples.

The friction coefficient \( f \) was calculated according to the formula:

\[ f = \frac{F}{P} \]  

where \( F \) – friction force, \( N \); \( P \) – normal loading force, \( N \).

The wear rate \( J_w \) value was defined according to the formula:
\[ J_h = \frac{Q}{qS_c L} \]  

where \( Q \) – sample mass loss, g; \( q \) – material density, g/cm\(^3\); \( S_c \) – geometrical area of the contact, cm\(^2\); \( L \) – slip distance, cm.

Fig. 2 presents the ECAP scheme that was chosen for strain hardening of the initial material [12, 13].

\[ \text{Fig. 2. ECAP scheme.} \]

The employed scheme allows achieving high degrees of accumulated strain as a result of shear in the conjugating channels. In this case the angle between the conjugating channels \( \varphi \) was 120°.

Studies on the evaluation of the adhesive bond shear strength and molecular constituent of the friction coefficient were carried out on the one-ball machine of friction at temperatures of 20, 150 and 300 °C according to the scheme that is presented in Fig. 3 [14].

\[ \text{Fig. 3. Scheme of testing of molecular constituent of the friction coefficient: 1 – tool steel R18 indenter; 2 – tested samples.} \]

Adhesive bond shear strength \( \tau_n \) was defined from the ratio:

\[ \tau_n = 0.75 \cdot \frac{M}{\pi \cdot \left( \frac{d_{1,2}}{2} \right)}, \]  

where \( d_{1,2} \) – diameters of prints on the tested samples, mm; \( M \) – indenter rotary moment, N mm.

Adhesive (molecular) constituent of the friction coefficient was defined as:

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

where \( p_r \) – normal pressure, MPa

\[ p_r = \frac{P}{\pi \cdot \left( \frac{d_{1,2}}{2} \right)^2}, \]  

where \( P \) – force of sample compression, N.

Results of experiments and their discussion

Figs. 4 and 5 present the charts with the results of tribological tests conducted according to the scheme “block-disk” (Fig.1).

\[ \text{Fig. 4. Dependence of the friction coefficient on the size of SiC particles} \]

\[ \text{Fig. 5. Dependence of the friction coefficient on the volume of powder filling} \]

It is seen from the charts that addition of powder filling of SiC to the magnesium alloy increases the friction coefficient. The lower the normal loading force and the slip rate, the higher friction coefficient.

In order to explain these results, let us consider the data received with the help of the one-ball machine of friction.

Fig. 6 demonstrates that the dependence of the adhesive bond shear strength \( \tau_n \) on the normal pressure \( p_r \) is described by the binomial dependence:

\[ \text{Fig. 6. Dependence of adhesive bond shear strength on the normal pressure in the contact with tool steel composition Fe-18W-4Cr-1,2V: a) - AZ91D in the initial state; b) - AZ91D + 3% SiC with an average particle size of 5 μm; c) - AZ91D + 3% SiC with an average particle size of 11 μm; d) AZ91D + 6% SiC with an average particle size of 11 μm; e) AZ91D + 3% SiC with an average particle size of 15 μm, f) AZ91D after 2 ECAP passes.} \]
where \( \tau_o \) — adhesive bond shear strength without normal loading force; \( \beta \) — piezocoefficient.

The molecular constituent of the friction coefficient \( f_m \) can be defined as:

\[
f_m = \frac{\tau_o}{p_r} + \beta
\]

It is seen from formula (7) that the molecular constituent of the friction coefficient increases, when the normal pressure \( p_r \) decreases. This fact explains the enhancement of the friction coefficient when the normal loading force reduces (Figs. 4 and 5).

Decrease in the slip rate reduces the temperature of the friction contact, which according to the data in Fig. 7 enhances the molecular constituent \( f_m \) and the total friction coefficient \( f \) (Fig. 4 and 5).

Increase of the friction coefficient after addition of SiC powder filling into the magnesium alloy can be explained by enhancement of the deformation constituent of the friction coefficient \( f_d \) (Figs. 4 and 5). It is known that in accordance with the mechanical and molecular friction theory [15] the deformation constituent of the friction coefficient is formed by the resisting forces of the deformation roller that runs in front of introduced irregularities to the surface of the softer contacting slipping bodies. The value of the deformation constituent of the friction coefficient \( f_d \) depends on the amount of introduced irregularities and their relative introduction can be defined analytically [15] or experimentally as:

\[
f_d = f - f_m
\]

The calculations of the values of the molecular constituent of the friction coefficient \( f_m \) conducted in the comparable conditions on the basis of experimental data given in Figs. 4, 5 and 7 demonstrate that addition of the SiC powder filling to the magnesium alloy enhances the value of the deformation constituent \( f_d \) from 0.09 to 0.20. The higher the \( f_d \) value, the higher the volume and size of SiC particles in the magnesium alloy. These particles characterized by high hardness are added to the contact surface of the counterbody, and the deformation constituent and total friction coefficient increase.

Solid SiC particles in the form of powder filling provide reduction of the wear rate of the dispersion-strengthened magnesium alloy (Fig. 8 and 9).

It should be noted that the wear rate decreases with the increasing size and volume of the filling particles in the magnesium alloy, as in this case the areas containing hard-wearing SiC particles increase. This effect can be observed on babbit bearings. The solid filling is added to the soft matrix of bearings.

The experimental data given in Figs. 6 and 7 testify to the fact that the magnesium alloy AZ91D after 2 ECAP passes is quite alternative to the composite magnesium alloy strengthened by the powder filling out of SiC. The preliminary deformation treatment of the initial magnesium alloy provides lower value of the adhesive constituent of the friction coefficient at a rather high bearing capacity of the frictional contact [16]. As the research results showed (Fig. 6), the bearing capacity of the frictional contact of the material processed by SPD technology is comparable with the composite material on the basis of the magnesium alloy that contains 3% SiC with an average particle size of 15 \( \mu \)m.

**References**


INFLUENCE OF THE SYNTHESIS METHOD ON THE CRYSTALLINE STRUCTURE, PHASE COMPOSITION AND PROPERTIES OF TiCrFeNiCuC EQUIATOMIC ALLOYS

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Abstract: Equiatomic alloys TiCrFeNiCuC were made by two methods of powder metallurgy – vacuum sintering and hot forging followed by annealing. In the process of sintering the TiCrFeNiCuC blanks, the influence of entropy of mixing resulted in the formation of solid substitution solutions mainly on the basis of the FCC lattice, and also formed titanium carbide (TiC_{0.58}). In samples obtained by hot forging and subsequent annealing, two carbides TiC and Cr_{0.74}C_{0.26} were found, and titanium carbide being formed with lower carbon content (TiC_{0.58}). In addition, the forged samples showed significantly higher values of the defect of the crystalline structure, which leads to increase in their hardness.

Keywords: EQUIATOMIC ALLOYS, MICROSTRUCTURE, PHASE COMPOSITION, HARDNESS, SINTERING, HOT FORGING.

1. Introduction

In the field of creating new classes of materials with increased physical, mechanical and operational properties, the approaches based on the development of high entropy alloys (HEAs) are the most promising.

A characteristic feature of such alloys is the content in their composition of not less than 5 basic elements, mainly in the equiatomic ratio. The presence of a large (not less than five) number of heterogeneous, but in an equal number of atoms, having different individual properties, imposes its specificity on the formation of a solid solution of high entropy alloys. The high entropy of mixing causes the minimization of the free Gibbs energy, which leads to the preferential formation of solid solutions with a BCC, FCC or FCC + BCC structure. The phases formed on the basis of solid solutions are more stable [1-3]. Alloys with such structures have high hardness, strength, wear resistance, oxidation resistance, etc. These properties of high entropy alloys are due to the slow diffusion of atoms in a multicomponent matrix, a significant distortion of the lattice, which arises in connection with the difference in the atomic dimensions of the constituent elements of the alloy, as well as the interaction between elements in phases based on a solid solution [4-9]. When giving carbon in the alloys, high entropy carbides will form.

To obtain HEAs the most widely used were various casting technologies [1-6]. However, in recent years, the methods of powder metallurgy are gaining increasing popularity in the development and production of these alloys [7-10].

The purpose of the work is to study the influence of the manufacturing method on the crystalline structure, phase composition and properties of the TiCrFeNiCuC equiatomic alloys.

2. Experimental Procedure

The initial Ti, Cr, Ni, Cu, Fe, and C powders with the purity of 99.5 - 99.9% were used as the starting elements for the preparation of the equiatomic alloys of the Ti-Cr-Fe-Ni-Cu-C system. Alloys were produced by two methods of powder metallurgy – vacuum sintering and hot forging with subsequent annealing.

The starting powders were dosed on an electronic scales. The charge of the equiatomic composition was prepared by mixing the powders in a drum mixer with a diagonal axis for 2 hours with the addition of alcohol. From the obtained mixture, cylindrical billets with a diameter of 20 and 40 mm at a pressure of 700 MPa were extruded in a steel matrix. Consolidation of powder blanks by hot forging was carried out on a doughstator press at a temperature of 1050 ° C in argon. Sintering of the samples and annealing of the forged samples were carried out in a vacuum induction furnace at 1200 °C for 2 hours.

X-ray diffraction studies were carried out on a DRON-3 X-ray diffractometer in filtered Co radiation by a step-scan method in the angular range 20÷130°. A quantitative micro-X-ray spectral analysis was performed on a Cameca MS-46 X-ray microprobe at a probe mode of 20 kV, 12 nA and a probe diameter of 3 μm. The microstructure of the alloys was studied with an XJL-17 optical microscope and with a JEOL Superprobe 733 scanning electron microscope. The density and porosity of the alloys were determined by hydrostatic weighing. The microhardness was measured on a PMT-3 device. The hardness was measured on a TK-14-250 hardness tester. The theoretical density of the alloy, calculated from the additivity formula, is equal to 6.55 g/cm³.

3. Experimental results and their discussion

X-ray diffraction studies of high entropy TiCrFeNiCuC alloys, obtained by different methods, revealed features both in the phase composition and in the defectiveness of their crystal unit cell. Regardless of the method of preparation, alloys had a heterogeneous structure. On the X-ray diffraction pattern of the alloy obtained after sintering at 1200 °C for two hours, a number of lines characterizing the phase with a FCC lattice are fixed, as well as TiC carbide. On the lines with the indices of the atomic planes (311) and (222), we can assume the presence of two phases with FCC lattices with close values of the crystal lattice parameter (Fig. 1, a). The phase with the BCC structure is fixed weakly.

Fig. 1. XRD patterns of TiCrFeNiCuC alloys, obtained by vacuum sintering (a) and hot forging with subsequent annealing (b).

On the X-ray diffraction pattern of the sintered alloy, the diffraction maxima (111) and (222) were divided into two components (Fig. 2). The calculated crystal lattice parameters for both FCC phases are: \( a = 0.36098 \) nm and \( a = 0.35877 \) nm. It is known that nickel and copper are systems with unrestricted solubility based on the structural type of FCC. It should be assumed that one phase of FCC with \( a = 0.36098 \) nm is formed with a high copper content (\( c_{Cu} = 0.36176 \) nm), another phase \( a = 0.35877 \) nm – with a high nickel content (\( c_{Ni} = 0.35195 \) nm). An analysis of the structural state of phases with a FCC structure indicates that both
phases of the FCC have a number of imperfections in their crystal lattice and a difference in the quantitative ratio of their defectiveness, characterized by the values of the parameters of the fine structure elements. Thus, for FCC with a high copper content with \( a = 0.30988 \) nm, the defectiveness of the crystal structure is denoted by the following parameters: coherent scattering region (CSR) = 36.2 nm, microdistortion \( \Delta a/a = 54.6 \times 10^{-3} \), dislocation density \( \rho = 8.2 \times 10^{11} \) cm\(^{-2} \). For a FCC structure with a high nickel content \( a = 0.35877 \) nm. Data on the imperfections of the FCC alloy structure is much higher in comparison with the analogous results for the phase with the predominant copper content and are denoted by the following parameters: CSR = 10.0 nm, \( \Delta a/a = 77.2 \times 10^{-3} \), \( \rho = 17.3 \times 10^{11} \) cm\(^{-2} \). The FCC phase, which is formed with the predominant content of the more ductile element of copper, naturally has a less distorted crystal lattice in comparison with the FCC lattice with a harder nickel base. This conclusion is confirmed by microhardness measurements: a FCC structure with a crystal lattice parameter equal to \( a = 0.36098 \) nm has a microhardness of 4.9 GPa, a structure with a crystal lattice parameter equal to \( a = 0.35877 \) nm has a microhardness of 6.8 GPa.

Along with solid solutions of the FCC type in the highly entropic TiCrFeNiCuC alloy obtained by sintering at 1200 °C for two hours, titanium carbide with a crystal lattice parameter of 0.43215 nm is formed. According to the dependence of the TiC cell parameter on the amount of carbon bound in it [12] in the sintered alloy, there is a TiC phase with an atomic ratio of carbon to titanium of 0.74 (TiC\(_{0.74}\)).

The formation of phases in highly entropic alloys, the appearance of two or three phases is associated with a certain electronic concentration in the alloy, with the difference in the atomic radii of the components that make up the alloy. Hot forging is a significant influence on the formation of the crystal structure of high entropy alloys. Hot forging of porous blanks can be considered one of the cycles of thermomechanical processing, during which a developed substructure is created. This developed substructure is the primary factor determining all other structural causes of thermomechanical hardening of steel. [11].

X-ray diffraction studies of the alloy TiCrFeNiCuC, obtained by hot forging and subsequent high-temperature annealing, indicate the formation of a heterophase structure of the alloy. The X-ray spectrum of the alloy is represented by phases of FCC, BCC, TiC and Cr,C\(_2\) carbides (Fig. 1 b).

Analysis of the X-ray spectrum of the alloy revealed the following features. Estimating the nature of the profiles of the X-ray lines of the FCC structure, several blurred profiles should be noted that describe the phase with the FCC grating, which is especially noticeable at large reflection angles. Thus, for a FCC lattice along lines with indices of atomic planes (311) and (222), it is possible to assume the presence of two phases with FCC lattices with close parameters. This is confirmed by calculations on the lines (222): \( a_1 = 0.36460 \) nm and \( a_2 = 0.35815 \). On the XRD pattern of the forging alloy, the diffraction maxima (111) and (222) were decomposed into two components (Fig. 3).

One of the phases with the parameter \( a_1 = 0.36046 \) nm \( a_2 = 0.35815 \) copper i.e. with a high copper content, another phase of FCC with \( a_2 = 0.35815 \) nm is closer to the nickel parameter, i.e. with a high content of nickel.

An analysis of the structural state of phases with a FCC structure indicates that both phases of the FCC have a number of imperfections in their crystal lattice and a difference in the quantitative ratio of their defectiveness, characterized by the values of the parameters of the fine structure elements. Thus, for the FCC lattice with a high copper content \( a = 0.36098 \) nm, the defectiveness of the crystal structure is denoted by the following parameters: CSR = 5.2 nm, microdistortion \( \Delta a/a = 90.4 \times 10^{-3} \), dislocation density \( \rho = 22.6 \times 10^{11} \) cm\(^{-2} \). For a FCC structure with a high nickel content \( a = 0.35815 \) nm. Data on distortion of the lattice of the FCC structure of the alloy is much higher in comparison with the analogous results for the phase with the predominant content of copper and are denoted by the following parameters: \( \Delta a/a = 119.8 \times 10^{-3} \), \( \rho = 42.0 \times 10^{11} \) cm\(^{-2} \). There is no grain fragmentation in the coherent scattering region (CSR = 112.3 nm, i.e., commensurate with the grain size), the structural defect is due to the distortion of the crystal lattice. The FCC phase, which is formed with the predominant
content of the more ductile element of copper, naturally has a less distorted crystal lattice in comparison with the FCC lattice with a harder nickel base. This conclusion is confirmed by microhardness measurements: a FCC structure with a crystal lattice parameter \( a = 0.36098 \text{ nm} \) has a microhardness of 5.5 GPa, a structure with a lattice parameter \( a = 0.35877 \text{ nm} \) has a microhardness of 7.3 GPa.

The most intense line (110) of the structure with a BCC lattice on the x-ray spectrum of the sample is indicated by a line of weak intensity, which indicates a small amount in the sample alloy. In addition to line (110), we can consider the line (211) belonging to the BCC structure as a weak diffuse reflex. Line (220) is almost overlapped with the background. The diffuse character of the BCC reflections is due to the distortion of the crystal lattice, which is confirmed by the quantitative characteristics of the fine structure elements. So the value of the regions of coherent scattering is 50.0 nm (probably somewhat overestimated as a result of overlapping of the part of the profile from the side of the small angle by the line of the FCC lattice (110)), microdistortions equal to \( 175.87 \times 10^3 \text{ cm}^{-2} \), the dislocation density is \( \rho = 62.0 \times 10^{11} \text{ cm}^{-2} \). The results on the distortion of the crystal lattice of the BCC phase are the largest for all the emerging highly entropic phases. The phase with the BCC structure is formed upon mutual dissolution of iron and chromium, which has the parameter \( a_{\text{bcc}} = 0.2858 \text{ nm} \), has so small a grain that it was impossible to measure the microhardness.

It was pointed out that on the XRD pattern of the alloy, in addition to a series of phase lines of FCC and BCC structures, a number of reflections belonging to TiC and Cr2C2 carbides. The TiC lattice parameter is 0.4311 nm, hence, the TiC phase is present in the alloy with an atomic carbon to titanium ratio of 0.58 (TiC/33). In the sintered alloy, the atomic ratio of carbon to titanium is 0.74.

The microstructure of the sintered and forged alloys consists mainly of two structural regions. According to micro-X-ray spectral analysis, the light phase has an increased content of Cu, Fe, and Cr. The darker phase is the result of the maximum interdiffusion of all elements of the alloy and has an increased concentration of Ni, Ti and C. Consequently, the dark phase contains TiC. In the forged alloy, a much greater dispersion of the structural elements is observed compared to the sintered alloy, as well as the presence of two carbides – TiC and Cr2C2, which is explained by the influence of hot forging.

![Fig. 4. Microstructures of sintered (a) and forged (b) equiatomic TiCrFeNiCuC alloys](image)

Analysis of the processes of structure formation of high entropy phases formed in alloys of TiCrFeNiCuC composition, inclusions of various compounds showed a significant increase in the defectiveness of crystal structures and, accordingly, an increase in the microhardness of both individual structural components and hardness of the alloy as a whole, using preliminary hot forging of porous blanks. In the sintered alloy, the hardness is 30 HRC, in the alloy with the preliminary hot forging, the hardness increased to 42 HRC (Table 1).

### Table 1. Characteristics of TiCrFeNiCuC alloys obtained

<table>
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<th>№</th>
<th>Production method</th>
<th>Density, g/cm³</th>
<th>Porosity, %</th>
<th>Hardness, HRC</th>
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<td>Sintering</td>
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<td>4.0</td>
<td>30</td>
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<tr>
<td>2</td>
<td>Hot forging and annealing</td>
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### 3. Conclusions

Thus, preliminary hot forging during the formation of a high entropy alloy intensifies the processes of structure formation, causes redistribution of carbon (with the formation of chromium carbide Cr2C2, titanium carbide TiC is formed with a smaller carbon content in TiC to 0.58), and also provides processes that lead to significant distortion of the crystalline lattice of the forming phases, which contributes to the strength of the alloys.

### References

SURFACE TREATMENTS AND COATINGS APPLICATION ON THE ALUMINUM PRODUCTS

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Abstract: The aim of this work is to present the influence of anodic surface treatment parameters on thickness and structure of an anodic layer formed on aluminum products.

The materials used in this study are the aluminum products from Alumil Company in Albania. The analyses of samples were performed using Optical Microscopy (Leica DMI 5000 M) for characterization of macrostructure of anodizing layer and Vickers micro-hardness (HMV-2 tester) of non-anodized aluminum products and anodized aluminum products. Aluminum product of the series A6060 are taken in Alumil Company in Albania. Comparing the results in this research (analyses) we have concluded the characteristics of anodizing layer in the aluminum product, which have improved and increase their surface and product performance.

Keywords: ALUMINUM ALLOY, MICRO-HV, OM, ANODAZING, MICROSTRUCTURE

1. Introduction

Surface treatments and coatings are applied to aluminum products to enhance their performance. In order to improve surface properties of final products, such as wear resistance, corrosion resistance - different types of surface treatments are applied. [1,2]

Anodizing is one the best technique for protective and decorative purposes is the most common method of superficial oxidation processes and is carried out through anodic oxidation. The usability of aluminum after anodizing depends mainly on the properties of oxide layers occurred during this process. [1,2]

Table one presents the chemical composition of A6060 [4]:

<table>
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<tr>
<th>Alloy</th>
<th>Si</th>
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<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
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<td>A6060</td>
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<td>0.029</td>
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</tbody>
</table>

Evaluation of the thickness of the oxide layer was carried out in the transverse section of the anodized profile, after polishing. Observations for thickness estimation of the oxide layer were performed on the 500x and 1000x metallographic microscope as well as the micro-hardness (Vickers) 400x magnification. [1,2,5]

The metallographic preparation of the samples and measurement are performed in Materials Science and Technology Laboratory, in Mechanical Engineering Faculty in Tirana-Albania. [1,2]

We focused the experimental part of our work on estimating the thickness of the anodized layer and its hardness. Performing Optical Microscopy using Leica DMI 5000 M software for characterization of macrostructure of anodizing layer and performing micro-hardness Vickers (HMV-2 tester) on aluminum products with anodizing treatment on the surface and also aluminum products without treatment. [1,2]

2. Discussion and Conclusions

- The A6060 products were coating with a layer anodizing and the level of strengthening was followed up and measured by micro-hardness test with 10gf, force applied for 10 sec in one indenter;
- The thickness of the anodized layer depends on the maintaining time in the anodizing bath;
- The A6060 products were coating with a layer anodizing and the level of strengthening was followed up and measured by micro-hardness test with 10gf, force applied for 10 sec in one indenter;
- In figure 1 it is shown the microstructure of sample from an aluminum profile products, taken from metallographic microscopy;

- The anodizing surface of aluminum products Based on the micro-hardness measurement results have higher hardness compared with the simple aluminum products without treatments in the surface;
- The micro - hardness of layer anodizing it is in the range between 420 – 560 HV comparing with the results of aluminum samples without treatments in the range between 55 – 70 HV.

Graph. 1. The results of micro-HV comparing the homogeneity of surface treatments

- Evaluation of micro-hardness of the oxide layer with thickness ~11microns determined with metallographic microscope by Leica Soft – provides the anodizing efficiency by increasing the hardness 8 times more versus aluminum products without treatments or coating on their surface.

REFERENCES


[5] Paul J.D. Whiteside, Jeffrey A. Chininis and Heather K. Hunt ‘Techniques and Challenges for Characterizing Metal Thin Films with Applications in Photonics’ Department of Bioengineering, University of Missouri, Columbia, MO 65211, USA; paulwhiteside@mail.missouri.edu (P.J.D.W.); jacrf5@mail.missouri.edu (J.A.C.)
EVALUATION OF MECHANICAL PROPERTIES OF DUCTILE CAST IRON AND INVERSE REGRESSION

ОЦЕНЩИВАНИЕ МЕХАНИЧЕСКИХ СВОЙСТВ ЧУГУНА
С ШАРОВИДНОГО ГРАФИТА И ОБРАТНАЯ РЕГРЕССИЯ

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Abstract: The evaluation of ductile cast iron is common foundry practice. For the correct non-destructive evaluation (NDE) of mechanical properties (ultimate tensile strength; relative lengthening; Brinell’s hardness; elasticity modulus) by means ultrasonic testing and inverse regression analysis are used.

Key words: MECHANICAL PROPERTIES, DUCTILE CAST IRON, INVERSE REGRESSION

1. Introduction
The ultrasonic testing of the mechanical properties of ductile cast iron [1,2,3] is a common practice in M+C HYDRAULIC.

There are methods of regression analysis are used. In literature there are dependencies between the structural characteristics of the cast iron \((F; P; N_G)\) and its mechanical properties \((E; V; N_G; R_m; HB)\), where \((F; P; N_G)\) are appropriate \(F, \%\) - quantity of ferrite and \(P, \%\) - quantity of perlite in the metal matrix, \(N_G, \%\) - nodular graphite contain; \(R_m\) - ultimate tensile strength; \(A_5\) - relative elongation; \(HB\) - Brinell’s hardness; \((E; V)\) - elasticity modulus. The following dependencies are considered [4-11]

\[
\begin{align*}
(1) & \quad (E; V) \Rightarrow (V_L, V_T), \\
(2) & \quad N_G = \eta(V_L), \\
(3) & \quad R_m = \gamma_0 + \gamma_1 V_L; \quad R_m = \beta V_L^2 HB; \\
(4) & \quad A_5 = A_5^{(0)} + A_5^{(1)} V_L; \quad A_5 = a(M V_L^2 / HB)^m; \\
(5) & \quad HB = h_0 + h_1 V_L,
\end{align*}
\]

where \((V_L, V_T)\) are velocities of longitudinal and transversal ultrasonic waves [8,11]. The coefficients in (2)-(5) are subject to determination and depend on the casting technology and the type of graphite in the casting. The dependencies (2) to (5) are regressions models from type

\[
(6) \quad (N_G; R_m; A_5) = F(V_L, HB),
\]

In regression analysis [12] the basic principle is “\((F; P; G)\) defines by \((N_G; R_m; A_5; HB)\)”, where \((F; P; N_G)\) - microstructure characteristics of, \((N_G; R_m; A_5; HB)\) - mechanical properties for ductile cast iron. In this sense, dependencies (2) to (5) are incorrectly. The correct approach is

\[
(7) \quad V_L = \Psi(N_G; R_m; A_5; HB),
\]

where \((F; P; G) \Rightarrow V_L\). In this article the models with one predictor \(X = \chi(N_G; R_m; A_5; HB)\) and order \(n\) are considered [12]

\[
(8) \quad V_L = \sum_{k=0}^{n} \beta_k X^k.
\]

The condition for choice, at \(X = 1\), of order \(m\), is

\[R^2 \rightarrow \max\] , where \(R^2\) is coefficient of determination.

Table 1.

<table>
<thead>
<tr>
<th>(m)</th>
<th>(R^2)</th>
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<tbody>
<tr>
<td>1</td>
<td>(R^2 = R^2(m = 1))</td>
</tr>
<tr>
<td>2</td>
<td>(R^2(m = 2) \approx (1.05 \pm 1.10) R^2)</td>
</tr>
<tr>
<td>3,4,5</td>
<td>(R^2(m = 3,4,5) \approx (1.06 \pm 1.13) R^2)</td>
</tr>
<tr>
<td>(m \geq 6)</td>
<td>The regression matrix is badly determined.</td>
</tr>
</tbody>
</table>

If \(m = 1\), then the values of \(R^2\) are relatively low. If \(m = 2\), then the values of \(R^2\) are rises with \(~ (5 \pm 10)\%\). If \(m = 3,4,5\), then the values of \(R^2\) are rises \(~ (1 \pm 3)\%\) and efforts to calculate it are not justified. If \(m \geq 6\), then the regression matrix is badly determined and calculations are not made.

Therefore, the optimal choice of the model (8) is one predictor \(X \Leftrightarrow (N_G; R_m; A_5; HB)\), and model order \(m = 2\).

2. Relations for ductile cast iron

2.1. Deterministic dependencies
In the theory of elasticity [10,11] is obtained (9)

\[
V_L = \frac{1 - \nu}{(1 + \nu)(1 - 2\nu)} \sqrt{\frac{E}{\rho}},
\]

where the elasticity modulus \(E; V\) respectively are Young’s modulus and Poisson’s coefficient, density of ductile cast iron \(- \rho, kg/m^3\). The deterministic dependence (9) is reduced to

\[
(10) \quad E = M(v) V_L^2,
\]

where

\[
M(v) = \rho \frac{(1 + v)(1 - 2v)}{(1 - v)} v = 0.5 - \frac{(V_L / V_T)^2}{1 - (V_T / V_L)^2}.
\]

For most ductile cast iron, the reference values for \(v\) are \(v \in (0.23 \pm 0.28)\). In fact, for ductile cast iron, Poisson’s coefficient changes to a very narrow boundary. By means
reference values $med(v) = 0.25$, $\rho = 7.31 \text{kg/m}^3$, $M = 6.092$ is obtain. Therefore, the dependence (10) is reduced to

(11) $E \approx 6V_L^2$.

2.2. Stochastic dependencies
According the experimental data, for ductile cast iron, from M+\textit{C HYDRAULIC} a polynomial models of (8) are considered

(12) $V_L = \sum_{k=0}^{2} \beta_k X^k$,

where $X \equiv (N_G;R_m;A_3;HB)$, $(\beta_0;\beta_1;\beta_2)$ subject to determination. It are direct regression problems.

The inverse regression problems are determine the confidence intervals $(X_L;X_R)$, when $V_L$ is measured. The equations for $(X_L;X_R)$ are [12]

(13) $\chi(X_{L,R}) + V_L = 0$,

where

$$\chi(X_{L,R}) = \frac{1}{2} \left[ \frac{1}{n} S_{XX} (X_{L,R} - \bar{X})^2 \right] \sum_{k=0}^{2} \beta_k X_{L,R}^k$$

number of measures $n$, $S_{XX} = (n-1)S \left( X, S, \bar{X} \right)$, by means Excel, MS Office are obtain.

The equations (13) are non-linear regarding $X_{L,R}$ and solved by the Newton’s method using a ZEROIN algorithm [11], on-line C++ compiler, at a specified root spacing. The ZEROIN algorithm is resistant and fast approaching.

3. Equipment
Image Analyzer Buehler Omnimet, Digital Ultrasonic Flaw Detector Siteman 150S, Tensile machine Testometric F300, Hardness tester ТШ-2М.

4. Experiment
Ten samples were made with varying percentages and graphite morphology and mechanical properties. They were determined for them $(N_G;R_m;A_3;HB)$ and $(V_L;V_T)$. Morphology of graphite $(N_G)$ was determined with a Buehler Omnimet image analyzer at an 8x image magnification. The mechanical properties $(R_m;A_3;HB)$ are determined by mechanical testing. The velocities $(V_L;V_T)$, Fig.1, according ASTM E 494:2015 are calculated.

Fig.1. Ultrasonic L-waves (a) and T-waves (b)

5. Inverse regression tasks
5.1. Polynomial models
According the experimental data, for ductile cast iron, confidence intervals $(X_L;X_R)$, are obtained.

![Fig.2. $(x = N_G,\% ; y = V_L, \text{m/s})$](image)

![Fig.3. $(x = N_G,\% ; y = HB, \text{kgf/mm}^2)$](image)

![Fig.4. $(x = R_m, \text{MPa} ; y = V_L, \text{m/s})$](image)

![Fig.5. $(x = A_3, \% ; y = V_L, \text{s})$](image)
5.2. Hybrid models

The introduction of hybrid models in the regression analysis is based on the following assumption. Factor combinations depend on one predictor [4-11]. For example $F(V_L; HB) = A_5$ and $\Psi(V_L; HB) = R_m$. Such an approach is expected $R^2$ will rise. On Fig. 7. and Fig. 8. specific dependencies are given.

6. Results

For data from M+C HIDRAULIC Plc the results of inverse regression analysis in Tables 2 - 8. are given. When comparing the results of (Fig.2) and (Fig.3.), it appears that using the model from (Fig.2.) has less scattering gives a little narrower boundaries evaluation of $N_G$, %. In this sense, the use of the model from (Fig.2.) is slightly better than the model from (Fig.3.).

7. Conclusion

The paper examined the possibilities and constructed correct models for assessing the degree of ductile cast iron spheronization and mechanical properties by measuring the velocity of propagation of longitudinal ultrasonic waves and Brinell hardness. The numerical values of the coefficients of the models were obtained as well as the coefficients for their determination. For this purpose, the respective inverse regression tasks are solved.

8. References

8. Voronkova L.V., Ultrasonic Testing Possibilities of Cast Iron Ingots, Th.2.2.3., ECNDT 2006, Roma, Italy.
9. Hanza S.S., D. Dabo, Characterization of cast iron using ultrasonic testing, Journal of Cr S NDT, No 18, p.3-7, ISSN 1847-9340, 2017