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INVESTIGATION OF ZINC COATED PANELS Nylofor® 2D Super

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Abstract: Zinc galvanized panels were ordered and delivered for the fencing of the factory yard. But immediately after receiving the panel from the deliverer, it was concluded that their quality is suspicious. These panels must fulfill strict standards requirement concerning their quality. To confirm this purchaser engaged the team from the Faculty of Technology and Metallurgy in Skopje to perform investigation and to check if the panels satisfy quality requirement. The performed investigation consists of the following testing’s: chemical composition of base metal (wire), wire diameter and tolerances, tensile test, weld shear strength test, mesh size and tolerances, coating, visual inspection of panels. Performed investigation confirmed that delivered panels didn’t fulfill necessary requirement for this type of fencing.

Keywords: ZINC COATING, PANEL, S NYLOFOR, WHITE RUST, ELECTRO RESISTANCE WELDING

1. Introduction
The Nylofor 2D & 2D Super system is, because of the high rigidity and security, recommended for professional fencing of schools, play grounds, parks, public buildings, factories and workshops, airports and military sites. The extra heavy horizontal wires make Nylofor 2D Super particularly suitable for the security of sport grounds too. The panels are extremely rigid due to the use of heavy welded mesh in conjunction with double horizontal wires. The coating technology should guarantee a long lifetime. The system includes panels in different mesh apertures and horizontal wires. The designation of the wire rod is C9D, and its WNo is 1.0304 – unalloyed steel. Chemical composition of the welding wire from unalloyed steel. Chemical testing are presented in table 1.

As can be seen from the formerly presented things, the quality of the panels is result of entirely performing of the quality installation. As can be seen from the table 1 obtained value for chemical composition fulfill the standard requirement, but measured values for carbon and silicon are much lower than values prescribed in standard.

2. Material and investigations
The subject of investigations in this research work are Panels Nylofor® 2D Super intended for fencing of factory yard - according with appropriate standard. The panels are produced by electrical resistance spot welded galvanized wires in accordance with EN 10223-7. The vertical wires have a barb at one side of the panel. The panel is reinforced by means of a horizontal double round wire at both sides of the vertical wire.

3. Results of the investigation
Chemical composition of base metal (Wire rods)
This test was performed according EN 10016-2 (ISO 16120). The designation of the wire rod is C9D, and its WNo is 1.0304 – wire from unalloyed steel. Chemical composition of the welding wire according standard requirement and values obtained by chemical testing are presented in table 1.

Table 1. Chemical composition of welding wire according EN 10016-2 (ISO 16120) and performed chemical analysis.

<table>
<thead>
<tr>
<th>Element, %</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. value</td>
<td>0.16</td>
<td>0.300</td>
<td>0.600</td>
<td>0.0350</td>
<td>0.035</td>
</tr>
<tr>
<td>Hor. wire</td>
<td>0.070</td>
<td>0.140</td>
<td>0.500</td>
<td>0.0179</td>
<td>0.008</td>
</tr>
<tr>
<td>Ver. wire</td>
<td>0.070</td>
<td>0.138</td>
<td>0.498</td>
<td>0.0182</td>
<td>0.008</td>
</tr>
</tbody>
</table>

As can be seen from the table 1 obtained value for chemical composition is beneath max values from standard requirement. It generally means that chemical composition fulfill the standard requirement. But, it has to be point out that measured values for carbon and silicon are much lower than values prescribed in standard.

Table 2. Outer wire diameter and tolerances

<table>
<thead>
<tr>
<th>EN 10218-2 Diameters and tolerances</th>
<th>Horizontal wire, [mm]</th>
<th>Vertical wire, [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylofor Super</td>
<td>8.00 ± 0.20 mm</td>
<td>6.00 ± 0.20 mm</td>
</tr>
<tr>
<td>Measured values</td>
<td>7.45, 7.49, 7.49</td>
<td>5.52, 5.53, 5.52</td>
</tr>
<tr>
<td></td>
<td>7.46, 7.46, 7.46, 7.46</td>
<td>5.53, 5.54, 5.55, 5.54</td>
</tr>
</tbody>
</table>

As can be concluded from table 2 measured values are beneath values for the outer diameters of Nylofer 2D and Nylofer 2D Super. It means they don’t satisfy standard requirement.

Table 3 Tensile testing of horizontal and vertical wire compared with standard requirement

<table>
<thead>
<tr>
<th>Vertical and horizontal wire, min, [N/mm²]</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal wire, [N/mm²]</td>
<td>473</td>
</tr>
<tr>
<td>Vertical wire, [N/mm²]</td>
<td>564</td>
</tr>
</tbody>
</table>

Results from performed tensile testing showed that vertical wire fulfills the standard requirements, but obtained results from tensile testing of horizontal wire are beneath the minimum values given in standard and don’t satisfy.

Weld shear strength test
Weld shear strength test was performed in accordance with EN 10223-7. Four randomly taken specimens (welds) were prepared and tested. According this standard, average shear strength shall not be less than 50% of the breaking load of the vertical wire. Obtained results are given in the table 4.

Table 4 Weld shear strength test

<table>
<thead>
<tr>
<th>Meas. value, [N]</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3125</td>
<td>3124</td>
<td>3765</td>
<td>3624</td>
<td>3410</td>
</tr>
</tbody>
</table>
As can be seen from the table 4, 50% of the minimum breaking load is 5939 N. Average value from four test measurement is 3410 N. It means that shear strength test didn’t fulfill standard requirement.

**Mesh size and tolerances**

Mesh size and tolerances are determined by EN10223-7 standard. Randomly chosen fields were tested. Requirements of the standard and measured values are given in table 5.

<table>
<thead>
<tr>
<th>Mesh size and tolerances Nylofor 2D super</th>
<th>Standard requirement</th>
<th>Measured values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distance between horizontal wires</td>
<td>200 ± 2 mm</td>
<td>198, 203, 197, 202, 201, 199, 200, 198, 200, 201</td>
</tr>
<tr>
<td>Distance between vertical wires</td>
<td>50 ± 2 mm</td>
<td>48, 49, 50, 50, 49, 50, 48, 50, 49, 48, 49, 49</td>
</tr>
</tbody>
</table>

Comparison between measured and obtained results showed pretty good results. Only too values didn’t satisfy standard requirement (horizontal wire bolded values).

**Zinc Coating**

Raw material i.e. steel wires are previously galvanized. Minimum zinc coating according with Betafence recommendation for the horizontal and vertical wires is 40 g/cm². Results from coating measurements are given in table 6. Obtained results from measurements were compared with requirement from ISO 1461 standard for zinc galvanized coating.

<table>
<thead>
<tr>
<th>ISO 1461</th>
<th>Coating min, [g/m²]</th>
<th>Coating min, [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard requirement</td>
<td>505</td>
<td>70</td>
</tr>
<tr>
<td>Measured values (horiz. wire)</td>
<td>711</td>
<td>100</td>
</tr>
<tr>
<td>Measured values (vertical wire)</td>
<td>1069</td>
<td>150</td>
</tr>
</tbody>
</table>

Obtained results show that zinc coating is much thicker compared with ISO 1461 standard requirement. Measured thickness value for vertical wire is two times higher than standard request.

**Visual inspection**

Inspected Nylofer 2D Super panels were laid on the wooden pallets in the factory yard. Every pallet with galvanized panels was separately inspected, and different types of defects were detected. As can be seen from the figure 3, pallets were protected with nylon coverage during transportation and storage. But this protection was generally damaged. General conclusion is that almost all panels have many different types of surface defects. From the most characteristic defects detected in the inspected panels were taken photographs which are given below. Photographs given in figure 1(a and b) concern to the white rust. White rust is type of surface defect which can appear on the surface of the fresh galvanized parts. The main reason for its appearing is presence of water (moisture) in contact with part and appropriate temperature. White rust is in fact Zn(OH)₂. Process of rust formation last until the last drop of water is present in contact with galvanized surface. Figures 2 refers to excess zinc coating on the galvanized bars. The reason can be improper temperature of molten zinc during galvanization. Figure 3 concerns to defect i.e. corrosion attack as result of mechanical damaging of the galvanized layer or bed surface preparation before galvanization start. Panels with defects like dross, flux, peelings and sapling are presented at figure 4. Vertical ribbed bars are not allowed for these panels (Figure 5), but they are used for panel’s production. Mechanically damaged panels during transport or storage can be seen at figure 6. Figure 7 show bed spot welds. It means that there is not strong connection between the bars.
However, the role of zinc coating is to protect the panel surface from corrosion. It’s a fact that galvanized coating normally has to be smooth, continuous and free from gross surface imperfections and inclusions. The surface of the steel wires should be completely covered with a uniform zinc coating whose thickness depend principally by the thickness of the steel being galvanized. During the visual control and measurement was found that zinc deposits are too thick and not uniform.

White rust (figure 1(a and b)) is a white powdery deposit formed from a natural corrosion process that can occur on any new zinc coated steel product. Zinc is a very durable coating for the purposes of providing sacrificial protection to the underlying steel substrate but, because it is reactive to water, great care must be taken in storing it correctly. That is why it is often referred to as “wet storage stain.” The white powder is actually zinc hydroxide – the substance formed when zinc reacts with water and air - and it gradually consumes the zinc coating; this process is most likely to happen in wet conditions with inadequate air circulation (improper packing of panels).

The actual thickness of galvanized coating achieved varies with steel section size, surface profile and surface composition. Actual coating weights are often much more than the minimum specified in the standard. Thicker coatings than those set out in EN ISO 1461 can give additional protection for use in particularly aggressive environments. For most applications, thicker coatings are rarely necessary.

The service life for the coating is determined by two factors, the environment and the coating thickness. Recent studies on the life of a galvanized coating show that a coating in an industrial environment will have 60% of the life of the same coating in a rural environment. In the neighborhood of company yard there is no such severe conditions.

Defects on the surface of the coating (figure 3) are influenced by many factors quality of raw material (wire), preparation of wires for galvanization, purity and temperature of zinc in bath, welding techniques and technology and many others. Molten zinc has to be smooth, continuous and free from gross surface imperfections and inclusions. The surface of the steel wires should be completely covered with a uniform zinc coating whose thickness depend principally by the thickness of the steel being galvanized. During the visual control and measurement was found that zinc deposits are too thick and not uniform.

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[5] EN 10244-2: Steel wire and wire products - Non-ferrous metallic coatings on steel wire - Part 2: Zinc or zinc-alloy coatings on steel wire,
[8] ASTM F 2453 / F 2453M: Standard Specification for Welded Wire Mesh Fence Fabric (Metallic-Coated or Polymer Coated) for Meshes fo 6in.² [3871 mm²] or Less, in Panels or Rolls, with Uniform Meshes
SURFACE QUALITY OF WOOD PLASTIC COMPOSITES COATED WITH SOLVENT AND WATER BASED PAINTS

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Abstract: This study investigated surface hardness, roughness, and abrasion resistance of hot press molded wood plastic composite (WPCs) panels coated two types paints, water- or solvent-based paints. The WPC panels are produced from different amounts of pine wood flour (30 to 60 wt%), virgin polypropylene (37 to 67 wt%) and 3 wt% maleic anhydride polypropylene (MAPP). The surface abrasion resistance and hardiness of the WPC panels painted with water or solvent based paints increased up to 50 wt% wood flour content, but further increment in the wood flour content decreased the abrasion resistance and hardness. The surface roughness of the painted WPCs increased with increasing wood flour content. The WPCs painted with solvent-based paints showed better surface quality as compared to the WPCs painted with water-based paints.

KEYWORDS: HYBRID COMPOSITES, MECHANICAL PROPERTIES, WOOD PLASTIC COMPOSITE, THERMOPLASTICS, WATER ABSORPTION, SURFACE HARDNESS.

1. Introduction

Coating Technology, a new process to coat wood plastic composites in virtually any color while enabling them to resist fading, heat retention, mold, mildew, stains and abrasion. The implementation of WPC with water-based paints could open up new application possibilities and markets in the construction sector, e.g. for façade and window sections. In the last few years, the WPC market in Europe has expanded rapidly and the outlook is viewed positively. In Germany, the current annual production volume is around 50,000 t, whilst Europe has an estimated capacity of around 120,000 t [1].

Among the reinforcing agents, natural fibers have significant advantages such as low cost, highly available and renewable, with low density and high specific properties as well as biodegradable and less abrasive to processing equipments. Among commodity thermoplastics, polypropylene (PP) possesses outstanding properties such as low density, good flex life, sterilizability, good surface hardness, very good abrasion resistance, and excellent electrical properties. However, the main drawback of PP is low modulus as compared to the wood. The purpose for the addition of cellulose-based fillers to thermoplastics is to reduce the cost per unit volume and to improve stiffness.

It is currently not possible to satisfactorily coat WPC surfaces with water-based paints. The reason for this is the low surface energy and the barely-existent functionality which result in bad wettability and lack of material anchorage for aqueous binders [1]. Solvent-based paints, sometimes referred to as "oil-based" or "alkyd" paints, contain a significantly higher level of organic solvents than water-based paints. These solvents are responsible for the strong odor noticeable in buildings that have been freshly painted. They are also potentially hazardous for both human health and for the environment which is why concerted efforts are being made to reduce or remove their presence in paints without negatively impacting on paint performance. water-based paints, often referred to as acrylic emulsions, are increasingly replacing organic solvents across a broad ange of paint applications and surface areas [2].

Appropriate coatings can provide outstanding scratch resistance, as well as provide a surface that is easy to clean. Appropriate coatings can seal the WPC to prevent moisture absorption, mold growth, and physical property reduction. Using coating systems can also enable homeowners to repaint their WPC to match new decoration schemes, or repair scratches or mars over time of use [3]. There is limited information about the effect of raw material formulation on the surface properties of WPCs painted with water or solvent based paints. In this study, the surface roughness, hardness, and abrasion resistance of painted WPCs produced with different amounts of wood and PP.

2. Materials and methods

2.1. Materials

PP granulates produced by Likom PP Co., Ukraine, was used as the polymer matrix (Fig. 1). Its density and melt flow rate (230°C /2.16 kg) were 0.90 g/cm³ and 6.5 g/10min, respectively. The compatibilizing agent, maleic anhydride modified homopolymer polypropylene (MAPP) (Optim 425, MFI/190°C; 2.16 kg = 110 g/10 min, density: 0.91 g/cm³), was supplied by Pluss Polymers Pvt. Ltd. in India.

Pine wood particles were obtained from the round woods by using a disc chipper with three knives, followed by grinding process in a laboratory type grinder. The average size of the wood flour without bark was 40 US-mesh (Fig. 2).

Fig. 1: Polypropylene and wood flour.

Fig. 2. Compound obtained from twin scriv co-rotating extruder.
The water based paint which was acrylic copolymer emulsion paint and solvent based paint which was long oil alkyd paint were supplied from a commercial paint manufacturer. The density and viscosity (DIN cup 4mm) of the water-based paint were 1.52 g/ml and 115 s, respectively. These properties were found to be 1.20 g/ml and 110 s for the alkyd paint, respectively.

2.2. Preparation of hot-press molded WPCs

The wood flour was dried overnight at 90 °C in a vacuum oven to melt blending. The pre-mixed wood flour, polypropylene, and coupling agent were fed into the main feed throat using a volumetric feed system. The pellets were then dried in an oven at 90 °C for 24 h after the extrusion process. The mat was prepared with the dried pellets by a hot compression molding process. The mixture was weighed and formed on an aluminum caul plate, using a 290 mm × 290 mm forming frame. A steel frame was used to prevent a lateral yielding of the dry-blend mixture during the hot pressing. Wax paper was used to avoid direct contact of the polypropylene flour with the metal platens of the hot-press. Subsequently, the pellets were compression molded in a hot press. The mats were hot pressed for 8 min under 5.5 MPa at 190 °C in a one-step process (Fig. 3). At the end of the hot pressing cycle, the panel was immediately moved from the hot press into a press at room temperature for cooling. 3 mm thick WPC panels were then trimmed to a final size of 100 mm × 100 mm.

![Image 43x409 to 286x530](Image 43x409 to 286x530)

Fig. 3: Production of hot pressed WPC boards.

A total of 16 experimental panels, 2 for each type of WPC panel, were manufactured. The air-dry density values of the specimens varied from 1.05 to 1.08 g/cm³. The raw material formulations used for the WPCs are presented in Table 1. The raw material formulations of the WPCs.

<table>
<thead>
<tr>
<th>WPC code</th>
<th>Wood flour (%wt)</th>
<th>Polypropylene (PP) (wt%)</th>
<th>MAPP (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30</td>
<td>67</td>
<td>3</td>
</tr>
<tr>
<td>B</td>
<td>40</td>
<td>57</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>50</td>
<td>47</td>
<td>3</td>
</tr>
<tr>
<td>D</td>
<td>60</td>
<td>37</td>
<td>3</td>
</tr>
<tr>
<td>E</td>
<td>30</td>
<td>67</td>
<td>3</td>
</tr>
<tr>
<td>F</td>
<td>40</td>
<td>57</td>
<td>3</td>
</tr>
<tr>
<td>G</td>
<td>50</td>
<td>47</td>
<td>3</td>
</tr>
<tr>
<td>H</td>
<td>60</td>
<td>37</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 1: The raw material formulations of the WPCs.

2.3. Paint application on the WPC panels

The solvent or water based paints were applied on the WPC boards by spray coating technique. The amount of the paint applied on the WPC surface was 200 g/m². The paint was uniformly applied on the surface of the WPC panels as shown in Figure 4.

![Image 361x693 to 499x799](Image 361x693 to 499x799)

Fig. 4: The application of the paint on the WPC board.

Curing of the paint was performed at room temperature for 24 h. The spray pressure and nozzle angle were 120-140 bar and 50°, respectively. The nozzle diameters for the water and solvent based paints were 0.48 and 0.33 mm, respectively. The 10 wt% water as thinner was added into the paint.

2.4. Measurement of surface roughness

Two samples with a size of 50 mm by 50 mm from each type of panel conditioned at 23 °C and 50% relative humidity were used for surface roughness evaluations. A total of ten measurements with a 15-mm tracing length, 5 along the sandmarks and 5 across the sandmarks, were taken from each face of the samples. The points of roughness measurements were randomly marked on the surface of test samples. A Mitutoyo SJ-301 surface roughness tester, stylus type profilometer, was employed for the surface roughness tests. Three roughness parameters characterized by ISO 4287 (1997) standard, respectively, average roughness (Ra), mean peak-to-valley height (Rz), and maximum peak-to-valley height (Ry), and root mean square roughness (Rq) were considered to evaluate the surface characteristics of the panels. Roughness values were measured with a sensitivity of 0.5 µm. Measurements were done at room temperature and pin was calibrated before the tests. The profilometer used for the measurements consisted of main unit and a pick-up which has a skid-type diamond stylus with 5 µm tip radius and 90° tip angle. The stylus traversed the surface at a constant speed of 10 mm/min and measuring force of the scanning arm on the samples was 4 mN (0.4 gf).

2.5. Abrasion resistance of the painted WPCs

The abrasion resistance of the painted WPCs was determined according to ASTM D4060 which was standard test method for abrasion resistance of organic coatings by the Taber abraser. The test specimen is mounted to the Taber Abraser turntable and rotated at a fixed speed under a weighted CS-10 abrading wheel. Initial and final abrasion levels were determined visually based on the initial indication of pattern fading and extremely worn out pattern on the paper, respectively. Rotations of the disks were consistently counted and corresponding values at abrasion levels were used to calculate average abrasion resistance. Four measurements, two for each specimen, were used for each WPC code.

2.6. Surface hardness of the painted WPCs

The surface hardness of the WPCs was determined according to ASTM D4366 – 14. The pendulum damping test has been found to have good sensitivity in detecting differences in coating hardness, where hardness is defined as resistance to deformation. A total of 10 measurements, 5 measurement for each specimen, were used for each WPC code.

3. Result and discussion

3.1. Surface roughness of the painted WPCs

The surface roughness values of the WPCs coated with solvent and water based paints are presented in Figures 5 and 6. As compared to the control WPC samples, the average surface
roughness (Rₐ) of the WPCs painted water-based paint slightly increased with increasing amount of wood flour while this was not observed for the WPCs painted with solvent-based paints. The average roughness of the WPCs painted with water-based paints increased from 2.36 to 2.75 µ as the wood flour content increased from 30 to 60 wt% in the WPC while this property was found to 3 to 2.5 µ for the WPCs coated with solvent-based paint. Previous studies reported that the increment in the filler content increased the surface roughness of the thermoplastic composites [4,5]. However in our study, it was observed that the surface roughness of the solvent-based paint coated WPCs decreased with increasing wood flour content.

3.2. Abrasion resistance

The results of abrasion resistance of the coated WPCs are presented in Table 2. In general, the abrasion resistance of the WPCs coated with water or solvent-based paints showed difference based on the wood flour content. The scratch resistance of the materials depends on the chemical composition, density and the hardness of the materials. The abrasion resistance of the materials is important when they are used as flooring material.

Table 2: The results of abrasion resistance of the painted WPCs

<table>
<thead>
<tr>
<th>Paint type</th>
<th>WPC code</th>
<th>Initial abrasion (cycle)</th>
<th>Final abrasion (cycle)</th>
<th>Average abrasion (cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-based paint</td>
<td>A</td>
<td>27</td>
<td>69</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>42</td>
<td>154</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>38</td>
<td>219</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>36</td>
<td>95</td>
<td>65</td>
</tr>
<tr>
<td>Solvent-based paint</td>
<td>E</td>
<td>57</td>
<td>141</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>42</td>
<td>180</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>51</td>
<td>172</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>28</td>
<td>78</td>
<td>53</td>
</tr>
</tbody>
</table>

4. Conclusions

The results of the research revealed that the surface properties of the WPCs coated with water or solvent based paints showed the differences based on the wood flour content. There was no significant difference in the average surface roughness values among the painted WPCs produced with the 30 wt% and 60 wt% wood flour. The highest abrasion strength and hardness were found in the coated WPC specimens produced with 50 wt% wood flour. Based on the findings obtained from the present study, it can be said that the WPCs prepared from the PP/wood flour/MAPP (47/50/3 wt%) had the optimum surface quality properties among the evaluated WPC codes.

5. Acknowledgement

This work was supported by Research Fund of the Istanbul University. Project number: BEK-20032. The authors wish to acknowledge Research Fund of the Istanbul University for financial support.

6. References

NICKEL FERRITE-ACTIVATED CARBON MATERIALS – PREPARATION AND PHOTOCATALYTIC EFFICIENCY FOR CLEANING OF MALACHITE GREEN AND REACTIVE BLACK 5 DYES UNDER UV-ILLUMINATION

NIKELOVA FERIT-AKTIVIRAN VYGLEN MATERIALI – POLUCHAVANIE I FOTOKATALITICHNA EFEKTIVNOST ZA OCHISTVANIE NA MALAHITOTO ZELENO I REAKTIVNO CHERNO 5 BAGIRILA

PÓD UV OBLÝCHVÁNE


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Abstract: Nickel ferrites having different stoichiometry supported on activated carbon (Ni$_{0.25}$Fe$_{2.75}$O$_4$-AC, Ni$_{0.5}$Fe$_{2.5}$O$_4$-AC, NiFe$_2$O$_4$-AC) were prepared by co-precipitation using nitrate precursors and activated carbon from peach stones and calcination procedure in nitrogen atmosphere. The physicochemical properties of these materials were studied by powder X-ray diffraction analysis (PXRD) and Mössbauer spectroscopy. The presence of spinel ferrite and additional hematite phases was established by PXRD. The photocatalytic properties of the so synthesized nickel ferrite-AC materials were tested and compared in oxidative degradation of Malachite Green (MG) and Reactive Black 5 (RB5) dyes under UV-light irradiation. The photocatalytic tests show that investigated samples lead to much higher degree of degradation of MG (86%–92%) compared with that of RB5 (17%–35%) due to their structure. The results proved that nickel ferrite-AC materials are more efficient photocatalysts for removal of MG as model contaminant from aqueous solution under UV light than RB5.

Keywords: NICKEL FERRITES-AC, MALACHITE GREEN, REACTIVE BLACK 5, PHOTOCATALYTIC DEGRADATION

1. Introduction

The development of efficient methods to reduce environmental contamination is of great practical importance. The heterogeneous photocatalysis is an outstanding method for purification of polluted waters [1]. Hazardous organic compounds are among the major factors of environmental pollution, especially in water media [2]. Synthetic dyes find wide application for coloring purposes in leather, textile, printing, food, cosmetic and plastic industries [3]. Water contamination caused by dyes is posing a problem throughout the world. Colour is the first aspect to be recognised in wastewater [4]. Spinel ferrites Fe$_x$O$_{4-x}$, M = Ni, Mg, Ca, Co) have narrow band gaps (~2.0 eV), magnetic separability, and chemical stabilities so their nanoparticles could be potentially applied as photocatalysts for decontamination of environment because of their superiority in complete utilization of natural sunlight [5,6]. The application of magnetic semiconductor nanoparticles for treatment of polluted waters is attractive research field. Nickel ferrites with general formula (AB$_2$O$_4$) are among the most versatile magnetic materials due to the high Curie temperature, high saturation magnetization, chemical stability and relatively high permeability [7]. The use of activated carbons as materials for the photocatalysts’ support shows many advantages because of the specific water surfaces, easy control of the surface chemistry and excellent adsorption capacity for organic compounds, high porosity and ability for recovering of active metal phase by burning the carbon support. The oxidative degradation rate under UV-light illumination is enhanced due to the porosity of the carbon feeding desorbed pollutant molecules to the photocatalytically active sites, suggesting also possible own photocactivity of the carbon support [8].

The nanosized composite NiFe$_2$O$_4$/active carbon has already been used to remove Alizarine Yellow R and Methyl Orange-azo dyes, from water [9]. The adsorption property of AC/NiFe$_2$O$_4$ magnetic composite was investigated with respect to Methyl Orange dye in ref. [10]. Another research group used the AC-NiFe$_2$O$_4$ as photo-Fenton catalyst for photo-Fenton degradations of Methylene Blue, Rhodamine B and Malachite Green as model pollutants, carried out in the presence of oxalic acid under λ > 400 nm visible light [11]. Zhao et al. [12] determined that NiFe$_2$O$_4$-graphene possesses significantly enhanced photocatalytic activity for the degradation of Methylene Blue under illumination of artificially simulated sunlight compared to bare NiFe$_2$O$_4$ nanoparticles. Photocatalytic activity of NiFe$_2$O$_4$/MWCNTs hybrids has been studied in the photocatalytic decolorization of Congo Red in aqueous solution under simulated solar light irradiation in ref. [13]. The multi-walled carbon nanotubes CNTs and NiFe$_2$O$_4$-MWCNTs were efficient adsorbents for the removal of Methylene Blue from polluted water [14]. The high photocatalytic activity of NiFe$_2$O$_4$/MWCNTs was established in the degradation of phenol and nitrophenols (o-nitrophenol, p-nitrophenol and picric acid) under UV light [15]. Ikenaga and coworkers determined that investigated activated carbon-supported ferrite had ten times higher hydrogen sulfide absorption rate than that of the ferrite prepared by the dry process [16]. The adsorptive ability of fly ash/NiFe$_2$O$_4$ composites has been tested for removal of Congo Red dye from an aqueous solution by the authors [17]. Singh et al. [18] showed that cobalt-doped nickel ferrite/MWCNTs nanocomposites demonstrated a significant catalytic activity in the photo-Fenton process in the degradation of Rhodamine B dye, which completely degraded the dye molecule in 15–25 min. The photocatalytic activity of nickel ferrite samples Ni$_x$Fe$_{3-x}$O$_4$ (0 ≤ x ≤ 1) in the degradation of Malachite Green dye under UV irradiation was discussed in previous investigations [19]. The present paper is focused on the synthesis, physicochemical and photocatalytic properties of nickel ferrite-activated carbon materials having different compositions in the degradation of aqueous Malachite Green and Reactive Black 5 dyes under UV light.

2. Experimental

2.1. Synthesis of the nickel ferrite-activated carbon samples

The nickel ferrite-activated carbon (AC) materials having different compositions Ni$_{0.25}$Fe$_{2.75}$O$_4$-AC, Ni$_{0.5}$Fe$_{2.5}$O$_4$-AC and NiFe$_2$O$_4$-AC (denoted as S1, S2 and S3) were synthesized by the co-precipitation technique. The starting aqueous solutions of 0.03M Ni(NO$_3$)$_2$•6H$_2$O (VWR Prolabo BDH chemicals) and...
Fe(NO₃)₃•9H₂O (Alfa Aesar) were mixed at a preset ratio. After that 2g of activated carbon were added to the mixture. The carbon was produced from peach stones (supplied by Laboratory for "Chemistry of Solid Fuels" at the Institute of Organic Chemistry with Centre of Phytochemistry). The 0.3M NaOH solution (Valerus Co.) was used as precipitant by adding it dropwise slowly into the mixture upon continuous stirring. The addition of precipitating agent was discontinued at pH = 12.5 and then the mixture was continuously stirred for one more hour. The so synthesized materials were then centrifuged and washed with distilled water until neutral reaction medium (pH=7) was reached. Further the obtained precipitates were dried at 110ºC for 3 hour in air media. The co-precipitated samples were thermally treated at 400ºC for 3 hours and 30 minutes in inert nitrogen atmosphere.

2.2. Powder X-ray diffraction analysis (PXRD)

The powder X-ray diffraction analysis was carried out on a Bruker D2 Phaser diffractometer within the range of 20 values between 5º and 65º using Cu Kα radiation (λ = 0.154056 nm) at 40 kV. The present phases were identified by using of JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997).

2.3. Mössbauer spectroscopy

The Mössbauer measurements were performed on apparatus Wissenschaftliche Elektronik GmbH, working at a constant acceleration mode, ⁵⁷Co/Rh source (activity ≈50 mCi) and α-Fe standard. The parameters of hyperfine interactions of Mössbauer spectral components: isomeric shift (IS), quadrupole splitting (QS), hyperfine effective magnetic field in the sites of iron nuclei (H eff), line widths (FWHM) and component relative weights (G) were calculated by computer fitting.

2.4. Photocatalytic investigations

The photocatalytic degradation of Malachite Green (MG) and Reactive Black 5 (RB5) dyes under UV-light irradiation was studied using obtained nickel ferrite/AC materials as photocatalysts. The photocatalytic experiments were carried out using polychromatic UV-A lamp illumination (18W) with maximum emission at 365 nm and illumination intensity 2.6 mW/cm². The reaction course was followed by UV-Vis spectrophotometer CamSpec M501. The aqueous solutions of Malachite Green (λmax=599 nm) and Reactive Black 5 (λmax=615 nm) dyes were with initial concentration 5 ppm and 20 ppm respectively. In order to establish adsorption equilibrium in system, the dye solution and photocatalyst were stirred in the dark for 30 min without any UV illumination. A semi-batch suspension photocatalytic reactor was equipped with two frits blowing tiny bubbles of air in order to saturate the solution in dissolved oxygen. The photocatalytic tests were carried at a constant stirring rate (400 rpm) under ambient conditions. The measurement of the photocatalytic efficiency of nickel ferrite – AC samples was performed by taking aliquot samples of the suspension out of the reaction vessel after regular time intervals. The powder was then separated from the aliquot solution by centrifugation before the UV–Vis spectrophotometric evaluation of the dye concentration, based on previous calibration. After that, the aliquot solution, together with the photocatalyst powder, were returned back into the reaction vessel, which ensured operation under constant volume and catalyst amount. The degree of degradation is estimated using dependence (C - Co/Co) x100, where Co and C are respectively initial concentration before turning on the illumination and residual concentration of the dye solution after illumination in the course of given time interval.

3. Results and discussions

Figure 1 represents the Powder X-ray diffraction patterns of the obtained calcined nickel ferrite – activated carbon materials showing the characteristic reflexes of non-stoichiometric and stoichiometric spinel nickel ferrite phase (PDF-86-2267; PDF-75-0449) and activated carbon also. The presence of additional hematite phase (PDF-89-0599) is registered in all thermally treated nickel ferrite-AC samples.

The recorded room temperature Mössbauer spectra of thermally treated nickel ferrite-AC samples are displayed in Figure 2. The Mössbauer spectra of prepared materials represent a superposition of the sextet and superparamagnetic doublet components. The sextet-type components could be assigned to the presence of spinel ferrite and hematite phases [20].

The photocatalytic activities of the investigated samples were measured using two hazardous textile dyes - Reactive Black 5 (RB5) and Malachite Green (MG) as model pollutants. Figure 3 is illustrating the reaction course of both dyes degradation in solution under UV-A illumination over the investigated photocatalysts. The adsorption capacities of samples S1, S2 and S3 towards model pollutant MG dye are higher than those for RB5 dye, which is probably due to the amino groups in MG reacting readily with acidic sites on the surface of the photocatalysts. After half an hour in the dark the UV lamp was switch on and the photocatalytic degradation is started. The rate of oxidative discoloration reaction of studied powders regarding the RB5 dye is lower than MG dye, which can be attributed to the higher stability of RB5 molecule having a much larger conjugated system of single and double bonds.
Mössbauer spectra of calcined nickel ferrite-AC photocatalysts.

Concentration changes of tested dyes based on changes in the intensity of the maximal absorbance peak at 599 nm for RB5 dye and at 615 nm for MG dye respectively, with the course of time.

Figure 4 shows degree of degradation of the dyes after 120 min under UV-A illumination over investigated photocatalysts. MG degradation conversion degrees of photocatalytic systems: S1, S2 and S3 are in the range 86–92%, while they degrade weaker RB5 dye (17–35%).

4. Conclusions

The nickel ferrite-AC photocatalysts were prepared by co-precipitation and calcination in inert atmosphere. The physicochemical characterization of the so synthesized samples by PXRD analysis and Mössbauer spectroscopy proved the existence of nickel ferrite and hematite as additional phase. Comparatively study of photocatalytic efficiency of the investigated materials confirmed the easier degradation of MG over RB5 dye in aqueous media. The tested photocatalyst Ni0.5Fe2.5O4-AC demonstrates the highest degree of degradation of MG (92%) and RB5 (35%) dyes compared to these over the other samples. The studies can be continued and extended further in the direction of involving TOC analysis of the total organic carbon in the decolorized solution thus evaluating not only the degree of discoloration but also the degree of total oxidation, which could shed some light on the different behavior of the two dyes. The present results determined that synthesized nickel ferrite-AC materials could be appropriate photocatalysts for removing of MG as contaminant from aqueous media.

Acknowledgements

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References


ВЗАИМОДЕЙСТВИЕ УПРОЧНЯЮЩИХ САПФИРОВЫХ ВОЛОКОН С МЕТАЛЛИЧЕСКОЙ МАТРИЦЕЙ ИЗ МНОГОКOMPONENTНЫХ СПЛАВОВ В КОМПОЗИТЕ СО СЛОЙСТОЙ СТРУКТУРОЙ ТВЕРДОФАЗНОГО ПРИГОТОВЛЕНИЯ

INTERACTION OF REINFORCING SAPPHIRE FIBERS WITH METALLIC MATRIX FROM MULTICOMPONENT ALLOYS IN THE COMPOSITE WITH A LAYERED STRUCTURE OF SOLID PHASE PREPARATION

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Abstract. A multilayer composite with a metal matrix of multicomponent alloys of iron and titanium and with reinforcing sapphire fibers was investigated. The composite obtained by diffusion welding under pressure of a multilayer package composed from foils of Fe- and Ti-alloys which were alternated with fragmented sapphire fibers. It is found that during the welding process of the packet at 1200°C for 45 minutes, a titanium alloy was actively interact with the oxide fibers. The alloy is based on iron, in contrast, was completely inert with respect to sapphire. The detailed examination of the data obtained by scanning electron microscopy and X-ray analysis is presented.

Keywords: composite, metal matrix, titanium alloy, an alloy of iron, diffusion welding, sapphire fiber, layered structure.

1. Введение

Техническая необходимость повысить рабочую температуру конструктивных элементов при одновременном увеличении их удельных механических характеристик на традиционном пути разработки новых сплавов приводит к полному расходованию возможностей последних [1]. Разработка композитных материалов с металлической матрицей позволяет использовать как достоинства металлов по их трещиностойкости, так и реализовать высокую прочность, жесткость и сопротивление ползучести некоторых армирующих волокон [2, 3].

Монокристаллические оксидные волокна изначально представляли потенциально эффективное армирующее средство для жаропрочных композитов с металлической матрицей. Такие волокна, получаемые из расплавов оксидов, например, методом Степанова, начали появляться с середины 1960-х годов. Однако, стоимость таких волокон, а также волокон, полученных позднее с помощью других известных методов, таких как EFG (edge-defined film-fed growth), LHFZ (laser heated floating zone directional solidification process), LHPG (laser heated pedestal growth) и μ-PD (micropulling-down), оказалась слишком высокой, чтобы применять их в конструкционных материалах [4].

Реальные возможности использовать оксидные волокна в композитах открывает метод внутренней кристаллизации [5]. При этом возникает ряд задач, решение которых призвано обеспечить получение конструкционного композитного материала с заданными свойствами. Первая из них заключается в выборе материалов волокна и матрицы, обеспечивающих, во-первых, их необходимое взаимодействие в процессе получения и эксплуатации изделия и, во-вторых, свойства композита. Так, например, различие в коэффициентах термического расширения материалов матрицы и волокна может привести к дроблению волокна на длины, не позволяющие реализовать их прочность в композите. Взаимодействие между волокном и матрицей формирует границу раздела между ними, в значительной степени определяющую и прочность композита, и его сопротивление ползучести. Результаты некоторых исследований этих и подобных факторов приведены в работах [6–11].


В приведенном библиографическом списке предлагаемая работа может занять важное место, так как посвящена исследованию слоистой структуры композитов твердофазного приготовления с упрочняющими фрагментированными волокнами из сапфира, полученными методом внутренней кристаллизации [4].

В данной работе методами растровой электронной микроскопии и рентгеноспектрального анализа исследовалась слоистая структура композиционного материала с монокристаллическими сапфировыми волокнами. Композит получали твердофазным способом с использованием диффузионной сварки (ДС) многокомпонентного пакета, составленного из фольг Ti- и Fe-сплавов, проложенных фрагментированными сапфировыми волокнами.

2. Конструкция и диффузионная сварка пакета

Сборка и конструкция пакета. Пакет (Fe)/Al2O3/(Ti), состоящий из фольг Ti- и Fe-сплавов, содержал 12 трехслойных модулей [(Fe)(Ti)(Fe)] и 11 (Ti)-фольг (табл. 1). Модуль составлен из элемента «книжной формы» [12], изготовленного из фольги Fe-сплава, и фольги Ti-сплава, вложенной в элемент. Перед сборкой пакета каждая фольга Ti-сплава с двух сторон «окрашивалась» клеящим раствором поливинилбутилгидрооксида в полиуретане, на котором до его застывания раскладывались фрагментированные...
Скорость набора температуры при нагреве также не процессе диффузионной сварки проводились под давлением. Таким образом, суммарное количество слоев равнялось 47, из которых 24 были из стали и 23 – из Ti-сплава. Между каждой слоями (Fe) и (Ti) размещались слои из сапфировых волокон (Al2O3), преимущественно ориентированных в направлении прокатки фольг. Габариты пакета – 25 × 40 мм.

Таблица 1. Данные о конструкции пакетов и режимах их диффузионной сварки

<table>
<thead>
<tr>
<th>Элементы конструкции и режимы ДС</th>
<th>Количество элементов, шт.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Пакет (Fe)/Al2O3/(Ti):</td>
<td>12</td>
</tr>
<tr>
<td>– модуль [(Fe)/(Ti)/(Fe)],</td>
<td>12</td>
</tr>
<tr>
<td>– элемент «книжной формы» из (Fe),</td>
<td>12</td>
</tr>
<tr>
<td>– отрезок (Ti)-фольги внутри (Fe)-элемента,</td>
<td>11</td>
</tr>
<tr>
<td>Число слоев (Fe)-сплава.</td>
<td>12 × 2 = 24</td>
</tr>
<tr>
<td>Число слоев (Ti)-сплава.</td>
<td>12 + 11 = 23</td>
</tr>
<tr>
<td>Число слоев Al2O3.</td>
<td>23 × 2 = 46</td>
</tr>
<tr>
<td>Суммарное количество металлических слоев.</td>
<td>24 + 23 = 47</td>
</tr>
<tr>
<td>ДС: 1150°С, 30 мин 1.5 МПа / 1200°С, 30 мин, 9.8 МПа и 15, 14.7 МПа</td>
<td></td>
</tr>
</tbody>
</table>

Диффузионная сварка. Пакет не содержал низкоплавких составляющих, поэтому нагрев, выдержка и охлаждение в процессе диффузионной сварки проводились под давлением. Скорость набора температуры при нагреве также не лимитировалась. ДС проводилась в 2 этапа при 1150 и 1200°С, общее время – 45 мин, давление поднималось ступенчато – 1,5, 9,8 и 14,7 МПа, что соответствовало нагрузкам 150 кН, 1,0 и 1,5 Т. Толщина пакета после ДС – 2,15 мм.

3. Методика исследования

Для исследования структуры композитов использовались растровая электронная микроскопия и рентгеновский спектральный анализ (РСА). Получение изображений объектов во вторичных и обратно-рассеянных электронах и РСА, выполнялись на цифровых электронных сканирующих микроскопах Tescan VEGA-II и CamScan MV230. Оба микроскопа имеют W-катоды и оснащены детекторами вторичных и отражённых электронов и энергодисперсионным рентгеновским микроканалоанализатором. Обработка спектров характеристического рентгеновского излучения производилась с помощью пакета программ, разработанной фирмой Oxford Instruments, в основу расчётной части которых заложен алгоритм внесения матричных поправок РАР [13]. Исследования производились при ускоряющем напряжении 20 кВ и токе электронного зonda 200 пА на образце кобальта. Размер электронного зonda – 0,16 мм.

4. Микроструктура композита

Структура поперечного сечения композита (рис. 1) состоит из множества извилистых слоев толщиной 65–70 мкм разделённых границами светлого тона и хаотически вклиненымися в них фрагментированными волокнами из сапфира. Однако даже при таком относительно небольшом увеличении можно видеть, что на участках с фрагментами сапфировых волокон и вблизи них границы светлого тона преобразовывались в тонкие прослоёки. На рис 1,6 они показаны стрелками.

При большем увеличении (рис. 2) видно, что вблизи волокна границы между слоями 2 трансформировалась в прослойки толщиной от 5 до 13 мкм, ограниченные дискретными светлыми границами, обозначенными встречными стрелками 1. Прослойки – это не что иное, как остатки Fe-сплава. А слой 2 образовались их двух слоев Ti- и Fe-сплавов на участках прямого контакта между ними в процессе диффузионной сварки и представляют собой комбинацию (Ti) + (Fe). Иная картина взаимодействия наблюдалась, если между слоями из различных сплавов вклинялся фрагмент волокна Al2O3.

Оказалось, что сапфир в процессе ДС при температуре 1200°С активно взаимодействует со сплавом на основе титана и совсем и нертен по отношению к сплаву на основе железа. В месте контакта сапфирового волокна и Ti-сплава уже после 45-ти минутной выдержки образуются обширные области взаимодействия (рис. 3). Подобная область присутствует и на рис. 2. Кроме того хорошо видно полное отсутствие какого-либо взаимодействия волокна и сплава на основе железа, расположенного с противоположной стороны волокна. Более того на этом же рисунке зафиксирован достаточно редкий случай, когда слой Ti-сплава попал между двумя фрагментами волокна.

На схеме слоистой структуры (рис. 4) такое место отмечено контуром 1 и при большем увеличении показано на рис. 5. Такие положения могут реализовываться, если два сапфировых фрагмента на границах между слоями окажутся расположенными точно друг против друга. Тогда между ними может оказаться отдельный участок слоя из Ti- или Fe-сплава. Об инертности сплава на основе железа по отношению к сапфиру свидетельствует рис. 6, на котором представлен уникальный случай, когда на протяжении 1 мм, не взаимодействующий с сапфиром, слой из Fe-сплава находится между сапфировыми волокнами (контур 2). Здесь его толщина составляет ~30 мкм. Это совпадает с толщиной исходной
фольги из сплава на основе железа, которая использовалась при сборке пакета.

Рис. 3. Показаны зоны взаимодействия сплава на основе Fe с волокнами из сапфира (светлые контуры) и зоны матрицы с противоположных от волокон ее сторон со сплавом железа (стрелки), шероховатой по отношению к волокнам

Рис. 4. Схема, объясняющая каким образом Ti- (1) или Fe-слой (2) может оказаться между фрагментами из волокон Al2O3

Рис. 5. Микроструктура Ti-слоя, находящегося между фрагментами сапфировых волокон (отмечено контуrom) и между сапфировым волокном и слоем Fe-сплава. ДС при 1200°C в течение 45 мин под давлением 14,7 МПа

Рис. 6. Микроструктура поперечного сечения пакета (Fe)/Al2O3/(Ti) после ДС: контур 1 – слой из сплава на основе титана между сапфировыми волокнами; контур 2 – протяженный (~1 мм) участок слоя из сплава на основе Fe между сапфировыми волокнами; стрелками показаны зоны взаимодействия слоев из сплава на основе Ti с волокном

Видно, что контраст слоев, заключенного между сапфировыми волокнами, который должен изменяться с изменением структуры, не меняется в сравнении с контрастом (Fe)-слоев, на удалении от фрагментов волокна. Такого нельзя сказать о контрасте участков Ti-слоя, «зажатых» между волокнами (контур 1) и попавших в зону взаимодействия с волокнами (на рисунке отмечены стрелками). Их контрастный рисунок резко отличается от того, что мы видим в зонах, свободных от волокон.

5. Рентгеноспектральный анализ

В помощь к результатам рентгеноспектрального анализа мы приводим рис. 7 со структурой участка, на котором он проводился.

Систематизация проведенного анализа дала следующие результаты.

1. Спектр 1. Сапфировое волокно Al2O3: 40.7 ат.% Al и 59.3 ат.% O.
2. Спектр 2. Слой, сформировавшийся в процессе ДС и последующего охлаждения на границе между сапфировым волокном и слоем из Ti-сплава. Его состав – 56.5 Ti, 37.8 Al, 4.7 Cr и 1.0 ат.% Mo, – из которого следует, что основными элементами образовавшегося слоя являются титан и алюминий. Суммарное содержание титана, хрома и молибдена равно 62,2 ат.%. Согласно диаграмме состояний Ti-Al это соответствует 2-фазной области из химических соединений Ме3Al и МеAl, где Ме = Ti, Cr и Mo, представляющих собой твердый раствор хрома и молибдена в Ti3Al и TiAl соответственно. Двухфазность этого слоя можно рассмотреть при большом увеличении на рис. 8: матрица серого цвета из соединения Me3Al + игольчатые выделения светло-серого контраста из MeAl, ориентированные перпендикулярно границам раздела слоев между Al2O3 и слоем Me3Al + (Ti).

Рис. 7. Микроструктура участка, где проводился рентгеноспектральный анализ: 1–10 — номера спектров локального анализа; 11–13 – то же для спектров по отмеченным площадкам

3. Спектры 3, 4 и 5 представляют 2-фазный слой из выделений твердого раствора (Tl) серого цвета – это спектры 4 и 5 – в матрице светло-серого цвета из Me3Al, где Me = Ti (54,9 ат.%), Cr (17,8 ат.%), Mo (6,7 ат.%) и Fe (0,5 ат.%). Суммарное содержание Me в соединении Me3Al составляет 79,9 ат.%, алюминий – 20,1 ат.%. Содержание элементов в твердом
расторе на основе титана (Тi): 93.6–95.4 Ti, 3.4–4.4 Al, 0.6–1.1 Cr, 0.4–0.6 Mo и 0.1–0.2 ат.%Fe. Заметим, что, по сравнению с первым слоем, здесь хром и молибден присутствуют в больших количествах, и появилось железо, которого в первом не было в составе титанового сплава.

Кинетика образования первого и второго двухфазных слоев представляется следующей. Формирование и рост слоев происходит в процессе ДС, а при охлаждении происходит выделение вторых фаз. В первом слое – это Me2Al, во втором – (Тi).

Спектр 11 даёт концентрации всех обнаруженных элементов во втором 2-фазном слое, средние по площади 23,5×47 мм: 75.8 Ti, 12.1 Al, 8.0 Cr, 3.5 Mo, 0.4 Fe и 0.2 Ni.

Далее, чтобы лучше отслеживать изменение содержания основных (сплавообразующих) элементов, приведем концентрационные профили обнаруженных элементов в зависимости от номера спектра или от расстояния, принимая за нулевую точку отсчета спектр 1 (рис. 9).

Выводы

Исходя из полученных данных, можно констатировать, что в процессе ДС под давлением и последующего (в течение ~1 ч) охлаждения со скоростью порядка 17 град/мин наблюдаются 2 самостоятельных процесса:

– между фольгами Тi-сплава и ЭП на границах Тi-сплав–ЭП происходит их твердофазное взаимодействие с образованием многокомпонентного сплава переменного состава;

– в местах локализации сапфировых волокон на границах волокно-титановый сплав при выдержке происходит диффузионное взаимодействие между Al2O3 и Тi-сплавом с образованием диффузионных зон из слоёв интерметаллических соединений MeAl и Me2Al, которые в процессе следующего за выдержкой охлаждения преобразуются в двухфазные слои MeAl + Me2Al и Me2Al + (Тi) соответственно;

– в отличие от границ волокно-титановый сплав на границах волокно-ЭП взаимодействие между Al2O3 и сплавом не наблюдалось.

Литература

Abstract: The paper presents the results of the synthesis of the xerogel of vanadium in the interaction of vanadium pentoxide and ammonium. It is shown that as a source of vanadium pentoxide can be used successfully vanadium carbonaceous - siliceous shales. Using obtained vanadate ammonium in receiving technology of vanadium xerogel is more cost effective process than the use for this purpose the chemical reagent. Integrated use of this unique raw material is a critical component of modern waste-free and environmentally friendly technologies to highlight not only the connection of valuable components, but also the raw material for the production of vanadium xerogels. Synthesized by sol-gel method based on vanadium oxide xerogel with partially ordered highly layered structures already are widely used in various fields of science and technology due to their unique properties. Scope xerogels vanadium: production photocatalysts, composites, membranes and ion exchange materials.

Keywords: siliceous shales, vanadium pentoxide, sol-gel method, xerogel, nanomaterials.

1. Introduction

Vanadium compounds are of great interest in terms of their use in processes for the preparation of anisotropic morphologies. [1] So-precipitated vanadium pentoxide in the presence of the template in the synthesis of compounds with highly complex structure, on which is formed a xerogel metal.

In practiced technology, vanadium pentoxide and its compounds which is raw material basis for the synthesis of the xerogel is derived from ammonium vanadate by its drying and calcination.

The source of ammonium vanadate in the Republic of Kazakhstan can serve as a carbon-siliceous shales Big Karatau deposit with reserves of hundreds of millions of tons of [2-3].

Organization of processing of uranium-bearing shale will not only comprehensively used in the mineral extraction along with uranium and vanadium, but also to solve environmental problems, as the vanadium compounds are relatively toxic reagents. Furthermore, the use of ammonium vanadate obtained xerogel vanadium technology will be more economical process than the use for this purpose the chemical reagent of the compound.

The elemental composition of the useful components shale besides uranium and vanadium are listed in Table 1.

Table 1: The elemental composition of carbon-siliceous shales Karatau

<table>
<thead>
<tr>
<th>Components</th>
<th>Contents, %</th>
<th>mineralogical consist</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>47.00</td>
<td>SiO₂</td>
<td>Amorphous</td>
</tr>
<tr>
<td>C</td>
<td>10.06</td>
<td>carbon</td>
<td>Amorphous</td>
</tr>
<tr>
<td>O</td>
<td>35.00</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>V</td>
<td>0.60</td>
<td>VO₂</td>
<td>Cubic</td>
</tr>
<tr>
<td>U</td>
<td>0.03</td>
<td>UO₂</td>
<td>Cubic</td>
</tr>
<tr>
<td>Mo</td>
<td>0.02</td>
<td>CaMoO₄</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>REE</td>
<td>0.10</td>
<td>REE</td>
<td>Sphere</td>
</tr>
</tbody>
</table>

The ratio of the basic components of oil shale is shown in Figure 1.

Integrated use of this unique raw material is a critical component of modern waste-free and environmentally friendly technologies to highlight not only the connection of the components but also the raw material for the production of vanadium xerogel, which represents the prospect of using both scientific and practical interest.

In the development process for the synthesis of the xerogel vanadium as the starting vanadium compound, ammonium metavanadate was selected, resulting in the processing of oil shale Greater Tau. The source was ammonium metavanadate crystallization process. After the crystallization process X-ray analysis has shown [4] that it contains 99.6% NH₄V'O₃.

Further, to obtain vanadium pentoxide as a raw material for the synthesis of the xerogel vanadium we used the ammonium metavanadate, highlighted earlier. X-ray analysis of the source of vanadium pentoxide, which is prepared from the vanadium solution has shown [5-6] that it comprises 98% V₂O₅ and 2% oxide of tetravalent vanadium VO₂.

It is found that the analyte vanadium compound substance has a pronounced crystalline structure.

It is known that most of the nanomaterials may be regarded as nanostructured materials having a hierarchical structure, and polyfunctional [7]. As noted above, the strategic direction of the preparation of such materials is the use of the principles of self-organization and self-assembly, allowing to achieve fast and efficient form of nanomaterials. The key to this approach is the use of different templates - intermediate controlling interaction at some level, and contributing to structural elements of a complex system in a certain way to self-organize.
2. Experimental procedure

In this paper, in order to synthesize a vanadium-containing gel as a template was used ammonia, which is participating in the formation of ammonia complex with vanadium-oxygen framework \( [\text{VO}_2]_n \text{m(OH)}_n \cdot n\text{NH}_3 \) \( \cdot n\text{H}_2\text{O} \). This results in the formation of the sol, and ammonia is used as a template. The use of ammonia as a template allows for the formation of the sol and gel, which can be used as a template for the synthesis of vanadium oxides.

Every 10 minutes the pH was measured and an aliquot of the test solution was used to determine the concentration of vanadium. When calculating the concentration of vanadium into account the dilution of the solution when introduced into a template.

3. Results and discussion

The results of the experiments are given in Table 2. Upon reaching pH 3.4 the solution slowly begins to thicken with the formation of vanadium compound with ammonia, rolling in the gel. From the results it can be observed that the sol is formed within 10 minutes, the gel is formed within 20 minutes, and the xerogel is formed within 30 minutes.

Controlling the gelling process was carried out by visual observation of external changes in the vanadium-containing solution in stages (Figure 2).

![Fig. 2 The sequence of formation of vanadium xerogel](image)

In order to study the composition and structure of the synthesized gel vanadium material was selected physical and chemical analysis of X-ray diffraction, electron microscopy, atomic force, infrared spectroscopy and thermogravimetric methods in comparison with the results of the analysis of raw materials [4].
INFLUENCE OF CHEMICAL COMPOSITION OF TOOL STEEL ON PERMANENT PLASTICITY DURING HEAT TREATMENT TRANSFORMATIONS

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Abstract: The work presents the research of permanent strain occurred when metallurgical transformations take place even under small stress applied externally lower than the yield stress of weaker phase. Four tool steel grades were tested: THG2000 (Uddeholm, Sweden), 20X13, 40X13 and 95X18 (GOST). All steel grades differ in carbon content and amount of alloying elements and behave differently when transformation plasticity occurs. This phenomenon was observed during bending test when bending stress was 100MPa and was less than 10 % of yield strength of the steel. The steel specimens were heated to 930-1050 °C temperature and then bent during air quenching. Plastic deflections were observed through all cooling process that involved martensitic transformation as well. Different effect of compression and tensile stresses on microstructure evolution during martensitic transformation was determined as both type of stresses formed in bent specimens.

Keywords: STEEL, TRANSFORMATION PLASTICITY, MICROSTRUCTURE, HEAT TREATMENT, STRESS

1. Introduction

Phase transformations in metals have a major influence on the material behavior in several common engineering applications. Steels exhibiting enhanced response to transformation-induced plasticity (high strength TRIP-steels for automotive production) are examples of the important role martensite formation can play [1, 2].

At temperatures above the martensite start temperature (Mₘ), austenite-to-martensite transformation can occur when the summation of the mechanical energy due to the externally applied stress and the chemical driving force exceeds a critical value. This transformation is known to be induced via stress-assisted nucleation at the same nucleation sites as those responsible for the athermal martensitic transformation that occurs during cooling [3]. An externally stressed specimen in the process of a phase transformation may show a significant nonlinear behavior, which is known as transformation plasticity [4-8]. Even under an externally applied load stress with the corresponding equivalent stress being small in relation to the “normal” yield stress of the material, plastic deformation occurs.

The austenite-to-martensite transformation and transformation plasticity as well directly depends on the amount of carbon level in the steel and it also depends on the yield strength of the material (initial phase – austenite). The steel with higher carbon content possess more stable retained austenite comparing to the low carbon steel and this can be due to the phenomenon that the transformation of this austenite is not obtained immediately [9].

Most alloying elements that enter into solid solution in austenite at high temperatures lower the martensite start temperature Mₘ during cooling with the exception of cobalt and aluminum [10]. It is also evident that the strong carbide forming elements like chromium, vanadium and molybdenum have an impact on martensitic transformation start temperature and on transformation plasticity as well [11, 12].

The aim of the work was to determine the influence of compression and tension stress on the transformation plasticity and evolution of microstructure of alloyed steel during quenching as recent scientific works do not show a general opinion [13-15]. Because of severe service conditions (high temperature, stress, corrosion, irradiation, etc.), alloy steels for the various utility industries must be sufficiently resistant to microstructural degradation. Therefore, the stability of the microstructure is one of the fundamental requirements concerning the industrial applicability of alloy steels [16]. The microstructural stability of martensitic high chromium steels is achieved by heat treatment consisting of austenizing, hardening and high-temperature tempering.

2. Methodology

The steel used for the investigation was THG2000 steel (Uddeholm, Sweden) alloyed with chromium, molybdenum and vanadium. The mentioned steel has a wide range of applications in indexable drills, milling cutters and transmission parts for automobiles due to its high resistance to abrasion at both high and low temperatures and resistance to thermal fatigue as well. For the investigation of influence of alloying elements differently alloyed steels 20X13, 40X13 and 95X18 (GOST 5632-72) were chosen for experiments for having effective comparison. Chemical composition of steel is presented in Table 1.

Table 1: Chemical composition of steel (% wt)

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>V</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>THG2000</td>
<td>0.39</td>
<td>1.00</td>
<td>0.40</td>
<td>5.30</td>
<td>0.15</td>
<td>1.30</td>
<td>0.90</td>
<td>Bal.</td>
</tr>
<tr>
<td>20X13</td>
<td>0.19</td>
<td>0.23</td>
<td>0.29</td>
<td>12.71</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
<td>Bal.</td>
</tr>
<tr>
<td>40X13</td>
<td>0.35</td>
<td>0.35</td>
<td>0.40</td>
<td>13.02</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
<td>Bal.</td>
</tr>
<tr>
<td>95X18</td>
<td>0.97</td>
<td>0.60</td>
<td>0.59</td>
<td>17.64</td>
<td>0.39</td>
<td>0.10</td>
<td>-</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

The specimens with rectangular cross-section were made with the dimensions 6 mm × 8 mm × 100 mm from hot rolled rod ∅ 11,2-14,0 mm. The specimens were austenitized in a protective environment (N₂+CO+CO₂) at 900 °C, 940 °C, 980 °C and 1020 °C for air quenching. The specimens were hardened choosing the different quenching temperature that allowed getting different solubility of carbides and thus the different composition of the solid solution of steel.

For the investigation of transformation plasticity, the austenitized specimen was placed at the special bending device [17] and air cooled. At the set temperature the specimen is loaded in bending load generated bending stress of 100 MPa and not exceeded 15 % of steel yield strength R_p0.2 at the certain temperature – yield strength of THG2000 is R_p0.2 = 730 MPa, at T = 550 °C [18]. The martensitic start temperature of the steel depends on austenizing temperature and for steel with the similar chemical composition is 270-370 °C [19], so, the mentioned temperature 550 °C was very approximate start of bending and it ensured that the martensitic transformation would start later and the very beginning of bending would be registered. The plastic deflection of specimen was measured in accuracy of 0.01 mm until the temperature of specimen reached room temperature.

It was also investigated the microstructure of the samples by monitoring with the laser analyzer LMA Carl Zeiss using a video camera YCH15 and with optical microscope Nikon with objective Nikon TU Plan Fluor 100x/0.90 and video camera Nikon DS-R2 16 MP. Following thermal or thermal-mechanical treatment, the samples for optical analysis were ground, polished, and etched in 3% Nital solution.
The temperature of specimen during heat treatment was measured by welded chromel-alumel thermocouple of 0.3 mm wire diameter.

3. Results and Discussion

Investigation of transformation plasticity of steel during air quenching from different austenitizing temperatures

The soft annealed microstructure of THG2000 steel is composed of a ferritic matrix and a big quantity of small disperse carbides of alloyed elements (Fig. 1). Distantly visible primary grain boundaries can be seen as well.

Fig. 1 Microstructure of steel THG2000 at annealed state

During air quenching of specimens of steel THG2000 after heating at austenizing temperature the martensite transformation did not start immediately. Increasing temperature of austenizing allowed solid solution to become more saturated with alloying elements (Cr, Mo), thus obtaining different \( M_s \) temperatures and different value of plasticity occurred during martensitic transformation (Fig. 2). The martensitic transformation started (circled part of the curves in Fig. 2) at about 370 °C for lower austenitizing temperature (900-940 °C) and decreased approximately to 310 °C for higher heating temperatures (980-1020 °C) as austenite became enriched with carbon and alloying elements after dissolution of small carbides at high temperature.

The total plastic deflection obtained after martensitic transformation had stopped fully and the specimen cooled down was the biggest for the lowest austenitizing temperature (Fig. 2).

Fig. 2 Plastic behavior of steel THG2000 specimens during air quenching from different austenitizing temperatures. \( T \) – temperature of specimen

The different amount of total plastic deflection after air quenching from different austenitizing temperatures showed the influence of different alloying degree of steel solid solution. The higher austenitizing temperatures were applied to steel specimens, the less the plastic deflections were obtained. Not only alloying of solid solution had influence on plastic deflection but also the content of retained austenite as increasing the temperature of heating raised its amount. Retained austenite remaining from heating till room temperature did not undergo any transformation thus decreased the plasticity of steel specimen during transformation.

Optical analysis of steel THG2000 showed the heterogeneous phase composition of steel composed of laths of martensite, hardly visible small carbides and probably retained austenite (further analysis will be provided for more precise phase composition) (Fig. 3).

Investigation of dependence between chemical composition of steel and transformation plasticity during air quenching

Less plasticity was obtained for THG2000 steel when compared with steels with different chemical composition: 20X13, 40X13 and 95X18 (GOST) that varied in carbon and chromium content (Fig. 4). This could be explained by the presence of vanadium content in THG2000 steel. As vanadium is strong carbide former (stronger than chromium [12]) the carbides remain stable up to very high heating temperatures almost melting ones. These carbides block plastic deformation during transformation of steel.

Fig. 3 Microstructure of steel THG2000 at air quenched state. Austenitizing temperature 1020°C

Fig. 4 Influence of chemical composition on plastic behavior of alloyed steel specimens during air quenching

For better understanding of plastic behaviour of steel during air quenching from austenitizing temperature it is necessary to know the phase composition of each steel grade and their critical temperatures. Such data is presented in Table 2.

Further investigations showed [11, 17], that transformation plasticity is very affected by amount of carbon in steel: the higher content of carbon was, the higher transformation plasticity was obtained. So, the data from Table 2 shows that during heating at austenitizing temperature only steel 20X13 had fully dissolved carbides, as it means, solid solution (austenite) saturated with approximately 0.2% carbon and 13% chromium. Other steels at the
same temperature contained also not dissolved carbides, that is, solid solution had less carbon and alloying elements. The steel specimens with smaller plastic deflection (Fig. 4) also contained retained austenite that did not transform during air quenching. As the transformation plasticity is related with transforming of austenite to martensite, less volume of formed martensite presented lower transformation plasticity.

Investigation of transformation plasticity of alloyed steel during tempering

The phenomenon of transformation plasticity can be observed not only during quenching of steel when martensitic transformation proceeds but also during tempering when quenched steel contains retained austenite and transformation of retained austenite to martensite happens. It could be explained like auto-deformation of steels parts that were affected by stress.

For determination of transformation plasticity of alloyed steel, the air quenched specimens were tempered at 200, 300, 400, 500 and 600 °C temperatures for 2 hours. As the specimens were curved after air quenching + bending, the difference in plastic deflection was measured after tempering at each temperature. The results are presented in Fig. 5.

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Austenizing T, °C</th>
<th>Phase composition at austenizing T</th>
<th>A1, °C</th>
<th>A3, °C</th>
<th>M1, °C</th>
<th>Phase composition after air quenching</th>
</tr>
</thead>
<tbody>
<tr>
<td>THG2000</td>
<td>1020</td>
<td>Austenite + carbides</td>
<td>840</td>
<td>870</td>
<td></td>
<td>Martensite + 8% retained austenite + carbides</td>
</tr>
<tr>
<td>20X13</td>
<td>1050</td>
<td>Austenite</td>
<td>820</td>
<td>900-950</td>
<td>320</td>
<td>Martensite + carbides</td>
</tr>
<tr>
<td>40X13</td>
<td>1050</td>
<td>Austenite + carbides</td>
<td>820</td>
<td>860-880</td>
<td>145-270</td>
<td>Martensite + carbides + low content of retained austenite</td>
</tr>
<tr>
<td>95X18</td>
<td>1050</td>
<td>Austenite + carbides</td>
<td>830</td>
<td>925-1100</td>
<td>260</td>
<td>Martensite (with 11% Cr and 0.25% C) + 17% retained austenite + carbides</td>
</tr>
</tbody>
</table>

Fig. 6 Change of plastic deflection of curved air quenched specimens of THG2000 steel after tempering at different temperatures for 2 hours. Austenizing temperature 1020 °C

4. Conclusions

Analyzing the results of experiments and sources of scientific literature, such conclusions were made:

- Transformation plasticity of steel THG2000 increased from 25% to 35% when austenizing temperature decreased from 1020 °C to 900 °C. The difference in plasticity is related with dissolution of carbon and alloying elements in solid solution at higher temperatures.

- Chemical composition of steel had influence on transformation plasticity of steel. The steel with solid solution saturated with the biggest content of dissolved carbon and alloying elements presented the highest transformation plasticity.

- Steel with fully transformed austenite to martensitic structure presented the highest transformation plasticity. Steels THG2000 and 95X18 showed the lowest transformation plasticity because of significant content of retained austenite comparing to the steel grades 20X13 and 40X18.

- Auto-deformation of curved steel specimens was determined for the ones austenitized at higher temperatures (980°C and higher) and for steels contained more retained austenite. The change of plastic deflection after air quenching and tempering at 700 °C was 3-7 %.

5. References


Determine the fatigue lifetime for aluminium alloy EN AW 2007.T3 during cyclic bending – torsion loading under in-and-out-of phase shift $\phi = 0^\circ$ and $\phi = 90^\circ$ using selected fatigue criteria

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**Abstract:** The article deals with determining of fatigue lifetime of aluminium alloy EN AW 2007.T3 during by multiaxial cyclic loading. The theoretical part deals with the fatigue and with the criteria for evaluation of multiaxial fatigue lifetime, in region low-cycle and high-cycle fatigue. The experimental part deals with modeling of combined bending - torsion loading and determining the number of cycles to fracture in region low-cycle and high-cycle fatigue and also during of loading with the sinusoidal wave form under in phase $\phi = 0^\circ$ and out phase $\phi = 90^\circ$.

**KEYWORDS: ALUMINIUM ALLOY, FATIGUE CRITERIA, SINUSOIDAL CYCLIC LOADING, MULTIAXIAL FATIGUE, STRESS**

### 1. Introduction

In the Earth's crust, aluminium is the most abundant (8.3% by mass) metallic element and the third most abundant of all elements (after oxygen and silicon). Aluminium is a relatively soft, durable, lightweight, ductile and malleable metal with appearance ranging from silvery to dull gray, depending on the surface roughness. It is nonmagnetic and does not easily ignite. Aluminium is one of the lightest engineering metals, having strength to weight ratio superior to steel. By utilising various combinations of its advantageous properties such as strength, lightness, corrosion resistance, recyclability and formability, aluminium is being employed in an ever-increasing number of applications. This array of products ranges from structural materials through to thin packaging foils [1, 2].

Multiaxial states of stress are very common in structures and components. Fatigue is usually a surface phenomena so that the state of stress is biaxial because the stress normal to a free surface is zero. Another relatively simple combination of different loads is offered by an axle loaded under combined bending and torsion. This loading combination was tested in our and also in many others experiments [3,4]. In spite of this fact, fatigue mechanisms are still not fully understood. This is partly due to the complex geometrical shapes and also complex loadings of engineering components and structures which result in multiaxial cyclic stress-strain states rather than uniaxial.

Multiaxial loading includes states of stress where the individual components of stress and strain can be either in-phase or out-of-phase, sometimes called proportional and nonproportional loading [5,6].

### 2. Fatigue criteria

Criteria valid for the fatigue lifetime calculation can be classified in three different categories: strain based methods, strain-stress based methods and energy based approaches. There are plenty of hypotheses used for evaluating a degree of damage caused by variable load [7, 8]. Life prediction methods which presume homogeneous material (free from cracks, inclusions or defects) at the outset of the investigation can be divided into strain-based (low-cycle fatigue) and stress-based (high-cycle fatigue) methods. There were chosen some fatigue criteria: Fatemi-Socie, SWT, Brown-Miller, Liu, Goodman, Sines, Findley and MCE fatigue criterion.

Fatemi and Socie [9] observed that the Brown and Miller’s idea could be successfully employed even by using the maximum stress normal to the critical plane, because the growth rate mainly depends on the stress component normal to the fatigue crack. Starting from this assumption, he proposed two different formulations according to the crack growth mechanism: when the crack propagation is mainly MODE I dominated, then the critical plane is the one that experiences the maximum normal stress amplitude and the fatigue lifetime can be calculated by means of the uniaxial Manson-Coffin curve; on the other hand, when the growth is mainly MODE II governed, the critical plane is that of maximum shear stress amplitude and the fatigue life can be estimated by using the torsion Manson-Coffin curve. Criterion has the following form:

$$\Delta \gamma = \frac{1}{2} \left( 1 + k \frac{\sigma_{max}}{\sigma_y} \right) \epsilon_f (2N_f)^{\eta} \left( 2 \times N_f \right)^{\gamma}$$

(1)

Smith, Watson and Topper (SWT) created a parameter for multiaxial load, which is based on the main deformation range $\Delta \epsilon$ and maximum stress $\sigma_{max}$ to the main plane. Criterion has the following form:

$$\sigma_{max} \Delta \epsilon = \frac{\sigma_f^2}{E} (2 \times N_f)^b \sigma_f \epsilon_f (2 \times N_f)^c$$

(2)

Brown and Miller [10] observed that the fatigue life prediction could be performed by considering the strain components normal and tangential to the crack initiation plane. Moreover, the multiaxial fatigue damage depends on the crack growth direction. Different criteria are required if the crack grows on the component surface or inside the material. In the first case they proposed a relationship based on a combined use of a critical plane approach and a modified Manson-Coffin equation, where the critical plane is the one of maximum shear strain amplitude. Criterion, which was created, has the following form:

$$\frac{\Delta \epsilon}{2} + S \times \Delta \epsilon = A \times \frac{\sigma_f}{E} \left( 2 \times N_f \right)^b + B \times \epsilon_f \times \left( 2 \times N_f \right)^c$$

(3)
Liu created a virtual model of the deformation energy, which is a generalization of the axial energy on the basis of prediction of fatigue life. Criterion has the following form:

$$\Delta W = \frac{4 \times \sigma f \times \epsilon f \times (2 \times N f)^{b+c}}{E} + \frac{4 \times \sigma f^2}{E} \times (2 \times N f)^{2b}$$ (4)

Goodman used main stresses for evaluating the fatigue under multiaxial loading. Normal stresses are calculated for each plane and their ranges are used for calculation of fatigue lifetime. If the point of the combined stress is below the relevant Goodman line then the component will not fail. This is a less conservative criteria based on the material ultimate strength yield point $S_{ut}$. To establish the factor of safety relative to the Goodman’s criteria can be written as:

$$\frac{K_f \times \sigma_{amp}}{S_{ut}} + \frac{\sigma_{mean}}{S_{ut}} = \frac{1}{f_f}$$ (5)

Sines published his works throughout the fifties of the last century. His criteria are very much alike, utilizing the amplitude of second invariant of stress tensor deviator (which corresponds to the von Mises stress) as the basis. Another term is added to the equation in order to cope with the mean stress effect – while Sines prefers the mean value of first invariant of stress tensor (i.e. hydrostatic stress $\sigma_0$). His resulting failure criterion can be expressed as:

$$\frac{\Delta \tau_{oct}}{2} + a \times (3 \times \sigma_{hmean}) = \tau_f \times (N_f)^b$$ (6)

Findley criterion is the first critical plane criterion. He suggested that the normal stress $\sigma_n$, acting on a shear plane might have a different linear influence on the allowable alternating shear stress, $\Delta \tau/2$. Criterion has the following form:

$$\frac{\Delta \tau}{2} + k \times \sigma_n = \tau_f \times (N_f)^b$$ (7)

Minimum circumscribed ellipse (MCE) – The origin of this method goes out from minimum circumscribed circle method (MCCM) [11]. This method was first presented by Papadopoulos. Its major feature is its explicitness in determination of mean shear stress. Papadopoulos later shows that such minimum circumscribed circle can be obtained by a search through all pairs and triads of points in the shear stress path, but such an approach can be very lengthy. The contrast in comparison with MCCM is clear – it should offer a better solution of phase shift effect problems. Nevertheless, as regards the definition of mean shear stress, it does not offer any new approach. For proportional loading this will always be a straight line and for non-proportional loading histories will have some complex shape.

$$\tau_a = \sqrt{\frac{R_a^2 + R_b^2}{4}}$$ (8)

Where: $\gamma_f$ is the fatigue ductility coefficient in torsion; $\phi_f$ is the fatigue ductility coefficient; $\sigma_f$ is the fatigue strength coefficient; $\sigma_0$ is the mean hydrostatic stress; $\sigma_n$ is the normal stress; $\sigma_{hmax}$ is the maximum stress; $\sigma_{hmean}$ is the mean stress; $\sigma_0$ is the stress in the direction of the axis y; $\tau_a$ is the equivalent shear stress; $\tau_f$ is the fatigue strength coefficient in torsion; $\Delta \epsilon_{max}$ is the maximum shear strain range; $\Delta \epsilon_1$ is the principal strain range; $\Delta \epsilon_{max}$ is the normal strain range; $\Delta \tau/2$ is the alternating shear stress; $\Delta \tau_{oct}$ is the octahedral shear stress; $\Delta W$ is the virtual strain energy; $N_f$ is the number of cycles to fracture; $S_T$ is the modified fatigue strength; $S_{ut}$ is the ultimate tensile strength; $f_f$ is the factor of safety applicable the fatigue; $E$ is the elasticity modulus in tension; $G$ is the elasticity modulus in torsion; $R_a$ is the major axis of the ellipse; $R_b$ is the maximum distance of stress point; $b$ is the fatigue strength exponent; $k$ is the fatigue strength exponent in torsion; $c$ is the fatigue ductility exponent in torsion; $A, B, S, k, a$ are material parameters.

3. Numerical calculations and results

In ANSYS software was created the model of the test bar. The real geometry of this component is shown in Fig.1. The rod bar had a circular shape with a defined section, in which was expected an increased concentration of stress and creation a fatigue fracture.

![Geometry of the test bar](image1.png)

**Fig.1 Geometry of the test bar**

The ends of this model were loaded by reversed bending moment on the one side and by reversed torsion moment on the opposite site. The values of presented stresses and strains in the middle of the rod radius were taken from computational analysis using finite element method. We used the following parameters in finite element model: used material was aluminum alloy EN AW 2007.T3 (AlCu4PhMg) with Young's modulus $E = 0.817x10^{11}$ Pa, Poisson number $\mu = 0.3$ and with the strength limit $R_a = 491$ MPa. From computational analysis can be seen that the area with greatest concentration of stresses or eventually the place with the higher deformation was localized in the middle of the rod radius (see Fig.2).

![Result of FEM analysis in ANSYS software](image2.png)

**Fig.2 Result of FEM analysis in ANSYS software**

25
Obtained values of the stresses from finite element analysis were next computational analyzed using Fatigue Calculator software. This is a program which can quickly calculate fatigue lifetime of selected material. After starting the calculation, Fatigue Calculator displayed the number of cycles to failure for different models of damage. In our calculation we considered with all multiaxial criteria described above which can be applied to low-cycle and also to high-cycle fatigue region. All the tests were performed under controlled bending and torsion moments. Frequency of each analysis was equal to 30 Hz. It was first detected the number of cycles to fracture for multiaxial low-cycle fatigue with amplitudes in the phase shift 0° and then out of the phase shift 90° for stress. The same was done for multiaxial high-cycle fatigue. The obtained numbers of cycles are processed into Wöhler curves $\sigma_{xx} - \log N_f$ for multiaxial cyclic combined bending - torsion loading. For multiaxial low-cycle fatigue with phase shift 0°, Wöhler curves are shown in Fig.3. For multiaxial low-cycle fatigue with phase shift 90°, Wöhler curves are shown in Fig.4.

### 4. Conclusion

All multiaxial models applied to fatigue lifetime calculation of aluminum alloy EN AW 2007.T3 increases with decreasing stress amplitude continuously in the cycles of number region. Comparing Wöhler curves for low-cycle fatigue (see Fig.7), for amplitudes of the load with phase shift 0° (solid lines) and for amplitudes of the load with phase shift of 90° (blank lines), it can be seen that some models (such as Fatemi-Socie and SWT) give higher resistance to fatigue damage in the phase shift than the synchronized load amplitudes. This may be caused by, that the bending loading and neither torsion loading not active with the maximum value on the sample at the same time during the phase shift, but alternately. In this way, as if the sample was loaded by lower value of stress or deformation in a given time (phase shift of 90°). For other models, this shift of amplitudes did not cause any significant changes and the differences are minimal.
Comparing Wöhler curves for high-cycle fatigue (see Fig.8), for amplitudes of the load with phase shift $0^\circ$ (solid lines) and for amplitudes of the load with phase shift of $90^\circ$ (blank lines), it can be seen that all models (except for Sines) gives a higher resistance against fatigue damage in the phase shift than in the synchronized amplitudes of loading. Probably the reason will be same as for low-cycle fatigue.

It was observed that a phase shift $90^\circ$ is the cause of "rotating" curves of fatigue life, which may have an impact on partial increase of fatigue life for the area of low-cycle and high-cycle fatigue.

5. Acknowledgements

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6. References

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THERMOCHEMICAL CALCULATIONS AND EXPERIMENTAL INVESTIGATIONS ON Mo-Ni-B ALLOY SYSTEM PRODUCED BY COMBUSTION SYNTHESIS

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Abstract: In this study, Mo-Ni-B alloy system which can be a new hard alloy alternative to tungsten base cemented carbides, was investigated by means of thermochemical calculations and experimental trials. Thermochemical calculations were carried out to estimate the adiabatic temperatures and possible product compositions in the alloys by using FactSage 7.0 thermochemical software. The combustion synthesis process was performed under normal gravity and air in Cu copper crucibles by using metal oxides (MoO3 and NiO), boron oxide (B2O3) as a boron source and aluminum (Al) as a metallic reductant. Alumina, (Al2O3) as a functional additive (diluent), were also added in order to reduce the adiabatic temperature of the reaction. Since the attained reaction temperatures for this system during the exothermic SHS process is so high (above 2000 °C), the reaction is self-sustaining and the melt consists of insoluble mixture of metallic compound and oxide phase which can be segregated under normal gravity force.

KEYWORDS: COMBUSTION SYNTHESIS, Mo-Ni-B, HARD ALLOY, THERMOCHEMICAL CALCULATIONS, FACTSAGE.

1. Introduction

Today, WC-Co MMCs are the mainstay of the manufacturing industry with a variety of applications including machining of many different metallic and nonmetallic materials [1]. According to the recent investigations, new hard alloys can be also successfully applied to wear resistance applications such as injection molding machine parts. For example, borides which have high corrosion resistance and strength can replace cemented carbides for some specific applications. A new hard alloy composite alternative contains a metal matrix of nickel as a binder and Mo-NiB-type boride as a hard phase. However, due to the poor sintering behavior of borides and the formation of brittle phases with metals during sintering, reaction boronizing sintering technique are mostly used in previous studies which requires high power and consequently higher costs [2].

Combustion Synthesis (or Self Propagating High Temperature Synthesis) is one of the alternative production techniques that can be used to produce refractory metal compounds such as carbides, nitrides, silicides, borides as well as other intermetallics and metal matrix composites. The process has several advantages such as very short processing time, simple operation, low initiation energy requirement and low cost. In a SHS process, after ignition, the combustion front is formed and propagates throughout the reactant mixture yielding the desired product [3]. This work aims to establish a scientific background for high energy efficient, fast and low-cost production of Mo-Ni-B hard metal system starting from the cheap oxides by combustion synthesis method.

2. Experimental Studies

The raw materials of the SHS experiments are MoO3 (99.5 wt. % pure, particle size < 60 μm), Al (99.6 wt. % pure and particle size <100 μm), NiO (99.0 wt. % pure and particle size <40 μm), Al2O3 (99.0 wt. % pure and particle size <50 μm). B2O3 was obtained by calcination of 99.5 % pure boric acid (H3BO3, Eti Holding Inc.) in nickel crucible at 800 °C for 2 hours followed by milling and sieving. After drying procedure of the powders in an oven at 110 °C for 2 hours, the mixture was prepared at different molar ratios. The SHS process was carried out in a copper crucible with the inner height of 200 mm and the inner diameter of 40 mm. The dried powder was mixed thoroughly in a Turbula mixer for 30 min. After the charge mixture was poured into the crucible and compacted thoroughly, a tungsten resistance wire was placed on the top of the compacted powder. The weights of the raw materials used in the experiments were shown in Table 1. The reaction was initiated by passing electricity through the resistance wire. After initiation, electricity was cut off and the crucible was left to cool to room temperature. The characterization studies were performed by using atomic absorption spectroscopy (AAS), X-ray florescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometers (WDS-EDS), and micro-hardness testing methods.

Table 1. Weights of initial raw materials for Mo-Ni-B systems

<table>
<thead>
<tr>
<th>Initial Raw Materials</th>
<th>Exp. No</th>
<th>Exp. No</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO3, g</td>
<td>76,1</td>
<td>76,1</td>
</tr>
<tr>
<td>NiO, g</td>
<td>29,6</td>
<td>44,9</td>
</tr>
<tr>
<td>B2O3, g</td>
<td>18,4</td>
<td>18,4</td>
</tr>
<tr>
<td>Al, g</td>
<td>52,1</td>
<td>56,3</td>
</tr>
<tr>
<td>Al2O3, g</td>
<td>8,6</td>
<td>9,8</td>
</tr>
</tbody>
</table>

3. Results and Discussions

A thermochemical calculation was carried out to estimate the adiabatic temperature (Tad) value and the possible product composition of the SHS reaction by using the advanced “Equilib” module of FactSage 7 developed by CRCT-ThermFact and GTT-Technologies22. In the calculations, FactPS, STGE2011, and FToxide were chosen as the most appropriate databases. In order to simulate the SHS reaction, 2 moles of MoO3, 0.5 mole of NiO, 1 mole of B2O3 were equilibrated with different moles of Al. The reactions of the process were assumed as adiabatic (ΔH=0) and the initial reaction temperature was selected as 25 °C. The adiabatic temperature value (Tad) is an important indicator to estimate whether a reaction is self-propagating or not. The adiabatic temperature change versus Al addition in the combustion reactions of the process were assumed as adiabatic (ΔH=0) and the initial reaction temperature was selected as 25 °C. The adiabatic temperature value (Tad) is an important indicator to estimate whether a reaction is self-propagating or not. The adiabatic temperature change versus Al addition in the combustion reaction is given in Figure 1. As can be seen, Tad can reach over 2700 °C, when the Al addition is selected between 7-8 moles. Figure 2 shows that when the Al content in the raw materials increases, reduction and liquid Mo-Ni-B alloy formation also increases. However, in order to get higher boron content, Al dissolution in the alloy is unavoidable for the specific initial composition. The amount of gas also increases with Al addition due to the formations of AlB2O24, BO2, Al2O3, NiO, B2O3, and (BO2)2g.
Figure 1. Thermochemical calculation for adiabatic temperature versus Al addition.

Figure 2. Thermochemical calculation for product composition versus Al addition.

The obtained SEM image of the specimen coded with NI1 is given in Figure 3. The EDS analysis shows that nickel reacted with excess aluminum to produce NiAl intermetallic which formed the matrix phase (1). The inner region of angular grains belong to MoB₂ phase (2) whereas the inner region are MoB (3). The mean hardness value of the specimen was found as 938.65 HV.

Figure 4 represents the obtained SEM image of the specimen coded with NI7. Since the initial NiO quantity is comparably higher than that of NI1, the excess Al reacted with high amount of Ni to form Ni₃Al phase. In the specimen, Mo₂NiB₂ region was also observed as gray angular form. The grains with white region represents MoB phase (3). The mean hardness value of the specimen was found as 943 HV.

4. Conclusion

It is possible to produce a Mo-Ni-B containing metal matrix composites from oxides by aluminothermic reaction. The formation of ternary boride Mo₂NiB₂ in the product is possible with nickel oxide addition. Due to the high amount of excess Al in the alloy, NiAl or Ni₃Al phases form in the matrix. This study is an ongoing project and further experiments and analyses will be carried out in the near future.

5. Acknowledgement

The authors are pleased to acknowledge the financial support for this research from TUBITAK (The Scientific and Technological Research of Turkey - Project No: 213M555) and Russian Foundation for Basic Research (Project No:14-08-91374).

6. References

INCREASE OF WEAR RESISTANCE OF METASTABLE AUSTENITE Cr-Mn-N STEEL DIFFUSION BORIDE COATINGS IN CONDITIONS OF ACTION THE EXTERNAL MAGNETIC FIELD

Abstract: In this paper it was investigated the formation of complex boriding diffusion layers on metastable austenite Cr-Mn-N steel powder method. Phase and chemical composition, thickness, microhardness and wear resistance obtained by layers of metastable austenite Cr-Mn-N steel. It is established that the application of an external magnetic field (EMF) leads to a redistribution of the proportion boride phases in the surface layers of the crystal lattice period changes. EMF allows in 1.5 – 2 times to reduce the period of saturation details, microhardness diffusion boride coatings increase to 20.5 – 21 GPa and increase their wear resistance in 2.4 – 3 times compared to steel without protective coating. Boriding a magnetic field will increase the microhardness boride coatings 6 – 7 GPa compared to the boriding without application of a magnetic field.

KEYWORDS: BORIDING, BORIDE LAYER, COPPER, STRUCTURE, DIFFUSION, FRICTION, MICROSTRUCTURE, MICROHARDNESS, WEAR RESISTANCE, AUSTENITE Cr-Mn-N STEEL

1. Introduction

Austenitic Cr-Mn-N steel refers to wear resistant steel in which metastable austenite during operation undergoes a phase change to create ε - martensite [1]. However, in the demanding conditions of intense loading at hydroabrasive wear in different corrosive environments, such as hydraulic gate fitting parts with Cr-Mn-N steel, a problem improvement operational characteristics [2]. An effective method is the use of chemical heat treatment (CHT) using boron and other saturation elements. CHT allows creating on the effective method is the use of chemical heat treatment (CHT) using magnetic field (EMF), and at simultaneous application.

To solve this problem, we used a complex diffusive saturation of the surface layer of Cr-Mn-N steel boron or boron and copper at simultaneous action of EMF.

To create a magnetic field coil (solenoind) used, which consisted of 635 windings ti res aluminum alloy, the size of 10x20 mm; the current strength – 60 A; the magnetic induction – 35 mT. For magnetic thermochemical treatment in coil placed high temperature furnace with crucible and packed in them saturated equipment PMT – 3 no less than 15 – 20 fields of view at a load of 0.49 – 0.98 N. Measuring accuracy microhardness was ±300 MPa.

Microhardness measurements were carried out on the equipment PMT – 3 no less than 15 – 20 fields of view at a load of 0.49 – 0.98 N. Measuring accuracy microhardness was ±300 MPa.

Research of the chemical composition of coatings performed microregnospectral analysis on electronic scanning microscope – SEM 106 with increasing in 2000 time, accuracy – 0.01% by weight. Determination of the chemical composition performed by EDS, calculation of quantitative chemical composition - the method of ZAF.

Phase composition, quantitative analysis phase, the periods of the crystal lattice, volume of elementary lattice phase, regions of coherent scattering in boride coatings were analyzed for X-ray diffractometer Ultima-IV of Rigaku (Japan), in the copper Ka monochromatic radiation.

Testing of coatings on the wear resistance performed on friction machine [7].

3. Results and discussion

Microstructural analysis established that after diffusion saturation Cr-Mn-N steel in boriding mixture during 5 hours formed diffusion layer with thickness up to 50 microns (Fig. 1, a), while the complex saturation with boron and copper during 5 hours diffusion saturation – up to 75 microns (Fig. 1, c). Overlay EMF at boriding during 2 hours leads to increases diffusion boride layer in 1.8 times (up to 90 microns) (Fig. 1, b), and in 1.3 times at the complex saturated with boron and copper (up to 100 micron) (Fig. 1, d).

Microstructure boride layer, shown in Fig. 1 (a) and Fig. 1 (b) has a layered structure and uniform distribution of phases over the cross section of a separate layer via presence inclusions of other phases, which are local dark zones in the structure layer. Coating consists of different phases with a grain size of 1 – 2 microns, multifaceted or droplike forms slightly elongated in the direction of the front diffusion of saturating elements. Typical for boride coating is presence the diffusion micropores, which oriented along the subsurface (Fig. 1, b). Boride layer structure formed at complex saturation with boron and copper in conditions of action EMF, has more pronounced layered nature with greater uniformity within a separate layer and a less quantity micropores (Fig. 1, d).
with boron and copper with simultaneous action EMF, the duration compared with the material base. Application EMF can increase steel get boride layers, microhardness which was 1.5 times with boron and copper without action EMF and in 6 times higher than microhardness boride coating obtained without action EMF – 18.0 GPa (Fig. 2). So boride layers in conditions of action EMF promotes improves microhardness of surface substratum up to 20.5 – 21 GPa. At the complete saturation in Cr-Mn-N steel boron and copper with simultaneous action EMF, observe formation more plastic boride diffusion layers with less microhardness in 1.2 times compared with boriding in conditions of action EMF (Fig. 2).

Along with this application the complete saturation with boron and copper with simultaneous action EMF leads to increases the microhardness in 1.4 times compared with the complete saturation with boron and copper without action EMF and in 6 times compared with the material base. Application EMF can increase microhardness boride coatings on 6 – 7 GPa, compared with boride coatings obtained without action ZMP. Microhardness distribution in the coating depending on the distance from the surface has stepped character and indicates on different phase composition by section boride diffusion layer (Fig. 2). At this the maximum hardness is formed in the surface layer FeB phases, thickness 10 – 15 microns.

Investigation of the distribution of elements over the cross section diffusion layer on samples of Cr-Mn-N steel after boriding and complete saturation with boron and copper in different physical - chemical conditions shown on Table 1 – 4 and Fig. 3 – 4. The point X-ray spectral analysis boride coating established that chromium, which is the main alloying element in Cr-Mn-N steel with containing up to 15% weight, unevenly distributed over the cross section of the diffusion layer. The main concentration of chromium is concentrated in the central and near-boundary up to matrix part boride coating. Since the thickness boride coating dependent on the conditions of saturation and composition of saturating environment, then in boride layers at the general thickness of the coating 45 – 50 microns maximum chromium content of 18 – 20 % weight detected at a depth of 15 – 30 microns. Outside boride layer of the chromium content decreases sharply up to 6 % weight (Fig. 3, a; Table. 1). For boride layer thickness 85 – 90 microns obtained in conditions of action EMF, the main part of the chromium with content from 17 % weight up to 24 % weight focuses on the depth of 30 – 65 microns boride layer (Fig. 3, b; Table. 2).

Investigation of the distribution microhardness by section boride diffusion layer on Cr-Mn-N steel shown in Fig. 2. It is shown that boriding allows to get diffusion coating with microhardness of surface substratum up to 14.5 GPa, and formation boride layers in conditions of action EMF promotes improves microhardness of surface substratum up to 20.5 – 21 GPa. At the complete saturation in Cr-Mn-N steel 13.0 GPa, and these layers obtained in conditions of action EMF – 18.0 GPa (Fig. 2). So after boriding with simultaneous action EMF on surface Cr-Mn-N steel get boride layers, microhardness which was in 1.5 times higher than microhardness boride coating obtained without action EMF and in 7 times higher than the microhardness base (2.5 – 3 GPa). At the complex saturation Cr-Mn-N steel boron and copper with simultaneous action EMF, observe formation more plastic boride diffusion layers with less microhardness in 1.2 times compared with boriding in conditions of action EMF (Fig. 2).

Along with this application the complete saturation with boron and copper with simultaneous action EMF leads to increases the microhardness in 1.4 times compared with the complete saturation with boron and copper without action EMF and in 6 times compared with the material base. Application EMF can increase microhardness boride coatings on 6 – 7 GPa, compared with boride coatings obtained without action EMF – 18.0 GPa (Fig. 2). So after boriding with simultaneous action EMF on surface Cr-Mn-N steel get boride layers, microhardness which was in 1.5 times higher than microhardness boride coating obtained without action EMF and in 7 times higher than the microhardness base (2.5 – 3 GPa). At the complex saturation Cr-Mn-N steel boron and copper with simultaneous action EMF, observe formation more plastic boride diffusion layers with less microhardness in 1.2 times compared with boriding in conditions of action EMF (Fig. 2).

Along with this application the complete saturation with boron and copper with simultaneous action EMF leads to increases the microhardness in 1.4 times compared with the complete saturation with boron and copper without action EMF and in 6 times compared with the material base. Application EMF can increase microhardness boride coatings on 6 – 7 GPa, compared with boride coatings obtained without action EMF – 18.0 GPa (Fig. 2).

Along with this application the complete saturation with boron and copper with simultaneous action EMF leads to increases the microhardness in 1.4 times compared with the complete saturation with boron and copper without action EMF and in 6 times compared with the material base. Application EMF can increase microhardness boride coatings on 6 – 7 GPa, compared with boride coatings obtained without action EMF – 18.0 GPa (Fig. 2).

Along with this application the complete saturation with boron and copper with simultaneous action EMF leads to increases the microhardness in 1.4 times compared with the complete saturation with boron and copper without action EMF and in 6 times compared with the material base. Application EMF can increase microhardness boride coatings on 6 – 7 GPa, compared with boride coatings obtained without action EMF – 18.0 GPa (Fig. 2).
separate inclusions of copper in the surface area boride phases (Fig. 4, Table 3, 4). The concentration of copper in separate areas of the surface substratum thickness up to 15 microns reached 96% weight, because on the X-ray diffraction fixed phase copper. Mostly copper located in the surface phase FeB. Outside inclusions of copper found gradual decrease its concentration over the surface substratum thickness up to 15 microns.

The results show that the lowest rate of wear by the end of period burnishing inherent boride coating obtained at complex saturation with boron and copper without action EMF, the duration of saturation 2 hours; b – complex saturation with boron and copper with simultaneous action EMF, the duration of saturation 2 hours (chemical analysis determined in the points +1, +2, +3, +4, +5, +6, +7, +8).

**Table 3. Chemical composition of the diffusion layer on Cr-Mn-N steel obtained after complex saturation with boron and copper without action EMF**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Position</th>
<th>+1</th>
<th>+2</th>
<th>+3</th>
<th>+4</th>
<th>+5</th>
<th>+6</th>
<th>+7</th>
<th>+8</th>
<th>% weight</th>
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<tbody>
<tr>
<td>Si (K)</td>
<td></td>
<td>0.04</td>
<td>0.06</td>
<td>0.03</td>
<td>0.03</td>
<td>0.08</td>
<td>0.00</td>
<td>0.03</td>
<td>0.00</td>
<td>0.70</td>
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<tr>
<td>V (K)</td>
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<td>0.37</td>
<td>0.54</td>
<td>0.37</td>
<td>0.37</td>
<td>0.26</td>
<td>0.32</td>
<td>0.28</td>
<td>0.30</td>
<td>0.12</td>
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<tr>
<td>Ti (K)</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cr (K)</td>
<td></td>
<td>1.38</td>
<td>3.86</td>
<td>3.32</td>
<td>1.16</td>
<td>5.34</td>
<td>5.35</td>
<td>5.44</td>
<td>3.37</td>
<td></td>
</tr>
<tr>
<td>Mn (K)</td>
<td></td>
<td>1.18</td>
<td>12.69</td>
<td>11.49</td>
<td>11.58</td>
<td>11.96</td>
<td>19.41</td>
<td>20.09</td>
<td>1.61</td>
<td></td>
</tr>
<tr>
<td>Fe (K)</td>
<td></td>
<td>81.59</td>
<td>81.90</td>
<td>83.25</td>
<td>86.64</td>
<td>81.80</td>
<td>74.55</td>
<td>74.00</td>
<td>94.19</td>
<td></td>
</tr>
<tr>
<td>Cu (K)</td>
<td></td>
<td>1.64</td>
<td>0.98</td>
<td>1.54</td>
<td>0.28</td>
<td>0.28</td>
<td>0.37</td>
<td>0.18</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4. Chemical composition of the diffusion layer on Cr-Mn-N steel obtained after complex saturation with boron and copper with simultaneous action EMF**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Position</th>
<th>+1</th>
<th>+2</th>
<th>+3</th>
<th>+4</th>
<th>+5</th>
<th>+6</th>
<th>+7</th>
<th>+8</th>
<th>% weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (K)</td>
<td></td>
<td>0.03</td>
<td>0.64</td>
<td>0.43</td>
<td>0.08</td>
<td>0.03</td>
<td>0.00</td>
<td>2.53</td>
<td>0.21</td>
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</tr>
<tr>
<td>V (K)</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.16</td>
<td>0.18</td>
<td>0.22</td>
<td>0.25</td>
<td>0.39</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>Ti (K)</td>
<td></td>
<td>0.07</td>
<td>0.00</td>
<td>0.22</td>
<td>0.06</td>
<td>0.08</td>
<td>0.04</td>
<td>0.10</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Cr (K)</td>
<td></td>
<td>0.54</td>
<td>0.39</td>
<td>3.28</td>
<td>12.92</td>
<td>13.10</td>
<td>25.77</td>
<td>26.57</td>
<td>50.62</td>
<td></td>
</tr>
<tr>
<td>Mn (K)</td>
<td></td>
<td>0.84</td>
<td>0.84</td>
<td>3.32</td>
<td>13.53</td>
<td>6.46</td>
<td>5.44</td>
<td>13.42</td>
<td>4.40</td>
<td></td>
</tr>
<tr>
<td>Fe (K)</td>
<td></td>
<td>2.63</td>
<td>2.17</td>
<td>5.60</td>
<td>70.64</td>
<td>79.71</td>
<td>68.05</td>
<td>54.76</td>
<td>44.03</td>
<td></td>
</tr>
<tr>
<td>Cu (K)</td>
<td></td>
<td>19.80</td>
<td>9.86</td>
<td>35.99</td>
<td>2.59</td>
<td>15.40</td>
<td>0.45</td>
<td>2.23</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

X-ray phase analysis of Cr-Mn-N steel with a diffusion coating established that at boriding without action EMF in the surface layer of 15 – 20 um formed phases FeB, (Fe, Cr)B and CrB (Fig. 5, a), and at the complex saturation with boron and copper without action EMF – phase FeB, (Fe, Cr)B and Cu (Fig. 6, a).

At the application EMF observed an increase a thickness of the boride coating and particular interlayer phase FeB. As a result, on the X-ray diffractograms surface layers boride coatings obtained after boriding in conditions of action EMF fixed the presence of phases FeB and (Fe, Cr)B (Fig. 5, b). After complex saturation with boron and copper with simultaneous action EMF, since formed coating of greater thickness than the boriding, then on the X-ray diffractograms fixed the presence of phases FeB and Cu (Fig. 6, b).

Overlay EMF leads to increases the separate layers boride phases and redistribution of quantitative correlation boride phases in the surface layers and changes of crystal lattice periods (Table 5). At the complex saturation with boron and copper volume share of copper in the surface layer, to the results of X-ray structural investigations was 2%, and at the CHT with simultaneous action EMF quantity of copper component in the surface phase FeB increased to 53.7%.

**Table 5. Parameters of crystalline lattice phase and quantity phase analysis of the surface Cr-Mn-N steel after boriding and complex saturation with boron and copper in different physical-chemical conditions**

<table>
<thead>
<tr>
<th>Process saturation</th>
<th>Name phase</th>
<th>Parameters of crystal lattice, Å</th>
<th>Volume (Å³)</th>
<th>Contents phases (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>FeB</td>
<td>+1</td>
<td>4,106</td>
<td>5,558</td>
</tr>
<tr>
<td>a</td>
<td>FeCrB</td>
<td>+2</td>
<td>14,537</td>
<td>7,316</td>
</tr>
<tr>
<td>b</td>
<td>CrB</td>
<td>+3</td>
<td>2,959</td>
<td>7,664</td>
</tr>
<tr>
<td>b</td>
<td>FeB</td>
<td>+4</td>
<td>4,105</td>
<td>5,540</td>
</tr>
<tr>
<td>b</td>
<td>FeCrB</td>
<td>+5</td>
<td>14,520</td>
<td>7,370</td>
</tr>
<tr>
<td>a</td>
<td>Cu</td>
<td>+6</td>
<td>3,615</td>
<td>3,615</td>
</tr>
<tr>
<td>a</td>
<td>Cu</td>
<td>+7</td>
<td>3,614</td>
<td>3,614</td>
</tr>
</tbody>
</table>

Boriding and complex saturation with boron and copper allows to increase the wear resistance of Cr-Mn-N steel as at the simultaneous action EMF, and without its influence (Fig. 7). Thus, the rate of wear Cr-Mn-N steel without coating for the first hour was 2,15 · 10⁻⁶ kg/m² · sec., while at the boriding without action EMF wear rate was 1,67 · 10⁻⁶ kg/m² · sec., and at the complex saturation with boron and copper without action EMF – 1,39 · 10⁻⁶ kg/m² · sec. Application boriding with the simultaneous action EMF leads to decrease the rate of wear for the first hour to 0,86 · 10⁻⁶ kg/m² · sec., and at the complex saturation with boron and copper with simultaneous action EMF to 0,65 · 10⁻⁶ kg/m² · sec. The results show that the lowest rate of wear by the end of period burnishing inherent boride coating obtained at complex saturation with boron and copper with simultaneous action EMF. At this the rate of wear layers saturation copper obtained with simultaneous action EMF in 4 times less than without coating. Continue the wear up to 2 hours showed that the rate of wear of the surface layers during this period was: Cr-Mn-N steel without saturation
1.53 \cdot 10^6 \text{ kg/m}^2 \cdot \text{sec},

boriding without action EMF – 1.39 \cdot 10^6 \text{ kg/m}^2 \cdot \text{sec},

complex saturation with boron and copper without action EMF – 0.97 \cdot 10^6 \text{ kg/m}^2 \cdot \text{sec},

boriding with the simultaneous action EMF – 0.78 \cdot 10^6 \text{ kg/m}^2 \cdot \text{sec},

complex saturation with boron and copper with simultaneous action EMF – 0.59 \cdot 10^6 \text{ kg/m}^2 \cdot \text{sec}.

On step 5 hour the wear rate diffusion layers was respectively of Cr-Mn-N steel without saturation 1.47 \cdot 10^6 \text{ kg/m}^2 \cdot \text{sec},

boriding without action EMF – 0.92 \cdot 10^6 \text{ kg/m}^2 \cdot \text{sec},

complex saturation with boron and copper without action EMF – 0.67 \cdot 10^6 \text{ kg/m}^2 \cdot \text{sec},

boriding with the simultaneous action EMF – 0.61 \cdot 10^6 \text{ kg/m}^2 \cdot \text{sec},

complex saturation with boron and copper with simultaneous action EMF – 0.51 \cdot 10^6 \text{ kg/m}^2 \cdot \text{sec}.

The application boriding with simultaneous action EMF Cr-Mn-N steel leads to diffusion redistribution Cr in the coating with a maximum concentration Cr of 24% weight on the depth 65 microns, and at the complex saturation with boron and copper with simultaneous action EMF – 50.5% weight Cr on the depth 60 microns.

It is shown that the microhardness of the surface layers Cr-Mn-N steel after boriding was 14.5 GPa, and at the boriding with simultaneous action EMF increased to 21.0 GPa. Microhardness surface layers obtained after complete saturation with boron and copper on Cr-Mn-N steel was 13.0 GPa, and layers obtained at the complex saturation with boron and copper with simultaneous action EMF – 18.0 GPa. In this way boriding and complex saturation with boron and copper with simultaneous action EMF allows increase the microhardness of the surface boride layers in 1.5 and 1.4 times respectively.

Wear resistance of Cr-Mn-N steel after boriding increase in 1.6 times, at this the coefficient of friction is 0.53, and at the boriding with simultaneous action EMF wear resistance Cr-Mn-N steel increase in 2.4 times, at this the coefficient of friction is 0.48. The complex saturation with boron and copper leads to increases the wear resistance Cr-Mn-N steel in 2.2 times, at this the coefficient of friction is 0.42, and at the complex saturation with boron and copper Cr-Mn-N steel with simultaneous action EMF wear resistance increase in 3 times, at this the coefficient of friction is 0.41.

The best wear resistance in conditions of dry friction have boride phases formed on Cr-Mn-N steel at complex saturation with boron and copper with simultaneous action EMF. It is explained of the change phase composition, morphology, increase a microhardness the diffusion coating and the presence separate accumulations of copper in surface zones boride layers, which performing the role of solid oils.

The best wear resistance in conditions of dry friction have boride phases formed on Cr-Mn-N steel at complex saturation with boron and copper with simultaneous action EMF. It is explained of the change phase composition, morphology, increase a microhardness the diffusion coating and the presence separate accumulations of copper in surface zones boride layers, which performing the role of solid oils.

5. References


THE EFFECT OF ADDING NIOBIUM ELEMENT (Nb) ON METALLURGICAL PROPERTIES OF Fe-Cr-C HARDFACING

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2- Department of Material Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran
E-mail: m.khanzadeh@iaumajlesi.ac.ir, masoodshirazi@yahoo.com

Abstract: In this study, the hard facing with Fe-Cr-C base welded wire and Fe-Cr-Nb-C cored welding wire by using submerged-arc welding method in single-pass, two-pass and three pass over the pieces of carbon steel (St37) was done. Cored welding wire Fe-Cr-Nb-C by an approximate ratio of 5.41 Cr to C ratio, was containing 5.6 to 7% of the niobium element. Scanning electron microscopy, optical microscopy, X-ray diffraction and point analysis, indicates the presence of carbides (Fe, Cr)7C3 and Nb2C in hardened samples with Fe-Cr-Nb-C welding wire. The results showed that with increasing number of hardened passes, the percentage of carbon, chromium and niobium concentrations increased and as a result the dilution percent was decreased that cause to increasing hardness and better performance. Test results indicate higher hardness of hardened samples with Fe-Cr-Nb-C welding wire compared to samples hardened with Fe-Cr-C welded base wire. With increasing number of of hard passes, hardness was increased, so that the highest and lowest hardness is related to three pass samples that was hardened with metal cored wire Fe-Cr-Nb-C. The reason of increased hardness in three-pass samples hardened with Fe-Cr-Nb-C metal cored wire was to with increasing in the number of hardened passes, dilution rate was reduced by the base metal and this cause to coarse and more uniform distribution of carbides.

KEYWORDS: COMPLEX CARBIDES, HARDFACING, SUBMERGED OPEN ARC WELDING, HARDNESS

1. Introduction

In this study, we tried to examine the effect of adding 5.6 to 7% niobium element to chromium alloy welding wire with an approximate ratio of 5.41 Cr to C ratio. Here, adding complex carbide either chromium carbide and niobium carbide by morphology and different distribution was created in the microstructure that by the shape, phases distribution and review of complex carbides on wear properties of new welded wire and precise linking of microstructure by metallurgical and mechanical properties is the goal of this research.

Materials and methods

In this study, plain carbon steel (St37) was used as the base metal with dimensions of 10 × 100 × 150 mm. In Table 1 was shown the chemical analysis of welding base wire Fe-Cr-Nb-C and Fe-Cr-C. Samples numbers and pass numbers for each test was shown in Table 2.

Surface hardening by submerged arc welding method was performed according to presented parameter in Table 3. Optical microscopy, Scanning electron microscope, XRD test, hardness and chemical composition analysis were carried out on welded samples.

Table 3. Welding parameters

<table>
<thead>
<tr>
<th>Process</th>
<th>Voltage</th>
<th>Current (A)</th>
<th>Welding Speed (cm/min)</th>
<th>Polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Submerged-arc welding</td>
<td>27-29</td>
<td>380-480</td>
<td>70-80</td>
<td>DCEP</td>
</tr>
<tr>
<td>Open arc</td>
<td></td>
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</tbody>
</table>

The chemical composition and microstructure

The chemical composition of surface and percentage of dilution in layers was shown in Table 5. As can be seen by increasing the number of hardened layers, carbon, chromium and niobium were increase and the rate of dilution has decreased.

In Figure 1 corner diagram of iron with the ternary structure Fe-Cr-C was shown. Location of samples 1, 2 and 3 in Figure 1 was shown in Table 4.

Fig 1. Corner diagram of iron with the ternary structure Fe-Cr-C

According to the chart, hardened samples with Fe-Cr-C welding base metal have been included M7C3 phase. Nucleation and growth of M7C3 carbides at 1350 °C was started and by over time from onset of freezing, melt carbon was reduced and eutectic transformation occurred. Also according to the percentage of carbon element, the resulting structure of the sample number 1 was hypo eutectic and examples 2 and 3 has been the hyper-eutectic.
In Figure 2 hyper-eutectic freezing diagrams from samples 4, 5 and 6 on the basis of chemical composition was indicated in Table 4. Considering the percentage of chromium and carbon, the resulting structure in the samples 4, 5 and 6 was of the hyper-eutectic. According to Figure 2, at a temperature of 1500 °C, M7C3 carbide was formed and then reaching to 1300 °C, M7C3 carbide was formed. Then, reaching a temperature of about 1170 °C, austenite was formed, and finally reducing the temperature to about 850 °C and frozen, ferrite phase was formed.

3.2. X-ray diffraction results

In Figure 3, X-ray diffraction results show that the phase Cr7C3, Fe3C, austenite-ferrite in three single-pass mode, two pass and three pass mode. Reason for the formation of Cr7C3 carbide, forming the chromium carbide element has been desire. In Figure 3 X-ray diffraction pattern of samples hardened with flux cored wire Fe-Cr-Nb-C was shown. X-ray diffraction results show that phases Nb2C, (Fe,Cr)7C3, Cr3C2, Cr2Nb, Fe3C, austenite-ferrite has been working on hard surfaces.

3.3. Grained microstructure

3.3.1. Optical microscopy (OM)

In Figure 4 images related to optical metallography of samples hardened with base welded wire Fe-Cr-C in single-pass mode, two pass and three pass was shown. As is shown, microstructure, consisting of tiny chrome carbide in the austenitic and ferritic field and distributed in accordance with the results of X-ray diffraction (Fig. 3). Increasing the number of hardened passes, due to reduced dilution of the base metal as it shown in Table 5, percent of chromium and carbon was increased and carbide size is larger, so that the sample 3 compared to the numbers 1 and 2 have been larger carbides. In Figure 5 an optical microscope image of the hardened sample with flux cored wire Fe-Cr-Nb-C was shown. Comparing Pictures 4 and 5 show that by adding 5.6 to 7 of weight percent of the element niobium to wire welding base Fe-Cr-C, carbides containing niobium and iron and chromium was shaped, which are in accordance with the results of X-ray diffraction (Figure 3) and this carbide was uniformly distributed in austenitic and ferritic field. The reason for this is that the element niobium is stronger carbide former element than chromium. As can be seen, with increasing number hardened passes, the sample size of carbides become greater such that sample number 6 (sample three assists hardened welding with Fe-Cr-Nb-C) compared to the 4 and 5 with carbide has been greater.

![Fig 2. Hyper-eutectic freezing diagrams of system [2]](image)

![Fig 3. X-ray Diffraction patterns of A: Fe-Cr-C B: Fe-Cr-C-Nb deposits](image)

![Fig 4. Optical microscopy of Fe-Cr-C layers A: one pass B: two pass C: three pass](image)

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>Cr</th>
<th>Nb</th>
<th>Percent of dilution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>76.8</td>
<td>3.67</td>
<td>1.23</td>
<td>0.42</td>
<td>0.013</td>
<td>17.6</td>
<td>0.0018</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>68.2</td>
<td>4.25</td>
<td>1.42</td>
<td>0.41</td>
<td>0.027</td>
<td>21.5</td>
<td>0.0021</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>63.3</td>
<td>4.85</td>
<td>1.43</td>
<td>0.37</td>
<td>0.087</td>
<td>23.8</td>
<td>0.0034</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>73</td>
<td>4.65</td>
<td>2.26</td>
<td>0.38</td>
<td>0.031</td>
<td>16.1</td>
<td>6.35</td>
<td>27</td>
</tr>
<tr>
<td>5</td>
<td>71.3</td>
<td>4.97</td>
<td>2.71</td>
<td>0.36</td>
<td>0.045</td>
<td>18.7</td>
<td>6.6</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>69.3</td>
<td>5.65</td>
<td>2.78</td>
<td>0.33</td>
<td>0.048</td>
<td>19.6</td>
<td>6.8</td>
<td>11</td>
</tr>
</tbody>
</table>
In Figure 6, Scanning electron microscope images of hardened samples with welded wire base Fe-Cr-C, was shown in three single-pass mode, two pass and three pass modes. According to Figure 6 (a), we can see that the structure of single pass mode composed of very fine carbides and whatever the number of hardened passes increased, carbides size gets bigger. The results of X-ray diffraction and optical microscopes images (Figures 3 and 4) the structure of hardened samples with Fe-Cr-C welding wire base was formed of chromium carbides in austenite and ferrite field. In Figure 7 SEM images of the samples 4, 5 and 6 have been hardened with flux cored wire Fe-Cr-Nb-C, was shown in three single-pass, two-pass and three-pass mode. As determined, and according to the results of X-ray diffraction and images of optical metallography (Figures 4 and 7) of the samples hardened with welded wire Fe-Cr-Nb-C,a microstructure with carbides containing niobium, iron and chromium in the austenitic and ferritic field was observed. By Comparing scanning electron microscopy (Figures 6 and 7) was shown that the number of hardened passes, the percentage of dilution is reduced, resulting in increased concentrations of niobium and carbide size become larger.

3.4. Element Analysis Test (EDS)

In Figure 8, the result of elemental analysis of the three-passes hardened by base welded wire Fe-Cr-C was shown. This analysis from the point A hardened sample with Fe-Cr-C Welding wire was shown in Figure 8. In this case, the maximum amount of iron, chromium and carbon is formed. By comparing the elemental analysis and X-ray diffraction results (Figure 3), determined that in the above example, chromium carbide is formed. In Figure 9 the results of the elemental analysis from point B on the hardened three-pass example by welding wire Fe-Cr-Nb-C was shown. Most of the elements in this carbide were niobium and carbon and so at point A, was formed carbide that containing (Nb,C).
hardened by wire Fe-Cr-Nb-C with 63.8 Rockwell hardness. As shown in Figures 4 to 7, with increasing the number of hardened passes, due to reduced dilution, increased value and hardness of the carbide elements.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>56.5</td>
<td>59</td>
<td>60.1</td>
<td>58.5</td>
<td>62.5</td>
<td>63.8</td>
</tr>
</tbody>
</table>

4. Conclusion
In this study, the effects of adding the element niobium on metallurgical properties hard weld base Fe-Cr-C were studied, the most important findings of the research include:

1. Hardening the surface with welded wire base Fe-Cr-C on plain carbon steel result in the formation of chromium carbide in austenitic and ferritic field.
2. By adding the element niobium to alloy system Fe-Cr-C, alloy of niobium carbides and carbide complex is formed in austenitic and ferritic.
3. With a reduction in dilution effect of increasing the number of hardened layers, the percentage of alloying element such as carbon, chromium and niobium which causes coarse carbides is increased.
4. The highest hardness is related to three-pass samples with flux cored wire Fe-Cr-Nb-C with a Rockwell C hardness of 8/63, but also the lowest hardness is related samples harden with to single pass welding with base Fe-Cr-C with hardness 56.5 Rockwell.

5. References
HEAT TREATMENT, MICROSTRUCTURE AND PROPERTIES OF 75Cr1 STEEL, FOR USE IN HEAVY LOADED ELEMENTS

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Abstract: This study aims to optimize the heat treatment of tool steel 75Cr1 which is used for heavy loaded elements in transmissions. A salt bath was used to quench and temper the steel at different temperatures. Mechanical tests and microstructural characterization were done to define the heat treatment parameters corresponding to the optimal performance of the elements. Optical microscopy, electron back scatter diffraction and x-ray diffraction were used to characterize the microstructure, while tensile tests and toughness tests were employed to determine the mechanical properties after different heat treatments. It was found that the yield strength decreases with increasing annealing temperature and that the toughness decreases with increasing annealing time and temperature. The changes of the mechanical properties are discussed in relation with the thermal treatment and the corresponding microstructures.

Keywords: HEAT TREATMENT, TOOL STEEL, MICROSTRUCTURE

1. Introduction

Important factors affecting competition in the automotive market are product quality, innovation and development time, price, reliability, safety, fuel economy and emission control [1]. The Continuously Variable Transmission (CVT) is a very efficient system with a high potential for future application in new generation vehicles. This type of automatic transmission provides low fuel consumption, no torque interruption during gear change and optimum power range of the engine [2]. Instead of using fixed gears, the CVT uses two pulleys connected by a pushbelt to transmit torque. The pushbelt is built up of hundreds of steel elements and two maraging steel ring packs. The elements are subjected to high cyclic loads and they should possess a high yield stress and wear resistance. Therefore a tool steel 75Cr1 is used for the production of the elements.

The steel is annealed at varying temperatures and soaking times and subsequently oil quenched and tempered. The steel contains chromium, which participates in the cementite formation. According to [3] the alloying elements partition between the austenitic matrix and the retained (undissolved) carbides during austenitizing. This partitioning fixes the chemistry and volume fraction of the carbides as well as the composition of the austenite. Finer carbides and a larger volume fraction of carbides will control the austenitic grain growth and can influence significantly the mechanical properties. Hence, the goal of the work is to understand better the influence of the heat treatment parameters on the strength, elongation and toughness of the elements made of 75Cr1 steel.

2. Experimental procedures

The nominal composition of the steel is given in Table 1. This high carbon low alloyed steel is classified as tool steel. The as received material has a thickness of 1.8 mm and is in the so called soft annealed (or spheroidization annealed) condition. In this condition the steel microstructure is ferrite with (Fe,Cr)3C carbides. The steel was subjected to 40 different heat treatments in a salt bath with varying annealing temperatures and times and subsequently oil quenched to form martensite. The different temperatures were 800, 820, 860 and 900 °C, and at each temperature the samples were soaked for 2, 4, 6, 8, 10, 12, 15, 20, 25 or 30 minutes before oil quenching. Afterwards all samples were tempered at 190 °C for 45 min. For every set of heat treatment parameters, 3 tensile samples, 30 samples for the toughness test and several extra samples for the microscopy tests were prepared.

Table 1: Nominal composition of 75Cr1.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>max.</th>
<th>max.</th>
<th>S</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>0.74-</td>
<td>0.80</td>
<td>0.25-</td>
<td>0.40</td>
<td>0.65-</td>
<td>0.80</td>
<td>0.025</td>
<td>0.30-</td>
<td>0.45 bal.</td>
</tr>
</tbody>
</table>

XRD analyses were performed with a Siemens Diffractometer D5000 with a molybdenum X-ray tube. The angular range of 25°-40° was scanned with a step size of 0.05° and 5 s/step. Using the formula of Cullity [4], the fraction of retained austenite was calculated for different heat treatments. The electron backscatter diffraction (EBSD) data were acquired in a FEI Nova 600 Nanolab at 20 kV and beam current 2.2 nA. The sample preparation consisted of mechanical and electrolytic polishing with A2 Struers electrolyte, followed by 40 min OP-U polishing with pressure less than 5 N. Tensile specimens were prepared according to the ASTM standard E8M-04 (gage length 50 mm). Tensile tests were carried out on a Zwick Z250 testing machine with a speed of 20 MPa/s until the yield point, and 0.0067 mm/s cross head speed for strain controlled plastic deformation until fracture. The Izod impact tests were executed on a Zwick/Roell HT55P machine.

3. Results

Equilibrium calculations of the Fe-C-Mn-Cr-Si system were performed using the Thermo-Calc software. From the Fe-C isopleth in Fig. 1 one can derive that for 0.75% C the A e1 and A ecm temperatures are 722 and 770 °C respectively and that ferrite, cementite and austenite are in equilibrium in the temperature range between 722 and 734 °C.

Fig. 1 Fe–C isopleth of the alloy; the carbon content of the 75Cr1 steel is indicated with a red dashed line.
Fig. 2 displays the variations in the equilibrium phase fractions for the 75Cr1 steel grade as a function of temperature. According to Thermo-Calc calculations cementite is the stable carbide among the other complex carbides. When the annealing temperature is above 734 °C, the maximum equilibrium cementite fraction is 1.6%.

The microstructure of the as received material in the soft annealed condition is visualized in Fig. 3. Etching with 4% HNO₃ in ethanol (4% Nital) for 8-11 s reveals clearly the grain boundaries and the spherical carbides (Fig. 3a). The volume fraction of carbides measured by quantitative metallography on multiple samples was about 12-13%. The EBSD maps (Fig. 3b, c) show that around 8% spherical iron carbides are present in the ferritic matrix. This underestimation of the carbide fraction measured with EBSD in comparison to the optical microscopy data is most probably due to the smaller area of the EBSD scan and the incorrectly indexing of some carbide orientations.

Fig. 4 shows the image quality and inverse pole figure maps of a sample annealed at 860 °C for 15 minutes which is oil quenched and afterwards tempered. The martensitic structure typical for high carbon steel is visible. In comparison with the starting material, less and smaller carbides can be observed. Some small regions of austenite in between martensite could be distinguished in Fig. 4c.
The effect of the annealing time on the tensile properties of the tool steel for 800°C is shown in Fig. 5a. The longer the austenitizing process, the larger is the loss of ductility. This effect is less clearly visible at higher annealing temperatures (Fig. 6). A summary of the values for the yield strength for all heat treatments is plotted in Fig. 5b. The increase of the annealing temperatures causes a decrease in the yield strength. On the other hand, if the annealing temperature is 860 °C or 900 °C, the yield strength increases at shorter annealing times. Correspondingly the elongation at fracture decreases with increasing temperature and increasing holding time, as can be seen in Fig. 6. The Izod impact test (Fig. 7) shows clearly that higher austenitizing temperatures and longer soaking times lead to a decrease in toughness.

The enrichment of the austenite matrix with carbon and alloying elements will lead to a decrease of the Ms temperature and as a consequence more untransformed austenite will retain at room temperature [4]. Retained austenite, depending on its carbon content and distribution in the microstructure, may contribute differently to the strength and ductility. A lower tensile strength can be observed after quenching and tempering in cases where the fraction of retained austenite is high. This austenite fraction can transform under strain during loading – this is the so called transformation induced plasticity (TRIP) effect. Additionally the very thin film-like morphology of the retained austenite situated between the martensite laths can contribute to the ductile fraction and correspondingly to an increase of the toughness [8,9]. On the other hand formation of the high carbon martensitic structures formed after short soaking times and low temperatures leads to an increase in strength (Fig.5b) and toughness (Fig. 7).

Hence the combination of high strength and high ductility could be obtained via quenching from low temperatures after short soaking times. High temperatures and high soaking times lead to lower strength and lower ductility.

5. Conclusions

The changes in the microstructure and mechanical properties of a tool steel 75Cr1 were studied as a function of the austenitizing temperature and time. It was found that:

- Lowering the annealing temperature and time leads to a higher strength and ductility due to less retained austenite. A lower annealing temperature also leads to less carbon saturation of the austenite and a more ductile material.
• High austenitizing temperatures and high soaking times will lead to a decrease in ductility.

Acknowledgements

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References


ADHESION ANALYSIS OF TITANIUM OXIDE NANOCOATINGS ON TITANIUM SURFACE

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Abstract: Ti and its alloys are mostly used for implant production. Their biocompatibility depends on the formation of thin TiO2 layer on the surface. It can be improved by modification of oxide structure in tubular. For biomedical applications, the adhesion of the coating layers is essential. The aim of the present paper is to investigate the adhesion of TiO2 nanocoatings on titanium surface.

Commercially pure Ti (CP Ti) and Ti-6Al-4V alloy samples were grinded, etched and anodized. The anodization was done in 0.5 wt.% HF electrolyte with duration of 7 hours for the CP Ti samples and 6 hours for Ti-6Al-4V alloy samples. The adhesion was investigated by tape and scratch tests. The critical loads that generate the first failures during the scratch test are used for characterization of the adhesion of the TiO2 nano-tubular coating. The critical loads were measured by CSEM-Revetest macroscratch tester under progressive scratching mode. The samples were characterized by SEM and EDX analysis. The areas around the critical load were further observed by optical and scanning electron microscopy for detail inspection of failure mechanism.

It was established that the higher micro-roughness of the surface of CP Ti sample after anodization is responsible for the detachment only of small areas of the nano-tubular coating situated mainly on the top surface. The lower micro-roughness of the sample made of titanium alloy and the presence of large flat areas lead to detachment of large coating’s portions. The scratch test reveals that the TiO2 nano-tubular coating on the CP Ti fails at an early stage (Lc1 ~ 8 N; Lc2 ~ 26 N), while that on the Ti-6Al-4V sample undergoes cohesive failure and completely fails at higher load values (Lc1 ~ 13 N and Lc2 ~ 40 N respectively). As titanium alloy is ductile material with higher strength than the CP Ti, it provides better support for the coating and produces higher critical loads.

Keywords: TITANIUM, Ti-6Al-4V, TITANIUM OXIDE, NANOTUBES, COATING ADHESION

1. Introduction

Titanium and its alloys are mostly used for implant production. Their biocompatibility depends on the formation of thin TiO2 layer on the surface [1,2]. It can be improved by modification of oxide structure in tubular, because the TiO2 nanotubes can mimic the dimensions of the natural bone components. Many research groups work on investigation of the biocompatibility of nano-tubular coatings on titanium implants.

It was established by S.Oh et al. [3] that the addition of nanotubes to the microstructured surface enhances multiple osteoblast behaviors, resulting in better in vivo osseointegration. The presence of a vertically aligned TiO2 nanotube surface on Ti foils improved the proliferation and mineralization of osteoblasts. According to the same group [4] the cell response depends on the nanotubes’ diameter, thus on small-diameter nanotubes, increased cell adhesion and growth with minimal differentiation is prevalent, while on larger-diameter nanotubes, mesenchymal stem cells are forced to differentiate specifically into osteoblast cells. It was established by N. Wang et al. [5] that 70 nm diameter is the optimum size for TiO2 nanotubes implants to obtain favorable osteoconductivity and osseointegration.

TiO2 nanotubes can be prepared by various techniques: sol-gel method, electrochemical deposition and anodization [4,6]. But anodization is preferred to the rest two processes because it provides strongly adherent TiO2 layer. The process is rapid, simple and inexpensive ensuring large array of titanium nanotubes [7-9].

For bio-medical applications, the adhesion and mechanical integrity of the TiO2 layer are essential. The adhesive strength between the anodic oxide films and the titanium substrate was reported to be from 11.7 MPa [3] to 25 MPa [9]. The bond strength between nanocoatings and titanium substrate is investigated mainly by tape test, tensile test or scratch test. Y. Parcharoen et al. [10] measured the adhesion of the hydroxyapatite coating to the substrate using ASTM D 3359-02 cross-cut tape test (B). They used 3M Brand Scotch tape which was firmly placed in the area and was pulled off at an angle as close to 180° as possible after 90 s. After that the surface morphology was investigated and the coating delamination was evaluated. During tensile test standard tensile testing machine is used [3,11-13]. The surfaces of the control samples and that with coatings are attached to the cylindrical rods with glue, adhesive tape or PMMA bone cements. Tensile loads are applied normally to the samples with crosshead speed of 0.5 – 1mm/min until interfacial failure occurs. The mean tensile bonding strength and standard deviation are calculated as well as the interface morphology is examined. The scratch test gives estimation of the adhesion strength of the coatings by determining the critical load Lc, which is defined as the load where film flaking starts [14].

The aim of the present paper is to investigate the adhesion of TiO2 nanocoatings on the surface of commercially pure titanium and Ti-6Al-4V alloy using both tape and scratch tests.

2. Experimental methods

Anodization

Round samples with dimensions 24 mm x 3 mm (diameter x thickness) were made of commercially pure (CP) Ti Grade-2 (99,5%) and Ti-6Al-4V alloy with chemical composition: Al-5,7%; Fe-0,13%; V-3,8%; O-0,089%; Ti-the rest (wt.%). The samples’ surface was grinded with sandpaper 300, 600 and 800. After grinding they were ultrasonically cleaned consecutively in acetone, ethanol and deionized water for 15 min in each media and dried with compressed air. On the next stage the samples were etched for 30 min in 0.5 wt.% HF acid, immediately rinsed with deionized water and dried. They were anodized in an electrolyte, containing 0.5 wt.% HF acid, at 25V for CP Ti and 30V for Ti-6Al-4V alloy. DC power supply and a graphite electrode as cathode were used. The process duration was 7 hours for CP Ti and 6 hours for Ti-6Al-4V alloy. Immediately after anodization the samples were rinsed several times with deionized water and dried with compressed air.

Adhesion tests

Two types of adhesion tests were done. The first one was made with Scotch Transparent Film Tape 640 of 3M with 12,7 mm width and adhesion to steel 30 N/100 mm. As this test gives only relative evaluation of the coatings adhesion we additionally did scratch test. The scratch tests were performed on the top surface of the sample with a CSM REVETEST Scratch Macrotester equipped with a Rockwell C diamond indenter of 200 µm radius. Progressive load scratching mode with normal force range of 1 N to 50 N was used.
in all experiments and at a speed of 10 N/mm. Critical load values (L_c) at which the failure event occurred for each sample were calculated as an average from at least five tests made in different areas to verify the obtained results. Scratch width at the critical loads was also measured using optical methods of localized regions of poor adhesion and failure for each scratch.

Samples characterization

The surface topography and morphology were observed with optical and scanning electron microscopies. Two SEM were used: high resolution field emission scanning electron microscope FEI Quanta 400 ESEM FEG (ESEM2) and SEM JEOL 733 which was subject to digitalization by a university project 2015 FMME 03. The EDX analysis was made on FEI Quanta 400 ESEM FEG (ESEM2).

3. Results and discussion

Anodization

The superficial morphology of both coated samples, shown in Fig. 1a and Fig.1b, discloses that the anodization of CP Ti produces step morphology with many small and deep craters that influences the subsequent treatment. Irrespective of their size, all of the present micro voids have defined boarders. The anodization of the alloy (Fig. 1c and Fig. 1d) reveals the fully lamellar microstructure between α and β lamellas. It can be stated that the surface micro-roughness of the CP Ti coated sample is higher compared to the alloy coated system.

Our previous investigations [15] showed that after 7 hours
anodization the surface of the CP Ti was covered with oxide layer with nanotubular morphology in 70-80% of the area and nanorods in the rest 30-20% (Fig.1b high magnification). The nanotubular structure consisted of nanotubes (NTs) with irregular shape and sizes with average internal diameter about 121 nm. After 6h anodization 80% of the surface of Ti-6Al-4V alloy sample was covered with comparatively well-shaped NTs (Fig.1d high magnification) with average internal diameter about 109 nm. EDX analysis on Fig. 2 shows that the NTs regions on the CP Ti surface consist of TiO₂. The presence of Al additionally to the Ti and O in the NTs regions on the Ti-6Al-4V alloy sample are evidence that the all elements take part in the anodization process.

Fig. 3 Surface morphology of anodized CP Ti sample after tape test.

Fig. 4 Surface morphology of anodized Ti-6Al-4V sample after tape test.
Adhesion (tape test)

Investigation of the coating’s adhesion by tape test shows that only small spots of the nano-tubular layer are detached from the surface of the CP Ti (Fig. 3). The detached areas are with round shape and sizes between 5-20 microns. They are situated preliminary on the top of the surfaces while in the grooves the adhesive tapes residues can be seen, as in very deep craters the adhesive cannot penetrate. After the tape test of the sample, made of Ti-6Al-4V alloy, large areas of the nano-tubular coating are detached mainly from the flat surfaces, while in the grooves the coating is not detached (Fig. 4). The alloy’s surface under the coating has high nano-roughness and morphology typical for basis of nano-tubular layer. This is an evidence for the mechanism of formation of TiO\textsubscript{2} NTs, proposed in [16].

So, in this experiment the micro-roughness plays important role on the results obtained. As the micro-roughness of the CP Ti sample is high, only the areas on the top surface can adhere well to the tape and can be detached, while no adhesive can penetrate into the deep grooves and craters, which prevents the coating’s detachment. The lower micro-roughness of the sample made of titanium alloy and the presence of large flat areas on its surface are preconditions for better adhesion to the tape and detachment of large coating’s portions.

Adhesion (scratch test)

Cohesion and adhesion of the coating is closely related to its wear and abrasion resistance during sliding in an increasing load mode because in both cases the failure originates in the coating. This failure is caused by application of the external force via wear/abrasive particles or sliding indenter during scratch test [17].

The experimental results of Chuan Ting Wang et al. [18] shows that the Ti substrate has a relatively low strength and poor wear resistance when it is subject to sliding or wear. Nevertheless the higher surface roughness, at the beginning of the track of the CP Ti coated sample, there is almost full contact between the stylus and the surface (Fig. 5a). Large asperity contact because of the ductile substrate provokes early spallation of the coating. The TiO\textsubscript{2} nano-tubular coating on the CP Ti fails at an early stage during the scratch test \((L_{c1} \sim 8\; N; \; L_{c2} \sim 26\; N)\) and the indenter causes progressive plastic deformation (Fig. 5b, Fig. 5c and Fig. 5d). The higher degree of deformation at the edge of the track is clearly seen in Fig. 5c. The appearance of high lateral accumulations of material and their size suggest that the coating has a low hardness. The direction of material moving under the influence of the loaded stylus is radial, which is clearly seen at the end of the test (Fig. 5d).

Going further, the acid etching of the metal prior the anodizing increases the hydrogen content near the surface that could lead to a decrease of the fatigue resistance and adhesion strength. The solubility limit of H in \(\alpha\)-Ti at room temperature is -0.04 at. % and the excess hydrogen could form small hybrid TiH\textsubscript{x} phases or microvoids that enhance localized plasticity [19].The observed semicircular failures along the track in the substrate material area (Fig. 5c and Fig. 5d) prove the reduction in the surface ductility of CP Ti substrate. However the circumferential cracking outside the scratch area is small and severe delamination or brittle failures are not found.

The SEM examination of the Ti-6Al-4V coated sample reveals that the TiO\textsubscript{2} nano-tubular film undergoes cohesive failure at higher load values \((L_{c1} \sim 13\; N)\) which means that 62.8% higher initial stage of failure than the other sample is measured. Although the higher loading, the type of the scratch track at the initial stage shows a small width (Fig. 6a) that is related to the higher hardness of the coating/substrate system. As shown in Fig. 6c the TiO\textsubscript{2} nano-tubular coating on the alloy completely fails at a higher load \((L_{c2} \sim 40\; N)\) or 53.8 \% higher than the CP Ti coated sample. The ductile alloy material with high strength provides better support for the coating and produces higher critical loads.
The dark lanes seen in Fig. 6a and Fig. 6b in the scratch path are regions stripped of the coating that contains some cohesive cracks (Fig. 6b). The increasing pulling force results in pushing aside some detached portions (Fig. 6c) of the surface material parallel to the scratch direction due to tensile cracking behind the stylus. These portions are significantly less in size which is a characteristic feature of harder materials or this fact could be related with the initial surface etching. At the end of the groove (Fig. 6d) the plastic push pad shows small semicircular cracks in front of the indenter.

Since the rate of hydrogen diffusion is higher by several orders of magnitude in β-phase than in α-phase [19], the absorbed hydrogen could be dissolved in the ductile β-phase and below the terminal solubility limit in β the hydrogen could diffuse in between the phases and the embrittlement of the substrate/coating interface should be less pronounced. In the place corresponding to the substrate material no failures of the ductile alloy are observed. The critical indentation widths of 0.112 mm and 0.147 mm (at Lc2) are observed for CP Ti and Ti-6Al-4V coated systems, respectively. It is obvious that the critical load increases with the increase of the coating/substrate hardness. This finding does not conflict to the results observed by the microstructural images.

4. Conclusions:

In this study the adhesion of titanium oxide nanocoatings on the surface of CP Ti and Ti-6Al-4V alloy were investigated by tape and scratch tests.

It was established that the higher micro-roughness of the surface of CP Ti sample after anodization is responsible for the detachment only of small areas of the nano-tubular coating situated mainly on the top surface. The lower micro-roughness of the sample made of titanium alloy and the presence of large flat areas lead to detachment of large coating’s portions.

The scratch test reveals that the TiO2 nano-tubular coating on the CP Ti fails at an early stage (Lc1 ~ 8 N; Lc2 ~ 26 N), while that on the Ti-6Al-4V sample undergoes cohesive failure and completely fails at higher load values (Lc1 ~ 13 N and Lc2 ~ 40 N respectively). As titanium alloy is ductile material with higher strength than the CP Ti, it provides better support for the coating and produces higher critical loads.

5. Acknowledgements

The anodization and the tape test were done in the Prof. Pulickel Ajayan’s laboratory in MEMS Department of Rice University, Houston. The work was supported by Fulbright grant. The scratch test and investigations were done in the University of Ruse “Angel Kanchev”, Bulgaria with the support of the university Project № 15-FMME-03 2015 “Improvement of the system of electron microscopic analysis of the materials realized by digitalization of the information received”.

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WEAR AND CORROSION RESISTANCE OF Ni-P COATING ON AA7075 ALUMINUM ALLOY

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Abstract:
This study was initiated to compare the wear and corrosion performances of an AA7075 quality aluminum alloy after electroless Ni-P process. The characterization of the coating was made by microscopic examinations, thickness, surface roughness and hardness measurements. Wear and corrosion performances of the uncoated and coated samples were investigated by using a reciprocating wear tester and a Potentiodynamic Polarization Scanning (PDS) technique, respectively. Formation of Ni-P layer on AA7075 aluminum alloy accompanied not only by remarkable increase in the surface hardness, but also caused significant improvement in wear and corrosion resistances.

Keywords: COATING, CORROSION, ELECTROLESS, WEAR.

1. Introduction
Aluminum and its alloys belong to the most important lightweight engineering materials [1]. Nowadays, lot of research work was done on aluminum and its alloys because of their exclusive properties such as high strength to weight ratios, high thermal conductivity and good corrosion protection [2, 3]. However, several drawbacks restrict the application of unprotected aluminum alloys, especially their low hardness and limited wear resistance. To improve the practical usage of aluminum alloys, many researchers have attempted to develop high wear-resistance strategies [4, 5]. Among different surface techniques, electroless deposition appeared as an attractive surface modification technique generating a micro-scale amorphous Ni-P layer to enhance wear and corrosion resistance of aluminum and its alloys [6, 7]. In order to assess the wear and corrosion behavior of this coating, the wear and corrosion experiments were carried out, and the results were compared with those of the 7075 aluminum alloy substrate.

2. Methods and Procedures
AA7075 disc-shaped samples with 25 mm diameter and 5 mm thickness were used as the substrate for the preparation of electroless NiP coating. This grade was chosen because it is very popular in aeronautics. The aluminum attracts easily with oxygen, hence the fine layer is allow to form on the surface. Therefore, it is difficult to coat the aluminum substrates covered with a very thin and imperious oxide film, so suitable surface preparation (mechanical grinding and polishing, alkaline cleaning with acetone and methanol, acid pickling and pretreatment) is required [8]. The commercial Ni-P electroless solution (DURNI-COAT DNC 520-9) containing 5 g/L nickel, 40 g/L NaH\textsubscript{2}PO\textsubscript{2} and suitable amounts of additive and stabilizer were used. The stirring rate of plating bath was about 250 r/min, using a magnetic stirrer and a polytetrafluoroethylene (PTFE) coated magnet with 2 cm length and 5 mm in diameter. The deposition was carried out in a 100 ml thermostated double wall beaker at 90 °C and pH 4.6 for 1 h to achieve a thickness of 13 μm.

Cross-sectional morphology of the electroless Ni-P coated sample was characterized by using an Optical Microscopy (OM). Mechanical properties of the uncoated and coated samples were examined by microhardness measurements and dry sliding wear tests. Microhardness tests were conducted on polished samples from cross section of the coating with a Vickers indenter under a load of 10 g for a dwell time of 10 s. Three microhardness measurements were obtained for each sample, and the average value was recorded. Dry sliding wear tests of the uncoated and coated samples were performed on a reciprocating wear tester operating in ball-on-disc configuration at room temperature. In this configuration, an Al\textsubscript{2}O\textsubscript{3} ball with a diameter of 10 mm was sliding forward and backward against the coatings with a sliding speed of 1.7 cm s\textsuperscript{-1}. Normal load of the test, sliding amplitude (wear track length) of the reciprocating motion and overall sliding distance were 2 N, 10 mm and 50 m, respectively. During the wear tests, the temperature and the relative humidity were maintained as 20±5 °C and 40±5 %, respectively. The friction coefficient force was continuously recorded during the tests. Width and depth of the wear tracks were measured by a surface profilometer (Surftest SJ 400) to calculate wear performance of the samples. Following the wear tests, wear tracks were examined by an OM.

The electrochemical corrosion tests were performed utilizing a typical three electrode potentiodynamic polarization test unit in the corroding media of aerated solution of 3.5 wt. % NaCl at room temperature. Before potentiodynamic polarization measurements, an initial delay of 45 min. was employed in order to measure the open circuit potential between working and reference electrodes. Potentiodynamic polarization curves were generated by sweeping the potential from cathodic to anodic direction at a scan rate of 1 mVs\textsuperscript{-1}, starting from – 0.25 up to + 0.25 V. Corrosion potentials (E\textsubscript{corr}) and corrosion current densities (i\textsubscript{corr}) were calculated using a Tafel type fit in the software. Finally, the surface images of the corroded samples were examined using an OM.

3. Results and Discussions
The cross-section morphology of the Ni-P coating detected by OM is illustrated in Fig. 1. Micrograph of the coating deposited on top of the aluminum alloy revealed that the coating has a good adhesion to the substrate and there is no discontinuity at the coating/substrate interface. Additionally, profilometry measurements indicated that the Ni-P coating has a roughness value Ra = 0.17 ± 0.01μm.

![Fig. 1 Cross-section micrograph of Ni-P coating.](image-url)

The microhardness value of the Ni-P coating is 204 HV\textsubscript{0.01}, while the microhardness of the uncoated sample is about 35 HV\textsubscript{0.01}. Thus, the electroless Ni-P coating caused to about a 5.8 fold increase in the hardness.
The results of wear tests for uncoated and coated samples are given in Table 1. It is seen that the Ni-P coating has lower friction coefficient and lower wear rate than those of uncoated sample. By taking into account the wear rates, it is quantified that wear resistance of the Ni-P coating is ~11 times higher than that of the uncoated sample.

Table 1: Friction coefficients and wear rates of uncoated and coated samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Friction coefficient</th>
<th>Wear rate x10^{-4} (m^3 N^{-1} m^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated Sample</td>
<td>0.5–0.75</td>
<td>111.5</td>
</tr>
<tr>
<td>Ni-P coating</td>
<td>0.44</td>
<td>9.89</td>
</tr>
</tbody>
</table>

The images of the wear tracks on the uncoated and coated samples along with the friction curves presented in Fig. 2 confirm the above findings. The images show the intensification of damage and roughness in the wear track, which is considerably lower for the Ni-P coating than for the uncoated sample (Fig. 2 a, b). Friction coefficients for the uncoated and coated samples used in the above experiments are shown in Fig. 2 c. The friction coefficient obtained for the Ni-P coating stabilizes after 30 number of cycle and shows a steady value of 0.44, whereas the friction coefficient for the uncoated sample shows a variable regime and a higher value (0.5–0.75).

The Ni-P coating shows great positive shift in corrosion potential and evident decrease in corrosion current density in comparison with the uncoated sample (Fig. 3). The corrosion potential $E_{corr}$ of the Ni-P coating is -767 mV and the corrosion current density $i_{corr}$ is $23.5 \times 10^{-6}$ A/cm². Meanwhile, the corrosion potential $E_{corr}$ and corrosion current density $i_{corr}$ of the uncoated sample are about -1050 mV and $47.9 \times 10^{-6}$ A/cm², respectively. Besides, an improved anticorrosion efficiency (IE) of the Ni-P coating than the uncoated sample could be calculated by Eq 1 [9]:

$$IE(\%) = 100 \times (I_A - I_B)/I_B; \quad (Eq \ 1)$$

where $I_A$ and $I_B$ are $i_{corr}$ of the Ni-P coating and uncoated sample, respectively. According to Eq 1, an enhanced anticorrosion efficiency (IE %) of the Ni-P coating is 50.9 % compared with the uncoated sample. The high corrosion resistance of the Ni-P coating is because of its amorphous characteristics; the absence of the defects in crystalline alloys such as grain boundaries, dislocations, stacking faults and other surface defects [10].

Figure 4 shows the OM images of the uncoated and coated samples after the corrosion tests. As shown in figure, the main failure mechanism for the uncoated sample was the pitting corrosion (Fig. 4 a). Many pits were seen on the uncoated sample, but the pits on the Ni-P coating did not formed (Fig 4 b).
4. Conclusion

The behavior of the substrate coated with electroless Ni-P was compared to that of the uncoated AA7075 aluminum alloy. Analyzing the properties of the uncoated and coated samples applied to the tests, one can conclude that:

1. Ni-P coating on AA7075 alloy is prepared by electroless deposition. The cross-section view of the Ni-P coating reveals that the coating is uniform, crack free and adherent metallic coating.

2. The hardness, wear and corrosion resistances of the Ni-P coating generated by electroless deposition are remarkably higher than those of the uncoated sample.

Acknowledgements

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5. Literature


THE SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE (GO) AND REDUCED GRAPHENE OXIDE (RGO)

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Abstract: In this study, graphene oxide (GO) was synthesized from graphite by using the Hummer method. GO was reduced using hydrazine hydrate to achieve reduced graphene oxide (RGO). GO and RGO powders synthesized by these methods can be used as fillers in the production of polymer matrix composite. These synthesized powders was examined in detail using the Zeta Potential (ZP) measurements, Ultraviolet Visible Spectrophotometer (UV-VIS), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) equipped with Energy Dispersive Spectroscopy (EDS) analyzer and Thermogravimetric-Differential Thermal Analysis (TG-DTA). All analysis results confirmed the GO and RGO considered as fillers in the production of polymer matrix composite can be prepared successfully.

Keywords: FILLERS, GRAPHENE OXIDE, REDUCED GRAPHENE OXIDE.

1. Introduction

Graphene, a single layer of carbon atoms densely packed in a honeycomb crystal lattice, is considered as promising versatile filler, due to its specific and unique structural, mechanical, and electronic properties [1-3]. However, graphene is hydrophobic and tends to agglomerate irreversibly [4], thus it does not disperse well in polymers and has a tendency to form phase separated composites [5]. To overcome these shortcomings, Graphene Oxide (GO) is prepared from oxidation of Graphite (GF) powder by Hummers method and Reduced Graphene Oxide (RGO) is synthesized from the reduction process of GO. GO is hydrophilic and contains epoxides, alcohols, lactols, ketones, and carbonyl groups, which can significantly affect the van der Waals interactions between the graphene layers (Fig.1) [6]. Easy synthesis and solution processability of GO as an inexpensive filler material encourage the production of polymer composites [7]. Also, the RGO sheets are usually considered as one kind of chemically derived graphene, just like GO [8, 9]. Stankovich et. al (2007) have examined the chemical reduction of exfoliated graphene oxide sheets with several reducing agents and found hydrazine hydrate (H$_2$NNH$_2$.H$_2$O) to be the best one in producing very thin graphene-like sheets [10]. The RGO became less hydrophilic due to the removal of oxygen atoms and thus precipitated. Hydrazine takes part in ring-opening reaction with epoxides and forms alcohols (Fig.1) [11].

In this study, GO and RGO powders was synthesized and the obtained powders were studied by ZP, UV-VIS, XRD, SEM, and TG-DTA analysis. The objective of this work is to synthesis graphene based fillers for polymer composites. Recently, attention has been renewed for producing graphene based materials because of its excellent thermal, mechanical, electrical and optical properties [12].

2. Experimental Details

GF powder, concentrated sulfuric acid (98%), potassium permanganate, 30 % H$_2$O$_2$ solution, hydrochloric acid and hydrazine hydrate were of reagent grade and purchased from Merck. All the reagents were used without further purification. All solutions were prepared using deionized (DI) water. GO was prepared from natural graphite (45µm nominal particle size) by the Hummers method [13]. Graphite (1 g) was mixed with 69 mL of concentrated H$_2$SO$_4$ and the mixture was stirred in an ice bath for around 30 min. After homogeneous dispersion of the graphite powder in the solution, K$_2$MnO$_4$ (8 g) was added slowly to the solution in an ice bath and the reaction mixture was stirred for 15 min. under a reaction temperature of 20°C. Then the ice bath was removed and the mixture was stirred at 35°C overnight to form thickened paste. Afterward, 70 mL of DI water was added slowly into the reaction solutions to avoid the reaction temperature rising to a limit of 98°C. After 2 h of vigorous stirring, 12 mL of 30 % H$_2$O$_2$ was added and the color turned golden yellow immediately. Finally, the mixture was then filtered and washed several times with 3 % HCl and DI water until pH 7 and dried at 65°C for 12 h to obtain GO powder. The obtained GO has a plenty of oxygen-containing functional groups in its graphitic backbone: carboxyl (COOH) and carbonyl (C=O) groups at the sheet edges and epoxy (C-O-C) and hydroxy (-OH) groups on the basal plane (Fig. 1) [14]. To prepare RGO, 0.1 g of GO was dispersed in 100 mL of DI water. Then 1 mL of hydrazine hydrate was added to the mixture and heated at 95°C for 12 h. After that, the mixture was filtered and the RGO was obtained as a black powder. Thus, the product obtained was washed with DI water several times.

Zeta potentials of powders dispersed in water using ultrasonic bath were measured by Zetasizer- NANO-ZS (Malvern Instruments Ltd., UK). Electronic absorption spectra of the powders were recorded in water solvent in the wavelength range of 200–400 nm at room temperature by using Lambda 25 UV-VIS spectrometer (Perkin Elmer, USA). The analyses of the powders were carried out by X-Ray Diffraction (XRD, PAN analytical, Empyrean) in the range of 5–50°. The surface morphology was examined by a Scanning Electron Microscopy (SEM, Supra 40VP, Zeiss). EDS analyses were performed on the same instrument. TG-DTA analysis (LABSYS evo, Setaram) was performed by heating the samples from 25°C to 600°C at a rate of 20°C min$^{-1}$ in a nitrogen atmosphere.

Fig. 1 Oxidation of GF to GO and RGO [11].
3. Results and Discussion

Zeta potential is an important indicator to determine the surface charge of the sheets and to characterize the stability of dispersions [15]. The zeta potential of GO and RGO dispersions was shown in Fig. 2 a, b.

Zeta potentials in Fig. 2 a, b were -41.3 and -3.81 mV for GO and RGO, respectively. The zeta potential of GO was high due to the presence of negatively charged OH and COOH groups [16]. The zeta potential value of RGO was -3.81 mV due to a decrease in oxygen functional groups [17]. As shown in Fig. 2 b, the zeta potential distributions of RGO were more regular than GO’s. High negative charge of GO and very low negative charge of RGO demonstrated excellent oxidation and reduction processes respectively.

![Fig. 2 Zeta potentials of (a) GO and (b) RGO.](image)

The oxidation and reduction progress were monitored by UV-VIS spectroscopy. As shown in Fig. 3 a, GO showed a maximum absorption peak at 291 nm which could be attributed to the n– n* transitions of C=O bonds [18]. As shown in Fig. 3 b, the UV-VIS spectrum of the RGO dispersion possesses one absorption peak at 323 nm. The absorption peak of GO at 291 nm red shifted into wavelengths around 323 nm due to the reduction progress [17].

![Fig. 3 UV-VIS spectra of (a) GO and (b) RGO.](image)

Figure 4 showed XRD patterns of the GF and prepared GO and RGO powders. In addition, 20 values and d-spacing data of the same materials are given in Table 1. The crystalline GF had a sharp characteristic peak at 20=26.4°. The corresponding interlayer distance was observed to be 0.33 nm. After oxidation, the diffraction peak shifted to 20=9.95° and the interlayer space increased to 0.88 nm (Table 1) [19]. The increase in the interlayer distance from 0.33 nm to 0.88 nm was due to oxygen-containing functional groups intercalated within the layered structure (Table 1) [16]. RGO exhibited a broader diffraction peak as shown in Fig 4. This indicated that the GO is completely exfoliated to a single layer of graphene [16].

![Fig. 4 X-ray diffraction patterns of GF, GO and RGO powders.](image)

Table 1: 2θ values and d spacing data obtained from XRD results

<table>
<thead>
<tr>
<th>Samples</th>
<th>2θ°</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF</td>
<td>26.4</td>
<td>0.337</td>
</tr>
<tr>
<td>GO</td>
<td>9.95</td>
<td>0.888</td>
</tr>
</tbody>
</table>

The SEM images of the GF, GO and RGO powders are shown in Fig. 5. It could be seen clearly from the SEM image of Fig. 5 a that GF had a thin plate stacked structure [20]. GO presented a worm-like structure randomly aggregated [21] (Fig. 5 b). According to EDS results of the GF and GO, oxygen content increased from 22.59 % to 47.95 % (Table 2). As shown in Fig. 5c, the SEM image of the RGO showed that wrinkle-like structure due to the rapid removal of oxygen-containing functional groups in GO [2]. According to EDS result of RGO (Table 2), only 14.28 % oxygen content remained which illustrated successful reduction of GO.

![Fig. 5 SEM images of (a) GF, (b) GO and (c) RGO.](image)
Fig. 5 SEM images of (a) GF, (b) GO, (c) RGO (magnification 30,000 KX).

Table 2: EDS results of GF, GO and RGO.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Oxygen Content (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GF</td>
<td>22.59</td>
</tr>
<tr>
<td>GO</td>
<td>47.95</td>
</tr>
<tr>
<td>RGO</td>
<td>14.28</td>
</tr>
</tbody>
</table>

TGA and DTG graphs for the GO and RGO powders were given in Fig. 6a, b and thermal parameters were summarized in Table 3. As shown in Fig. 6a, GO showed two steps of decomposition. The first weight loss for the GO was observed in 78°C corresponding to the loss of water molecules. GO showed a major weight loss at the temperature range of 170–200°C which can be attributed to the removal of most of the oxygen-containing functional groups. The step at 558°C was related to pyrolysis of the remaining oxygen-containing groups as well as the burning of ring carbon (Fig.6a and Table 3) [9-22]. GO exhibited about 13% residual weight at 600°C. This demonstrated its excellent thermal stability [2]. As shown in Fig. 6b, RGO exhibited two steps degradation; the first step commencing at 51°C was due to the loss of water molecules. The second step degradation at 491°C involved the pyrolysis of the hydroxyl, epoxy functional groups, yielding CO, CO₂, and steam [10]. RGO exhibited only 56% weight loss at 600°C, which was much lower than that of the GO (Table 3), indicating a significantly decreased amount of oxygenated functional groups [18].

Table 3: Thermal parameters for the GO and RGO powders. (20 °C/min heating rate, under nitrogen atmosphere).

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C) range</th>
<th>Weight loss at 600°C (%)</th>
<th>Residue at 600°C wt. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>78, 185, 558</td>
<td>87</td>
<td>13</td>
</tr>
<tr>
<td>RGO</td>
<td>51, 491</td>
<td>56</td>
<td>44</td>
</tr>
</tbody>
</table>

4. Conclusion

In summary, GO powders were successfully produced by Hummer’s method and chemical reduction of GO using hydrazine hydrate was characterized using various techniques. Analysis results indicated that GO could be prepared and reduced into RGO successfully. GO and RGO powders synthesized by these methods can be used as fillers in the production of polymer matrix composites.

5. Literature


EFFECT OF THE MARBLE POWDER AND WOOD POWDER CONTENT ON THE TECHNOLOGICAL PROPERTIES OF THERMOPLASTIC COMPOSITES

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Abstract: The waste powder produced during the manufacture of marble, which is presently mostly discarded in landfills, has the potential for higher-valued usage. Recycling marble waste powder will contribute to the protection of nature as well as economic gain. The goal of this study is to investigate the potential use of marble waste powder as filler in the thermoplastic composites with wood. Thermoplastic composites were manufactured by adding marble factory waste powder and wood powder in different ratios to polypropylene (PP). Maleic anhydride grafted polypropylene (MAPP) were used as coupling agent to improve interfacial adhesion between hydrophilic wood–fibers and thermoplastic composites. Although mechanical properties of the composites decreased with increasing content of the marble powder, the water absorption of the composites significantly decreased with increasing content of the marble powder.

KEYWORDS: THERMOPLASTIC COMPOSITES, TECHNOLOGICAL PROPERTIES, WOOD POWDER, MARBLE POWDER,

1. Introduction

Studies of polymer composites mixing with organic or inorganic fillers have steadily increased due to the advantages of the fillers in economic and environmental aspects. Organic wood fibers have characteristics of low density, biodegradability, and sustainable productivity [1, 2], and inorganic fillers have attracted great attention because of their cost efficiency, abundance [3]. The fillers (organic or inorganic materials) generally increase stiffness, strength, and hardness of polymer composites by hybridization [4, 5, 6]. Inorganic and organic fillers have long been considered as a future candidate to replace glass fiber or carbon fiber in thermoplastic composites, and thus, it can help resolving environmental issues and taking economic advantage over those artificial fibers [7].

Marble, used frequently in construction applications, is utilized by an industry that produces a significant amount of solid waste during the cutting process. Recycling the marble powder produced during cutting is an important issue because of the current development of environmental awareness and costs for filler [8]. It is estimated that approximtely 2.2 million tons of marble blocks are processed in Turkey annually, of which 660,000 tons of marble powder is thrown out without being recycled. If that potential material is evaluated in industry, it is provided significant gains to the economy [9]. The unused marble powders have significant effects, not only economically, but environmentally as well. The large number of marble processing facilities in the world is the cause of the intensification of marble waste areas, which negatively affect the environment and natural beauty, especially in the regions where these facilities are located [10].

When studies on the economic use of marble wastes were examined, it was observed that they related on the construction sector in general, such as using marble powder wastes in filler processes, the manufacture of light construction blocks, improving floors with marble powder, and as an additive substance in the manufacture of cement [9, 11, 12, 13, 14, 15, 16, 17]. Excluding the use of wastes from marble processing facilities as construction materials, it was observed that they are used as powder wastes reduced to different dimensions as a raw material decoration in architecture, a filler material, and as an additive substance for agricultural purposes [18, 19].

The use of organic wastes of wood industry and agricultural industry as an additive substance in the manufacture of thermoplastic composites has drawn a lot of attention in recent years. In previous studies, in addition to waste wood fibers, some other natural fibers such as kenaf [20], jute [21], sisal [22], flax [23], hemp [24], coir [25], pine cones [26], walnut shell [27], and sunflower stalk [28] have been investigated, and positive results have been obtained. Although some inorganic fillers such as talc [29], kaolin [7], clay [30], boron-nitride [31], and zinc-borate [32] have widely been adopted in thermoplastic composites with wood fiber, to our knowledge, there are no reports on the utilization of marble waste powders as a filler in thermoplastic composites.

The objective of this study was the manufacture of thermoplastic composites by adding marble powder and wood powder in different ratios to polypropylene and studying their physical and mechanical properties. We aimed to investigate the effect of marble powder content on the density, water resistance and mechanical properties of the thermoplastic composites.

2. Materials and methods

2.1. Materials

The waste marble powder were obtained from the collected liquid precipitation ponds at a factory manufacturing traventine marble powders in Denizli, Turkey. The technical compositions of the traventine marble are given in Table 1. The marble powders were passed through a mesh screen and retained on a 0.25-mm mesh screen (Fig.1). The marble powders were then oven-dried to a moisture content of 0 to 1% using a laboratory oven at 100 °C for 48 h, and then stored in a sealed container.

Wood particles were obtained from beech (Pinus nigra Arnold var. pallasiana, oven-dry q = 0.490 g/cm³) lumbers by using laboratory type disc chipper with three knives. The moisture content of the wood particles, as determined by oven-dry weight, was found to be 40–50% prior to the treatment. The wood particles were ground in a laboratory Wiley grinder. The wood powder passing through a US 35-mesh screen was retained by a US 80-mesh size. The wood powder was dried in a laboratory oven at 102 °C for 24-h to a moisture content of 0–1% based on the oven-dry weight of wood ant then stored in a polyethylene bag.

Polypropylene (PP) (melting temperature = 160°C, density = 0.9 g/cm³, melt flow index at 230°C and 2.16 kg = 6.5 g/10 min) produced by Petkim Petrochemical Co. (Izmir, Turkey) was used as the polymeric material. MAH-grafted PP (MAPP-OPTIM-415 with the reactive modifier MAH (MAH content = 1 wt %)) was supplied by Pluss Polymers Pvt., Ltd. (New Delhi, India).
Table 1. Technical Properties of the Marble (Test report of Demirkayalar Marble Company, Denizli, Turkey, 2009).

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Travertine Marble</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>Mohs</td>
<td>3 to 3.5</td>
</tr>
<tr>
<td>Unit Weight</td>
<td>g/cm³</td>
<td>2.44</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
<td>2.66</td>
</tr>
<tr>
<td>Particle Size</td>
<td>μm</td>
<td>~250</td>
</tr>
<tr>
<td>Water Absorption in Atmospheric Pressure</td>
<td>By weight (%)</td>
<td>1.62</td>
</tr>
<tr>
<td>Water Absorption Under Pressure</td>
<td>By weight (%)</td>
<td>3.94</td>
</tr>
<tr>
<td>Porosity</td>
<td>%</td>
<td>3.94</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>N/mm²</td>
<td>54.4</td>
</tr>
<tr>
<td>Compressive Strength After Freezing</td>
<td>N/mm²</td>
<td>50.8</td>
</tr>
<tr>
<td>Degree of Pores</td>
<td>%</td>
<td>3.94</td>
</tr>
<tr>
<td>SiO₂</td>
<td>%</td>
<td>1.91</td>
</tr>
<tr>
<td>F₂O₃</td>
<td>%</td>
<td>79.10</td>
</tr>
<tr>
<td>MgO</td>
<td>%</td>
<td>1.15</td>
</tr>
<tr>
<td>CaO</td>
<td>%</td>
<td>2.43</td>
</tr>
</tbody>
</table>

Fig. 1. Waste marble powder

2.2. Composite Manufacturing

The marble powder, wood powder, PP, and MAPP granulates were pre-blended in a mixer and then processed in a 30-mm conical, co-rotating, twin-screw extruder (Aysa Instrument Com., Istanbul, Turkey) with a length to diameter ratio of 30 : 1. The raw materials were fed into the main feed throat with a gravimetric feed system. The barrel temperatures of the extruder were controlled at 170, 180, 190, and 190°C for zones 1, 2, 3, and 4, respectively. The temperature of the extruder die was held at 200°C. The extruded strand passed through a water bath and was subsequently pelletized. These pellets were stored in a sealed container and then dried for about 3–4 h before they were injection-molded. The temperature used for the injection-molded samples was 170–190°C from the feed zone to the die zone. The WPC samples were injected at an injection pressure between 45 and 50 kg/m² with a cooling time of about 30 s. Finally, the samples were conditioned at a temperature of 23 ± 2°C and a relative humidity of 50 ± 5% according to ASTM D 618-08.

The formulations of the composites are given in Table 2.

2.3. Mechanical properties

The flexural properties, modulus of rupture (MOR), and modulus of elasticity (MOE) were measured in three-point bending tests with a standard material testing system at a crosshead speed of 1.3 mm/min in accordance with ASTM D 790-03. The MOR and MOE values of the samples with dimensions of 127 × 12.7 × 3.2 (thickness) mm³ were determined at ambient conditions of 23 ± 2°C and 50 ± 5% relative humidity according to ASTM D 618-08. The tensile tests were conducted according to the ASTM D 638. Tensile specimens [dogbone shape (Type III)] were tested with a crosshead speed of 5 mm/min in accordance with ASTM D 638. Seven specimens were tested for each composite formulation.

Table 2: The raw material formulations of the WPCs.

<table>
<thead>
<tr>
<th>WPC code</th>
<th>Wood powder (%wt)</th>
<th>Marble powder (%wt)</th>
<th>Polypropylene (PP) (wt%)</th>
<th>MAPP (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>50</td>
<td>47</td>
<td>3</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>40</td>
<td>47</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>20</td>
<td>30</td>
<td>47</td>
<td>3</td>
</tr>
<tr>
<td>D</td>
<td>30</td>
<td>20</td>
<td>47</td>
<td>3</td>
</tr>
<tr>
<td>E</td>
<td>40</td>
<td>10</td>
<td>47</td>
<td>3</td>
</tr>
<tr>
<td>F</td>
<td>50</td>
<td>0</td>
<td>47</td>
<td>3</td>
</tr>
</tbody>
</table>

2.4. Water resistance

Thickness swelling (TS) and water absorption (WA) tests were carried out according to ASTM D 570-05 specifications. The test samples were in the form of disks 50.8 mm in diameter and 3.2 mm in thickness. Ten replicate samples were tested for each WPC formulation. The conditioned samples were placed in a container of distilled water maintained at a temperature of 23 ±1°C. The weights and thicknesses of the samples were measured at different time intervals during the long period of immersion. At the end of 24, 168 (7 days), and 672 (28 days) h of submersion, the samples were removed from the water one at a time, all surface water was wiped off with a dry cloth, and the samples were weighed to the nearest 0.001 g and measured to the nearest 0.001 mm immediately. The value of WA as a percentage was calculated as follows:

\[ WA(t) = \frac{W(t) - W_0}{W_0} \times 100 \]

The value of the TS as a percentage was calculated as follows:

\[ TS(t) = \frac{T(t) - T_0}{T_0} \times 100 \]

where TS(t) is the thickness swelling at time t (%), T₀ is the initial thickness of the sample, and T(t) is the thickness at time t. The density of the sample was measured on the TS sample.

3. Result and discussion

3.1. Mechanical properties

The mechanical properties of the WPCs are presented in Table 3. The MOR of the WPCs decreased with increasing content of the marble powder. In particular, the MOR more decreased as the amount of marble powder was above 30 wt% (Figure 2). The addition of 10 wt% marble powder improved the MOE considerably. Further increment in the marble content up to 50 wt% decreased the MOE of the composites but still it was higher than that of the control group without marble powder (Table 3, Figure 3).

Table 3: The results of the mechanical properties of the composites.

<table>
<thead>
<tr>
<th>WPC code</th>
<th>MOR (N/mm²)</th>
<th>MOE (N/mm²)</th>
<th>Tensile Strength (N/mm²)</th>
<th>Tensile Modulus (N/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>55.3</td>
<td>(3,49)*</td>
<td>3616.0</td>
<td>31.0</td>
</tr>
<tr>
<td>B</td>
<td>55.0</td>
<td>(0,93)</td>
<td>4843.2</td>
<td>(3,39)</td>
</tr>
<tr>
<td>C</td>
<td>54.0</td>
<td>(0,93)</td>
<td>4763.3</td>
<td>28.9</td>
</tr>
</tbody>
</table>
The tensile strength and tensile modulus of the composites are shown in Figures 4 and 5, respectively. As increased the marble content of composites, both the tensile strength and the tensile modulus decreased. Specifically, as the amount of marble content was above 20 wt%, the tensile strength and modulus decreased remarkable when compared to the composites having 20 wt% and below. The decreament ratio in the tensile strength was more pronounced than the decreament ratio in the tensile modulus.

### Table 4: The results of water resistance of the composites.

<table>
<thead>
<tr>
<th>WPC code</th>
<th>Water Absorption (%)</th>
<th>Thickness Swelling (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>One day</td>
<td>One week</td>
</tr>
<tr>
<td>A</td>
<td>0.21</td>
<td>0.56</td>
</tr>
<tr>
<td>B</td>
<td>0.19</td>
<td>0.47</td>
</tr>
<tr>
<td>C</td>
<td>0.17</td>
<td>0.47</td>
</tr>
<tr>
<td>D</td>
<td>0.12</td>
<td>0.32</td>
</tr>
<tr>
<td>E</td>
<td>0.11</td>
<td>0.18</td>
</tr>
<tr>
<td>F</td>
<td>0.09</td>
<td>0.09</td>
</tr>
</tbody>
</table>

* Standard deviations

### 3.2. Water resistance

The results of water resistance are presented in Table 4. In general, the water absorption and thickness swelling decreased with increasing amount of the marble powder and decreasing amount of wood powder (Table 4, Figures 6 and 7). The water absorption and thickness swelling of composites sharply decreased when the amount of marble content reached to 30 wt%. The highest water absorption and thickness swelling values were found in the specimens produced with 50 wt% wood powder while the lowest values were found in the specimens produced with 50 wt% marble powder as seen Figures 6 and 7.

**Fig. 2: The MOR of the composites**

**Fig. 3: The MOE of the composites**

**Fig. 4: The tensile strength of the composites**

**Fig. 5: The tensile modulus of the composites**

**Fig. 6: The water absorption ratios of the composites**
4. Conclusions

The results of the research revealed that the increase in the amount of the marble powder in the composites had a negative effect on the mechanical properties of the composites while the increase in the amount of the wood powder had a positive effect. One exception of this was observed in the MOE values where the MOE of composites improved considerably with the addition of 10 wt% marble powder and then decreased again with the further increment in the marble content up to 50 wt%. The decrease in the mechanical properties of composites was more remarkable when the marble content in the composites was over 20 wt%. The water absorption and thickness swelling decreased with increasing amount of the marble powder and decreasing amount of wood powder.

5. Acknowledgement

This work was supported by Research Fund of the Istanbul University. Project number: BEK-20082. The authors wish to acknowledge Research Fund of the Istanbul University for financial support.

6. References

SOME PHYSICAL AND MECHANICAL PROPERTIES OF TURKISH HAZELNUT (CORYLUS COLURNA L.) WOOD

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Abstract: The aim of this study was to determine some of the physical and mechanical properties of Turkish hazelnut (Corylus colurna L.) wood. Hazelnut is an endemic species in Turkey and the trees used for the study were taken from the Pınarbaşı District of Kastamonu Province. As a result of experiments carried out to evaluate the physical properties, it was found that the values of dry and air dry density were 0.636 g/cm³ and 0.672 g/cm³, radial, tangential and longitudinal swelling values were 4.60%, 7.48% and 0.41%, radial, tangential and longitudinal shrinkage values were 5.11%, 8.49% and 0.59%, respectively. According to the related standards, the mechanical properties of bending strength (98.5 N/mm²), modulus of elasticity in bending (8273.4 N/mm²), compressive strength parallel to the grain (5.09 N/mm²), and hardness values of cross, radial and transverse sections (72.55 N/mm², 47.32 N/mm², 46.13 N/mm², respectively) were also determined.

Keywords: TURKISH HAZELNUT, CORYLUS COLURNA, MECHANICAL PROPERTIES, PHYSICAL PROPERTIES

1. Introduction

Turkish hazelnut (Corylus colurna L.), one of the endemic species in Turkey, has a smooth stem and can reach 80 cm in diameter and 15-20 m in height. Some trees in Kale Forest District of Bolu Regional Forest Headquarter have attained a diameter of 1 m and height of 30-35 m 1.3 and trees growing in graveyards and at the edges of fields in Merkeşler village in Bolu Province were measured at more than 80 cm in diameter. This tree species is rarely used in the timber industry because its technological properties are not well known. Turkish hazelnut grows naturally in western Anatolia (Kazdağı/Bolu, Kastamonu and Yenice/Karabük) and eastern Anatolia (Rize and Trabzon). It can grow at an altitude of 1600 m in Yığılcı/Düzce, Köstebek Forest/Nalıhan, Kastamonu between Azdavay and Cide and on Gavar Mountain in Tosya, and in Amasya on Sana Mountain. It is found at 1160 m in Ayancık, Çingen Konağı and Zindan/Sinop, and at 800 m in Mihalıççık, Çatacak Forest/Eskişehir. Turkish hazelnut trees are most commonly located in the northwest of the country at a vertical distribution of between 800-1700 m, in small groups or individually, together with other species such as oak, beech, maple and fir.2 The wood of this species is red in color and when well-polished is used for the manufacture of furniture.3

Forest villagers in the mid and western Black Sea region have made use of Turkish hazelnut for the production of wooden souvenir items and furniture. When assessing the possibility of utilizing tree species in terms of suitable areas of the forest products industry, it is very important to determine the chemical, physical, mechanical, drying, machining and conservation properties of those tree species. At present, only the anatomical properties of the Turkish hazelnut tree have been investigated for this purpose. This study is very important because the technological properties of this tree species have not been previously determined. Accordingly, Turkish hazelnut has been underutilized in the forest product industry. Depending upon the development of increased industrial applications, this tree could be more widely cultivated. Nonetheless, to begin with, the wood properties of the Turkish hazelnut must be determined. The aim of this research was to investigate the physical and mechanical properties of Turkish hazelnut and to interpret the results with regard to possible industrial utilization.

2. Materials and Methods

In order to examine the distribution areas of Turkish hazelnut, sample trees belonging to this protected species were taken from Pınarbaşı District in Kastamonu Province. An official description of the study area is given in Table 1.

Table 1: Study area data

<table>
<thead>
<tr>
<th>Area No.</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regional Forest Headquarters</td>
<td>Kastamonu</td>
</tr>
<tr>
<td>Forest Management Directorate</td>
<td>Pınarbaşı</td>
</tr>
<tr>
<td>Division No.</td>
<td>160</td>
</tr>
<tr>
<td>Location</td>
<td>Kastamonu Province, Pınarbaşı District, Kurtgirmez Mountain, east of Büyükkaş Hill</td>
</tr>
</tbody>
</table>

Coordinates: 41° 35' 43.6" (N) 33° 13' 29.2" (E)

Table 2: Sample trees

<table>
<thead>
<tr>
<th>Sample Tree No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direction</td>
<td>East</td>
<td>East</td>
<td>West</td>
<td>East</td>
<td>North</td>
<td>West</td>
</tr>
<tr>
<td>Flora</td>
<td>Buxus</td>
<td>Buxus</td>
<td>Buxus</td>
<td>Buxus</td>
<td>Buxus</td>
<td>Buxus</td>
</tr>
<tr>
<td>Altitude (m)</td>
<td>1290</td>
<td>1290</td>
<td>1290</td>
<td>1290</td>
<td>1290</td>
<td>1290</td>
</tr>
<tr>
<td>Slope(%)</td>
<td>30</td>
<td>30</td>
<td>47</td>
<td>30</td>
<td>30</td>
<td>41</td>
</tr>
<tr>
<td>Diameter (cm)</td>
<td>50</td>
<td>29</td>
<td>35</td>
<td>33</td>
<td>31</td>
<td>27</td>
</tr>
<tr>
<td>Dry branch (m)</td>
<td>6.90</td>
<td>6.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet branch (m)</td>
<td>6</td>
<td>10.30</td>
<td>11.90</td>
<td>9.40</td>
<td>5.85</td>
<td>10.40</td>
</tr>
<tr>
<td>Height (m)</td>
<td>16.35</td>
<td>11.20</td>
<td>14.90</td>
<td>12.60</td>
<td>14.10</td>
<td>13.80</td>
</tr>
<tr>
<td>Middle diameter (cm)</td>
<td>27</td>
<td>26</td>
<td>25</td>
<td>23</td>
<td>24</td>
<td>20</td>
</tr>
</tbody>
</table>

In order to determine the physical properties, a total of 32 sections, 15 cm in length, were taken from each sample tree at heights of 0.30 m, 1.30 m, 2.30 m, 2.40 m, 3.60 m, 8.30 m and 10.30 m. A total of five sample logs, 1.5 m in length, were taken from each sample tree for mechanical testing, according to TS 2470 (1976) standard.

The physical properties of oven and air dry density (TS 2472, 1976)4, radial, tangential (TS 4083, 1976)5 and volumetric (TS 4085, 1983)6 shrinkage, and radial, tangential (TS 4084, 1976)7 and volumetric (TS 4086, 1983)8 swelling were investigated. The mechanical properties of bending strength (TS 2474, 1976)9, modulus of elasticity in bending (TS 2478, 1976)10, tensile strength perpendicular to the grain (TS 2476, 1976)11, impact bending strength (TS 2477, 1976)12, compression strength parallel to the grain (TS 2595, 1977)13 and Janka hardness (TS 2479, 1976)14 of Turkish hazelnut wood were also examined.

First, sections obtained from the sample trees were cut and left under a covered outdoor area until the fiber saturation point was
reached. The specimens for physical tests were then prepared according to standards. A total of 400 specimens for density and 50 specimens for each of the other physical tests were prepared. All samples used for the physical and mechanical tests were acclimatized according to TS 642 ISO 554 (1997) to attain the air dry state (12%). The section parts used for physical test specimens are shown in Figure 1.

![Image](Fig 1: Timber used to prepare the mechanical test specimens. The timber sections used for mechanical test specimens are shown in Figure 2.)

The density test results of Turkish hazelnut along with the values of other broad-leaved native species in Turkey are given in Table 5.17

**Table 5: Density values of some Turkish wood species.**

<table>
<thead>
<tr>
<th>Species</th>
<th>No. of samples (N)</th>
<th>Mean (X)</th>
<th>Standard deviation (s)</th>
<th>Max. value (Xmax) (g/cm³)</th>
<th>Min. value (Xmin) (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turkish hazelnut</td>
<td>50</td>
<td>0.636</td>
<td>0.07</td>
<td>0.817</td>
<td>0.405</td>
</tr>
<tr>
<td>Beech</td>
<td>50</td>
<td>0.64</td>
<td>0.06</td>
<td>0.66</td>
<td>0.453</td>
</tr>
<tr>
<td>Oak</td>
<td>50</td>
<td>0.67</td>
<td>0.09</td>
<td>0.69</td>
<td>0.412</td>
</tr>
<tr>
<td>Chestnut</td>
<td>50</td>
<td>0.59</td>
<td>0.09</td>
<td>0.63</td>
<td>0.363</td>
</tr>
<tr>
<td>Elm</td>
<td>50</td>
<td>0.64</td>
<td>0.06</td>
<td>0.68</td>
<td>0.412</td>
</tr>
<tr>
<td>Maple</td>
<td>50</td>
<td>0.59</td>
<td>0.09</td>
<td>0.63</td>
<td>0.363</td>
</tr>
<tr>
<td>Alder</td>
<td>50</td>
<td>0.49</td>
<td>0.09</td>
<td>0.53</td>
<td>0.254</td>
</tr>
<tr>
<td>Ash</td>
<td>50</td>
<td>0.65</td>
<td>0.09</td>
<td>0.69</td>
<td>0.412</td>
</tr>
<tr>
<td>Poplar</td>
<td>50</td>
<td>0.41</td>
<td>0.04</td>
<td>0.45</td>
<td>0.254</td>
</tr>
<tr>
<td>Lime tree</td>
<td>50</td>
<td>0.49</td>
<td>0.05</td>
<td>0.53</td>
<td>0.363</td>
</tr>
</tbody>
</table>

As seen in Table 5, except for alder, poplar, and lime tree, the density values of Turkish hazelnut are similar to those of other broad-leaved tree species. Turkish hazelnut has medium density according to the classification values presented by Bozkurt and Erdin (1990)18.

The shrinkage test results of Turkish hazelnut and other broad-leaved native species in Turkey are given in Table 6.17

**Table 6: Shrinkage values of some Turkish wood species.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Radial</td>
</tr>
<tr>
<td>Turkish hazelnut</td>
<td>4.60</td>
</tr>
<tr>
<td>Beech</td>
<td>5.0</td>
</tr>
<tr>
<td>Oak</td>
<td>4.0</td>
</tr>
<tr>
<td>Ash</td>
<td>5.0</td>
</tr>
<tr>
<td>Elm</td>
<td>4.6</td>
</tr>
<tr>
<td>Maple</td>
<td>3</td>
</tr>
<tr>
<td>Alder</td>
<td>4.4</td>
</tr>
<tr>
<td>Ash</td>
<td>5.0</td>
</tr>
<tr>
<td>Poplar</td>
<td>3.5</td>
</tr>
<tr>
<td>Lime tree</td>
<td>5.5</td>
</tr>
</tbody>
</table>

In terms of density, the values of Turkish hazelnut are similar to those of beech, whereas its shrinkage values are lower. This is a positive feature. In terms of radial, tangential and volume shrinkage values, Turkish hazelnut is classified as being 'moderately...
shrinkable’. The ratio of tangential and radial shrinkage is 1.62, which is only slightly lower than the general mean ratio of 1.65. The difference between tangential and radial shrinkage is 2.88%. With a value greater than 2.5, as in this case, the deformation risk increases during the wood drying.20

The swelling test results of Turkish hazelnut and other broad-leaved native species in Turkey are given in Table 7.21-24

Table 7: Swelling values of some Turkish wood species.

<table>
<thead>
<tr>
<th>Species</th>
<th>Radial</th>
<th>Tangential</th>
<th>Longitudinal</th>
<th>Volumetric</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turkish hazelnut</td>
<td>5.11</td>
<td>8.49</td>
<td>0.59</td>
<td>14.18</td>
</tr>
<tr>
<td>Beech</td>
<td>5.2</td>
<td>12.6</td>
<td>0.3</td>
<td>17.8</td>
</tr>
<tr>
<td>Oak</td>
<td>5.0</td>
<td>10.0</td>
<td>-</td>
<td>14.9</td>
</tr>
<tr>
<td>Maple</td>
<td>4.8</td>
<td>9.3</td>
<td>0.16</td>
<td>14.4</td>
</tr>
<tr>
<td>Poplar</td>
<td>4.3</td>
<td>8.2</td>
<td>0.3</td>
<td>12.8</td>
</tr>
</tbody>
</table>

The difference between tangential and radial swelling is 3.38%. When this value is greater than 3, as in this case, the risk of deformation increases during the wood drying.20 Although the risk of deformation is decreased with higher sorption values and a lower difference between radial and tangential sorption values, the deformation risk is increased with lower sorption values and a higher difference between radial and tangential sorption values.20

The mechanical test results of Turkish hazelnut and some other broad-leaved native species in Turkey are given in Table 8.17

Table 8: A comparison of mechanical test results of some Turkish wood species.

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>Turkish Hazelnut</th>
<th>Beech</th>
<th>Chestnut</th>
<th>Ash</th>
<th>Oak</th>
<th>Hornbeam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bending strength</td>
<td>98.5</td>
<td>112</td>
<td>77</td>
<td>120</td>
<td>108</td>
<td>160</td>
</tr>
<tr>
<td>Modulus of Elasticity</td>
<td>8273.4</td>
<td>130</td>
<td>82</td>
<td>900</td>
<td>13400</td>
<td>11056</td>
</tr>
<tr>
<td>Impact bending</td>
<td>0.71</td>
<td>0.9</td>
<td>0.57</td>
<td>0.65</td>
<td>0.78</td>
<td>0.8</td>
</tr>
<tr>
<td>Compression strength</td>
<td>50.1</td>
<td>57</td>
<td>50</td>
<td>52</td>
<td>65</td>
<td>82</td>
</tr>
<tr>
<td>Tension perpendicular</td>
<td>5.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The bending strength of Turkish hazelnut is moderate. But its MOE is low. In other words, under a certain load it shows more deformation (bending). Its compression strength is also moderate. It exhibits high impact bending, and for this reason it can be employed where high impact performance is needed. At the same time, Turkish hazelnut wood can be considered for applications that require bending properties, because it has a relatively high impact bending strength comparable to that of beech, oak, ash, elm and maple. Turkish hazelnut displays high hardness parallel to the grain. The same point is also true for hardness perpendicular to the grain.

4. Conclusion

Because of its high hardness value, Turkish hazelnut wood can be used for parquet flooring, and it is also suitable for the production of sports equipment, machine parts, tool handles, stairs, furniture and other wooden structures, especially in areas exposed to shock. In addition, as its bending properties are considered to be appropriate for certain applications, further bending tests must be performed to investigate these possibilities; however, the chemical, anatomical, drying and machining properties should also be taken into account.

5. References

PRODUCTION OF LAYERED MDF PANEL HAVING FINE FIBERS IN FACE LAYERS AND COARSE FIBERS IN CORE LAYER FOR FURNITURE INDUSTRY

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Abstract: MDF (Medium Density Fiberboard) which is one of the wood-based panels used for industrial applications such as furniture, building materials, and laminate flooring. The conventional MDF panels are produced using single layer in the mat forming machine. In this study, it is aimed to produce layered MDF panel for the furniture industry. The surface layers of the MDF consist of fine wood fibers, while the core layers consist of coarse fibers. The advantages of three layer MDF are as follows: (1) The amounts of wood and adhesive can be decreased by using the coarse fibers used in the core layer of the MDF, (2) The fiber production capacity of the defibrator can be increased using coarse fibers, which positively affects the energy saving in the defibrator, (3) The splitting caused by side screw withdrawal resistance can be prevented using coarse fibers.

Keywords: MDF, FINE FIBERS, COARSE FIBERS, FURNITURE INDUSTRY, LAYER

1. Introduction

Conventional wood-based composites are manufactured products made primarily from wood with only a few percent resin and other additives. A useful way to classify conventional wood-based composites based on specific gravity, density, raw material, and processing methods is shown in Figure 1.

The term of fiberboard includes hardboard, medium-density fiberboard (MDF), and cellulosic fiberboard. Several things differentiate fiberboard from particleboard, most notably the physical configuration of the wood element. Because wood is fibrous by nature, fiberboard exploits the inherent strength of wood to a greater extent than does particleboard.

Fiberboard is normally classified by density and can be made by either dry or wet processes (Fig. 1). Dry processes are applicable to boards with high density (hardboard) and medium density (MDF). Wet processes are applicable to both high-density hardboard and low-density cellulosic fiberboard. The following subsections briefly describe the manufacturing of high- and medium-density dry-process fiberboard, wet-process hardboard, and wet-process low-density cellulosic fiberboard.

2. MDF Production

MDF is engineered wood-based panel materials made by bonding together wood fibers with a synthetic resin adhesive. Medium Density Fiberboard (MDF) is used the most commonly which is made by drying process. MDF is used extensively in factory-assembled and ready-to-assemble furniture, as well as in cabinets, underlayment, drawer fronts, molding, and countertops due to its ability to be produced in molded form, as well as in straight-edged flat panels.

Medium density fiberboard (MDF) is primarily used for industrial applications such as furniture, building material, and laminate because of its good mechanical and economical aspects is usually high in strength, easy to machine, and has good weathering properties (Suchsland and Woodson, 1986).

MDF can be manufactured with either softwood or hardwood species. Most MDF is composed primarily of softwood, although some individual brands may contain a higher percentage of temperate hardwood, depending on the location of the factory to the local forest resource.

Manufacturing Process

A typical process involves reducing wood down to small chips, which are then thermally softened and mechanically refined into fibers. These are then mixed with a synthetic resin binder. The resonated fibres are dried and then formed into a mattress ready for pressing. The mattress is pressed between heated polished press plates to the desired thickness.

Standard forms of MDF typically have densities as follows:
• Average density: 700 kg/m³ to 800 kg/m³
• Core density: 600 kg/m³ to 700 kg/m³
• Face density: 1000 kg/m³ to 1100 kg/m³

MDFs can have densities that range from below 450 kg/m³ up to 800 kg/m³ and above.

The Types of MDF which are used in furniture industry commonly;
• Fine Thickness MDF
• Middle-Coarse Thickness MDF
• Coarse Thickness MDF

Fine thickness MDF has 1.8-2.5 mm thickness. Its usage areas are such as drawer stands, furniture or cabinet backs and door panels.

Middle-Coarse Thickness MDF has 3-6 mm thickness. Almost all furniture's main structure consists from middle-coarse MDF.

Coarse Thickness MDF has 45-60 mm thickness. It can be used for architectural purposes and belt or column in buildings.

The face of particleboard usually consists of fine wood particles and the core is made of coarser material. The result is a smoother surface for laminating, overlaying, painting or veneering.

The purpose of this project is producing MDF by using thinner fibers for the surface and a bit more coaster fibers for the core differently from particleboard.
In this study, it is aimed to produce layered MDF panel for the furniture industry. The surface layers of the MDF consist of fine while the core layers consist of coarse fibers. The MDF panels having different face and core layer ratios could be produced using different defibrator disc gap, which results in different fiber sizes. In the production of layered MDF production, the MDF companies should change their mat forming system, which look like the mat forming of three layers particleboard.

Thus, there will be some advantages such as;
1. The amounts of wood and adhesive can be decreased by using the cores fibers used in the core layer of the MDF.
2. The fiber production capacity of the defibrator can be increased using cores fibers, which positively affect the energy saving in the defibrator.
3. The splitting caused by side screw withdrawal resistance can be prevented using core layer consist of coarse fibers.

3. Available Methods for Manufacturing

Some methods for the realization of this production are below:

a. Change the wood species used
b. Change the size of fibers (figure 2)
c. Make some changes the density profile of wood material (figure 3)
d. Change amount of adhesive

Changing the wood species using on the surface and core layers of MDF is one of the most important influence to decrease splitting during the screwing. According to this information, soft wood fibers (such as pine fibers) using on the surface of MDF while hard wood fibers (such as beech or oak fibers) using on the core of MDF.

During the conventional produce of MDF fine fibers are used on the core layer. It is caused side splitting during screwing because of MDF core layers having harder and denser structures. To prevent this, it should consist of coarse fibers.

The density profile mainly means that a density changing in the board thickness. If the density of the core layer is decreased, side splitting is diminished during the screwing.

Boards which are used coarse fibers inside the core layer, require less amount of adhesive. In this way, companies’ adhesive costs are declined.

4. Conclusion

In this study, it is intended to reduce side splitting, high costs because of using excessive adhesive and high density problems and to overcome the problems mentioned before. This study is a preliminary study due to has not completed yet and lack of relevant literature. The limits of this study are the process of preparation of fibers and the absence of information to be compared due to the literature scarcity.

In the future, it is recommended that for researchers who will perform similar research to use different wood species, different density profile values and mechanical sifting system.

5. Acknowledgement

This work was supported by The Scientific and Technological Research Council of Turkey (TUBITAK), Project number: 1140263. The authors wish to acknowledge TUBITAK for financial support.

6. References

SURFACE ROUGHNESS EVALUATION OF ALUMINUM MATRIX COMPOSITES AFTER DRY SLIDING WEAR TESTS

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Abstract: Aluminum matrix composites composed of Al, Al-5.6 wt.% Cu (Al5.6Cu), Al-7 wt.% of alpha brass α-Al0.8Zn0.2 (Al7CuZn) and Al-9 wt.% of nickel brass Cu0.6Al0.3Zn0.1Ni0.05 (Al9CuZnNi) as the matrix and 15 vol.% of TiC and synthesized Al-Ti-C master alloy (MA) as the reinforcement were successfully fabricated by hot forging. Sliding wear tests were conducted at different velocity and loads using a pin-on-disc apparatus and under dry conditions. The results of the investigations indicate that the coefficient of friction significantly lower in composites with Al-Ti-C master alloy then that reinforced with TiC, while the wear rates are lower in composites with Cu additions. The post-test analysis of the material damage mechanisms were examined by optical profilometer.

KEYWORDS: MASTER ALLOY, HOT FORGING, WEAR TESTS, ROUGHNESS, 3D PROFILOMETRY MEASUREMENTS

1 Introduction

The tribological behavior characteristics of aluminum matrix composites (AMC) strengthened with various ceramic particles (TiC, B4C, TiB2, Al2O3, SiC) have been extensively studied to determine the effect of different combinations of matrix and reinforcement on wear behavior [1] whilst the AMC with synthesized master alloys (MA) as a reinforcement has not been systematically investigated so far.

The master alloy is an intermediate material of finely-dispersed second phase (mostly ceramic phase) in the metallic or intermetallic matrix, in the form of porous mass or sponge, [2;3] prepared by in-situ processing techniques involving a chemical reaction resulting the formation of thermodynamically stable reinforcing ceramic phase. Therefore in our work, master alloy was prepared from elemental powders of Al, Ti and C to subsequently application for producing hot forming composites mixed with aluminum powder. It is assumed that, as a result of in-situ reaction in the synthesized master alloy the grain boundaries between the particles of the strengthening phase TiC and aluminum will be free of oxides, which greatly increases the interfacial strength, titanium carbide particles themselves are of submicron size and homogeneously distribute in the volume, which increases mechanical properties of AMC, provides in effective load transfer and decreases the wear rates. [4]. However, presence of brittle titanium aluminides particles in such composites has a deleterious effect on the mechanical properties, which is why to investigate a wear behavior of such composite materials especially compared with Al/TiC composite materials is in great interest. [5-7]

Studying the topographical features of the worn surfaces morphologies (craters, cracking, transfer layer, plastic deformation, fatigue, shear fracture, etc.) also one of the important investigation subject for many decades, because it helps to evaluate wear conditions, predicting wear behavior and controlling wear processes. Wear quantification techniques are based on mass or geometric measurements. The widely used technique to calculates the wear volume loss is gravimetric wear measurement, but this method is not very useful when the wear damage involve both abrasive and adhesive mechanisms. Usage of stylus or optical profilometers could be good additional method to evaluate not only the wear volume or depth, but also the local development of the wear damage on the sample surface due to standardized roughness parameters calculated from 2D or 3D profiles [8-10].

Thus, the aim of the present work is to study the wear behavior of aluminum matrix composites after dry sliding tests under different conditions of applied load and speed, in order to determine their effect on friction coefficient, surface roughness and clarify the damage mechanisms.

2 Experimental procedure

AMC composed of Al, Al-5.6 wt.% Cu (Al5.6Cu), Al-7 wt.% of alpha brass α-Al0.8Zn0.2 (Al7CuZn) and Al-9 wt.% of nickel brass Cu0.6Al0.3Zn0.1Ni0.05 (Al9CuZnNi) as the matrix and 15 vol.% of TiC and previously synthesized master alloy (MA) of composition 20Al-64Ti-16C (wt.%) as the reinforcement, were prepared as follows: raw powders of matrix material and reinforcement additives were ball milled in planetary mill for 7.5 minutes, then compacted at 500 MPa, heated in a furnace under argon atmosphere at the temperature of 600 °C and hot forged. Throughout the text, abbreviations of the following type will be used: Al-TiC, Al-MA represents samples containing 15 vol.% of reinforcement phase with aluminum matrix and Al5.6Cu-MA, Al7CuZn-MA, Al9CuZnNi-MA – samples with alloyed matrix. Table 1 shows the values of Brinell hardness, density and ultimate tensile strength for test materials after hot forging.

Table 1: Mechanical properties of aluminium matrix composites

<table>
<thead>
<tr>
<th>Materials</th>
<th>HB, MPa</th>
<th>Density, g/cm³</th>
<th>UTS, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-15TiC</td>
<td>319</td>
<td>2,647</td>
<td>156,6</td>
</tr>
<tr>
<td>Al-15MA</td>
<td>615</td>
<td>2,896</td>
<td>187</td>
</tr>
<tr>
<td>Al5.6Cu-15MA</td>
<td>958</td>
<td>3,036</td>
<td>151,1</td>
</tr>
<tr>
<td>Al7CuZn-15MA</td>
<td>927</td>
<td>2,849</td>
<td>140,6</td>
</tr>
<tr>
<td>Al9CuZnNi-15MA</td>
<td>879</td>
<td>2,946</td>
<td>145,7</td>
</tr>
</tbody>
</table>

Cylindrical samples were examined under dry sliding condition against a counterface of G51320 steel having a hardness of 63-65 HRC using a pin-on-disk machine at different applied loads (10, 20 and 30N) and speed (1 – 4 m/s), for a constant sliding distance of 1 km. The mass loss of the specimens was measured with an analytical balance. Sliding surface was examined under optical microscopy XJL-17AT and roughness parameters were identified by optical profilometry to explore the possible wear mechanism.

3 Results and discussion

Fig. 1 shows the microstructure of the composites materials after hot forging. The grey phase corresponds to Al, the dark phase – master alloy (Fig. 1, a, b), which is consist of two main phases, i. e. TiC, Al and weak additions of titanium aluminides [7]. In composite with alloyed matrix (Fig. 1, c, d, e), could be seen white phase corresponds to Cu, alpha and nickel brass.

Fig. 2 represents the wear rates of Al-15TiC and Al-15MA. It was found; those tested materials maintain only 10 N load and work properly at 1 m/s and 2 m/s sliding speed, where mass los the highest for Al-15TiC, but further increasing of sliding speed results to adhesion between the composite materials and the steel counterface.

It can be seen from the abrupt raise of wear rate values at 3 m/s (Fig. 2), from the formation of transferred layer on the counterface surface (Fig. 3) and the visible traces of extensive plastic deformation – presents of numerous voids, cracks and...
delimitation in worn surface of Al-15TiC, Al-15MA composite materials (fig. 4 a, c).

3D profiles of Al-15MA indicates (fig. 4 d), that a layer of material has been removed as debris from these areas and that the debris is in the form of thin sheets. The examination of the Al-15TiC 3D profiles (fig. 4 b) reveals the plastic flow of the matrix material and hard particles spalling. All this assumption is in good correlation with increasing of surface roughness parameters, especially in maximum valley depth \( R_v \) and maximum peak height \( R_p \) (Table 2).

The results of the investigations shows that the coefficient of friction lower in composites with Al-TiC master alloy (0.2-0.3) then that reinforced with TiC (0.4-0.38), probably because of better mechanical properties of the Al-15MA.

To improve the wear resistance of AMC were decided alloyed matrix material with 7 wt.% of alpha brass \( \alpha-Cu_{0.8}Zn_{0.2} \) and 9 wt.% of nickel brass \( Cu_{0.64}Zn_{0.31}Ni_{0.05} \), which noticeably increase hardness of the composites compared to Al-15TiC, Al-15MA and decrease tensile strength (table 1).

There are grooves and ridges running parallel to one another in the sliding direction on the worn surface of the composites with alloyed matrix as shown in Fig. 5 (a, c e). It seems, that grooves are deeper in the Al5.6Cu-15MA and Al7CuZn-15MA then Al9CuZnNi-15MA, but the lower surface roughness parameters from the table 2 indicate that Al5.6Cu-15MA more wear-resistant. The 3D profiles after friction tests (Fig. 5 b, d, f) has rather smooth surface, unlike uneven surface with traces of extensive plastic deformation in the case of Al-15TiC and Al-15MA. The variation of were rate and coefficient of friction with sliding speed exhibit a load dependence and illustrated in Fig. 6 and Fig. 7.
The variation of wear rate and coefficient of friction with sliding speed exhibit a load dependence and illustrated in Fig. 6. With an increase of the sliding speed and applied load wear rate of the samples increase and coefficient of friction decrease. Under 10 and 20 N all materials have close wear rate values, but load and speed extension to 4 m/s and 30 N respectively leads to significant loss of mass in Al7CuZn-15MA, Al9CuZnNi-15MA composites. It is clear from the obtained dates, that Al5.6Cu-15MA exhibits the lowest value of coefficient of friction, wear rate and roughness parameters.

**Conclusion**

According to the microstructural and 3D profile analysis, friction coefficient, wear rate and roughness parameters measurements of aluminum matrix composites, the best wear behavior exhibits samples of Al reinforced with 15 % of Al-Ti-C master alloy compared to Al-15TiC composite and composites with Cu addition due to better mechanical properties.

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**Fig. 5** The microstructure of the worn surfaces of a) Al5.6Cu-15MA, b) Al7CuZn-15MA, c) Al9CuZnNi-15MA and their 3D surface profiles respectively. The applied load is 30 N, and the sliding velocity is 4 m/s.

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**Fig. 6** Wear rate and friction coefficient of AMC, alloyed with Cu, alpha and nickel brass and with 15MA as a function of sliding speed and applied load.
Reference


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EFFECT OF FIBER ON PROPERTIES OF SELF-REINFORCED PHENYLONE

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Abstract: Now there are a number of important scientific and technical problems of producing fibers with a specified set of properties and high quality indicators, process optimization and efficient processing of their applications. In this context, the aim of this work was the possibility of creating new self-reinforced polymer composites based on aromatic polyamide phenylone reinforced with organic fibers. The properties of self-reinforced composites based on aromatic phenylone are presented. It is shown that the optimum fiber content are 5-10 wt.% in the polymer matrix.

Keywords: AROMATIC POLYAMIDE, ORGANIC FIBERS, ORGANOPLASTICS

1. Introduction

Composite materials have been a synonymous to technological progress for a long time and its prospects are doubtless. Currently, a large number of synthetic polymeric materials with a valuable set of properties are received. If the first synthetic polymers were only replacing natural materials, but further high-molecular compounds of new types which were significantly different from the natural, which have in some cases, specific unique properties have been synthesized [1].

Progress in many areas of technology certainly dependent on the production of synthetic fibers with specific properties. However, organic filaments as fillers for composites have been recognized recently [2]. But their appearance suggests an organic composites as the most promising and indispenable structural materials [3]. The use of synthetic fibers in the composite contributes to further development of aviation and rocket and missile engineering etc. For example, in aircraft applications organic composites enabled to reduce the mass of the aircraft on 30% [4].

In connection with the foregoing, the aim of this work is to develop a process of getting samples of self-reinforced organic plastics with high strength characteristics. The main stages of the method developed by us are as follows. Selected components are aromatic polyamide - phenylone C-1 and organic fiber – phenylone.

2. Methods and subjects of investigation

Phenylone aromatic polyamide C-1 (TS 6-05-221-101-71) was used as a binder; this represents finely divided pink powder with a bulk density of 0.2 - 0.3 g / cm³ and a specific viscosity of 0.5 % in dimethylformamide solution with 5 % of lithium chloride not less than 0.75, characterized by the following properties: density of 1.35 g / cm³, toughness of 20 kJ / m², hardness of 18 HRB, the tensile breaking stress of 100 MPa.

Table 1. Compound press-composition

<table>
<thead>
<tr>
<th>Filler</th>
<th>Content, mass, % Based</th>
<th>Content, mass, %</th>
</tr>
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<tbody>
<tr>
<td>Fibers phenylone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>Aromatic polyamide</td>
<td>95</td>
</tr>
<tr>
<td>10</td>
<td>phenylone C-25P</td>
<td>90</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>85</td>
</tr>
</tbody>
</table>

For the reinforcement of phenylone C-1 heat resistant organic fiber were selected from aromatic polyamides phenylone fiber (2-3 mm long, the strength of 69 kgf / mm², an elongation of 15-20%, the elastic modulus of 900 - 1200 kgf / mm², density of 1.37-1.38 g / cm³).

Press-composition of the compound: C-25P phenylone +5-15 mass % of organic fibers (Table 1) was prepared by mixing the components in a rotating electromagnetic field in the presence of ferromagnetic particles. The tablets were charged in a mold preheated to 523K, heated to 593-598K and maintained at this temperature for 10min, 10min without pressure and under pressure of 30 MPa. To fix the shape of a product, the goods were cooled under pressure to a temperature of 523 K and pushed out of the mold later.

Physical-mechanical properties: strength (σ\_{c},comp.), relative deformation (ε) and elastic modulus (E) under compression were determined by a device SANS (according to NSS of China GB/T 2569-1995) on loading 10 ton and at speed 2 mm/min. Operational speed range – 0.05-500 mm/min. Samples 10 mm in diameter and 12 mm in height were used for researches.

Fig.1. The distribution of fibers in a polymer matrix with filler content:

a - 0; b - 5; c - 10; d - 15 wt.%

Electron microscopic studies were carried out with samples of materials that can withstand 3 minutes in liquid nitrogen and then were subjected to brittle fracture. On freshly prepared fracture in vacuum (10-4mm.merc.st.) the carbon film of 500-700 A thick was
improvement is observed in injection of 5-10 mass % of organic (by 1.2 – 1.5 times). Especially significant compression strength of fibers. As to elastic modulus, it increases only by 5 -10 mass%.

Phenylone increases directly proportional to organic fibers content. It is established that compression limit of initial aromatic polyamide values in excess of 3.1 GPa, and an increase of relative deformation. The results and their discussion

3. The results and their discussion

Considering the fact that machinery is one of the main branches where developed organic fiber-reinforced plastics are used, in particular – details of movable connections. Special emphasis during studying of its physical-mechanical properties got compression strength, because this factor allows to predict load-bearing capacity of friction knot completed with details from organic fiber-reinforced plastics.

As a result of mixing the starting components, it was obtained a uniform distribution of the organic fiber organoplastics (fig.1).

Fig.2. Physical and mechanical properties of phenylone and organic plastics and on its basis

These organoplastics have high compressive strength - more than 200 MPa, elastic modulus at a content of 5-10 wt.% reaches values in excess of 3.1 GPa, and an increase of relative deformation. It is established that compression limit of initial aromatic polyamide phenylone increases directly proportional to organic fibers content (by 1,2 – 1.5 times). Especially significant compression strength improvement is observed in injection of 5-10 mass % of organic fibers. As to elastic modulus, it increases only by 5-10 mass% percentage content, further it starts decreasing (fig.2).

This increase can be explained by inter-compound filling effect, when fiber particles are placed on the boundaries of super-molecular structures in drawback sections and influence on macromolecules flexibility. Nearby filler surface there is limitation of supermolecular structures mobility, which doesn't depend on polymer and filler nature. It leads to a certain change of material elasticity [5,6]. For phenylone globular structure with traces of intense destruction is characteristic. The mutual arrangement of the supermolecular structures is different from the original one, which is characterized by denser packing. The improving of strength properties of organic plastics based on phenylone can be explained by good adhesion of the polymeric binder with the fiber and converting the globular structure into fibrillious one.

Macromolecules of phenylone degrade less intensively than in aliphatic polyamides [7]. No significant changes at the molecular level are confirmed by the results of infrared spectroscopy. Spectrogram of base phenylone and that of wear particles are identical, except for a slight displacement of the absorption band in the frequency range 1500-1550 cm⁻¹, which is proof of the rupture of hydrogen bonds.

Fig. 3. The structure of the starting polymer and organoplastic (magnification x8000)

Analyzing the test conducted earlier [8,9], it was revealed that the optimum content of the fibers in the polymer matrix is: phenylone - 5 wt%. The results indicate the prospects for further research in this area and provide a basis to recommend organoplastics for the manufacture of construction materials.

4. References

MECHANICAL PROPERTIES OF WOOD POLYPROPYLENE COMPOSITES PRODUCED BY USING RESIN IMPREGNATED PAPER WASTE

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Abstract: In this study, it was evaluated some mechanical properties of polypropylene composites reinforced with resin impregnated paper waste (MIPW) obtained from the particleboard and fiberboard factories. To meet this objective, resin impregnated paper waste and pine wood flour were compounded with polypropylene with coupling agent (MAPP) in a twin screw co-rotating extruder and then was manufactured by injection molding process. Injection molded composites were prepared from the wood flour, MIPW powder and polypropylene with maleic anhydride-grafted polypropylene (MAPP) at 10, 20, 30, 40, and 50 wt % contents of the MIPW powder. The tensile and flexural properties of wood polypropylene composites filled with resin impregnated paper waste were decreased. But still, the test results showed that the MIPW can be efficiently used as reinforcing filler for polypropylene composite due to satisfactory mechanical properties of the composites.

Keywords: WOOD - POLYPROPYLENE COMPOSITE, MECHANICAL PROPERTIES, RESIN IMPREGNATED PAPER WASTE

1. Introduction

Wood plastic composites (WPCs) have attracted considerable attention from industry in recent years. WPCs approximately have average annual growth rate of 18% in Northern America and 14% in Europe.¹,² The use of wood flour or fiber as fillers and reinforcements in thermoplastics has been gaining acceptance in the applications of commodity plastics in the past few years.³ The advantages of using a wood component in thermoplastic composites are that the biomass resource is nonabrasive, low in cost, widely available, sustainable, high filling levels possible, high specific properties, lower density per weight of raw material, flexible, and recyclable.⁴ The physical form can vary from fine wood flour to wood fibers.⁵ The cost and performance of the final composite products dictate the form of the wood to be used in the plastics. The typical plastics used in this technology are various types of polyethylene, PP, and polyvinyl chloride.

Current growth rate of the WPC market is 22% for North America and 51% for Europe.⁶ Decking for outdoor applications represent the largest market for WPCs both in North America and Europe and in both regions growth is most rapid in the decking segment.⁷ WPC market share in the European decking sector is estimated to be around 6%. In Europe, total WPC production amounts to 120 thousand tons (excluding product destined for the auto industry). Around 68 thousand tons of this production is currently destined for the decking sector. The positive growth in WPC decking has led manufacturers to introduce residential construction applications such as sidings, roofing, windows, door frames, and outdoor furniture. Further expansion into the residential construction industry and development of applications for the furniture industry require an understanding of the fire performance of the WPCs.

Biocomposites reinforced with wood fibers and mineral fillers have attracted a great attention as alternative materials. Particularly, researches with regard to WPC (wood plastic composite) materials have been continuously increased within the last 20 years because of the advantageous characteristics of each constituent in composite materials.⁸ Among the reinforcing agents, natural fibers have significant advantages such as low cost, highly available and renewable, with low density and high specific properties as well as biodegradable and less abrasive to processing equipment.⁹ Among commodity thermoplastics, polypropylene (PP) possesses outstanding properties such as low density, good flex life, sterilizability, good surface hardness, very good abrasion resistance, and excellent electrical properties.¹⁰ However, the main drawback of PP is low modulus when compared with the wood. The purpose for the addition of cellulose-based fillers to thermoplastics is to reduce the cost per unit volume and to improve stiffness. Enhancing bending and tensile properties of the filled-polypropylene (PP) composites can expand applications in buildings and structures. There have been different attempts to improve the bending and tensile properties of flat-pressed thermoplastic composite panels. One option is to incorporate nanoscale reinforcing fillers such as nanoclay and carbon nanotube into the composite panel.¹¹,¹²

In the recent years the use of the resin impregnated decorative and overlay paper sheets has significantly increased in the furniture and laminate flooring industries in European countries and Turkey. As a result of increasing decorative and overlay paper sheet production, the amount of the impregnated paper waste produced by square-trimming the paper has dramatically increased in the factories. The impregnated paper waste is a major challenge for recycling due to the high volume needed worldwide and its low biodegradability. The amount of this dry waste is considerable, running up to 400 t/year in just a medium sized paper impregnating factory.¹³ A better approach for this material is through reusing or recycling in order to decrease the permanent waste volume. Because of its good bondability, the use of recycled alpha cellulose papers containing the melamine resin can be an alternative way for waste minimization. In a previous study, it was reported that impregnated decorative paper waste can be used successfully as a binder of particleboard.¹⁴

Mechanical properties of polypropylene composites filled with melamine impregnated paper waste (MIPW) instead of wood flour were investigated according to ASTM standards. Injection molded composites were prepared from the wood flour, MIPW powder and polypropylene with maleic anhydride-grafted polypropylene (MAPP) at 10, 20, 30, 40, and 50 wt % contents of the MIPW powder.

2. Experimental

2.1. Materials

Pine wood (Pinus sylvestris L.) was used as lignocellulosic filler in the thermoplastic composites. Air-dry density, modulus of rupture (MOR), modulus of elasticity (MOE), and compression strength of poplar wood are 0.52 g/cm³, 98 N/mm², 11700 N/mm², 54 N/mm², respectively.¹⁵ Pine wood having a moisture content of 20–30% based on the oven-dry weight of the wood was processed by a rotary grinder and retained on a 60-mesh screen.
The waste decorative and overlay papers were supplied from Yıldız Entegre Company, which has melamine impregnated paper line in Kocaeli, Turkey. They were obtained from the edge trimming of partially cured, dried melamine papers used for low pressure laminates from the production line. Polypropylene (PP) \((T_m = 160 \, ^\circ C, p = 0.9 \, g/cm^3\), and MFI/230 \(^\circ C/2.16 \, kg = 6.5 \, g/10 \, min\) was used as the polymeric material produced by Petkim Petrochemical, Turkey. Maleic anhydride-grafted PP [MAPP-OPTIM-425; reactive modifier maleic anhydride (MAH) content = 1 wt %] was obtained from Pluss Polymers, India.

2.2. Methods

2.2.1. Preparation of injection-molded PP composite samples

The wood flour, melamine impregnated paper waste, PP matrix, and MAPP granulates were processed in a 30-mm co-rotating twin screw extruder with a length-to-diameter \((L/D)\) ratio of 30:1. The barrel temperatures of the extruder were controlled at 170 \(^\circ C\), 180 \(^\circ C\), 185 \(^\circ C\), and 190 \(^\circ C\) for zones 1, 2, 3, and 4, respectively. The temperature of the extruder die was held at 200 \(^\circ C\). The extruded strand passed through a water bath and was subsequently pelletized. The pellets were stored in a sealed container and then dried to the minimum moisture content of 1–2% in a laboratory oven before the injection molding. The temperature used for injection molded samples was 180–200 \(^\circ C\) from feed zone to die zone. The PP composite samples were injected at injection pressure between 4 and 5MPa with cooling time of about 20 s. Finally, the samples were conditioned at a temperature of 23 \(^\circ C\) and relative humidity of 50% according to ASTM D 618.\(^{16}\) Air dry density values of the filled PP samples varied from 0.99 to 1.04 g/cm\(^3\). Polypropylene, pine wood flour, resin impregnated paper waste and the coupling agent were then weighed according to the formulations given in Table 1.

### Table 1: Comparison of the injected molded composite types.

<table>
<thead>
<tr>
<th>Composite type</th>
<th>Wood flour (wt%)</th>
<th>Melamine Impregnated Paper Waste</th>
<th>Polypropylene (PP) (wt%)</th>
<th>MAPP content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>50</td>
<td>0</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>A</td>
<td>40</td>
<td>10</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>B</td>
<td>30</td>
<td>20</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>20</td>
<td>30</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>D</td>
<td>10</td>
<td>40</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>E</td>
<td>0</td>
<td>50</td>
<td>50</td>
<td>3</td>
</tr>
</tbody>
</table>

2.2.2. Determination of Mechanical Properties

The flexural properties of the specimens with dimensions of 127 \(\times 12.7 \times 3.2\) (thickness) \(\times 10^{-3}\) \(\text{mm}^3\), flexural modulus and strength, were measured in three-point bending test using a standard material testing system (Lloyd) at a crosshead speed of 1.3 \(\text{mm/min}\) in accordance with ASTM D 790.\(^{17}\) Tensile strength and modulus of the specimens [dogbone shape (Type III)] were tested with a crosshead speed of 5 \(\text{mm/min}\) in accordance with ASTM D 638.\(^{18}\) Ten replicate specimens were tested for the tensile and flexural properties of each composite formulation.

3. Results and discussion

3.1. Mechanical Properties

In this study, six different groups were manufactured and their mechanical properties were determined. The flexural and tensile values of the WPC (Control group), melamine impregnated paper waste filled polypropylene composites are presented in Table 2. The highest and lowest results in flexural strength of composite types were found to the control group (compost of 50% wood flour, 50% PP, %3 MAPP) and group B (compost of 30% wood flour, 20% MIPW, 50% PP, %3 MAPP), respectively. The highest and lowest results in flexural modulus of composite types were found to group A (compost of 40% wood flour, 10% MIPW 50% PP, %3 MAPP) and group E (compost of, 50% MIPW 50% PP, %3 MAPP), respectively.

### Table 2: The flexural and tensile values of the WPCs.

<table>
<thead>
<tr>
<th>Composite type</th>
<th>Flexural Strength (MPa)</th>
<th>Flexural modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>54.70</td>
<td>3565</td>
<td>31.8</td>
<td>3842</td>
</tr>
<tr>
<td>A</td>
<td>49.2</td>
<td>4061</td>
<td>29.0</td>
<td>3467</td>
</tr>
<tr>
<td>B</td>
<td>34.1</td>
<td>3596</td>
<td>20.3</td>
<td>2963</td>
</tr>
<tr>
<td>C</td>
<td>39.2</td>
<td>3167</td>
<td>27.8</td>
<td>3043</td>
</tr>
<tr>
<td>D</td>
<td>41.7</td>
<td>3074</td>
<td>30.23</td>
<td>2881</td>
</tr>
<tr>
<td>E</td>
<td>42.4</td>
<td>2670</td>
<td>26.2</td>
<td>2619</td>
</tr>
</tbody>
</table>

The results of the tensile strength test were similar to the results of the flexural strength test. Control group (contents of 50% wood flour, %50 PP, %3 MAPP) among composite types was given to 31.8 MPa the highest result in tensile strength but B group (compost of 30% wood flour, 20% MIPW, 50% PP, %3 MAPP) was given to 20.3 MPa the lowest result of that. The highest and lowest values in tensile modulus are given to the control group (3842 MPa) and E group (2619 MPa), respectively.

According to the result of this study, melamine impregnated paper waste used instead of the wood flour in WPC production were observed to reduce the flexural properties of WPC. The reduction in the flexural strength of the samples due to MIPW content was mainly attributed to the poor compatibility between thermoset MIPW and polypropylene, which forms weak interfacial regions. Poor dispersion of the fillers in the polymer matrix could be reason for lower tensile strength for the samples with content of the MIPW. Since there was not good bonding between the MIPW and polymer matrix, test samples were broken at lower loads.

4. Conclusion

The results of this study showed that the MIPW was capable of serving as new reinforcing filler in the manufacturing of polypropylene composite materials, which reduced cost and environmental benefits. In general, the flexural and tensile strengths of the composites decreased with the MIPW flour content. The test results showed that the MIPW could be efficiently used as reinforcing filler for polypropylene composites with MAPP used for decking products, due to satisfactory mechanical properties of the composites.

5. References

5. Jacobson, R. E.; Rowell, R.; Caulfield, D.; Sanadi, A. R. United States based agricultural “‘waste products’” as fillers in a...


