COMPOSITES ON THE BASE OF INDUSTRIAL WASTES
I. PHYSICO-CHEMICAL PROPERTIES OF Fe-Ni SLAG

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ABSTRACT

With a view to utilize industrial wastes (metallurgical slag and waste glasses) the physico-chemical properties of Fe-Ni slag from the “refining” and “melting” processes are investigated. Compact samples of the metallurgical slag are produced by milling, pressing and sintering ceramics technology. They are characterized for: chemical and granulometric composition, structure; mechanical (density, porosity, modulus of elasticity and bending strength) and thermal properties (temperature range of sintering, temperatures of softening and melting, relative thermal expansion and temperature coefficient of linear expansion).

Keywords: metallurgical slag, slag utilization, slag mechanical and thermal properties.

INTRODUCTION

The main problem in the production of metals and new materials are the waste products (slag, scoria, waste powders, etc.). More than 2 million tons of industrial wastes are deposited annually in the EU territory.

The wastes from the industry and households contain high concentration of toxic substances, heavy metals, organic substances and soluble salts [1-3]. Wastes processing by reduction of the noxious and toxic substances occupies central place for environment preservation as a method for environment protection.

For protection of the environment against pollution by toxic elements, recycling of the chemical wastes is carried out [4]. Recycling and encapsulation are expensive industrial processes [5]. The development of technologies for treatment of industrial wastes on the site that they are produced and their transformation after recycling in new qualitative materials is a project of the 21st Century. For that purpose methods and technologies are developed which require a minimum quantity of energy and time. The environmentally detrimental components can be transformed in inert products, for instance, by the technologies of melting and atomization that encapsulate the heavy metals and completely decompose the organic substances. The glass phase which is a component of many waste materials plays the role of an encapsulating coating. By mixing the glass with the environmentally detrimental substances and subsequent thermal treatment, products of multi-barrier structures are obtained [6], i.e. structures similar to the natural minerals or such as those of the glass. The crystal materials transform into a new product while the glass al-
allows fixation (encapsulation) or decomposition of the toxic elements in the material to concentration corresponding to the requirements of ecology.

The metallurgical slag is the main waste in the ore processing in metallurgy with particle size above 10 mm. According to its chemical composition it is subdivided in ferronickel, ferrochromium, calcium ferrite, etc. [7]. The metallurgical slag is a multi-component system characterized by high percentage content of Si-, Ca-, Fe- and Mg-oxides of high porosity due to the presence of glass phase (5 - 30 %). The absence of detrimental to nature components in the slag composition makes its application easier.

The degree of slag vitrification and crystallization depends on its chemical composition and structure. The molecular ratio of Si- and O- atoms (N_o = Si/O) for Fe-Ni slag is in the range of 0.323 - 0.352 and determines the percentage content of the crystal phase in the material [8]. The pyroxene modulus, \( M_{pv} = 2 + (\Sigma R^2+(\Sigma R^4 + \Sigma R^6)) \), where R means the oxides with the given valence, also affects the structure of the composites of the glass ceramics type [9], as well as: the formation of tetrahedral crystal phase, the interaction of the components in the glass phase and the development of the thermal process [10]. For Fe-Ni-slag \( 2.72 \leq M_{pv} \leq 2.95 \).

The metallurgical slag is also used as initial raw material for production of new materials useful for the other applications [11-17], some of which are presented in Table 1.

The physico-chemical properties and the thermal behavior of these products most of all depend on the structure of the material and on the conditions of synthesis [18].

The metallurgical slag (similarly to the waste powders) is used as raw material in the cement industry [19-20], e.g. the slag obtained in the blast-furnace production is used for the production of Portland cement [21]. The slag is activated by a solution of sodium silicate (water glass) and sodium sulfate, waste powders; lime and others are used for additives. The cement produced solidifies in a short time and possesses high strength.

The waste powder additive to the calcium ferrite slag improves the mechanical properties of the Portland cement [22] and increases its corrosion resistance [23-25].

Matelepsy et al. [26] have tested the stability and mechanical strength of Portland cement produced from slag in an alkaline medium and have found out that activators such as NaOH, Na2SiO3, Na2O, Na2CO3, etc. affect positively the alkaline slag (i.e. result in formation of pores and caverns in the cement structure). These activators influence the process of „hydration” and the cement microstructure [27].

Ecologically compatible cement which does not contain heavy metals is developed on the base of metallurgical slag [28]. The detoxication is performed by melting the slag in an electrical furnace at temperature between 1300 - 1500°C. During the process of „melting”, the heavy metals and non-organic components from the slag are „frozen” in the glass matrix as a result of which a stable product, non toxic for the environment is obtained [29-30].

In the pyrometallurgical processes for production of copper from copper sulfate [31], ferrosilicate slag remains as an waste [32] and it can be used as a raw material for production of bricks for the needs of the construction [33]. These products have high corrosion resistance and stability between 1250 - 1350 °C [34].

Bricks for the construction are manufactured from the waste slag, the chemical and mechanical properties of which are investigated by a number of researchers. For instance, Ibrahim et al. [35] study the mechanical characteristics of bricks produced from slag, in the composition of which 10 to 25 % anorthite, mullite and quartz are included. In case of addition of 40 - 60 % feldspar to the initial raw material (at the temperature of synthesis 1250 °C) products are obtained with me-

| 1 | Construction | Portland cement, fillers (ballast), thermal insulation materials, etc. |
| 2 | Chemical industry | Catalysts, pigments, filters for ion exchange, etc. |
| 3 | Ceramics | Ceramic sheets, tiles, porcelain filters, dust collectors, diffusers, aerators, etc. |
| 4 | Other applications | Luminescent materials, Acoustic absorbers, etc. |
Mechanical strength in the range from 37 to 47 MPa. Midzul et al. [36], examine slag for similar application which contains ≈ 65 % Fe-oxides and Chop [37] studies the properties of products made from manganese-silicate slag. All the authors show that if the products contain ≤ 10 - 30 % of that type of slag then the temperature of synthesis decreases to 990 - 1040°C, the absorption of water also decreases to 10 %, and the coefficient of thermal expansion becomes higher. If the portion of the slag in the products is 50 - 80 % at different quantity of SiO₂, Al₂O₃, Li₂O and TiO₂ and they are synthesized at 860 - 880 °C (τ = 2h), the compression strength is increased to 25 - 51 MPa. A mixture of slag and clay, after synthesis at temperature 1000 - 1200°C, shows different micro heterogeneity, while slag containing 10 % FeO vitrifies easier [38]. Other authors [36, 39] examine calcined granulated slag for production of bricks that meet the approved standards and are comparatively cheaper.

The porcelain tiles are characterized by decorative surface, good homogeneity, low level of water absorption (≈ 0.1 %), good mechanical properties, abrasivity, resistance to low temperatures and chemical agents (acids, detergents, bases), etc. [40]. In the glaze composition slag rich in silicate components might be present because the silicate in combination with additives which decrease the melting temperature leads to strengthening of the structure during the time of drying and synthesis [41, 42].

Metallurgical wastes and glass are used for production of compact and porous glass ceramic materials [43] at controlled heat treatment [44,45]. They find application in the production of electronic components [46], optical sensors [48], additives for biomedical products [47], catalysts, membranes, sensors [48], composite materials [49], etc.

The use of slag of various chemical and mineralogical composition in the production of glass ceramic materials results in manufacture of products of variable microstructure and mechanical properties. The nature and character of the crystalline phase and the microstructure of the materials affect the technical characteristics of the final product [50]. For instance, the glass ceramic materials produced from a mixture of metallurgical slag, clay, sand and catalyst possess high chemical resistance [51]. Zhunina et al. [52] investigate the crystallization of the glass phase produced of easy to melt calcium clay. The crystal materials obtained are composed mainly of pyroxene but at the same time they contain Cr₂O₃ and TiO₂, that are very effective as catalysts of the process „crystallization”. During the crystallization of a mixture of cast granite and dolomite, a material composed of alkaline aluminopyroxene, mellite and olivine is produced [53]. When using Egypt clay, MgCO₃, Li₂CO₃, sand and a small quantity of catalyst which accelerates the crystallization we obtain a glass ceramic material of lower coefficient of thermal expansion as compared to that the glass [54]. A glass ceramic material containing mono-mineral pyroxene is synthesized from slag rich in basalt [55]. Such materials possess good mechanical properties, excellent abrasive ability and high chemical resistance. Other researchers investigate the crystallization of glass ceramic materials produced from a mixture of mono-pyroxene and basalt [56]. The product obtained from pyroxene is characterized by good abrasive ability. The glass ceramic products produced of basalt slag find application in other fields as well [57].

The metallurgical slag in the composition of which Si- and Al-oxides predominate may be used as a raw material for the production of ceramic filters, aerators and diffusers applied in the treatment of industrial gases and purification of waste waters [58, 59]. The glass ceramic products obtained show good chemical, physical, microbiological and mechanical properties as well as resistance to sharp temperature variations [60, 61]. The presence of heavy metals in the slag such as Sn, Sb, Cd, Ba, As, Sr, Zn, Pb, Mo, is eliminated by the use of waste glass which fixes them in the composite matrix during the liquid phase synthesis [62, 63]. Polyurethane foam can be used as forming agent for the porous ceramic structure [64]. The porosity of the ceramic filters will depend on the foam concentration and pore structure [65].

**EXPERIMENTAL**

The chemical composition of the raw materials is determined by atomic absorption spectroscopy with an atomic absorption spectrophotometer Rank Hilger, Atom-Spek H-1580.

The differential thermal analysis (DTA) and the thermogravimetric analysis (TGA) are performed with the apparatus Netzsch STA-409 (heating rate - 10°C
min\(^{-1}\) in the range 20 - 1400°C, atmosphere - air). A thermomicroscope Leitz 5 (heating rate in the range 20-1500°C - 10°C min\(^{-1}\)) was used for determination of the melting point and the areas of sintering and softening. The apparatus Philips PW 1820 (CuK\(_\alpha\)-radiation, Ni-filter, examination range - 2θ = 6 - 50°) was used for carrying out the X-ray structure analysis (XRA).

The planetary-motion mixer Fritsch pulverisette 5 with Al\(_2\)O\(_3\)-balls has been used for milling and mechanical activation of the raw materials; milling time 1-3 hours, medium - alcohol + water. Mesh analysis (mesh Retsch STR 36 D-42781 Haan) was performed for determination of the granulometric composition. The specific surface of the powders is defined by means of BET Micromerits Gemini. The powder morphology was studied by a scanning electron microscope Leica S 440i at magnification 50 - 2000 times.

For the first sintering stage uniaxial press Weber Pressen KIP 100 of pressures 10 - 400 MPa was used. The molds have the shape of a parallelepiped (dimensions: a = 60 mm, b = c = 4-6 mm) and cylinder (diameter f = 35 mm). The density was determined by two methods: direct (in case of known geometrical dimensions of the samples, \(r = m/V\)) and hydrostatic (for samples of undefined geometry) in operation medium - water. The theoretical density was determined by the theoretical densities of the component phases and their volume concentrations by the equation: \(x_r = x_r^c + (1-x)r^c\) where: \(x_r\) - theoretical density; \(x\) - mass part of the waste powders (slag); \(r^c\) - density of the waste powders (slag); \(r^c\) - density of the waste glass. For determination of the sample porosities the following equation was used: \(\theta = 1 - \rho/\rho_r\), where: \(\rho\) - actual density of the composites.

The mechanical tester Netzsch 401/3 was used for determination of the elasticity modulus (Young’s modulus) and bending strength (compact samples of parallelepiped shape polished in advance by a diamond paste of particle size 9 μm were examined).

A dilatometer Netzsch 402E (heating/cooling rate - 2°C min\(^{-1}\); test range – 20 – 600 - 20°C) was used for testing the thermo mechanical characteristics of the sintered materials: coefficient of thermal expansion, temperature variation of ΔL/L and thermodynamic stability.

RESULTS AND DISCUSSION

Two types of metallurgical slag from Kavadarcı (Macedonia) have been investigated: slag from the process „refining” (Slag-R) and slag of the process „melting” (Slag-M).

The chemical composition of Fe-Ni slags (Table 2) shows that they are multi component silicate systems of high Fe\(_2\)O\(_3\), FeO, SiO\(_2\), CaO and MgO content. The vitrification and crystalization of the system depend on the chemical composition. Figs.1 and 2 show the particle morphology.

The SEM micrographs show that the powder of the slag possesses significantly higher geometrical activity because it is much more disperse than the waste powders. This is due to the preliminary milling of the slag (in ball and planetary-motion mills) that it has undergone before sintering.

Table 3 presents the granulometric composition of the slag. The fraction of particle dimensions < 0.045 mm has the largest relative share. This granulometric composition is produced after milling of the slag before the process of sintering. Slag of the same granulation is used in further experiments. Table 4 presents the phase composition of Fe-Ni slag obtained after XRA was carried out.

Table 5 presents the thermal characteristics of the ferronickel slag.

These studies show that Slag-R has higher sintering range (1250 - 1500°C) and melting point higher than 1500°C, as compared to Slag-M (1260 - 1370°C), because the content of the difficult to melt oxides in it is much higher.

![Table 2. Chemical composition of ferronickel slag.](image)

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Slag-R, mass %</th>
<th>Slag-M, mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(_2)O(_3)</td>
<td>1.59</td>
<td>2.48</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.25</td>
<td>0.28</td>
</tr>
<tr>
<td>SO(_3)</td>
<td>0.92</td>
<td>0.87</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>0.11</td>
<td>0.33</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>32.65</td>
<td>17.62</td>
</tr>
<tr>
<td>FeO</td>
<td>46.28</td>
<td>31.42</td>
</tr>
<tr>
<td>CaO</td>
<td>7.84</td>
<td>4.48</td>
</tr>
<tr>
<td>MgO</td>
<td>5.40</td>
<td>9.66</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>1.25</td>
<td>11.25</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>1.80</td>
<td>19.80</td>
</tr>
<tr>
<td>NiO</td>
<td>0.61</td>
<td>0.31</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05</td>
<td>0.33</td>
</tr>
<tr>
<td>CoO</td>
<td>0.19</td>
<td>0.14</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Σ</td>
<td>98.96</td>
<td>99.04</td>
</tr>
</tbody>
</table>
The densities of Slag-R and Slag-M are 5.04 g cm\(^{-3}\) and 3.58 g cm\(^{-3}\), respectively.

The fraction < 0.045 mm and molds of parallelepiped shape and dimensions of the operation volume 60x5x5 mm\(^3\) (pressing force - 30 MPa; plasticizer - 1 % solution of polyvinyl alcohol (PVA) were used for making pressed samples of Fe-Ni-slag.

The sintering was performed at \(T = 900, 950, 1050, 1100, 1150\) and \(1200\)°C, in a chamber furnace (air atmosphere; \(V_\text{heating} = 10^\circ\text{C min}^{-1}\); holding at the final temperature - 2 hours).

It is found out that Slag-R increases its geometric stability at heat treatment up to 1200°C, while when using Slag-M, and similar conditions of sintering, deformed samples are produced (there is degassing in the volume of the samples at \(T > 1150\)°C).

The color of the sintered compact samples of both types of Fe-Ni slag is different: from light red for Slag-M to black for Slag-R, which is due to the almost two times higher quantity of Fe-oxides (Fe\(_2\)O\(_3\) + FeO) in their composition (Slag-R - 78.93 %, Slag-M - 49.04 %).

### Table 3. Granulometric composition of the waste slag.

<table>
<thead>
<tr>
<th>Diameter, mm</th>
<th>Slag-R, mass %</th>
<th>Slag-M, mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 1.0</td>
<td>0.7</td>
<td>0.0</td>
</tr>
<tr>
<td>-1.0 + 0.5</td>
<td>4.4</td>
<td>0.0</td>
</tr>
<tr>
<td>- 0.5 + 0.25</td>
<td>7.0</td>
<td>7.1</td>
</tr>
<tr>
<td>- 0.25 + 0.125</td>
<td>17.0</td>
<td>9.8</td>
</tr>
<tr>
<td>- 0.125 + 0.063</td>
<td>17.1</td>
<td>14.9</td>
</tr>
<tr>
<td>- 0.063 + 0.045</td>
<td>23.6</td>
<td>26.2</td>
</tr>
<tr>
<td>&lt; 0.045</td>
<td>30.2</td>
<td>42.0</td>
</tr>
</tbody>
</table>

### Table 4. XRA of the ferronickel slag.

<table>
<thead>
<tr>
<th>Slag-R</th>
<th>Eskolite (Cr(_2)O(_3)) – amorphous phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag-M</td>
<td>Hematite (Fe(_2)O(_3))</td>
</tr>
<tr>
<td></td>
<td>Diopside (CaMgSi(_2)O(_6))</td>
</tr>
<tr>
<td></td>
<td>Olivine (MgFeSiO(_4)) - amorphous phase</td>
</tr>
</tbody>
</table>

When the sintering temperature of the pressed samples is increased (Slag-M) from \(T = 900\)°C (2h) up to \(T = 1200\)°C (2h) their color also changes from light red to grayish-black.

Samples of different density (porosity) are produced by varying the sintering temperature – Table 6.

It is seen in Table 6 that Slag-R has almost two times lower density compared to that of Slag-M, which is because of its lower reaction ability. That is a result of considerable differences in the chemical composition and in the concentrations of the phases present in the two types of slag. On the other hand the modulus of elasticity and the bending strength of Slag-R are higher than those of Slag-M at similar temperatures of synthe-

![Fig. 3. Curves of the relative thermal expansion ΔL/L during heating/cooling of Slag-R.](image-url)
Table 5. Thermal characteristics of the ferronickel slag.

<table>
<thead>
<tr>
<th>Slag type</th>
<th>Sintering temperature, °C</th>
<th>Softening temperature, °C</th>
<th>Melting temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag-R</td>
<td>1250</td>
<td>1500</td>
<td>&gt; 1500</td>
</tr>
<tr>
<td>Slag-M</td>
<td>1260</td>
<td>1370</td>
<td>1480</td>
</tr>
</tbody>
</table>

The temperature dependences of the relative thermal expansion (ΔL/L) during heating/cooling (20 → 600 → 20°C) of Slag-R and Slag-M are identical. The absence of hysteresis in these dependences shows that Slag-R and Slag-M are systems of thermodynamic equilibrium (Figs. 3, 4).

The temperature variation of ΔL/L is presented as a polynomial of III order:

Slag-R: \( \Delta L/L = -0.302 + 0.018T - 2.317 \times 10^{-5}T^2 + 2.501 \times 10^{-6}T^3 \)

Slag-M: \( \Delta L/L = -0.232 + 0.015T - 1.365 \times 10^{-5}T^2 + 1.302 \times 10^{-6}T^3 \)

The temperature coefficient of linear expansion \( \alpha \) can be calculated by the equation:

Slag-R: \( \alpha = 0.018 - 4.634 \times 10^{-5}T + 7.503 \times 10^{-6}T^2 \)

Slag-M: \( \alpha = 0.015 - 2.730 \times 10^{-4}T + 3.906 \times 10^{-6}T^2 \)

The technical coefficient of thermal expansion for Slag-R is 12.9 \( \times 10^{-6} °C^{-1} \), and for Slag-M 11.6 \( \times 10^{-6} °C^{-1} \).

**CONCLUSIONS**

The following conclusions can be formulated as the result of the investigations carried out:

- By milling, pressing and sintering compact samples of metallurgical slag are produced: from the processes of „refining” – Slag-R and „melting” – Slag-M;
- The sintered samples are in thermodynamic equilibrium. They are characterized for: chemical and granulometric composition, structure; mechanical (density, porosity, elasticity modulus and bending strength) and thermal properties (temperature range of sintering, temperatures of softening and melting, relative thermal expansion and temperature coefficient of linear expansion).

**Acknowledgement**

The authors acknowledge gratefully the financial support for this work from the Ministry of education and science of R. Bulgaria (contract BM-7/05) and the Ministry of education and science of R. Macedonia.

Table 6. Density, porosity and mechanical properties of the examined slags.

<table>
<thead>
<tr>
<th>Slag type</th>
<th>Temperature of synthesis, °C</th>
<th>Density, g/cm³</th>
<th>Porosity, %</th>
<th>Young’s modulus, GPa</th>
<th>Bending strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag-R</td>
<td>1100</td>
<td>3.21</td>
<td>36.3</td>
<td>27.3</td>
<td>41.5</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>3.25</td>
<td>35.5</td>
<td>29.0</td>
<td>47.8</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>3.28</td>
<td>34.9</td>
<td>39.4</td>
<td>48.7</td>
</tr>
<tr>
<td>Slag-M</td>
<td>900</td>
<td>2.25</td>
<td>37.2</td>
<td>6.1</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>2.36</td>
<td>34.1</td>
<td>6.2</td>
<td>14.0</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>2.38</td>
<td>33.5</td>
<td>6.7</td>
<td>17.8</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>2.48</td>
<td>30.7</td>
<td>16.1</td>
<td>26.0</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>2.76</td>
<td>22.9</td>
<td>25.2</td>
<td>49.9</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>2.93</td>
<td>18.2</td>
<td>29.1</td>
<td>51.0</td>
</tr>
</tbody>
</table>
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