Refractory ceramic materials are used in the processes taking place at high temperatures. In most refractory materials consist of oxides and combinations thereof. Refractory materials are mostly produced from six oxides: SiO$_2$, Al$_2$O$_3$, MgO, CaO, Cr$_2$O$_3$ and ZrO$_2$, which are located in the melting temperature of 1700 °C to 2825 °C [1, 2]. Depending on the prevailing operating conditions of the various refractory lining. They are used in several industries: iron and steel, foundries, glass, cement, etc. Approximately 65% of the world consumes refractory iron and steel. In Poland, as a result of activities of the Polish steel industry iron and steel consumed is about 50% of the total refractory materials. Refractory materials are used both in steel furnaces (arc furnaces, induction furnaces, oxygen converters) in blast furnaces for smelting pig iron and ladle during casting and machining of steel (including the main steelmaking ladles and indirect). In the manufacture of steel using a variety of types of refractory materials.

They are used as lining the shaft electric arc furnace (including materials magnesia, magnesia-carbon) and the materials used in the main tanks (materials dolomite, dolomite-magnesite, magnesia-spinel, magnesia-chrome). In both cases, the constant and direct contact with the liquid steel, undoubtedly affect the chemical composition of the materials used refractories. Wear of refractory materials used in the above-described objects is greatest due to the virtually constant contact with the liquid steel. Steel melted in steel furnaces or converters tapped into the ladle. Poured into a vat of steel slag with an average temperature above 1600 °C. Slag is a protective layer in the tank steel bath before cooling too quickly. Along with the high temperature affects the ladle lining therefore also slag.

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The most aggressive of the slag are oxides FeO, MnO and MgO. Destructive to the working refractory impingement steel poured from the furnace, and the turbulence in the same vessel [3, 4]. The decrease in steel ladles life is affected by types of secondary metallurgy run (argon, heating, vacuum degassing). Fuel ladle refractory is in the range 3–30 kg/ton of steel. Refractory materials are subject to continuous wear, thereby generating a significant amount of waste. It is, therefore, to obtain information about the chemical composition changes, especially in terms of metal content and harmful substances. This information will be helpful in choosing the appropriate form of re-use and waste refractory materials utilized.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

The study used part of the main ladle linings designed for repair. Portion downloaded came from a refractory tank with a capacity of 150 ton of parts exposed to constant contact with the liquid steel (metal zone). Tests were also performed for new materials for the refractory lining of the vessel. Samples were taken from the Steelworks ZWW (Rolled Product Plant), Celsa – Huta Ostrowiec in Ostrowiec Świętokrzyski.

2.2. Research methodology

The surface of the ladle refractory samples were tested with the main scanning electron microscope, Hitachi (SEM) S-3500N equipped with manual Noran EDS analyzer. The study included both test scanning surface of the melt in contrast secondary electron (technique – SEM SE), as well as the chemical analysis was performed using X-ray spectroscopy of an energy dispersive (EDS). The samples of the new and waste material derived from the refractory lining of the ladle steelmaking performed a qualitative and quantitative analysis of chemical composition by X-ray spectroscopy of an energy dispersive (EDS). Using EDS qualitative analysis can determine what elements are present in the different areas of the sample based on the presence or absence of the characteristic peaks in the spectrum. The purpose of the quantitative analysis is to determine the relationship EDS element content based on the comparison of the peak intensities of the elements in practice. The quantitative analysis of the content of all elements is normalized to 100%. Point analysis was performed for both the chemical composition as well as an analysis of selected areas of the charge.

3. RESULTS AND DISCUSSION

Chemical analysis performed using X-ray spectroscopy with an energy dispersive (EDS) showed in the unused material presence of refractory elements such as C, Mg, O, Al, Ca, Si. Figure 1 shows photomicrographs of the analyzed areas of new refractory materials. Figure 2 presents spectrograms of the analyzed areas of unused refractory materials.
Fig. 1. Photomicrographs of selected areas: A (a), B(b), C(c) of a new refractory materials
Fig. 2. Spectrograms of selected areas: A(a), B(b), C(c) of the analyzed new materials.
Table 1. Area analysis of new refractory materials

<table>
<thead>
<tr>
<th>Area analysis</th>
<th>Chemical composition [% wt.]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>A</td>
<td>65.98</td>
</tr>
<tr>
<td>B</td>
<td>67.42</td>
</tr>
<tr>
<td>C</td>
<td>70.36</td>
</tr>
</tbody>
</table>

Table 2. Point analysis of new refractory materials (area C)

<table>
<thead>
<tr>
<th>Point analysis</th>
<th>Chemical composition [% wt.]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>48.65</td>
</tr>
<tr>
<td>2</td>
<td>93.71</td>
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<tr>
<td>3</td>
<td>36.28</td>
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<tr>
<td>4</td>
<td>72.26</td>
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<tr>
<td>5</td>
<td>88.84</td>
</tr>
<tr>
<td>6</td>
<td>13.79</td>
</tr>
</tbody>
</table>

Fig. 3. Photomicrographs of a new C(a) and used A’ (b) refractory materials with marked analyzed points

Marked points of point analysis are presented in Figure 3a. Chemical composition of analyzed new material are shown in Table 1 and Table 2. Analogous tests have been performed for the used refractory material. The results of which are summarized in Table 3 and Table 4. Photomicrographs of the analyzed areas are shown in Figure 4 and the corresponding
spectrograms are presented in Figure 5. It also provides micrographs of the point analysis of the A’ area (Fig. 3b). Quantitative chemical analysis and EDS new and used materials showed that the chemical composition was different.

Fig. 4. Photomicrographs of selected areas: A’ (a), B’ (b), C’ (c) of a used refractory materials

146
Fig. 5. Spectrograms of selected areas: A′ (a), B′ (b), C′ (c) of the analyzed used materials
The appearance of small amounts of potassium and iron can be observed in the used refractory materials (Tabs 3, 4). Potassium is one of the group of alkaline elements, and its penetration into the structure of the ladle lining accelerates degradation. Alkalis penetrate the crystal lattice of carbon and causes intergranular stress and cracking units. In the test material was not observed the presence of lead and zinc, which also show a destructive effect on the lining of the ladle. The absence of lead, is probably related to the fact that lead is usually collects in the lower part of the furnace or ladle and samples were 1/2 ladle wall height. We currently offer material for steelmaking ladle working lining covers the area of slag products, bath and bed. They are often used magnesia-carbon materials, with small differences in chemical composition depending on the zone. These are products having a low content of fluxes containing carbon, preferably in the form of graphite, which is a component of magnesite is limited by the wetting material and the steel slag [5]. They are becoming an alternative to the existing solutions, which are used in metal products dolomite. Durability of MgO-C lining ladle steelmaking depends on many factors including the capacity of the tank, the composition of the slag and is approximately several melts. In addition to changes in the chemical composition of the used refractory materials is also observed increase porosity of the work within the 9–12% [6].

4. CONCLUSIONS

The research provided information on how to change the concentration of elements in new and used refractory materials. The change in the observed level of concentration does
not limit the use of these wastes in the industrial processes. The Polish metallurgical plants, which produce waste refractories, their selection is made to re-incorporation in thermal devices. Refractory waste that can not be re-built, and the state allows you to use them again in the production of refractory materials are bought by producers and recycled. Refractory waste that can not be reused because of the degree of destruction and slaggling are dumped in landfills. The search for alternative methods of waste management of refractory materials should be taken into account first of all the type and amount of material, the content of the ingredients, impurities, lining life and economic benefits.

Possible directions of disposal of waste refractories are used in the blast furnace process (as a flux), sintering ore, alteration in the oxygen converter, road aggregate, in the production of ferroalloys, tiles, glass, and as a thickener sludge. Consider also the possibility of refractory materials used as fertilizer to fertilize the soil. For this purpose, it would be necessary to conduct further analysis taking into account the diversity of materials, samples from different heights vat and migration of elements.

REFERENCES


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