STUDY OF MEDIEVAL CERAMICS EXCAVATED AT THE MONASTERY OF KARAACHTEKE (VARNA, BULGARIA)

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ABSTRACT

Various medieval unglazed and glazed ceramic artifacts discovered during archaeological excavations at the monastery of Karaachteke near Varna (Bulgaria) are for the first time chemically and structurally characterized by ICP-OES, XRD, SEM-EDS and the Archimedes method aiming to understand the technology of medieval ceramics production.

The unglazed artifacts water absorption ranges from 10 mass % to 15 mass %, which indicates that the ceramics are well sintered and most probably fired at a high temperature, ca 950°C - 1050°C. The artifacts contain a certain amount of coloring oxides (Fe₂O₃ + TiO₂), which determine their slightly red color. The phase composition indicates the presence of crystalline phases of quartz and plagioclase, the amount of which differs in the different samples. SEM proves the presence in the sintered ceramic body of coarse quartz grains having a size of 0.05 mm to 0.3 mm. This leads to the conclusion that highly sandy clay or ceramic body containing red firing clay and coarse grain quartz sand was used.

The study of the glazed artifacts proves that a transparent lead glaze prepared at a firing temperature of ca 950°C - 1050°C was widely used in the Middle Ages. Some of the objects are typical sgraffito pottery, which indicates that the ceramic masters during this period could produce ceramic bodies, engobes and glazes using different raw materials compositions. Other glazed artifacts refer to the type of the famous Preslav ceramics having a white ceramic body and transparent green glaze of the Seger formula PbO.0.16Al₂O₃.2SiO₂ and firing temperature higher than 1000°C.

Keywords: medieval ceramics, SEM, structure, glazes.

INTRODUCTION

The ceramics are the most common and abundant materials found by archaeological excavations. Their chemical and mineral composition, as well as their forms and decorations, are among the main elements of multilateral study which gives information on the organization of production, business and trade relations, cultural influences and differences between regions and ages. The overall knowledge of a ceramic material and its properties requires the identification of the composition-structure-properties relations that are strictly dependent on the technology applied.

Various unglazed and glazed ceramic artifacts found during archaeological excavations at the monastery Karaachteke by Prof. Casimir Popkonstantinov (University of Veliko Tarnovo), Assoc. Prof. Rosina Kostova (University of Veliko Tarnovo) and Valentine Pletnyov (Regional Museum, Varna) in the period from 2011 to 2013 are a subject of the current research. Extensive excavations and research have begun in 1995, and with some interruptions, are continuing today.

The monastery of Karaachteke near Varna (Bulgaria) is one of the largest monasteries at the Balkans. It was discovered at the beginning of the XXth century by the founder of the Bulgarian archeology Karel Shkorpil. The monastery Karaachteke was most probably built at the end of the IXth and the beginning of the Xth century and was inhabited until the XVIIIth century. The ceramics found differ - without ornaments or decorated by reliefs
and parallel or grid cross lines, with green transparent glaze, the so called sgrafito ceramics of the XIIth - XIVth century and such from the Ottoman period - from the XVth to the XVIIIth century. A sign of the intense monastery life refers to the found textured and painted pottery from white clay. Some of the dishes are imported from Byzantium, while other are in the style of the „Preslav painted ceramics“ from the end of IXth and the beginning of the Xth century [1 - 2].

The study of medieval pottery presents a definite interest aiming to meet the level of ceramics development during that period. The authors of this research are experienced in the study of ceramic glazed and bodies, frits and decoration [3 - 10]. They present their results obtained in the study of the chemical and structural characterization of unglazed and glazed medieval pottery found during archaeological excavations at Karaachteke monastery near Varna (Bulgaria).

**EXPERIMENTAL**

The unglazed ceramic artifacts studied are shown in Fig. 1. Those indicated by UG1 are found at a depth of 1,0 m to 1.2 m, those labeled as UG2 are discovered at a depth of 1 m, while other ceramic artifacts, labeled as UG3 and UG4 - at a depth ranging from 0.60 m to 0.80 m. The glazed ceramic artifacts indicated by G1, G2, G3 and G4 are found at a depth of 1 m and are shown in Fig. 2.

The analysis was carried out with the application of (i) ICP - OES following samples dissolution in an acid solution, performance of a classical silicate analysis and alkali fusion; (ii) XRD using XRD Diffractometer "TUR-M62" with CoKα radiation; (iii) SEM using a scanning electron microscope SEM 525 M (Philips) with an energy dispersive spectrometer EDS - EDAX 9900; (iv) the Archimedes method for determination of water absorption of ceramic artifacts.

**RESULTS AND DISCUSSION**

The results from the chemical analysis of the unglazed artifacts composition are given in Table 1. SiO₂ and Al₂O₃ are the most important oxides found in the ceramic body. The slightly red color is determined by coloring oxides (Fe₂O₃ + TiO₂). It is also found that they contain more than 3 mass % alkali oxides like K₂O and Na₂O. The water absorption determined varies from 10 mass % to 15 mass %, which is most probably due to sintering at temperatures ca 950°C - 1050°C. The samples phase composition determined by XRD indicates the presence of crystalline phases of quartz and plagioclase.

<table>
<thead>
<tr>
<th>Artifacts</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>TiO₂</th>
<th>MnO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>SO₃</th>
<th>P₂O₅</th>
<th>LI</th>
</tr>
</thead>
<tbody>
<tr>
<td>UG1</td>
<td>70.55</td>
<td>15.47</td>
<td>5.60</td>
<td>1.43</td>
<td>1.40</td>
<td>0.78</td>
<td>0.05</td>
<td>1.05</td>
<td>2.57</td>
<td>1.38</td>
<td>0.09</td>
<td>0.26</td>
</tr>
<tr>
<td>UG2</td>
<td>70.75</td>
<td>13.57</td>
<td>5.0</td>
<td>1.54</td>
<td>3.14</td>
<td>0.69</td>
<td>0.07</td>
<td>0.74</td>
<td>2.54</td>
<td>&lt;0.03</td>
<td>0.11</td>
<td>1.06</td>
</tr>
<tr>
<td>UG3</td>
<td>66.41</td>
<td>17.54</td>
<td>5.91</td>
<td>1.38</td>
<td>1.65</td>
<td>0.74</td>
<td>0.05</td>
<td>0.73</td>
<td>3.54</td>
<td>&lt;0.03</td>
<td>0.14</td>
<td>1.06</td>
</tr>
<tr>
<td>UG4</td>
<td>65.3</td>
<td>18.56</td>
<td>5.89</td>
<td>1.46</td>
<td>2.05</td>
<td>0.86</td>
<td>0.05</td>
<td>0.83</td>
<td>3.09</td>
<td>&lt;0.03</td>
<td>0.06</td>
<td>1.28</td>
</tr>
</tbody>
</table>
of an amount varying in the different samples (Fig. 3).

The chemical composition and the microstructure of the glazed ceramic artifacts was determined by SEM-EDS. Fig. 4 shows a scanning microscope photograph and local chemical analysis by EDS of the glazed ceramic artifact denoted by G1 in Fig. 2. Coarse quartz grains of a size of 0.05 mm to 0.30 mm, immersed in a sintered ceramic matrix, are clearly visible in the ceramic body. The ceramic matrix contains 35.56 % of Al$_2$O$_3$, 55.49 % of SiO$_2$, 1.69 % of K$_2$O, 1.12 % of CaO, 1.04 % of TiO$_2$, and 5.11 % of Fe$_2$O$_3$. The presence of coloring oxides determines the light red color of G1. These results show that a very sandy clay, which was not apparently digested but used in the form in which it was extracted or passed through a sieve of 0.5 mm, was used. The content of quartz sand grains in the ceramic body results from the presence of a transparent lead glaze having a high thermal expansion coefficient. The glaze chemical composition is as follows: 5.89 % of Al$_2$O$_3$, 28.51 % of SiO$_2$, 0.04 % of K$_2$O, 0.33 % of CaO, 0.93 % of Fe$_2$O$_3$, 64.30 % of PbO. It is most probably obtained using two raw materials: 70 % of PbO and 30 % of clay. It is applied either by dipping the green ceramic body in the glaze followed by single firing or directly to a biscuit ceramic body followed by double firing. The latter is assumed on the ground of its relatively good water absorption, resulting from the ceramic body sintering at ca 950°C - 1050°C. The high content of lead oxide (64.30 %) in the glaze indicates that the temperature of the second glaze firing is lower by 50°C - 100°C and is done in a strongly oxidizing environment, because otherwise it would have been reduced. The oxidizing environment affects the glaze color, which varies from yellowish-brown due to the lead glaze to brick-red which
results from the ceramic body bleed through the glaze.

Fig. 5 shows a scanning microscope image and local chemical analysis of the glazed ceramic artifact designated in Fig. 2 by G2. SEM analysis shows the presence of two layers in the ceramic body - glaze and engobe. There is a relief decoration of dark red lines, while the color of the artifact is yellowish brown. On the ground of visual evaluation and analyses data this artifact is attributed to the typical sgraffito pottery.

SEM study of artifact G2 shows that the ceramic body comprises open pores and grains of quartz, which are smaller compared to those observed in G1. The chemical composition of the ceramic body includes 2.44 % of MgO, 25.95 % of Al$_2$O$_3$, 57.14 %, of SiO$_2$, 3.13 % of K$_2$O, 0.59 % of CaO and 10.75 % of Fe$_2$O$_3$. The ceramic body has a higher content of Fe$_2$O$_3$, compared to that of the engobe and glaze, which explains the dark red color of the relief ornaments. The dark red coloration of the medium layer is determined by an interaction connected with the engobe removal in the course of the manufacture and the direct contact between the reactive lead glaze and the ceramic body. Unlike G1, this artifact shows the presence of engobe, relatively more sintered than the ceramic body. It is composed of MgO (1.24 %), Al$_2$O$_3$ (34.06 %), SiO$_2$ (50.52 %), K$_2$O (6.70 %), CaO (2.63 %), Fe$_2$O$_3$ (2.71 %), TiO$_2$ (1.29 %), PbO (0.85 %). It can be argued that it is composed of fireclay, potassium feldspar, quartz sand and dolomite as the recipes to prepare ceramic bodies and glazes were known during this period of ceramic development. The role of the engobe is to cover the ceramic body preventing the reaction between the glaze and the ceramic body or to control this reaction when required to provide decorative ornaments of a specific color. The lead glaze is transparent of the Seger formula PbO.0,13Al$_2$O$_3$.1,3SiO$_2$ and firing temperature of 940°C -960°C. Such ceramics can be produced by a single firing or by double firing [9, 10].

SEM of glazed ceramic artifact G3 /Fig. 6/ with white ceramic body and green transparent glaze shows that this artifact is also glazed by typical lead glaze of the following chemical composition: Al$_2$O$_3$ (3.99%), SiO$_2$ (33.89%), K$_2$O (0.10 %), CaO (0.23 %), Fe$_2$O$_3$ (0.55 %), PbO (61.25%). The composition of the ceramic body reveals that it is prepared from quite pure white fireclay, possibly washed, which requires a high firing temperature. The ceramic body has closed pores and water absorption
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of 15.0 %. The lead glaze is transparent of the Seger formula PbO.0,16Al₂O₃.2SiO₂ and firing temperature above 1000°C. Apparently this ceramic artifact belongs to the famous Preslav ceramics.

SEM of the glazed ceramic artifact (labeled as G4 in Fig. 2) of a red ceramic body, green glaze and black lines ornaments is presented in Fig. 7. It is seen that it contains glaze, engobe and ceramic body. This artifact is peculiar because the black decorative ornaments are made by engraving the body after the engobe application which results in engobe absence between the glaze and the body and besides determines the higher thickness of the glaze. Furthermore, the direct contact between the reactive lead glaze and the ceramic body containing Fe₂O₃ at a concentration of 10 mass % explains the black color obtained. This is shown in Fig. 7. SEM shows more porous engobe (of a chemical composition of 1.02 % of MgO, 16.52 % of Al₂O₃, 62.81 % of SiO₂, 5.77 %, of K₂O, 4.84 %, of Fe₂O₃, 1.29 % of TiO₂ and 9.04 % of PbO) when compared to the ceramic body, which is more sintered. The recipe composition of the engobe includes quartz sand and potassium feldspar PbO in addition to clay, as most probably the engobe is only homogenized but not ground. The reaction between the glaze and the engobe gives green color usually obtained under reducing conditions. The latter are provided in this case by Fe₂O₃ content. The glaze has the Seger formula PbO.0,15Al₂O₃.1,9SiO₂ and firing temperature 1000°C - 1020°C [9, 10].

Fig. 8 shows the chemical composition of the interface between the engobe and the glaze, the chemical composition of the black line, the chemical composition of the interface between the black line and the ceramic body and the chemical composition of the glaze. The areas near the contact between the engobe and the glaze, as well as between the glaze and the ceramic body are studied by SEM - EDS. It is found that the chemical components migrate in both directions. The lead from the glaze enters the engobe and body, while K, Ca, and Fe dissolve in the reactive lead glaze.

CONCLUSIONS

Unglazed and glazed medieval ceramic artifacts from the monastery Karaachteke (Varna, Bulgaria) are chemically and structurally analyzed by ICP-AES, XRD and SEM-EDS aiming to estimate the level of
medieval ceramic manufacturing. It is found that SiO$_2$ and Al$_2$O$_3$ are the main oxides in the ceramic body of the medieval pottery. The artifacts contain also a certain amount of coloring oxides (Fe$_2$O$_3$ + TiO$_2$), which determines the slightly red color. The water absorption of the medieval pottery is in the range of 10 - 15 mass %, which provides the assumption that the artifacts are well sintered, probably at high temperatures of ca 950°C - 1050°C. The phase composition study shows that quartz and plagioclase are present in amounts which differ in the samples investigated. SEM proves the presence of coarse quartz grains of a size of 0.05 mm to 0.3 mm in a sintered ceramic body. This leads to the conclusion that either highly sandy clay or ceramic body, consisting of red firing clay and quartz sand of dimensions of 0.05 mm to 0.3 mm were used. Thus a high thermal expansion coefficient of the ceramic body is obtained in the course of firing which is in fact required for the coordination with the transparent lead glaze.

The study of the glazed artifacts indicates that transparent lead glaze with firing temperatures ca 950-1050°C is widely used in the Middle Ages. The sintered ceramic body is obtained using clay of a high Fe$_2$O$_3$ content, quartz sand and potassium feldspar. It is concluded that the glazed artifacts G2 and G4 are typical sgraffito pottery. This indicates that the ceramic masters in the middle ages knew how to make ceramic bodies, engobes and glazes from compositions containing different raw materials.

It is proven that artifact G4 is of the type of the famous Preslav ceramics with a white ceramic body and transparent green glaze of the Seger formula PbO.0,16Al$_2$O$_3$.2SiO$_2$ and a firing temperature higher than 1000°C. It is found that the chemical elements are migrating in both directions within the contact layers between the engobe and the glaze as well as between the glaze and the ceramic body. Pb from the glaze enters the engobe and the body, while K, Ca, and Fe dissolve in the reactive lead glaze.

REFERENCES