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Fractographical Characteristic of Admixtures in Medieval Pottery

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Abstract

The principal aim of the investigations described in the paper was to characterize the structure of fragments of ceramic vessels found in the region of Wyszogród, Poland, and dated from 7th to 9th century. The ceramic fragments were examined by optical and scanning electron microscopy. The material was subjected to qualitative and quantitative analyses. The qualitative description included the identification of the kind of admixtures, determination of their distribution and description of the structure of the ceramic matrix. This was done using fractographic examinations of vessel fractures which permitted identifying the shape, color, and admixture distribution, and also enabled us to observe the structure of the ceramic matrix in particular cracks and delaminations. The quantitative analysis consisted of the measurements of the size of the admixtures. Observations combined with a point analysis of the chemical composition performed in a scanning electron microscope supplemented the examinations of the kind and structure of the admixtures. The admixtures were characterized using the methods of quantitative description.

Keywords: Pottery, Fractographic examination, Clay

CHARAKTERYSTYKA FRAKTOGRAFICZNA DOMIESZEK W ŚREDNIOWIECZNYCH WYROBACH GARNCARSKICH

Głównym celem badań opisanych w artykule była charakterystyka budowy odłamków naczyń ceramicznych znalezionych w okolicach Wyszogrodu w Polsce, datowanych na VII-IX wiek. Odłamki ceramiczne badano za pomocą mikroskopu optycznego i elektronowego mikroskopu skaningowego. Materiał był przedmiotem analizy jakościowej i ilościowej. Opis jakościowy obejmował identyfikację rodzaju domieszek, oznaczenie ich rozkładu oraz opis budowy osnowy ceramicznej. Zrealizowano to za pomocą badań fraktograficznych odłamków naczyń, które pozwoliły na identyfikację kształtu, barwy i rozkładu cząstek domieszki, a także umożliwiły obserwację budowy osnowy ceramicznej, a w szczególności pęknięć i rozwarstwień. Na analizę ilościową składały się pomiary rozmiaru cząstek domieszek. Obserwacje połączone z analizą punktową składu chemicznego, przeprowadzone za pomocą elektronowego mikroskopu skaningowego, uzupełniły badania rodzaju i struktury domieszek. Domieszki charakteryzowano przy użyciu metod opisu ilościowego.

Słowa kluczowe: wyroby garncarskie, badanie fraktograficzne, glina

1. Introduction

Ceramic materials, including clay, have been known and used for making various products and vessels of everyday use for hundreds of years. Ceramic potteries are artifacts of the past found in great numbers at archeological sites. Among relics of the early Middle Ages, the ceramic pottery is often the dominant or even sole archeological find [1]. Investigations of archeological ceramic vessels give us certain knowledge about the way our ancestors lived, the materials they used, and the techniques they employed for making ceramic products. In addition to the knowledge of ancient technologies of vessels we can also answer some questions concerning the civilization and culture in those years, and even the origins of old tribes.

Archeologists use the age of the discovered ceramics for determining the age of other finds. The knowledge of the structure and mineral composition of archeological artifacts permits their dating more precisely.

Studies on archeological ceramics are also important for materials engineering. They deliver valuable information about the material, its structure and minerals used as admixtures, and also about the changes the material underwent during hundred years it stayed in the soil. On the other hand, materials engineering with its research techniques provides useful tools for examining archeological objects, including products made of clay.

The techniques used for examining archeological ceramics include, for example, optical microscopy [2, 3], scanning electron microscopy (SEM) [2], transmission electron microscopy (TEM) [4], Mossbauer spectrometry [5], and X-ray diffraction [6].

Archeological objects to be examined in the present study were found in the Wyszogród region in Poland. During the archeological excavations conducted in this region, archeologists found various fragments of clay vessels [1].

Early-medieval ceramic vessels were made using classic technique, *i.e.* by mixing appropriate raw materials, placing the mixture in a mould, drying it and, finally, firing (once or many times). The main raw material was clay, often added the second phase (mineral admixtures like sand, debris) in order to reinforce the structure. The vessels were hand-shaped from clay ribbons and rolls. After drying they were fired in a bonfire. The debris was prepared from naturally crumbled granites, sand or gravel, or by grinding or hammering eroded or burned out stones [7].

The mineral admixtures were added to clay in order to improve its properties. For example, an addition of sand increased the resistance of the vessel to elevated temperatures. Additives could also make the mixture more fatty or lean. A lean mixture absorbs less water, and thereby facilitates and shortens drying and firing. The debris, on the other hand, permits the firing temperature to be lowered [8].

Some of the second phases observed in the clay matrix are also common impurities, which left after the process of the vessels forming. Their existence could be an evidence of using local source. The present paper is the part of the work, whose aim is to adapt the methods and techniques of characterization microstructure and properties of materials used in materials science and engineering to archeological artifacts. Especially, for archeologists knowing the minerals, which were added intentionally or left as impurities, could help to conclude about the clay source region, and as a consequence about the trade exchange or migration of our ancestors.

2. Examination methods

The investigations began with macroscopic observations of the ceramic vessels, first with the naked eye and then with a stereoscopic microscope (FUTUR TECH 3E) at a low magnification. The aim was to find differences in the color of the clay matrix, to distinguish the admixtures, and to estimate the roughness of the surface.

The next stage included a microscopic analysis of selected fragments of the vessels, such as fractures left after chipping and selected smooth surfaces, using a Hitachi-S3500N scanning electron microscope. We also examined the chemical composition in certain points of the clay matrix and in places where admixtures had been identified. The macro- and microscopic photographs were used for determining the size of the additives, the measure being taken to be their average chord [9].

3. Results and discussion

Since admixtures, *i.e.* foreign particles added purposely to the basic material (clay), are important components of the structure of ceramic vessels, our attention was focused on their observations and attempts to identify them basing on their shape, color and size.

Macroscopic observations revealed additives with sizes above 0.1 mm and larger. Smaller admixtures could only be found at larger magnifications using a scanning electron microscope. Table 1 gives the average chords of the admixtures determined by macroscopic observations and identified in the scanning electron microscope. Fractographic examinations revealed differences in shape, color and morphology of the admixtures.

It appeared that the admixtures that predominated in the samples examined were of two kinds. The admixtures of the first kind have spherical or irregular shapes and are brick-red in color. In many cases, the color of the admixtures is non-uniform, in certain places, as is the case e.g. in sample N3, it is light-gray with a fatty luster. The size of these admixtures ranges from 0.5 to 4 mm.

Basing on literature data [10] we may suppose that the admixtures found in this sample are plagioclase ($Na[AlSi_3O_8]$) or lepidocrocite ($FeO[OH]$). This is not, however, certain since other minerals, such as quartz (SiO_2) or barite ($BaSO_4$+[Cu,Sr]), look in a similar way and, thus, the precise identification is difficult [11].

The other group of characteristic admixtures contains transparent, colorless particles with a glassy luster (Fig. 2). These admixtures are especially numerous in samples N1 and N4. In sample N1, their size ranges from 0.1 to 1 mm, and in sample N4 – from 0.5 to 2.0 mm.

The lack of color, transparency and glassy luster suggests that these admixtures are quartz. Again, however, it cannot be taken to be sure since the appearance of muscovite $KAl_2[(OH,F)_2/AlSi_3O_{10}]$ is similar [10, 11].

Table 1. Size, color and shape of the admixtures.

Sample	Average size (stereographic microscope) [mm]	Size spread (stereographic microscope) [mm]	Average size (SEM) [mm]	Size spread (SEM) [mm]	Color and shape
N1	0.55	0.1 – 1	0.25	0.005 – 0.3	Transparent, grayish white, spherical and irregular
N2	2	1 – 3	0.1	0.04 – 0.1	Grayish white, transparent, brick-red
N3	2.25	0.5 – 4	0.5	0.01 – 1	Transparent, brick-red in color, spherical
N4	1.25	0.5 – 2	0.1	0.01 – 0,2	Transparent, irregular
N5	2	1 – 3	0.2	0.1 – 0,2	Transparent, spherical
N6	2.05	0.1 – 4	0.01	~0.01	Transparent, irregular
N7	0.55	0.1 – 1	0.3	0.01 – 0.5	Brick-red, transparent, spherical, irregular
N8	1.25	0.5 – 2	0.5	0.5	Grayish white, irregular
N9	1.5	1 – 2	0.5	0.02 - 1	Brick-red, transparent, irregular

a)

b)

Fig. 1. Macroscopic observations of sample N3: a) magnification 7x, and b) magnification 20x.

The clay matrix of the ceramic vessel material was also examined. It has been found that its structure is laminar, which is characteristic of the manual technique of making ceramic pottery. We also found delaminations and cracks that surrounded the matrix. These are the evidence that the bond between the admixtures and the matrix is weak.

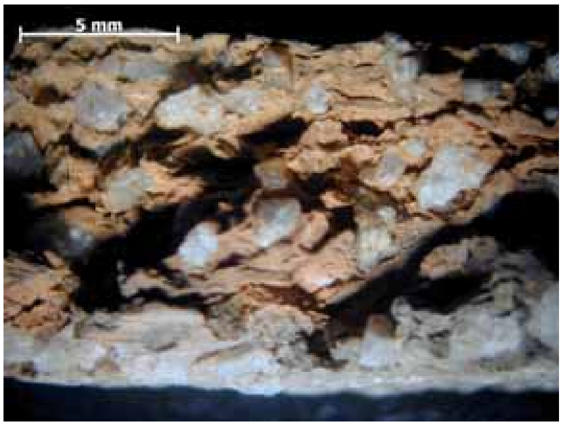
Examinations in a scanning electron microscope combined with an analysis of the chemical composition were conducted at selected places of the matrix and in certain regions of admixtures. The chemical composition was examined in the admixtures sized from 50 to 100 μm, since these constituted the most numerous group. The chemical analysis was performed by the EDS method and showed that the main component of the admixtures was silicon. A SEM image of such an admixture and the results of the chemical analysis are shown in Fig. 3. The percent contents of the individual elements are given in Table 2.

We may suppose from the spectrum of Fig. 3b that the predominant admixture in this micro-region is silicate. This is confirmed by the high intensity of the peaks from the lines Si-K and O-K. The spectral analysis also reveals the presence of Fe, Al (lines Fe-K and Al-K) and vestigial amounts of Na, Mg, P, Cl, Ca and Ti.

In a few samples, SEM examinations identified admixtures with a characteristic white color (high contrast) and a size of 100 μm. The chemical analysis has shown that they contain great amounts of iron. A SEM image of such an

a)

b)



c)

d)

Fig. 2. Macroscopic observations of the samples: a) N1 magnification 7x, b) N1 magnification 20x, c) N4 magnification 7x, d) N4 magnification 20x.

admixture found in sample N9, and the spectrum of elements taken at point 1 on the surface of this sample are shown in Figs. 4a and 4b, respectively. The percent contents of the individual elements present in this micro-region are given in Table 3.

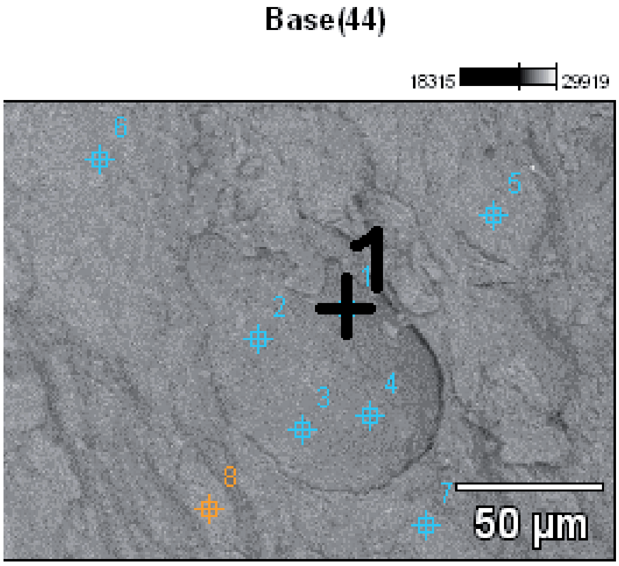


Fig. 3a. Image of a micro-region on the surface of sample N4; chemical analysis made at point 1.

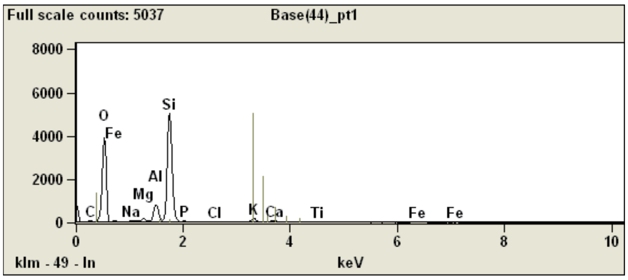


Fig. 3b. Spectrum of the elements present in the micro-region examined (point 1 in Fig. 3a).

Table 2. EDS results obtained from a micro-region on the surface of sample N4.

Element	Concentration [wt%]
O – K	56.02
Na – K	0.36
Mg – K	0.54
Al – K	4.11
Si – K	29.82
P – K	0.36
Cl – K	0.17
K – K	2.53
Ca – K	1.82
Ti – K	0.50
Fe – K	3.78

We can see from the above examinations that the micro-region examined contains a mineral admixture with a high content of Fe, which is confirmed by the high intensity of the peak from the line Fe-K. We also observe here traces of Al, K, Ca and Mn. Judging from the presence of Fe, this admixture may be magnetite or hematite [10, 11].

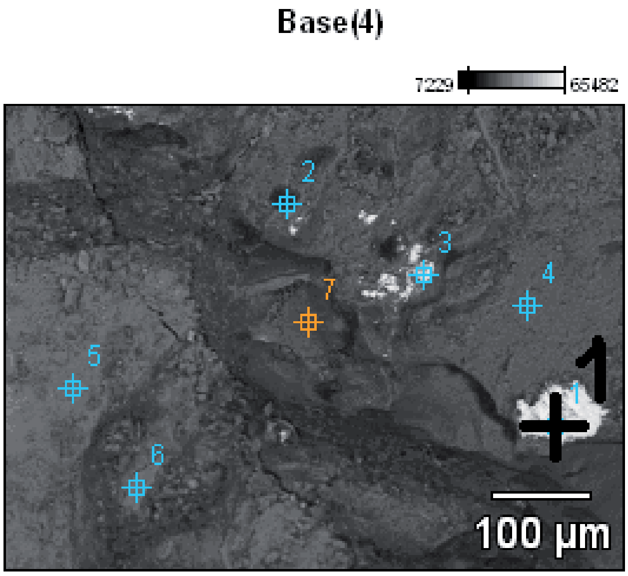


Fig. 4a. Image of a micro-region selected on the surface of sample 9; chemical analysis performed at point 1.

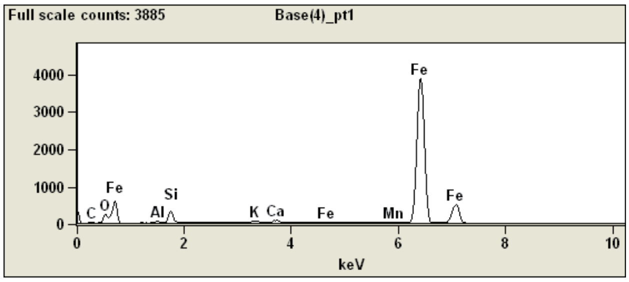


Fig. 4b. Spectrum of the elements present in this micro-region (made at point 1 in Fig. 4a).

Table 3. EDS results obtained for the micro-region shown in Fig. 4a (sample N9).

Element	Concentration [wt%]
O – K	7.70
Al – K	0.69
Si – K	3.20
K – K	0.27
Ca – K	0.55
Mn – K	0.66
Fe – K	86.93

4. Summary

The results of macro- and micro-examinations of fragments of ancient ceramic vessels, presented in this paper, were obtained during the first cycle of comprehensive studies which have been initiated in co-operation between the Institute of Materials Engineering, Warsaw University of Technology, and the Institute of Archeology and Ethnology, Polish Academy of Sciences.

The studies performed so far have proved a high usefulness of fractographic examinations for investigating archeological objects. These examinations, conducted at various magnifications, beginning with observations with the naked eye and ending at analyses of images magnified several hundred times, permit us to reveal the structure of the clay matrix and to characterize the admixtures introduced into it, intentionally or left in the pottery as impurities which were not removed during the sintering.

In view of their highly varied structures, sizes and shapes, the admixtures can be identified using both stereoscopic microscopy and scanning electron microscopy. The two methods are complementary to one another and both should be used when the identification of the admixtures with particularly varied sizes is concerned. Stereoscopic microscopy is a very useful tool for identification of various mineral admixtures, since it permits determining their color which often varies within the body of a given admixture. In a scanning electron microscope, on the other hand, differences between the kinds of admixtures are represented as the differences in contrast. In addition, the point chemical analysis permits identifying the elements present in a given admixture. It should however be noticed that many minerals which commonly occur as admixtures show similar features as to the structure, color and content of elements. This makes their unequivocal identification very difficult.

The clay matrix of the ceramic vessels examined was found to be laminar, which is typical of hand-made products. A characteristic delamination between the matrix and the admixtures was also observed. In all the nine samples taken from various vessels but found at the same archeological site, the structures of both the clay matrix and admixtures have very similar features. It should be noted that, even though the vessels were discovered at the same archeological site, they were found at various depths, which means that they should be dated from different time periods (7th to 9th century). Nevertheless, the methods of preparing the ceramic mass and the production technique were similar.

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