A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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ANALYSIS OF THE STRUCTURE OF ARCHEOLOGICAL OBJECTS – CERAMIC POTTERY

ANALIZA STRUKTURY OBIEKTÓW ARCHEOLOGICZNYCH – NACZYŃ CERAMICZNYCH

The aim of the present study was to check whether the research methods used in materials engineering could be useful for examining archeological ceramic pottery. The experiments were conducted with the use of stereoscopic microscopy, scanning electron microscopy, and optical profilometry. The examined material included pieces of the archeological clay vessels excavated from various sites and dated at two various historical periods. The first group includes samples from the 5^{th} century B.C. from Biehla (Germany) and Starosiedle (Poland), the second group consists of fragments of vessels of the 10^{th} century A.D. from Starosiedle (Poland) and Rosenhof (Germany). The structure of the matrix and the mineral admixtures distributed throughout it were analyzed on the cross-sections of the archeological material. The examinations were performed using the fractographic method and optical profilometery, which permitted determine the shapes and morphology of the admixtures, examine their embedding in the matrix material (clay), and also revealing possible layers or delaminations within the matrix.

Keywords: pottery, clay, admixtures, stereoscopic microscopy, optical profilometry

Głównym celem pracy przedstawionej w artykule było wykorzystanie metod badawczych stosowanych w inżynierii materiałowej do badania ceramiki archeologicznej. Do badań zastosowano mikroskopię stereoskopową, skaningową mikroskopię elektronową oraz profilometrię optyczną. Materiałem do badań były fragmenty glinianych naczyń archeologicznych pochodzących z różnych okresów historycznych i z różnych miejsc, odpowiednio: Biehla i Starosiedle – V w. p.n.e.; Starosiedle i Rosenhof – X w. Analizie poddana była budowa osnowy oraz rozmieszczone w niej domieszki mineralne. W tym celu zastosowano badania faktograficzne i badania przy użyciu profilometru optycznego powierzchni płaskich powstałych w wyniku cięcia materiału archeologicznego. Badania te pozwoliły na obserwację kształtu, morfologii domieszek, a także stopnia „obtoczenia" ich przez materiał osnowy – glinę, oraz obecności warstw i rozwarstwień w osnowie.

1. Introduction

Ceramic has been known to man since the beginnings of the earliest civilizations. The wide application range of this material was due to the easy access to the raw material, i.e. clay and to its advantageous properties. Vessels made of clay have been commonly used in households almost to the present times, and this is the reason why they are found abundantly at archeological sites [1]. Ceramic products undergo no structural changes during many-year exposure in the soil, thus, they are useful for reconstructing ancient cultures and technologies [2]. Thanks to their durability, pieces of clay vessels have become a useful tool for dating other archeological objects [3].

Archeological ceramics is also an interesting object for materials engineers. Fragments of clay vessels may be considered to be simple composite materials where the clay is the matrix, and the debris, sand or straw are fillers called admixtures by the archeologists. Intentionally added to the thick clay grains of sand, rubble stone, ground bones or fragments of pottery hereinafter referred to as admixture. However, clay also contains in its composition to the minor minerals, which the tests shall also be treated as an admixture.

For decorative purposes, the manufacturers of ancient vessels often embellished them by covering their surfaces with various patterns. These ornaments were most often in the form of lines or grooves made with simple tools. Important features to be examined are the condition of the surface of the vessels, the structure of the matrix, the kind and chemical composition of the admixtures, and also their bonds with the matrix. Thanks to the knowledge of the structure of ancient everyday vessels, we can know how our ancestors managed with the technological problems.

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Among the various techniques used for examine archeological ceramics optical microscopy [4], X-ray diffraction, scanning electron microscopy [5], and spectroscopy (including infrared spectroscopy) can be bentioned [6].

The examinations reported in the present paper were realized in co-operation between employees of the Materials Engineering Department, Warsaw University of Technology, and the Institute of Archeology and Ethnology, Polish Academy of Sciences.

The examined materials were fragments of ceramic vessels found at various sites (Starosiedle, Biehla, Rosenhof) dated at various centuries (5th century B.C., and 10th century).

The aim of the studies was to check the usefulness of various research methods employed by materials engineers for characterize the structure of clay vessels pieces. Results obtained with permit to get knowledge about the technology and origins of the raw materials, to estimate the similarities between the manufacturing methods used during the past years, and to verify some archeological hypotheses. For example, from the technological point of view for archeologists is important to knows if the pottery was made by hand, wit or without using pottery wheel. However, this article is not geared to prove special hypotheses but identify the research methodology helpful in studies of archaeological ceramics. The examination methods employed in the present study included macroscopic examinations i.e. observations with the naked eye and in a microscope at low magnifications, and then, observations at higher magnifications using electron scanning microscopy. The surface topography was analyzed too.

2. Materials and methods

The materials examined were fragments of archeological ceramic vessels found during archelogical excavations at various sites. Found fragments of ceramic vessels from two different places and periods, respectively: 5th century B.C. – Biehla (Germany) and Starosiedle (Poland), and 10th century A.D. – Rosenhof (Germany) and Starosiedle (Poland).

The examinations started from macroscopic observations with the naked eye and using FUTURE TECH 3e and Olympus SZX10 stereoscopic microscopes at a low magnification (20-25x). The aim was to find the differences in the color of the clay matrix and mineral admixtures, in the shape and size of the admixtures and their distribution, and also to estimate the roughness of the sample surface. Then the samples were examined (30-1200x) using a HITACHI 2600N scanning electron microscope, which permitted us to identify the fine admixtures invisible during the macroscopic observation, to estimate the degree in which the mineral particles were embedded by the clay, and also to observe in fractographical terms the clay matrix. In addition to the microscopic observations, a point chemical analysis of the admixtures and matrix was performed. The roughness, admixture distribution and decorations present on the outer surfaces of the samples were examined on cross-sections of the samples (obtained by cutting out a piece of the vessel fragment examined) using a WYKON NT 9300 optical profilometer.

3. Results and discussion

Important components of the structure of clay vessels are mineral admixtures purposely added into the clay matrix in order to improve its properties. The macro- and microscopic observations performed revealed how the admixtures were diverse. As an example, Fig. 1 shows photographs of the structure of the ceramic vessel fragments with visible admixtures.

The admixtures differ in shape, color, and size (Fig. 1). The differences of color and shining of admixtures are visible in stereoscopic microscope. However, because of the black and white photographs are presented, admixtures with characteristic features are marked on figures by arrows. The most frequently occurring admixtures, found in all the samples examined, are colorless and vitreous (Fig. 1). Vitreous admixtures are especially visible in Fig. 1A (indicated by the arrow in Fig. 1A) The samples excavated at Biehla (5th century B.C.) contain large brick-red admixtures (indicated by the arrow in Fig. 1B). The samples from Starosiedle (10th century A.D.) contain admixtures of various colors, e.g. black with the metallic luster (indicated by the arrow in Fig. 1C). All the samples examined contain aglomerates of various minerals differing in color (Fig. 1D).

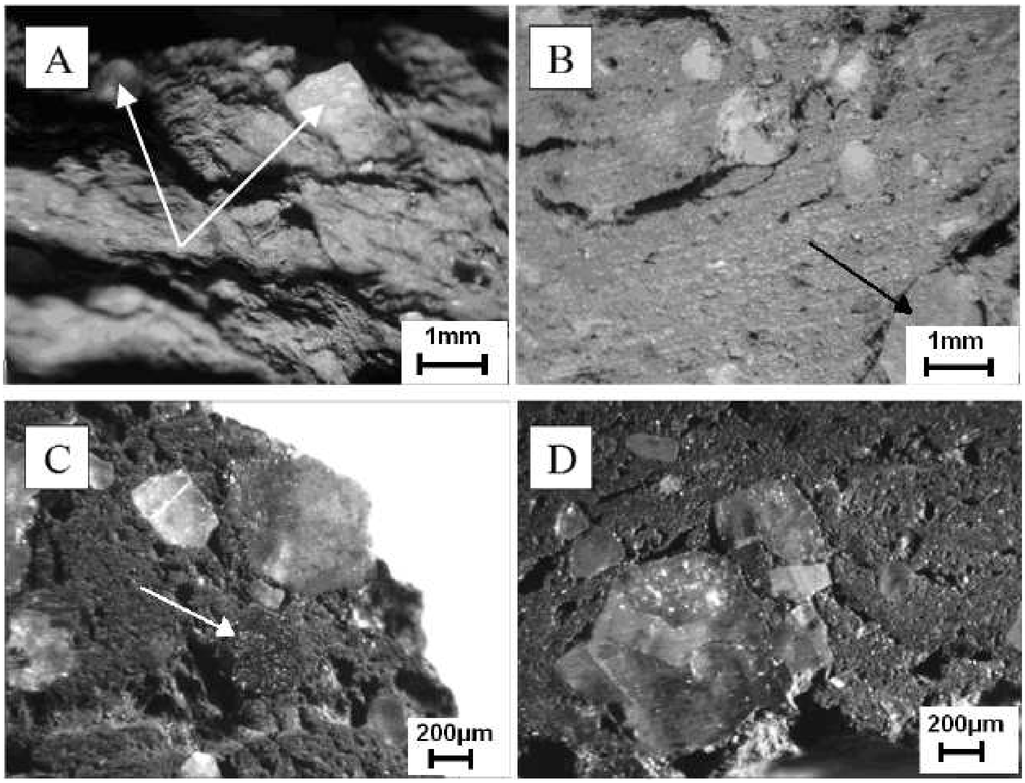

Fig. 1. Stereoscopic microscope image of the vessels pieces: A) Starosiedle (5th century B.C.), magn.20x (vitreous admixtures); B) Biehla (5th century B.C.), magn.20x (brick – red admixtures); C) Starosiedle (10th century A.D.) – magn.25x (black with metallic luster admixtures); D) Rosenhof (10th century A.D.), magn.25x (agglomerates of various minerals differing in color).

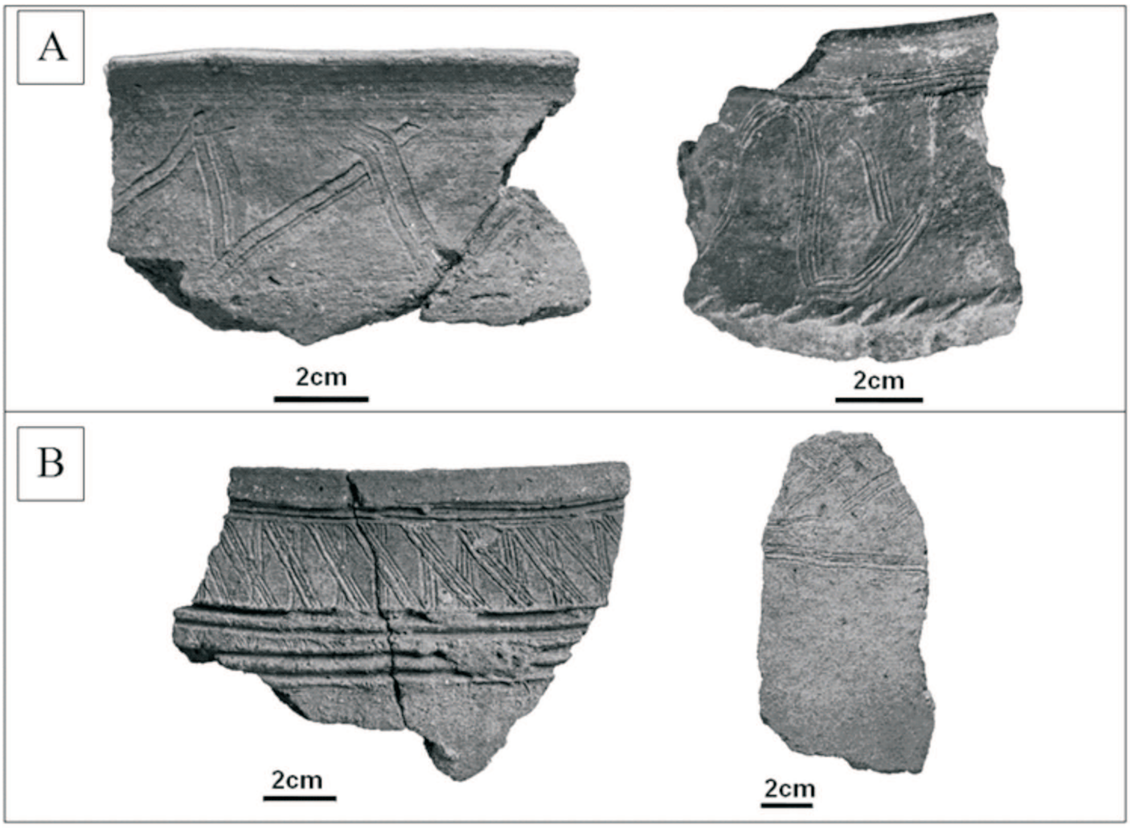

Fig. 2. Macroscopic photographs of fragments of the ceramic vessels: A) samples found in Starosieldle (10th century A.D.); B) samples found at Rosenhof (10th century A.D.)

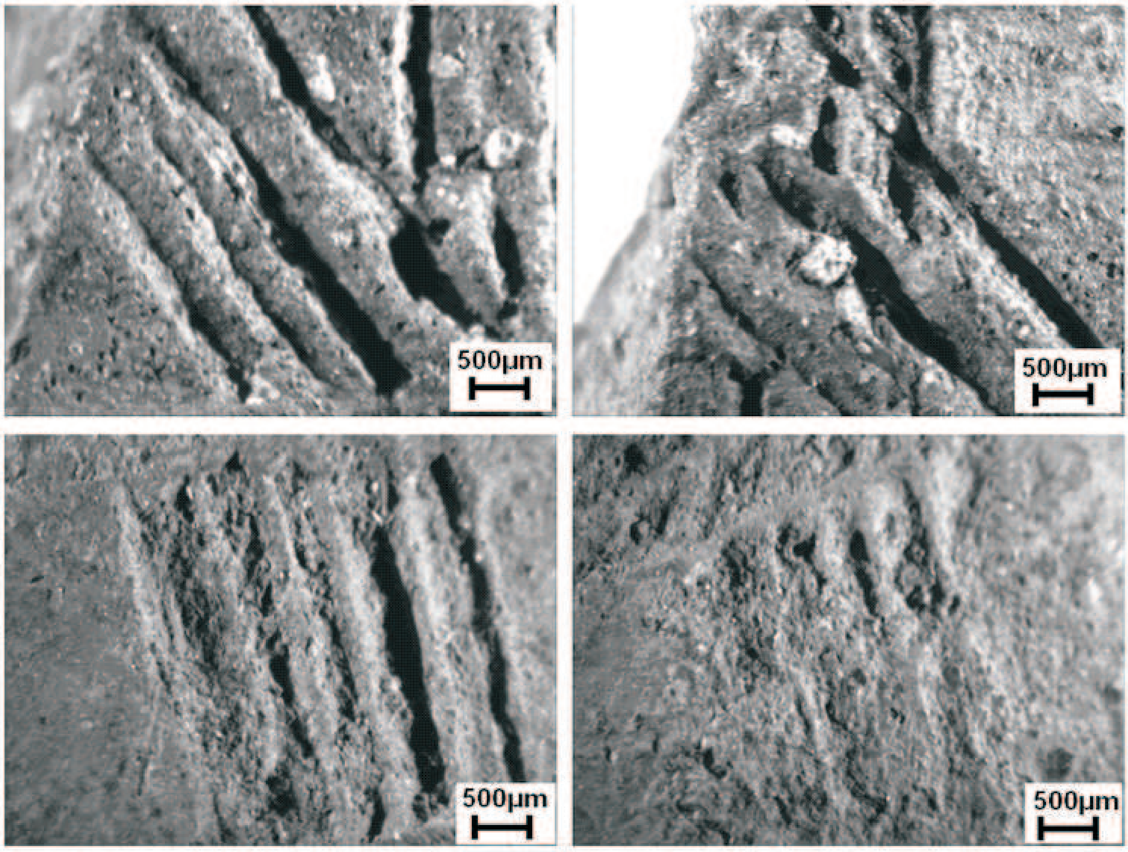

Fig. 3. The surface of a vessel found at Rosenhof (10th century A.D.), stereoscopic microscope image, decorative ornaments visible

The samples from the 10th century A.D. are embellished with ornaments and other decorations. In our study we examined these adornments using a digital camera and a stereoscopic microscope (Figs. 2 and 3). We can see from the macroscopic observations that the ornaments have various forms: wavy lines (Fig. 2A), deep grooves irregularly spaced (Fig. 2B), finger-made cavities, and zigzag lines (Fig. 2). Observations at greater magnifications using a stereoscopic microscope confirm that these ornaments were made with simple tools such as small sticks or just fingers.

SEM examinations permitted us to observe the admixtures of the various kinds, shapes, and sizes (Figs. 4-7).

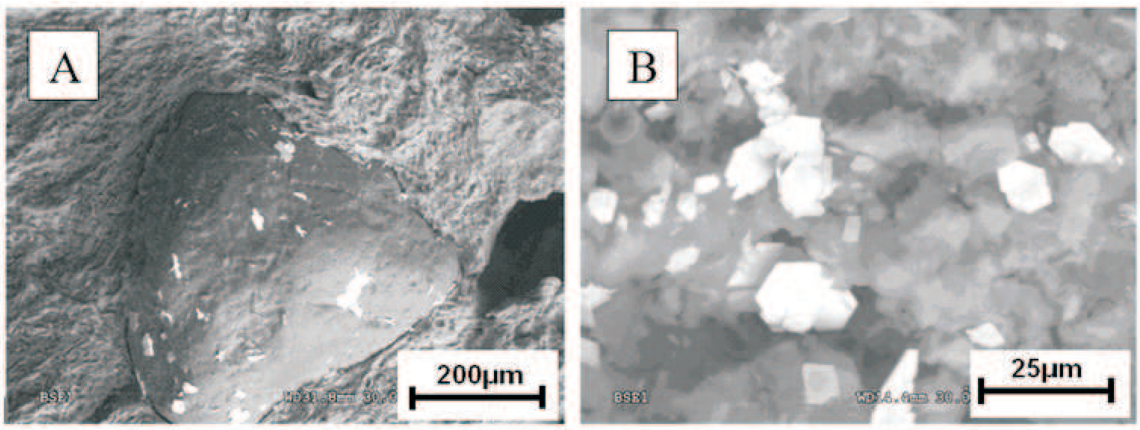

Fig. 4. Samples from Starosiedle (5th century B.C.): A) large admixture with a rounded shape; B) small admixtures with sharp edges; the lamellar structure of the admixtures are visible

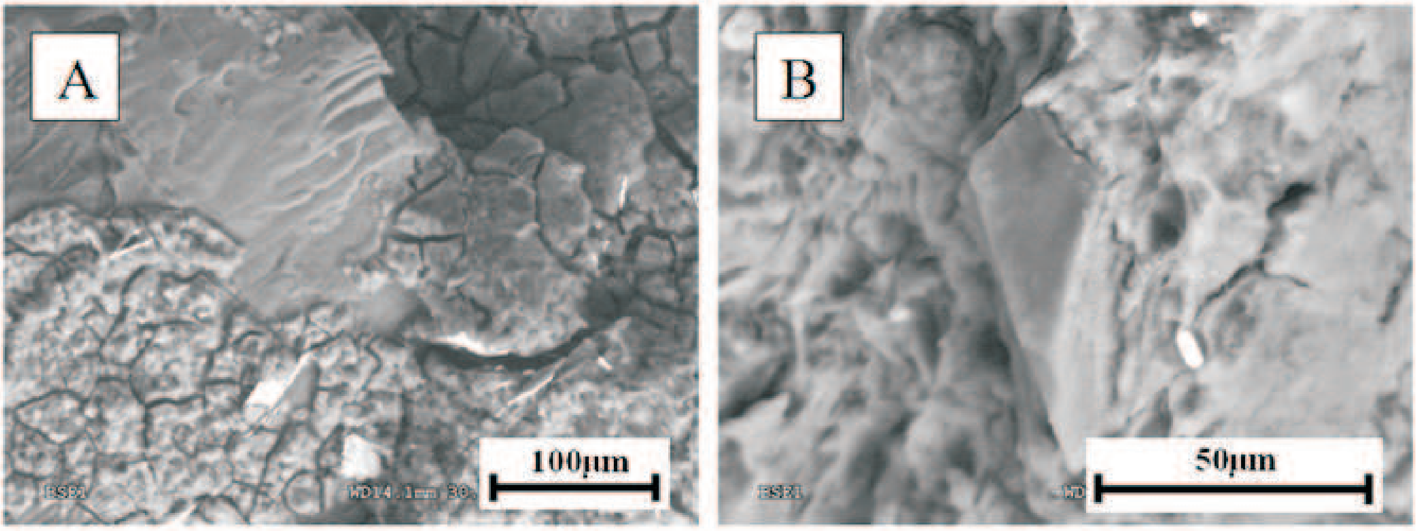

Fig. 5. Samples from Biehla (5th century B.C.): A) small admixture with step-like jumps, B) small sharp-edged admixture

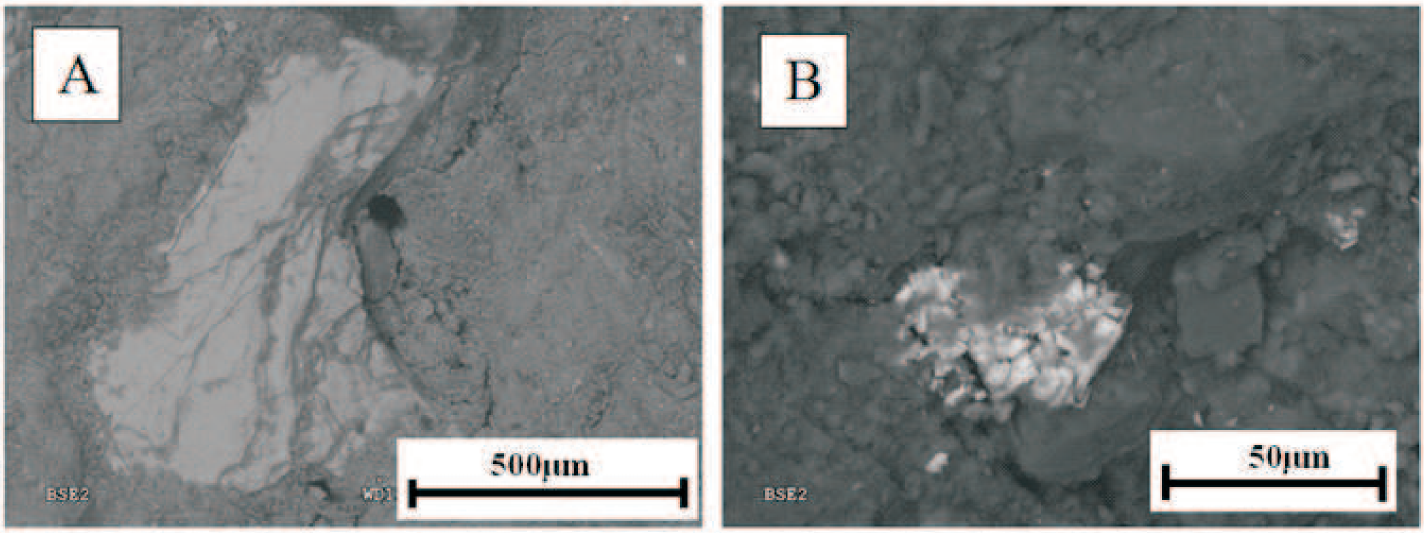

Fig. 6. Sample from Starosiedle (10th century A.D.): A) large admixture with step-shaped cracks, B) agglomerate of small admixtures

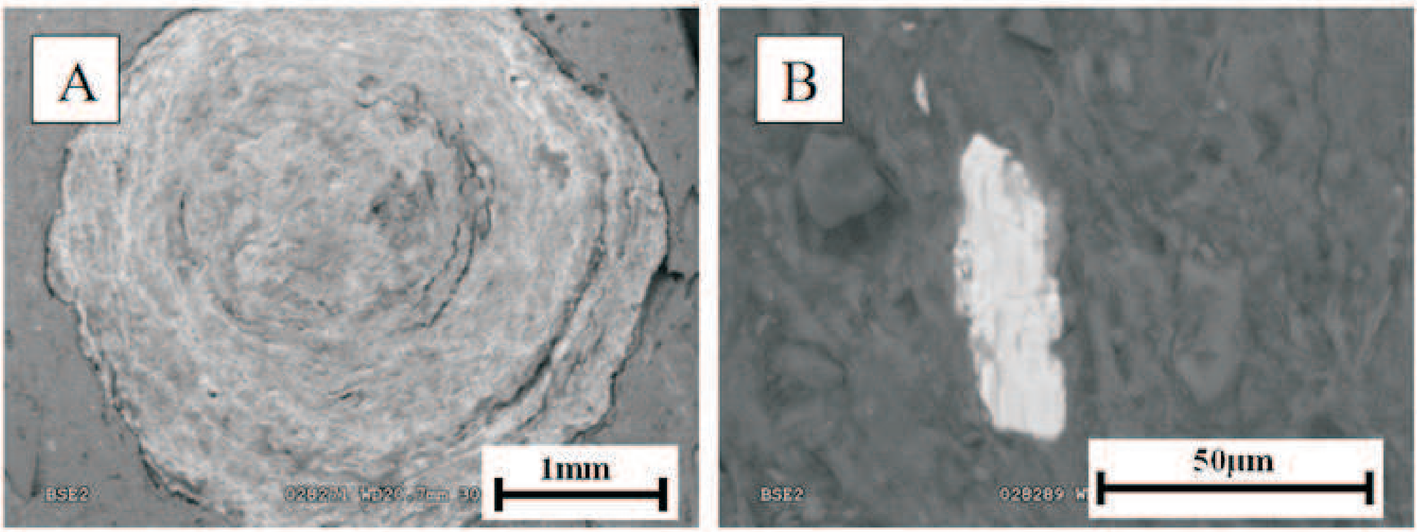

Fig. 7. Samples from Rosenhof (10th century A.D.): A) large spherical admixture, B) elongated rounded-edge admixture

As shown by SEM results, the size of the admixtures ranges from 3mm to 3μm (Figs. 4-7). Their shapes greatly vary from spherical (Fig. 7A), thorough irregular, to elongated with rounded edges (Fig. 7B). We can also see fine particles which concentrate to form agglomerates (Figs. 4B and 6B). The structure of the matrix and admixtures is similar in all the samples examined, irrespective of their age (5th B.C. or 10th A.D.), see Figs. 4-7. In all the samples the matrix has a lamellar structure. Most of the admixtures are weakly embedded by the matrix, which can be inferred from the delaminations observed at the admixtures/matrix interfaces.

The diversity of the chemical composition of the admixtures is reflected by the varied contrast of their images, and is confirmed by the results of the EDS examinations.

The chemical composition, i.e., the identification of the elements present in the mineral admixtures and in clay, was examined within the matrix and the admixtures by a point analysis in a scanning electron microscope. Taking into account the possible errors inherent in the EDS X-ray microanalysis such as a contamination with carbon which reduces the intensity of X-ray radiation from the elements examined [7], we identified the elements present in the samples and estimated their proportions. An example of such an analysis is shown in Fig. 8.

Within the region examined (Fig. 8A) we can see a spherical admixture with a diameter of about 300μm. The chemical analysis has shown that it contains a great amounts of silicon (high intensity of spectral lines), iron (>9wt%), oxygen, aluminum (>8wt.%), and also other elements such as potassium and magnesium, which may indicate an admixture of the mica group. However, there is no enough evidently proof of exact type of mineral.

The topography of the surface of the samples, within the regions of admixtures and decorations, was examined using an optical profilometer.

Fig. 9 shows a cross-section of a sample (Starosiedle, 10th century A.D.) with visible mineral admixtures, in particular an aglomerat of several smaller admixtures represented by the varying color within this region.

The surface of the same vessel fragment with visible decoration in the form of grooves arranged in parallel are presented at Fig. 10. The image visualizes the substantial depth of the grooves with respect to the vessel surface which must result in its considerable roughness. This is confirmed by the high value of the roughness parameter Ra (79.40μm).

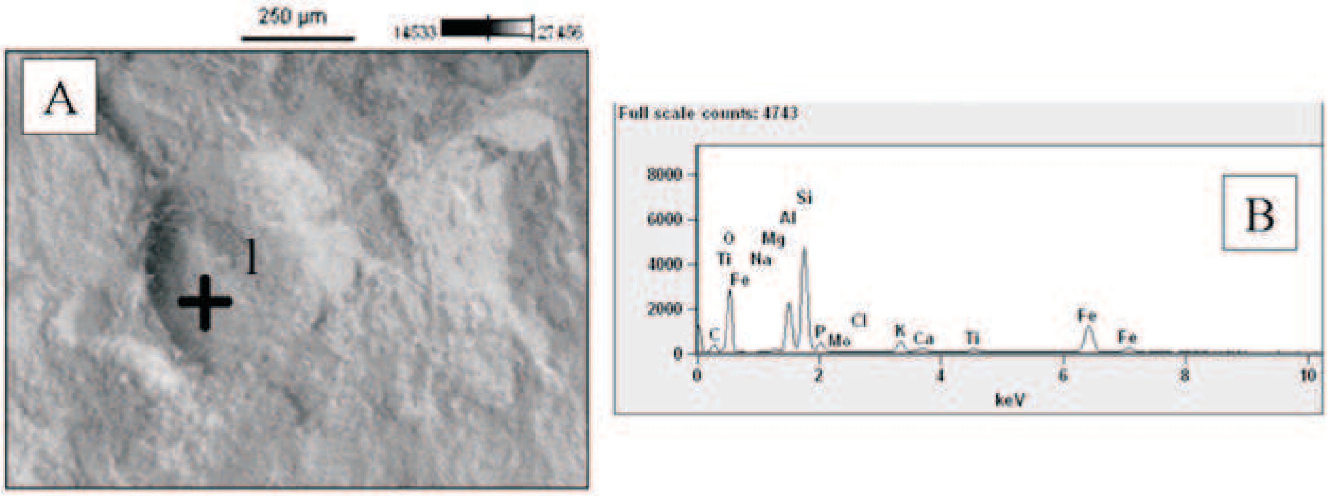

Fig. 8. EDS image of the micro-region examined on the surface of a sample from Starosiedle (10th century A.D.): A) area subjected to the analysis – measurement point designated by the number 1, B) spectrum of the elements obtained at point 1

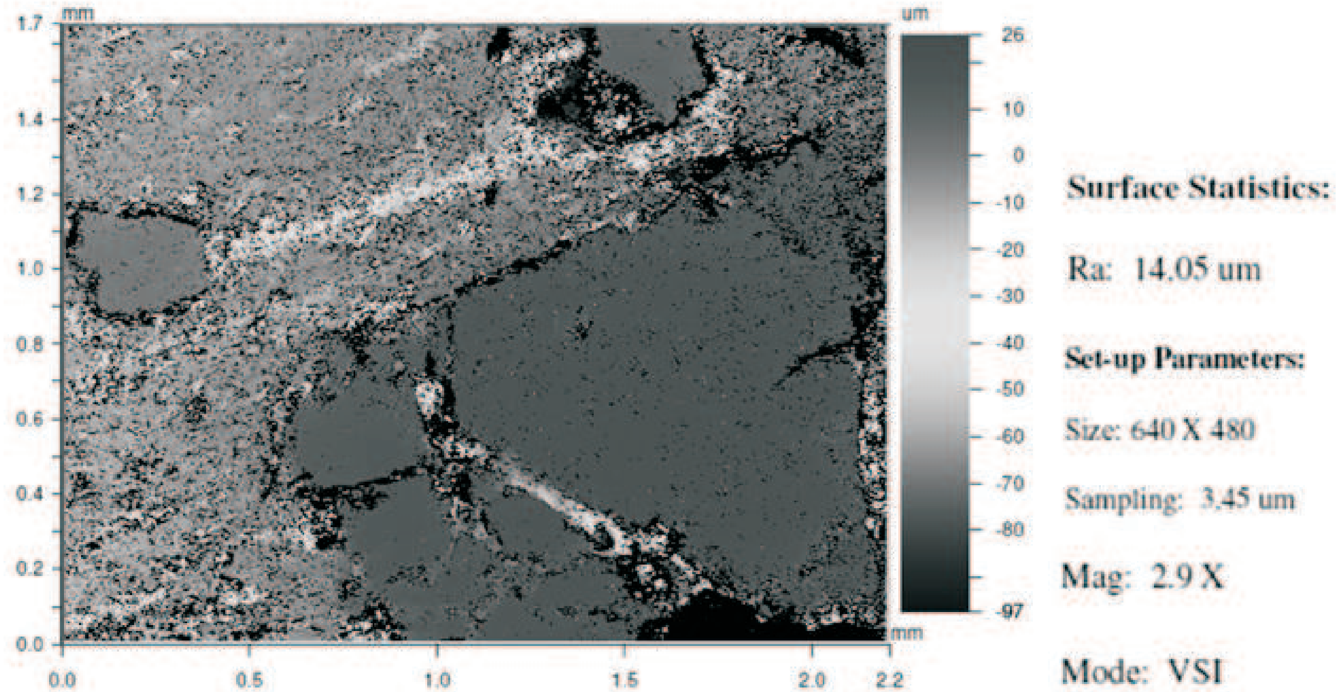

Fig. 9. Sample from Starosiedle (10th century A.D.)

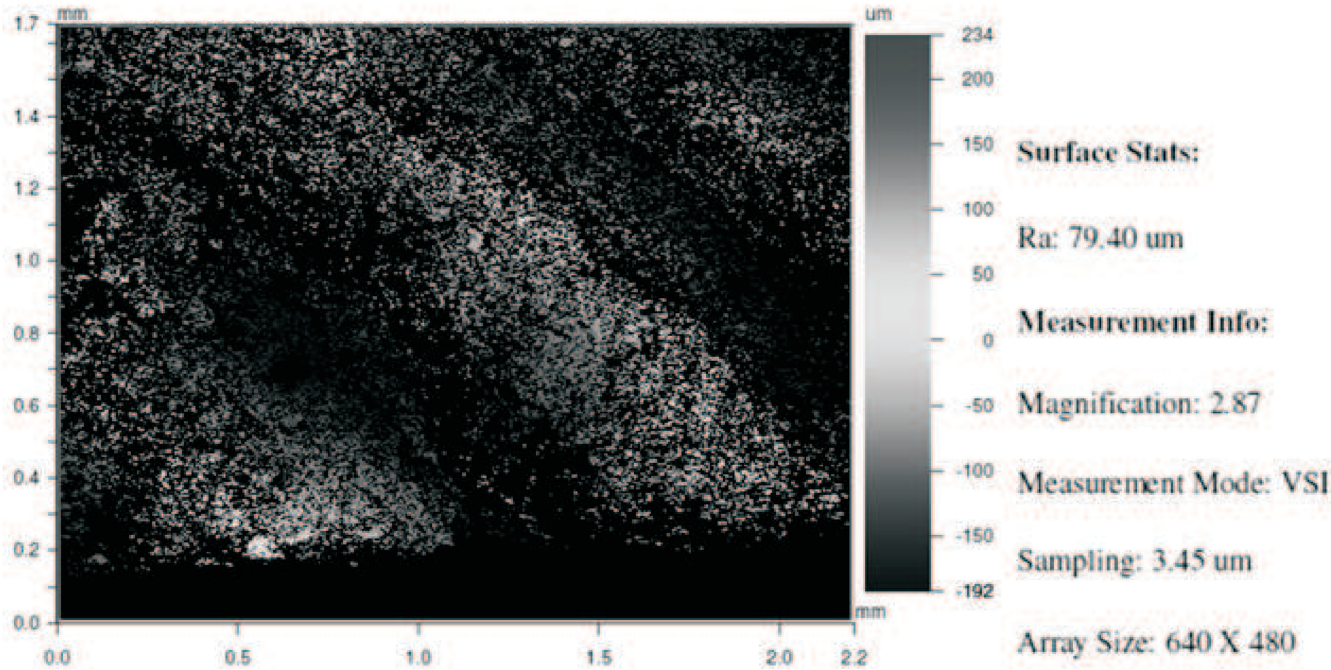

Fig. 10. Sample from Starosiedle (10th century A.D.)

4. Conclusions

Macroscopic examinations permit us to describe the structure of the ceramic samples, in particular to identify the admixtures, determine their shapes, size, distribution, and also to distinguish between their varied colors which are indicative of their varied chemical compositions. The structure of all the samples appeared to be similar irrespective of the site of their origin and of their age (5th century B.C. and 10th century A.D.). All the materials examined contained admixtures with similar morphologies and sizes (the size range from 3 to 3000μm). The admixtures often occurred in the form of aglomerates and were weakly embedded in the matrix material. The structure of the matrix was also similar in all the samples: it was laminar and cracked. Examinations of the laminar structure of the matrix confirmed that the vessels were hand-made. The macroscopic examinations also permitted observation of the various embellishments and ornaments present on the ceramic vessels (pottery from the 10th century A.D.).

Examinations in a scanning electron microscope revealed the fine admixtures (below 5μm) present in the matrix material and enabled us to observe the variety of their shapes which varied from spherical through rounded-edge elongated to regular with sharp angular edges.

The EDS chemical analysis permitted identifying the elements present in the admixtures, because the results of this analysis are not unequivocal, it is possible only to identification the group of mineral, but not the specific mineral.

Profilometry permits imaging the surface topography of the ceramic samples and also observing fragments of decorative patterns present on the sample surface.

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REFERENCES

[1] http://www.archeologia.bitmar.net (1.07.2009).
[2] E. Sobierska, P. Gubernat, P. Wyszomirski, R. 49, 8-14 (1998).
[3] http://archeowiesci.wordpress.com/ (1.07.2009).
[4] B. Gomez, C. Doherty, Archaeometry **42**, 109-118, 1 (2000).
[5] M.F. Ownby, C. Ownby, E.J. Miksa, Journal of Archaeological Science **31** 920040, 31-38.
[6] G. Verlaj, K. Janaki, A. Mohammed Mustafa, R. Palanivel, Applied Clay Science **43**, 303-309 (2009).
[7] A. Szummer, Podstawy ilościowej mikroanalizy rentgenowskiej, Warszawa 1994.

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