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ABOUT THE SINTERING OF HISTORICAL "YELLOW BRICKS" OF SOFIA

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ABSTRACT

The historical "yellow cobblestones" of Sofia are a very well sintered ceramic clinker with practically zero water absorption. However, the high amount of crystal phase formed, which explains the extraordinary mechanical properties of this remarkable material, is in formal contradiction with its low final porosity. In fact, in the modern ceramics clinkers the crystallinity is similar or inferior, but the reached degree of sintering is lower; as a result, the mechanical properties are reduced.

The aim of this report is to elucidate some peculiarities of the densification process of "yellow ceramics bricks" because such information is essential for the eventual successful production of replica of this emblematic pavement.

The chemical and phase compositions of original "yellow paving bricks" together with those of modern clinker from "Vitosha" boulevard in Sofia were evaluated by XRF and XRD analysis, respectively. The structures of both ceramics were investigated with density measurements and SEM.

Their densification behaviour was estimated by re-sintering of milled original samples by Hot Stage Microscopy (HSM) tests. The results elucidate that the sintering temperature of the historical clinker is inferior, and their sintering interval is significantly narrow. This peculiarity is explained by the rapid decreasing of apparent viscosity with temperature rise.

Finally, by secondary holding at the sintering temperatures and subsequent fast quenching of a "yellow brick" sample, it is demonstrated that some phase formation occurred during the industrial cooling step. This result explains both the good degree of densification and the better properties of the "yellow cobblestones".

Keywords: ceramics, sintering, cultural heritage.

INTRODUCTION

The "yellow cobblestones" are a historical pavement, which was used to cover the central streets of Sofia in 1907 - 1908. This emblematic luxury material was produced in the Budapest ceramic factory "Kőbánya Brickworks Pesten Rt." (KGTP) and imported in Bulgaria by the ceramic factory "Isida" - Novoselsi (today Elin Pelin).

By using local marl clays KGTP mainly produced building bricks for the needs of the Hungarian capital [1]. In the middle of 19-th century the production reached 15 million pieces, while in 1867 its amount growths to 30 million bricks.

Later, by using the same raw material and after modification of the technology and increasing of the sintering temperature, a new high quality clinker ceramic, named " keramit", was developed [2]. The patent certificate issued by the Hungarian Royal Patent Office reports that this invention was patented on 28 September 1903. According to the data of KGTP for the period between 1879 and 1934, the area of paved roads with "keramit" in Budapest, together with these in other Hungarian and foreign cities, was approximately 1 km^2 [3].

About 60 decares of the material was used as pavement in Sofia. Today (i.e., near 120 years ago) the whole reserved space is two times smaller; in addition, many of yet existing "yellow cobblestones" are broken or cracked.

In 2013, with a decision of the Sofia Municipal Council, this pavement was declared a cultural heritage. This means that it must be documented, described, studied, and, if repairs are needed, restored to the same condition. This is the main reason that the last decade different groups have been trying to study "yellow" ceramics or to synthesize somewhat similar material [4, 5].

The present work is also a part of this activity. It is related to the BSF project "Use of Bulgarian marl raw materials with additives from other natural and industrial sources for the synthesis of high-quality ceramics of the "yellow" pavers type".

It practically restarts our preliminary research, made during a project with Sofia Municipality from 2014 under the "EUROPE" Program entitled "Study of the composition, structure, properties and method of obtaining the yellow paves in Sofia". The proposed working plan of this first project included the following three stages:

I: Historical Reference. Initial research. Preliminary studies with the yellow pavers to establish composition, structure and main operational characteristics.

II: Development of method and composition for obtaining blocks for outdoor pavements of the "yellow pave" type.

III: Development of technology for serial production.

Regardless of the successful preliminary first stage of the project, which funding was symbolic, Sofia Municipality showed no interest in continuing the collaboration with our group. As a result, after 8 years, we decide to restart our research without the participation of Sofia Municipality.

Now, our ambition is to create a material practically identical to the "yellow paving stones", and highlight some important technological details for their modern production, using appropriated Bulgarian raw materials.

In present work are reported some results for the composition, structure and sintering behaviour of the original "yellow ceramics bricks". In order to demonstrate better some of the particularities of this historical paving material, these results are compared with data, obtained with the modern clinker, used for paving of pedestrian zone of "Vitosha" boulevard in Sofia. Both studied pavements are presented in Fig. 1.

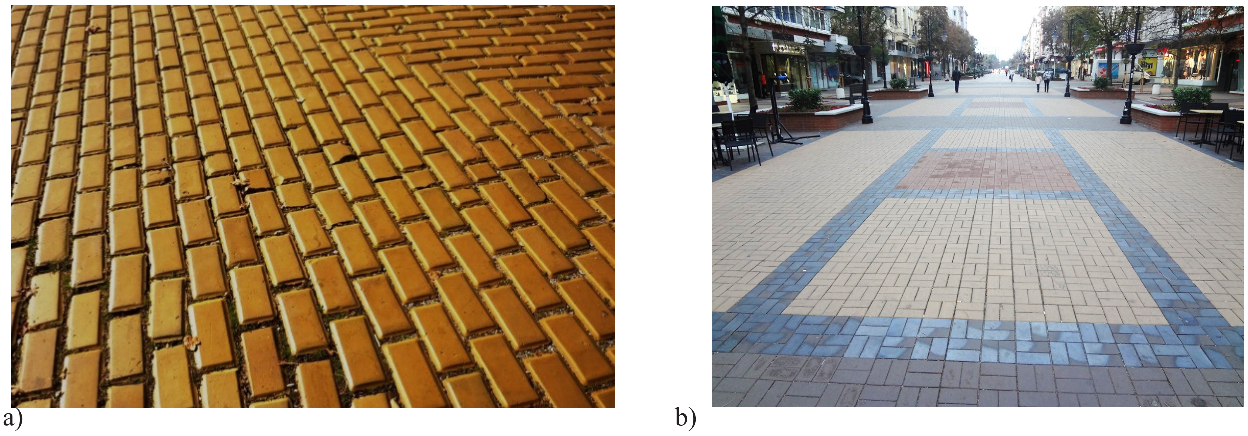
EXPERIMENTAL

The chemical compositions of both ceramics were evaluated by XRF analysis (Zetium Spectrometer – Malvern Panalytical).

Powder XRD patterns of the studied samples were recorded on an Empyrean Powder X-ray diffractometer (Malvern Panalytical, Netherlands), using Cu radiation (λ = 1.5406 Å) at 40 kV and 30 mA and PIXcel3D detector. Phase identification was carried out using the HighScore Plus program.

The sintering behaviour was investigated by Hot Stage Microscopy (ESS HSM-1400 Expert System) at 10°C min^{-1}.

The structure of ceramic samples was evaluated by



a)

b)

Fig 1. Images of the studied clinkers, (a) - historical paving of Sofia, (b) - modern clinker from pedestrian zone of "Vitosha" boulevard.

traditional routes. The apparent, ρ_a, skeleton, ρ_s, and absolute, ρ_{as}, densities of the samples and their water absorption, WA, were determined. ρ_a was estimated by precise micrometer and balance, while ρ_s and ρ_{as} by gas pycnometer (AccyPy1330, Micromeritic) before and after crashing and milling the samples below 26 μm, respectively. WA was measured after 3 h boiling in distillate water with conductivity less than 5 $\mu S.cm^{-1}$. Then, the results were used to evaluate closed, P_C, and open P_O porosity:

$$P_C = 100 \text{ x } \frac{\rho_{as}-\rho_s}{\rho_{as}} \qquad (1)$$

$$P_O = WA \text{ x } \rho_a \qquad (2)$$

The structure of ceramics was studied by Scanning Electron Microscopy (JEOL JSM 6390) after crashing of samples and Au metallization.

RESULTS AND DISCUSSION

The result of XRF analysis of both samples, labelled YP (yellow pavement) and MC (modern clinker), respectively, are reported in Table 1.

MC has a composition, formally belonging to three axial systems: clay-feldspar-silica, containing relatively high percentages of silica and alumina and moderate percentages of alkali oxides. It is somewhat similar to "soft" porcelain or stoneware, but contains higher percentage of iron oxide and unusually high amount of TiO_2.

The XRD pattern of MC sample is presented in Fig. 2.

Table 1. Chemical compositions of studied ceramics (wt. %).

	YB	MC
SiO_2	53.5 ± 0.3	57.4 ± 0.4
TiO_2	0.6 ± 0.1	5.2 ± 0.2
Al_2O_3	14.6 ± 0.3	17.4 ± 0.3
Fe_2O_3	5.2 ± 0.2	8.4 ± 0.2
CaO	17.1 ± 0.3	1.1 ± 0.1
MgO	5.1 ± 0.2	2.6 ± 0.1
BaO		1.2 ± 0.1
K_2O	2.8 ± 0.1	3.6 ± 0.1
Na_2O	1.1 ± 0.1	2.6 ± 0.1

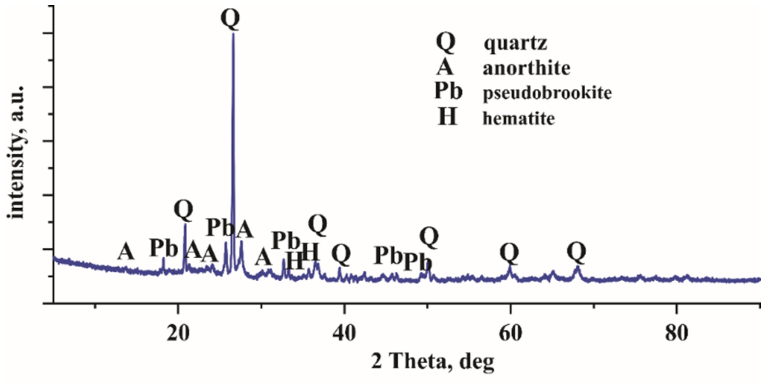


Fig. 2. XRD pattern of MC sample.

It shows that the main crystal phase is residual quartz, together with lower amounts of plagioclase (anorthite s.s.), hematite and pseudobrookite (Fe_2TiO_5), which is typical yellow-brown pigment for the ceramic sector [6]. This result is in a good agreement with the chemical composition. It can be assumed that iron oxides play the role of flux while the Fe_2TiO_5, similarly to the quartz, can be considered as a filler.

The sintering mechanism of traditional ceramics is well known [7 - 9]. It starts with the melting of fluxes and then, with the increasing of temperature and/or holding time, the amount of formed liquid phase growths due to dissolution of quartz and metakaolin. In this manner the percentages of SiO_2 and Al_2O_3 in the melt increase with the rise of its amount. Thus, a drastic viscosity fall doesn't occur with the temperature increase, which leads to larger sintering interval and good manufacturability.

Typically, in a well sintered traditional ceramic with near zero water soaking, the liquid phase, formed during the heat-treatment, entirely vitrifies forming between 60 and 70 % glassy phase [8, 9]. When the crystallinity is higher reached degree of sintering is usually lower.

The chemical composition of YP is uncommon for the traditional bricks and clinkers. It is characterized by a lower amount of silica and alumina and very high percentage of lime; in addition, it contains about 5 wt % MgO and 5 % iron oxides and very low percentages of alkali oxides. This analysis confirms that the parent Hungarian raw material was marl with a specific chemical composition. The XRD pattern of YP sample is presented in Fig. 3 and shows that the main crystal phases are pyroxenes and plagioclase, in an approximate ratio of 2/1. These result also are in agreement with the reported chemical composition.

Typically, the main carbonate mineral in the marls is calcite, while in the Pest pits it seems that the percentage of dolomite was also high. This peculiarity is crucial for the "keramit" production and explains many of its specifics.

In principle, the marls are not considered as very appropriate raw materials for the bricks production. The main problem is related to the higher plasticity of batches, which limits the molding possibilities and leads to an undesirably high shrinkage when a good degree of sintering can be reached. Another problem is that a complete transformation of CaO, formed after the limestone decarbonization, into new crystalline and amorphous phases should be ensured, because the presence of unreacted "active" CaO in the building ceramics might lead to lime-popping [10].

However, if some technological features are clarified or additional procedures are introduced, marls could be

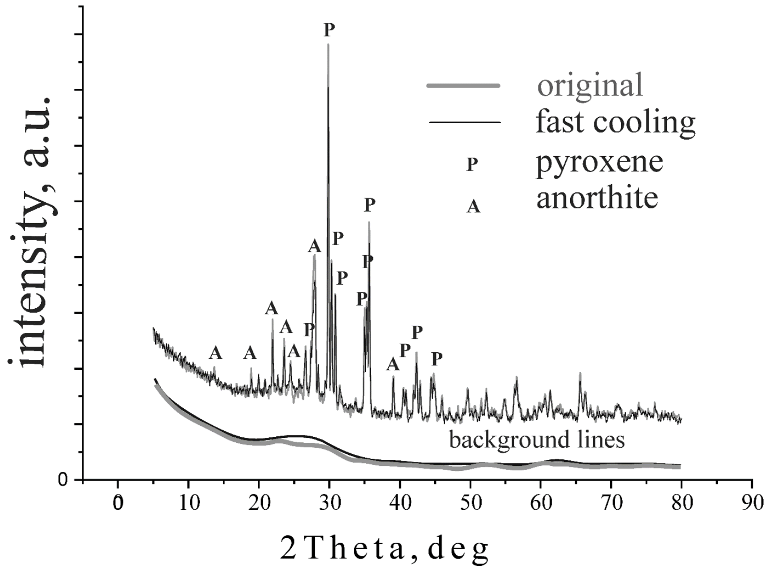


Fig. 3. XRD pattern of YP and YP-Q samples.

successfully used to produce various types of ceramics. So, if no other suitable local clays are available, the production of "marl" bricks becomes an acceptable practice [11 - 13]. In fact, the use of marls in the brick production is also popular in northern Bulgaria [14, 15].

In our previous studies with ceramics, based on the high amount of industrial wastes, also are reported results for building ceramics with reduced silica and high CaO percentage [16, 17]. Some of the obtained samples are characterized by very low open porosity, high crystallinity, and exceled mechanical properties (i.e. the characteristics valid also for the original "keramit").

In these works, the sintering and the phase formation were explained mainly by the position of the ceramics in appropriated phase diagrams. If the composition is close to eutectic, the amount of formed liquid phase changes significantly at minor variations of sintering temperature, which creates serious technological problem. On the contrary, if the composition of ceramics is close to that of the main crystal phase, the crystallinity is too high and sintering temperatures close to the liquids can be reached. So, most appropriate are intermediate compositions, where the densification carries out between the eutectic and liquids temperatures, and the amount and composition of formed melt phase is controlled by the lever rule.

The densification and phase formation of the original "keramit" might be explained in a similar way. This approach is diverse by the description of sintering of a traditional ceramic, which is related to the formation of high amount of viscous liquid phase as a result of dissolution of quarts and metakaolin.

The different sintering trends of both ceramics were demonstrated by the HSM test using original samples, milled below 75 µm. It might be assumed that these re-sintering curves give acceptable preliminary information for the temperatures of densification and deformation of studied compositions.

Fig. 4 shows the resulting plots, while photos of the samples at different characteristic temperatures are presented in Fig. 5. The temperatures, corresponding to these "fixed" points for a HSM test and the related viscosities, proposed by Scholze, are summarised in Table 2 [18].

The re-sintering of the modern clinker starts at about 1130°C and up to 1290°C deformation is not observed. This "sintering interval" (i.e. the temperature difference between T_{FS} and T_{MS}), corresponding to a viscosity decrease at about 60 times, is large, the sintering rate is moderate and, as a result, the reached shrinkage at 1250°C is about 10 %. This result demonstrates manufacturability and good ability to withstand

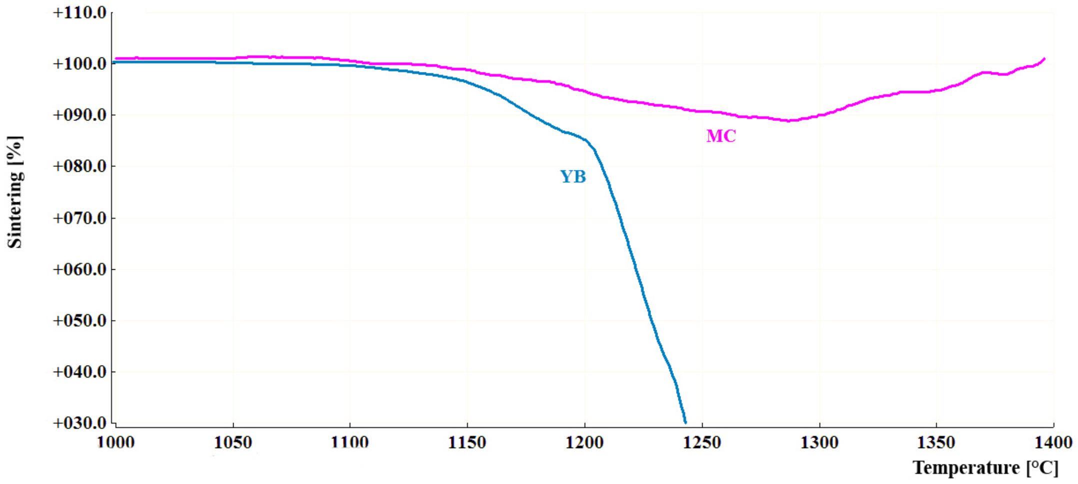


Fig. 4. HSM isothermal re-sintering plots of MC and YP.

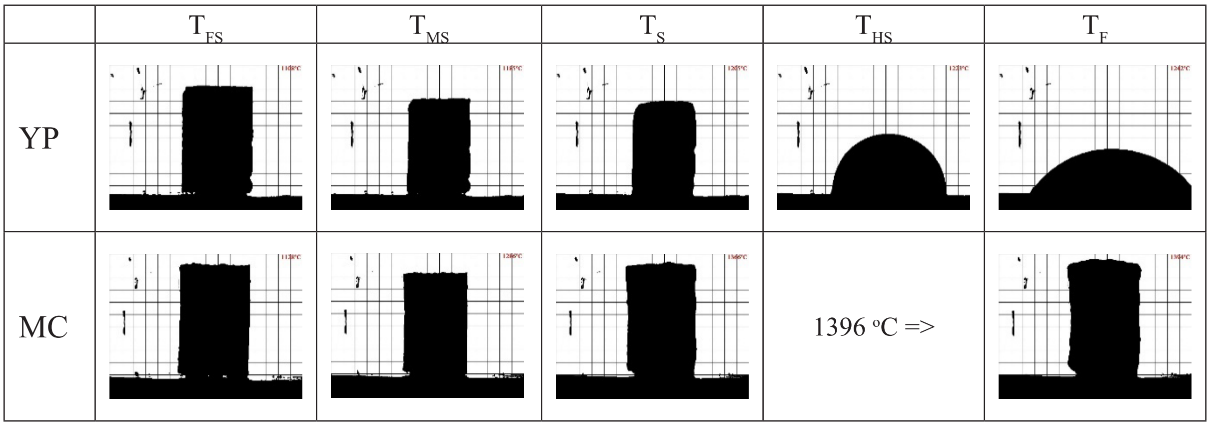


Fig. 5. HSM photos of MC and YP re-sintered samples at different characteristic temperatures.

Table 2. Characteristic temperatures, °C and viscosities η, Pa s^{-1} according HSM test.

	Log η	YP	MC
First Shrinkage (T_{FS})	9.0	1108	1128
Maximum Shrinkage (T_{MS})	7.2	1185	1286
Softening (T_S)	5.1	1205	1366
Half Sphere (T_{HS})	3.6	1223	
Flow (T_F)	3.1	1242	

temperature variations during the sintering. This behaviour is also confirmed by the XRD result from Fig. 2. In fact, shown relatively high crystallinity is an important factor that prevents pyroplastic deformation.

With the increasing temperature, typical over-firing, related to slow bloating of the sample, starts. The "softening" point, which corresponds to a viscosity of about 10^5 Pa s^{-1} is at 1340 - 1360°C, but no drastic change in the sample's shape is observed up to 1400°C (see the last photos in Fig. 4. These results can be explained only if some unmelted crystal phase remains in the sample. In fact, after 1 h holding at 1250°C MC samples with weight of 10 - 15 g forms somewhat as a ceramic foam, which yet contains residual quartz and pseudobrookite.

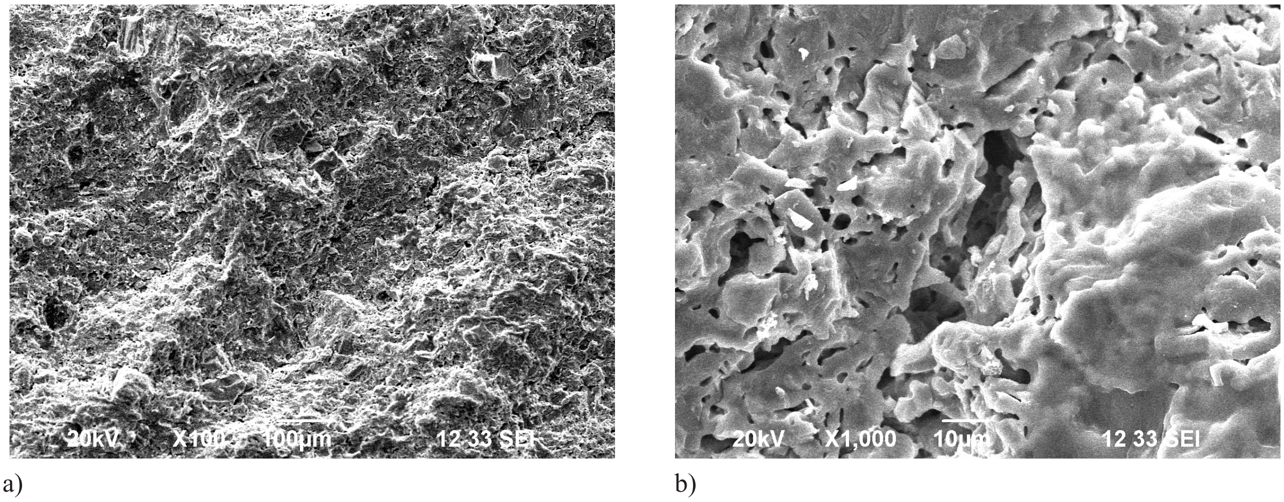
At the same time, the original "keramit" starts to re-sinter at about 1110°C, and already at about 1200°C, deformation of the sample is observed; at about 1230 - 1240°C it is totally melted. The "sintering interval" is two times shorter than one in MC and occurs at lower temperature. After T_{MS} the viscosity rapidly decreases with about three-four orders only for 50 - 60°C, which can be explained by rapid melting of the crystal phases.

These results elucidate that the amount of crystal phase, as well as the related apparent viscosity, vary significantly with temperature: at 1100°C the crystallinity and the apparent viscosity are so high that the densification is inhibited, while at 1200°C the sample already is deformed and the shrinkage is more than 20 %. It might be assumed that the eutectic temperature of the original composition is at about 1080 - 1100°C, while the liquids one - at about 1190 - 1210°C [17]. In fact, during the parallel test (1 h heat-treatment at 1250°C) YB sample melted entirely, forming a black glass. Its XRD pattern show a wholly amorphous structure.

In this case, the sintering mainly depends by the amount of crystal phase, corresponding to the working temperature. Below the eutectic temperature the crystallinity is high and the sintering is inhibited, while close to liquids it is too low and deformation occurs. This means that the densification of "keramit"

Table 3. The densities, water adsorption, and corresponding open and closed porosities of MC, YP and YP-Q samples.

	MC	YP	YP-Q
Apparent density, g cm^{-3}	2.32 ± 0.01	2.54 ± 0.01	2.53 ± 0.01
Skeleton density, g cm^{-3}	2.678 ± 0.003	2.564 ± 0.002	2.562 ± 0.002
Absolute density, g cm^{-3}	2.716 ± 0.002	2.851 ± 0.002	2.802 ± 0.002
Water soaking, %	5.5 ± 0.2	0.4 ± 0.1	0.5 ± 0.1
Open porosity, %	12.8 ± 0.3	1.0 ± 0.2	1.2 ± 0.2
Closed porosity, %	1.4 ± 0.2	10.1 ± 0.2	8.6 ± 0.2



a) b)

Fig. 6. SEM images of fracture of MC at low (a) and higher (b) magnifications.

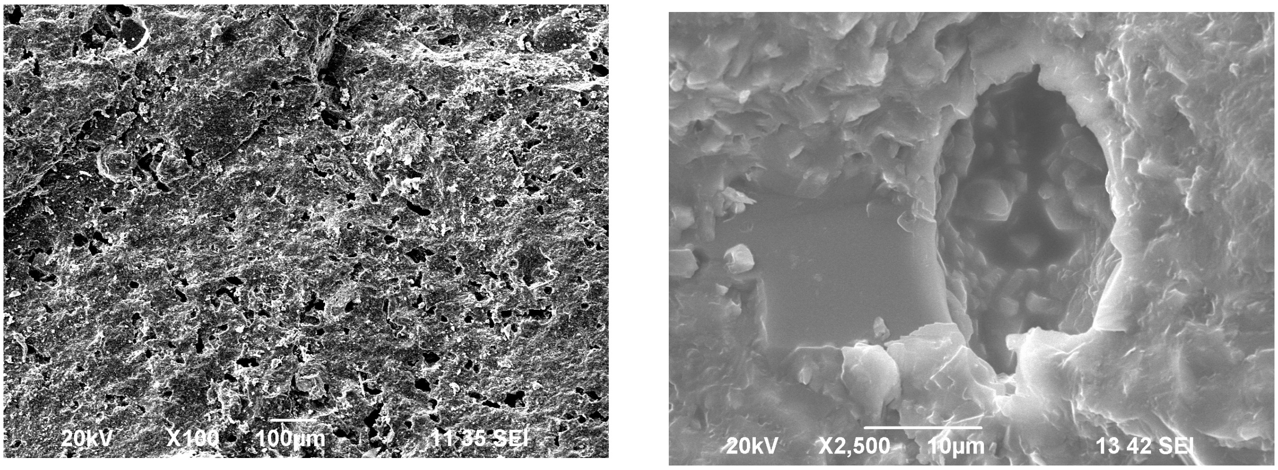
should be carried out in a narrow sintering interval with minimal temperature variations. Probably low working temperatures at about 1120 - 1140°C, coupled with longer holding times, were used for the production of the “historical pavements”.

The results for the densities, water adsorption and corresponding open and closed porosities of YP and MC samples are reported in Table 3.

The modern clinker is characterised with ~5.5 water soaking, corresponding to ~13 % open porosity, while the closed porosity is below 2 %. These values elucidate that an intermediate degree of sintering, when the transformation of open into closed porosities started, is reached. These porosity results are typical for the facing and clinker bricks. The expected compressive strength and bending strength of products with similar characteristics are 30 - 50 MPa and 10 - 25 MPa, respectively [19].

The SEM images of fracture of MC are shown in Fig. 6. The homogeneous structure of the material is elucidated in Fig. 6a, while Fig. 6b (at higher magnification) confirms the uncompleted degree of sintering and shows the presence of open residual pores with an irregular shape.

At the same time, the water absorption in YB is near zero, while the closed porosity is about 10 %, which value is a little higher than that for a well sintered modern glass porcelain [8, 9]. The exceled degree of sintering is



a) b)

Fig. 7. SEM images of fracture of YB at low (a) and higher (b) magnifications.

demonstrated in Fig. 7a, whereas a typical closed pore with semi-spherical shape and the elevated crystallinity of the material are elucidated in Fig. 7b.

The mechanical properties of this historical pavement, measured during our previous project by the colleagues from University of Architecture, Civil Engineering and Geodesy - Sofia, also are amazing: compressive strength of 290 ± 15 MPa and bending strength of 45 ± 10 MPa (i.e. values surpassing 2 - 3 times these of the modern clinker pavements). Considering the size of original bricks and the period of their production these values are remarkable.

Similar results can be explained by the combination of very good degree of sintering and high crystallinity, which however formally contradict each other. In principle, in the traditional ceramics, the higher is the crystallinity more difficult is the sintering.

In order to clarify this interesting densification behaviour an additional test was made. Original YB sample (with weight of about 15 g) was heat-treated at 1130°C for 3 h and then quenched in water. The densities of thus obtained specimen, labelled YP-Q, are added in Table 3, whereas the corresponding XRD pattern is compared with that of YP in Fig. 3.

The differences between apparent and skeleton densities of YP-Q and YP are low and similar to the experimental errors. At the same time, the absolute density of quenched sample is lower with about 0.05 g/cm^3, which decrease the closed porosity with ~1.5 %. This density decreasing corresponds to a lower crystallinity in YP-Q with about 10 - 15 wt %, which is consequence of the density difference between crystal and amorphous states (at about 15 and 5 % for pyroxene and anortite, respectively) [20, 21].

Fig. 3 also confirms the reduced crystallinity in YP-Q. Peak intensities of the present crystalline phases are lower as compared with those of the original sample, whereas the amount of the X-ray amorphous phase is higher as evidenced by the intensity of the amorphous halo.

These results indicate that during the repeated heat-treatment a part of the crystalline phase melts and subsequently, due to the rapid quenching, does not recrystallize again. This clarifies that the amount of liquid phase, participating really in the sintering, is higher than that in YP (i.e. that a part of crystal phase, presented in the original yellow cobblestones, is formed during the cooling step). It can also be noted that the density changes accompanying this crystallization do not affect water absorption and only increase slightly the closed porosity.

Somewhat similar densification was also demonstrated in other ceramics with higher crystallization trend and improved mechanical properties [16, 17]. This behaviour is different from that of traditional ceramics, where the liquid phase controlling the sintering vitrifies at cooling.

CONCLUSIONS

The chemical and phase compositions of the "yellow cobblestones" of Sofia differ from these of the modern clinkers, laid in the Bulgarian capital in recent times. In addition, the historical pavement is characterized with unusually good degree of sintering and the formation of high amount of pyroxene and anorthite crystal phases, which explains its extraordinary mechanical properties.

However, the high crystallinity is in formal contradiction with the exceled degree of densification. This peculiarity is explained by some phase formation, occurring during the cooling step, which increasing the crystallinity and porosity of the final product.

Acknowledgments

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