Mössbauer and X-ray study of the firing process for production of improved roofing tiles

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Abstract The effects of firing atmosphere parameters on the microstructural characteristics and physical properties of clay roofing tiles were studied. For these investigations, ^{57}Fe Mössbauer spectroscopy, X-ray diffractometry and dilatometry were used. XRD of the raw material exploited from the clay pit belonging to the roofing tile factory "Potisje-Kanjiza", revealed the presence of montmorillonite, kaolinite, illite and some chlorite clay minerals, as well as, quartz, albite, calcite and dolomite. Gradual changes were observed both in the ^{57}Fe Mössbauer spectra and X-ray diffractograms with samples fired in reducing CO/N_2 gas atmosphere at temperatures between 700 and 1060 °C. These changes reflect the dehydroxylation processes, oxide (Fe_3O_4) formation, carbonate decomposition, densification and new silicate (plagioclase) formation. The firing conditions in reducing atmosphere were determined to produce roofing tiles with improved properties.

Keywords Clay roofing tiles · Firing in reducing atmosphere · Microstructure · ^{57}Fe Mössbauer spectroscopy · X-ray diffractometry

1 Introduction

The firing of ceramic roofing tiles is the most important technological process which determines the properties of the product. The common firing processes use

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oxidising atmosphere [1–4]. However, firing in reducing atmosphere can lead to improved mechanical and exploitation characteristics in the case of the heavy clay raw material originating from the Pannonian basin. The problem of the ceramic systems based on Kanjiza clay materials is the composition of the melt phases formed after the decomposition of the clay minerals. Namely, these phases are not able to wet properly the alkali earth oxides obtained after the decomposition of the carbonates. The expected new crystalline phases are not formed in the required quality and quantity [5]. One possible way to overcome this problem is the lime-bonding improvement by performing the firing process in reducing atmosphere of right composition. In previous studies [6–9] the thermal behavior of different clays during firing has been investigated involving Mössbauer spectroscopy.

The aim of our present work was to elucidate the influence of mineral composition and iron micro-environments of the industrial raw material mixture used for the production of roofing tiles on the properties of the final product fired in reducing atmosphere. For these investigations, ^{57}Fe Mössbauer spectroscopy, X-ray diffractometry and dilatometry were used.

2 Experimental

The raw material was exploited from the clay pit belonging to the roofing tile factory "Potisje-Kanjiza". The exploited clay raw material, Kanjiza deposit (northern Serbia), is formed from two layers. The upper layer (yellow clay) is a loess-deposit of 950 m length and 5 m depth which contains a relatively small amount of clay minerals (under 23 m/m%) but it is rich in quartz, carbonates (above 20 m/m%) and feldspar minerals. The second layer (called blue clay) is 950 m long and 8 m deep. It predominantly contains clay minerals; illite, montmorillonite, kaolinite and chlorite. The industrial raw material mixture used for the production of clay roofing tile and also for our experiments consists of 80 % blue clay and 20 % yellow clay. The preparation, forming and drying were performed according to industrial technological procedures [10]. The materials were fired in a dilatometer or in conventional industrial conditions in flowing air or in 5 v/v % CO/N_2 gas atmosphere at different temperatures between 700 °C and 1060 °C.

The dilatometric measurements were performed with a Bähr-DIL 802L dilatometer using a heating/cooling rate of 5 K/min with a 15 min long plateau at the peak temperature.

SEM micrographs were recorded with a JEOL, JSM–6460HV electron microscope.

Powder X-ray diffractograms of the samples were measured by a computer controlled DRON-2 X-ray diffractometer using Fe K$_\alpha$ radiation and a β filter. The diffractograms were recorded between 5° and 95° in (2θ), with a goniometer speed of 0.2° min^{-1} at room temperature. The evaluation of the XRD patterns was made by the EXRAY code. For identification of the phases the ASTM X-ray diffraction data were used.

^{57}Fe Mössbauer spectra of powdered samples were recorded in transmission geometry with a conventional Mössbauer spectrometer (KFKI) working in constant acceleration mode. The γ-rays were provided by a 3×10^9 Bq ^{57}Co/Rh source. The measurements were performed at room temperature. Isomer shifts are given relative

Fig. 1 XRD patterns of the raw material (**a**) and its states after firing in reducing atmospheres at 700 °C (**b**), 800 °C (**c**), 900 °C (**d**), 1000 °C (**e**) and 1060 °C (**f**). Notation of the mineral phases: Q-quartz, A-albite, C-calcite, D-dolomite, I-illite, M-montmorillonite, Ch-chlorite, K-kaolinite P-plagioclases, Ol-olivine, and Am-amorphous material
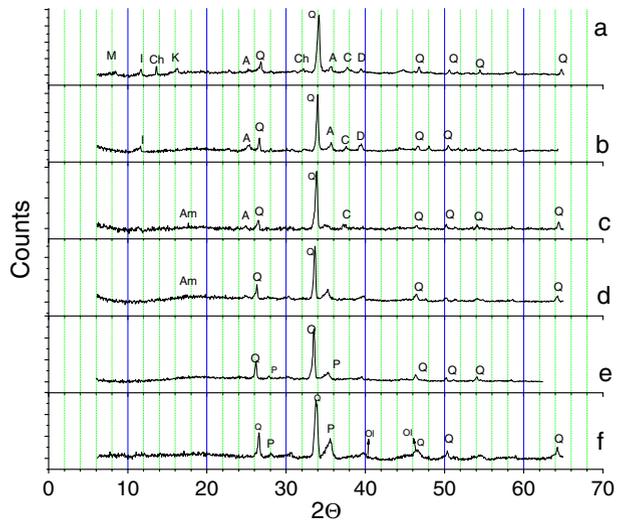
to α-iron. The Mössbauer spectra were analyzed by least-square fitting of Lorentzian lines by the help of the MOSSWINN code [11].

The water absorption capacity, frost resistance and flexural strength of the final products were measured by conventional tests used in the quality control at the roofing tile factory "Potisje-Kanjiza".

3 Results and discussion

The XRD patterns of the raw material mixture and of the material fired in reducing atmosphere between 700 °C and 1060 °C are presented in Fig. 1. The computer evaluation of diffractograms revealed that the starting material contained 26 wt% quartz, 18 wt% albite, 3 wt% calcite, 5 wt% dolomite, 13 wt% montmorillonite, 19 wt% illite/ kaolinite and 16% chlorite. This composition corresponds well enough to those obtained previously for the industrial raw material mixture originated from the Kanjiza deposit [5, 12].

XRD of the fired samples reflect the decomposition and transformation of mineral phases. Most of clay minerals, except illite, decomposed already at 700 °C (Fig. 1b), while plagioclases have began to form only at around 900 °C and their occurrence increased with the firing temperature (Fig. 1d–f). The appearance of amorphous phase can be well seen in the XRD (Fig. 1c, d). The observed transformation of the clays during the firing in reducing atmosphere can be explained by the earlier (i.e., at lower temperature) occurrence of clay dehydroxylation, carbonate decomposition and subsequent processes than in the case of firing in oxidizing atmosphere.

This is demonstrated by the results of the dilatometric investigations (Fig. 2), which indicated different firing behavior of the material mixture in reducing atmosphere and in oxidizing atmosphere. The difference in dilation curves in Fig. 2 at a given temperature above 700 °C shows easier clay dehydroxylation, carbonate decomposition and densification in the case of firing in reducing atmosphere. The

Fig. 2 Comparison of the dilatometric curves: raw material fired in reducing and oxidising atmosphere
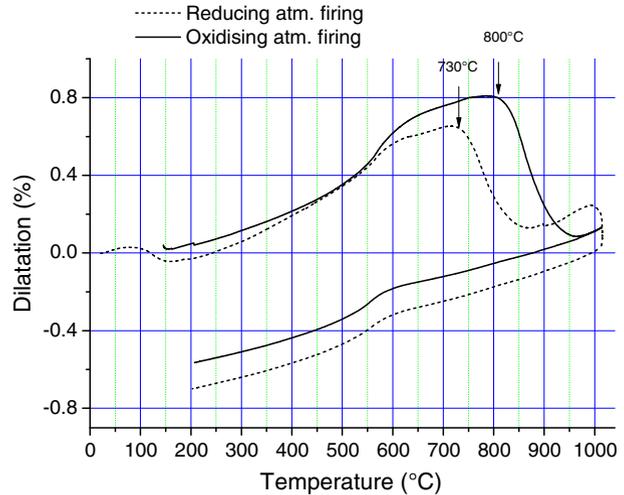
comparison of dilatometric curves mainly between 730 °C and 800 °C as well as above reveals that different consolidation phenomena take place in different atmospheres. The higher total shrinkage in reducing atmosphere can indicate a higher degree of vitrification [12], which is demonstrated in SEM micrographs in Fig. 3.

Room temperature ^{57}Fe Mössbauer spectra of samples before and after firing in reducing atmosphere at selected temperatures can be seen in Fig. 4. Although the spectra are shown in high velocity range in order to show the appearance of sextets of iron oxides in certain cases together with the changes in the paramagnetic components, all spectra were recorded and evaluated in a narrower velocity interval, too. Several trials were made to find optimum spectral decomposition including different combination of multiplets of Lorentzians according to existing models and using also quadrupole splitting distributions. The Mössbauer parameters belonging to possible decomposition of spectra found to be optimum are depicted in Table 1. The spectrum of the raw material was decomposed into 3 doublets. To assign the spectral components to the iron-bearing mineral phases present in the sample (montmorillonite, illite, kaolinite and chlorite), one needs to know the spectra of the individual pure components, but even then a unique interpretation will sometimes be difficult or impossible, either because the spectrum cannot be decomposed in a unique fashion into individual components, or because different iron-bearing components have very similar Mössbauer patterns. We assigned doublets D1 and D2 to Fe^{3+} occupying M1 and M2 sites in the clay silicates. Doublet D3 is associated with Fe^{2+} microenvironments in the silicates. Our interpretation of the spectrum of raw material is consistent with the XRD results and with those reported earlier [6, 13].

The spectra of the fired samples were fitted into four doublets as well as two sextets when magnetically split components (at 700 °C firing) appeared. The Mössbauer parameters of these doublets are denoted by D2, D3, D4 and D5 in Table 1. In the case of the fired samples only doublet D2 is belonging to Fe^{3+} microenvironments, doublets D3, D4 and D5 are associated with Fe^{2+} species.

We have found significant changes in the spectra (Fig. 4b–f) and in the parameters (Table 1) with the firing temperature and in comparison to those of the raw material.
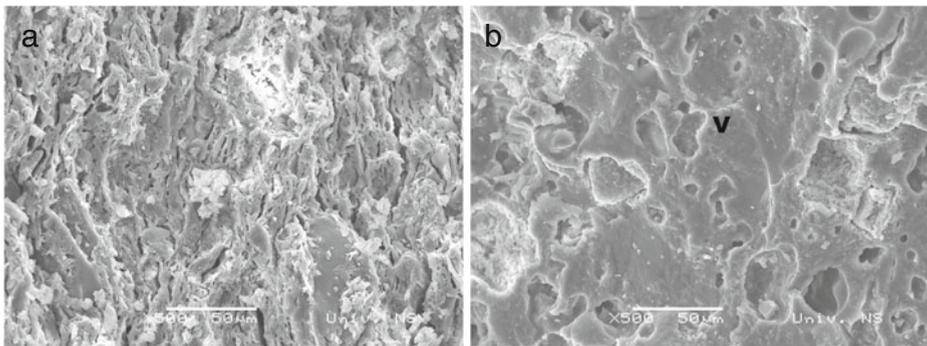
Fig. 3 Typical view of the microstructures. SEM images (Magnification: ×500) of (**a**) a sample fired in oxidizing atmosphere at 1060 °C and (**b**) a sample fired in reducing atmosphere at 1060 °C, V labels vitrified regions

Instead of the two Fe^{3+} doublets, D1 and D2, characteristic of the initial stage, a new Fe^{3+} doublet D2 with altered quadrupole splitting appeared after firing at 700 °C, the relative occurrence of which and also its quadrupole splitting gradually decreased with the firing temperature. At the same time, new Fe^{2+} doublets, D4 and D5, were found in the spectra already for 700 °C firing temperature. The relative area of doublet D5 increased gradually with the firing temperature. There is no significant change in parameters of doublet D3 till 800 °C firing. However, an abrupt change of the quadrupole splitting of doublet D3 was found upon firing the sample at 1060 °C.

Similar spectral changes have already been found previously in the studies of firing of different clays [6–9]. The assignment of the components and their association with the process of firing we are suggesting here are also consistent with those of the previous works.

Quadrupole doublet D2 can be attributed with Fe^{3+} octahedral sites in the decomposing clay lattices. The increase of the quadrupole splitting of this component with the firing temperature reflect undoubtfully the dehydroxylation process in excellent agreement with all previous works [6–9]. Doublet D3 can be mainly connected with illite, based on its corresponding Mössbauer parameters [14] and due to the presence of illite till 800 °C indicated by XRD (Fig. 1). Furthermore, under reducing conditions, a similar Fe^{2+} doublet component, associated with remaining and dehydroxylated clay, has been found which did not show any characteristic change until 800 °C in other works [6]. In the spectrum of the sample fired at 700 °C the appearance of sextets S1 and S2 clearly evidenced magnetite (Fe_3O_4) formation. This is consistent with the earlier observation [6] that the layer structure of the clays breaks down at around 700 °C under reducing conditions, while iron may show up in crystalline magnetite phase forming from the resultant amorphous material. Doublets D4 and D5 can be partly associated with Fe^{2+} in the amorphous phase formed during the decomposition of clay minerals. The decomposition products of the layered silicates and the accessory minerals like calcite and dolomite recrystallise into new high temperature phases [7]. All transitions between the decomposition products of the clay minerals and the high temperature phases proceed through an amorphous phase. The amorphous phase can play an important role in plagioclase formation and vitrification processes at higher firing temperatures. In the case of

Fig. 4 ^{57}Fe Mössbauer spectra, recorded at room temperature; raw material (**a**) and its states after firing in reducing atmospheres at 700 °C (**b**), 800 °C (**c**), 1060 °C (**d**)
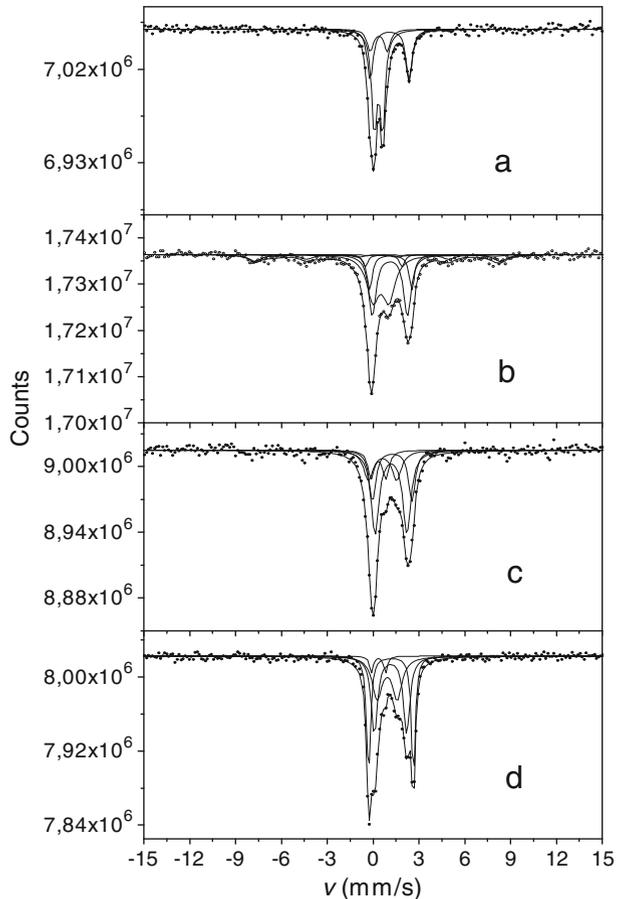
firing at 1060 °C, doublets D3, D4 and D5 can be partly assigned to Fe^{2+} in newly formed crystalline silicates. Based on the characteristic Mössbauer parameters of minerals, doublet D3 observed for sample fired at 1060 °C can be attributed to olivine [15–17]. The formation of olivine is confirmed by our XRD results. Olivine has already been found as newly formed phase after firing clays in reducing atmosphere [6, 18]. Doublets D4 and D5 may be assigned partly to iron-bearing plagioclase. The isomer shift and quadrupole splitting of doublets D4 and D5 match those which were reported for plagioclases [19, 20]. The presence of plagioclase is clearly shown by the XRD (Fig. 1e and f). Members of plagioclases (anorthite and albite) have already been shown in the case of calcareous clays after firing [21–24].

Considering the reducing atmosphere firing of a wide range of clays, a large variety of Fe^{2+} bearing mineral phases may form above 1000 °C strongly depending on mineral composition and conditions of firing [6].

On the other hand, the Mössbauer spectra reflect a gradual increase in the Fe^{2+}/Fe$_{total}$ ratio with the increase of the firing temperature in reducing CO/N$_2$ atmosphere. The possible correlation of Fe^{2+}/Fe$_{total}$ ratio with the formation of technologically favorable microstructure will be discussed elsewhere.

Table 1 Mössbauer parameters of the raw material and its states after firing process in reducing atmospheres at 700 °C, 800 °C and 1060 °C

Firing temperature °C	D1			D2			D3			D4			D5		
	A %	δ mm/s	Δ mm/s	A %	δ mm/s	Δ mm/s	A %	δ mm/s	Δ mm/s	A %	δ mm/s	Δ mm/s	A %	δ mm/s	Δ mm/s
–	36	0.37 ± 0.01	0.49 ± 0.02	33	0.37 ± 0.01	0.88 ± 0.02	31	1.13 ± 0.01	2.62 ± 0.01						
700*				27	0.35 ± 0.01	1.22 ± 0.01	27	1.15 ± 0.01	2.60 ± 0.02	21	1.08 ± 0.01	2.11 ± 0.02	9	0.89 ± 0.01	1.30 ± 0.02
800				16	0.35 ± 0.01	1.08 ± 0.01	29	1.19 ± 0.01	2.62 ± 0.01	36	1.15 ± 0.01	2.11 ± 0.02	19	0.89 ± 0.01	1.50 ± 0.02
1060				5	0.35 ± 0.01	0.92 ± 0.01	33	1.17 ± 0.01	2.92 ± 0.02	35	1.14 ± 0.01	2.11 ± 0.01	27	0.92 ± 0.01	1.30 ± 0.02

* in this case sextets of magnetite ($\delta = 0.29$ mm/s, B = 49.1 T, and $\delta = 0.67$ mm/s, B = 45.6 T) also occurred in 14%

Table 2 Physical and mechanical properties of clay roofing tiles after firing in various atmospheres

Firing atmosphere	Water absorption capacity (wt.%)	Water absorption capacity under vacuum (wt.%)	Frost resistance T value*	Frost resistance Number of cycles	Breaking strength (kN)
Oxidizing	11.91 ± 0.05	16.07 ± 0.05	0.750 ± 0.01	5	2.1 ± 0.2
Reducing atmosphere (5 %CO/N_2)	6.60 ± 0.05	11.66 ± 0.05	0.571 ± 0.01	25	2.3 ± 0.2

*Coefficient of impregnation according to DIN 52251–3. The lower value belongs to higher frost resistance

Table 2 shows that improved properties (lower porosity, higher frost resistance, better flexural strength) were obtained in the case of the products fired in reducing atmosphere in comparison with the ones fired in oxidizing atmosphere.

4 Conclusion

The effect of firing process in reducing atmosphere was studied on the microstructure and phase composition of roofing tile material originated from Kanjiza factory, Serbia. ^{57}Fe Mössbauer spectroscopy and XRD reveal gradual changes in Fe^{2+}/Fe_{total} ratio and phase composition of silicate minerals after firing process in reducing CO/N_2 gas atmosphere at temperatures between 700 °C and 1060 °C. The changes obtained by XRD, dilatometry and Mössbauer spectroscopy were associated with dehydroxylation, oxide (Fe_3O_4) formation, carbonate decomposition, vitrification and new silicate formation processes. Improved properties of roofing tiles were obtained after firing process in reducing atmosphere. Our results give technological parameters for the production of high quality roofing tiles and facing bricks with improved properties.

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