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Original scientific paper

PHASE TRANSFORMATIONS OF AMORPHOUS SiO_2 IN DIATOMITE AT TEMPERATURE RANGE OF 1000–1200°C

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A b s t r a c t: The phase transformations of the amorphous SiO_2 have a very important role in the application of diatomite in the production of ceramic products. Therefore the phase transformations of diatomite are observed with the use of DTA and TGA at temperatures up to 1100°C, and diatomite in powder state heated at temperature 1000–1200°C for a period of 1 and 2 hours. DTA and TGA analyzis show that during thermal treatment up to 1100°C the diatomite remains in its amorphous phase. Roentgen-structural examinations of probes heated at 1000–1200°C for a period of 1–2 hours show no presence of crystalline phases at 1100°C. XRD examinations of probes heated at 1200°C show presence of the crystalline phases cristobalite and quartz. The samples was heated at 1200°C for a period of 2 hours, and was observed with an increase of the cristobalite content compared with quartz. SEM and TEM examinations results of diatomite heated at 1200°C for a period of 2 hours show that the probes undergoes sintering followed by reduced porosity.

Key words: amorphous SiO_2; diatomite; thermal treatment; phase transformations

INTRODUCTION

Amorphous SiO_2 is widely used in the production of various ceramic products (refractory, oxide ceramics, nuclear, etc). Therefore this results in the great interest especially in studying the phase transformations of amorphous SiO_2 during the heating process at various high temperature ranges, treated or later used as ceramic products.

The first phase diagram of SiO_2 is published by C.N. Fenner [1] in the year 1913. Since then there are numerous of examinations for the single component SiO_2 systems that have been performed, but still even today there are certain uncertainties which are subject to further examinations.

S. Z. Carroll-Porczynski [2] in his paper shows that clear precipitate of SiO_2 ($SiO_2 \cdot H_2O$) during heating at the temperature range of 1000–1500°C undergoes crystallization of low temperature cristobalite as well as low temperature quartz. I. Patzak [3] in his paper concludes that during heating of various types of SiO_2 almost always cristobalite is obtained, while tridymite is very rarely obtained and this is as result of the presence of various impurities. J. J. Endell [4] proves that during heating of kieselguhr in the temperature range of 1000–1050°C other than cristobalite there are very fine crystals of quartz formed as well. M. Kantzer and M. Mezard [5] concludes that during the heating process of SiO_2-gel at 1050°C besides cristobalite there is quartz formed.

L. S. Birks and J. H. Schulman [6] have studied the influence of additives such as magnesium carbonate, calcium carbonate, strontium carbonate, barium carbonate and manganese carbonate in the crystallization of amorphous SiO_2 in the temperature range of 1200–1300°C. O. W. Flörke [7] concludes that SiO_2-gel during heating and in the presence of alkali metal oxides crystallizes to cristobalite and quartz. T. Tokuda [8] concludes that during a period of one hour of ignition at temperature of 1370–1390°C of high purity amorphous SiO_2 (aerosol) comes to crystallization, formation of quartz, whereas at temperatures above 1400°C there's only presence of cristobalite.

I. Patzak [9] comes to the conclusion that the amorphous SiO_2 with impurities such as alkali metals, alkaline-earth metals, aluminum or OH-ions, in the temperature range of 870–1470°C is followed by phase changes and it crystallizes in

cristobalite, partially through quartz. During these examinations there is no presence of tridymite evident.

Crystalline forms of SiO_2 are shown in the following scheme:

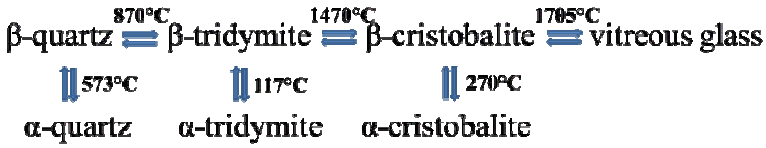

Fig. 1. Phase transformation of SiO_2 [10–11]

Thermal treatment of natural diatomite in the temperature range of 600–1200°C with an analysis on the new formed phases is shown in publication [12]. Crystallization of amorphous SiO_2 and the impact of certain impurities on the crystallization of amorphous SiO_2 are shown in publications [13–18]. Some properties and structural examinations of diatomites from various locations are shown in publications [19–22].

EXPERIMENTAL

Raw material

As raw material is used diatomite from village of Rožden (Kavadarci region), Republic of Macedonia [23]. Based on the chemical composition of the raw material shown in Table 1, it can be concluded that the material is diatomite with a high percentage of SiO_2 (92.97%).

Table 1

Chemical composition of diatomite

Oxides	Mass %
SiO_2	92.97
Al_2O_3	1.52
Fe_2O_3	0.21
TiO_2	0.06
CaO	0.43
MgO	0.19
MnO	0.01
SO_3	0.05
P_2O_5	0.09
K_2O	0.26
Na_2O	0.08
LOI	3.86
Total	99.73

X-ray analysis was performed on the diatomite, and the results of the examination are shown in Fig. 2.

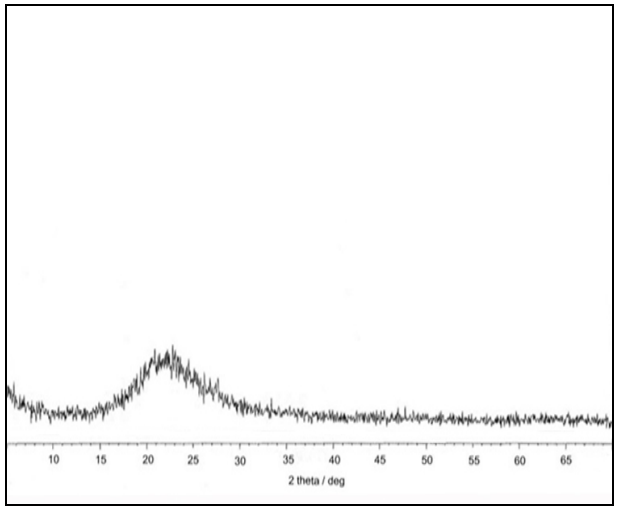

Fig. 2. XRD analysis of diatomite

Based on the XRD analysis of diatomite it can concluded that the raw material is in amorphous phase and there are no indications of crystalline modifications of SiO_2 (quartz, cristobalite and tridymite). X-ray examinations were performed with the DRON X-ray diffractometer under the following conditions: Cu K_α radiation, wavelength $\lambda = 1.54056$ nm, Testing interval 70°, registration voltage 38 kV, current intensity 18 mA.

SEM analyses

Scanning electron microscopy photographyes of diatomite are shown in Figures 3 and 4.

In Figure 3 is shown SEM photography of diatomite where clearly can be seen the skeletons of

microorganisms, while Figure 4 shows the porosity of diatomite with open pores, with dimensions c.c. 250 nm.

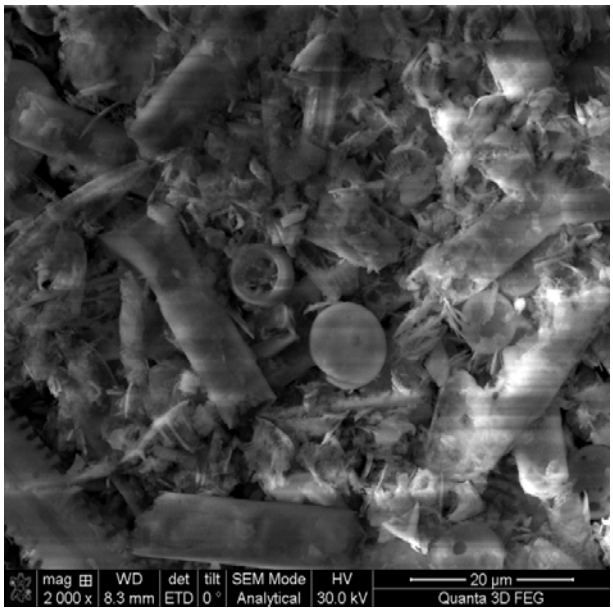

Fig. 3. SEM of diatomite

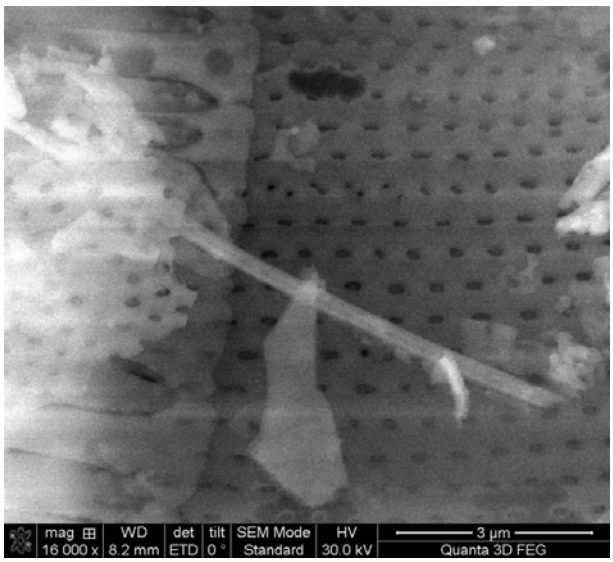

Fig. 4. SEM of diatomite

Thermal treatment of diatomite

Differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) of diatomite were performed with Stanton Redcroft, England, apparatus, under the following experimental conditions: temperature range from 20 to 1200°C; speed of heating 10 °C/min; sample mass 11.7 mg; gas environment – air; material carrier – ceramic pot. The results of DTA/TGA for diatomite are shown in Figure 5.

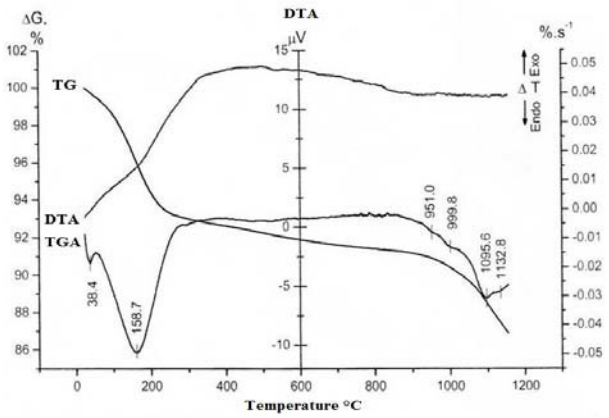

Fig. 5. DTA/TGA of diatomite

Thermo-gravimetrical analysis shown in Figure 5 shows an intensive loss in weight in the temperature interval of 30–200°C and 900–1200°C. The endothermic peak at 158°C is as result of the loss of the absorbed water from the surface and the open pores, while the second loss of mass during the temperature range of 900–1200°C is due to the loss of the hydrated water.These analyses show that the material doesn't crystallize even after a thermal treatment at 1000°C, and that it remains amorphous.

X-ray examinations

X-ray examinations are performed on diatomite heated at temperatures of 1000°C and 1200°C for a period of 1 and 2 hours. X-ray diffractometers of samples heated at 1000°C for a period of 1 and 2 hours are shown in Figures 6 and 7.

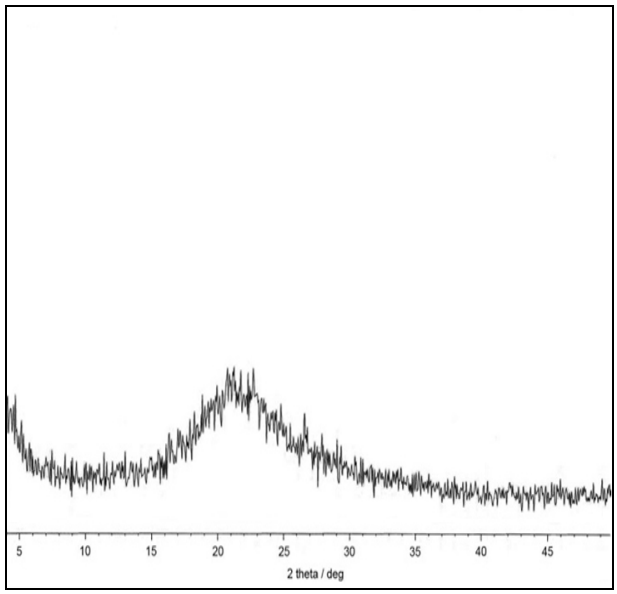

Fig. 6. XRD of diatomite heated at 1000°C for 1 hour

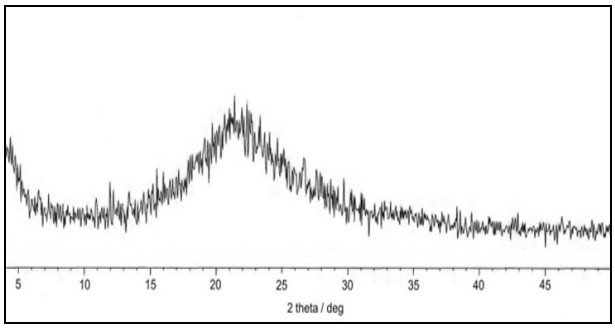

Fig. 7. XRD of diatomite heated at 1000°C for 2 hours

Based on the shown diffractograms in Figures 6 and 7 it can be concluded that after the thermal treatment the amorphous SiO_2 in diatomite does not crystallize.

X-ray diffractograms of samples heated at 1200°C for a period of 1 and 2 hours are shown in Figure 8 and Figure 9.

XRD examinations of probe heated at 1200°C for a period of 1 hour (Figure 8) show that during this thermal treatment comes to crystallization of the amorphous SiO_2 in cristobalite and quartz.

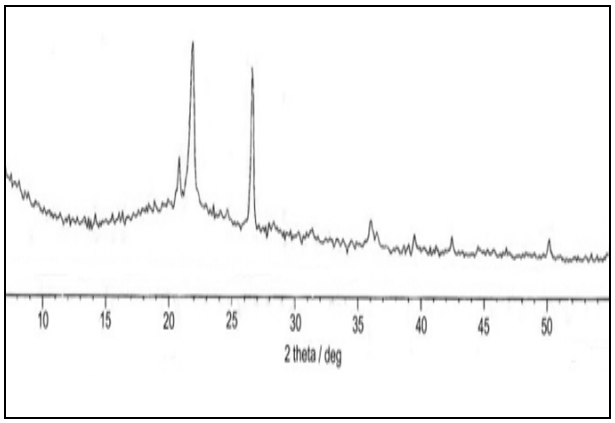

Fig. 8. X-ray of diatomite heated at 1200°C for 1 hour

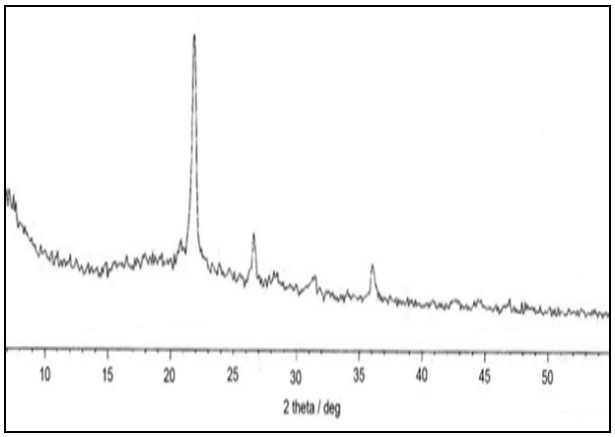

Fig. 9. X-ray of diatomite heated at 1200°C for 2 hours

Based on the results of the diffractogram of probes heated at 1200°C for a period of 2 hours (Figure 9), it can be concluded that the amorphous SiO_2 crystallizes in cristobalite and quartz. In this probe the concentration of cristobalite is much higher than the concentration of quartz. This indicates that the crystallization of the amorphous SiO_2 in diatomite to a cristobalite phase goes through the quartz phase.

SEM analysis of diatomite

SEM photography's of diatomite heated at temperature 1200°C for a period of 2 hours are shown in Figure 10 and Figure 11.

SEM analysis of diatomite heated at 1200°C for a period of 2 hours (Figure 10 and Figure 11) shows that there is sintering of the diatomite which results in the growth of particles, i.e. agglomeration, as result of which comes to the lowering of its porosity.

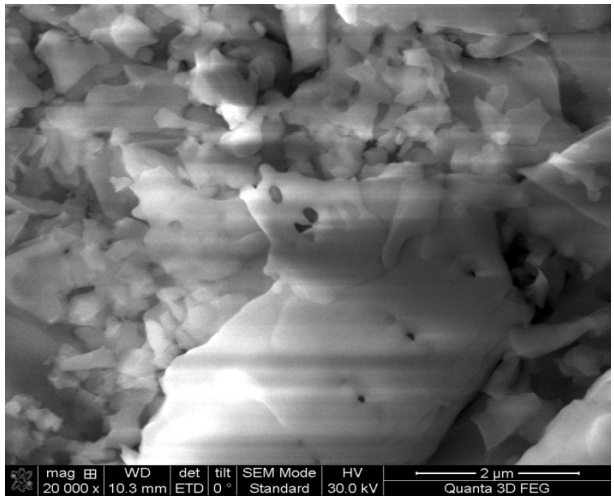

Fig. 10. SEM of diatomite heated at 1200°C for 2 hours

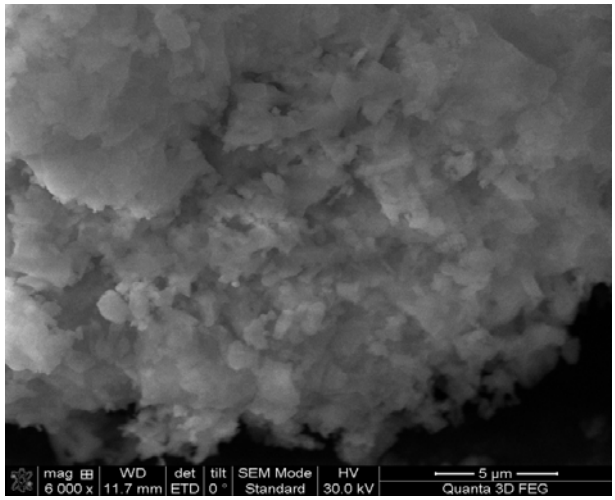

Fig. 11. SEM of diatomite heated at 1200°C for 2 hours

TEM analysis

Results of the TEM analysis performed of diatomite heated at 1200°C for a period of 2 hours are shown in Figures 12 and 13.

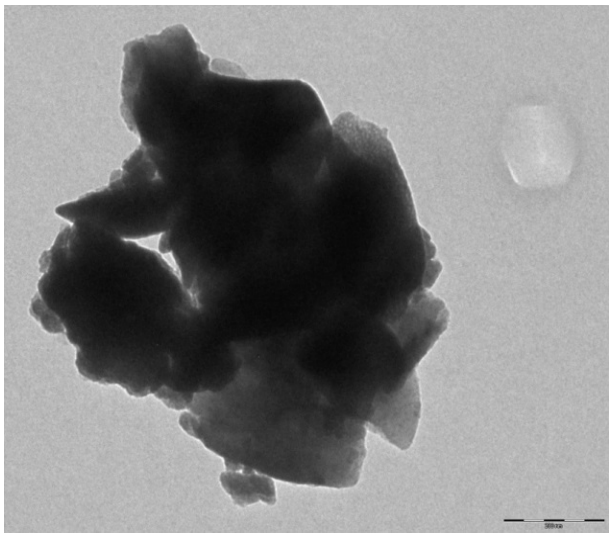

Fig. 12. TEM of diatomite heated at 1200°C for a period of 2 hours

TEM analysis of diatomite thermally treated at 1200°C for a period of 2 hours confirms the results obtained with SEM. Figure 12 and Figure 13 show agglomeration of diatomite particles as result of the sintering process.

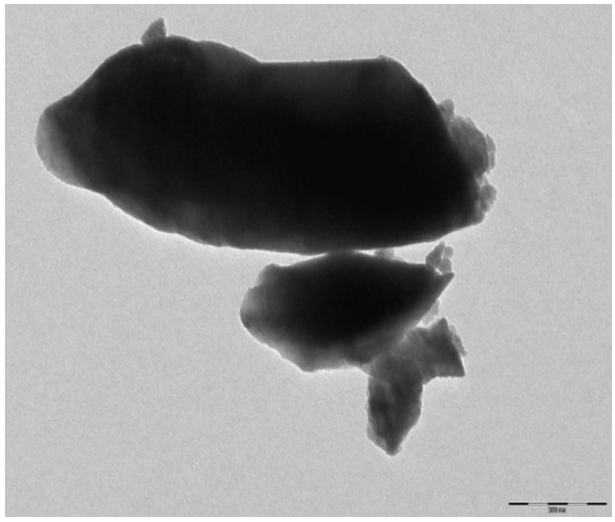

Fig. 13. TEM of diatomite heated at 1200°C for a period of 2 hours

CONCLUSION

For the examination of the phase transformations of the amorphous SiO_2 in diatomite from Rožden (Kavadarci region), differential thermal analysis and thermo-gravimetrical analysis are performed while heating up to 1100°C and the diatomite in powder state is heated at temperature range of 1000–1200°C for a period of 1 and 2 hours.

DTA and TGA of diatomite is performed with a speed of heating 10°C/min up to 1100°C, and it shows that up to this temperature (1100°C) the amorphous SiO_2 does not crystallize.

XRD examinations of diatomite heated in powder state at temperature range of 1000–1200°C for a period of 1 and 2 hours show the following: probes heated at 1100°C for a period of 1 and 2 hours remain amorphous, while the probes heated at temperature of 1200°C for a period of 1 and 2 hours undergoes partial crystallization of the amorphous SiO_2 in quartz and cristobalite. The probe heated at 1200°C for a period of 2 hours shows increase of the cristobalite phase compared to quartz. This indicates that the crystallization of the amorphous SiO_2 in diatomite to a cristobalite phase goes through the quartz phase.

SEM and TEM examinations of samples heated at 1200°C for a period of 2 hours show that it comes to sintering of the sample with the appearance of agglomerates or growth of grains, accompanied by a decrease in porosity.

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Р е з и м е

ФАЗНИ ТРАНСФОРМАЦИИ НА АМОРФЕН SiO_2 ВО ДИЈАТОМИТ ВО ТЕМПЕРАТУРЕН ИНТЕРВАЛ 1000–1200 °C

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Клучни зборови: аморфен SiO_2; дијатомит; термички третман; фазни трансформации

Фазните трансформации на аморфен SiO_2 имаат исклучително важна улога при примена на дијатомеитот за производство на керамички производи. Поради тоа се следени фазни трансформации на дијатомеитот со примена на DTA и TGA во температурен интервал до 1100°C, како и при жарење на дијатомеитот во прашкаста состојба на температура од 1000 до 1200°C во времетраење од 1 и 2 часа. DTA и TGA покажуваат дека при термички третман на дијатомеитот до 1100°C не доаѓа до кристализација на аморфниот SiO_2. Рендгено-структурните испитувања на пробите, жарени на 1000–1200°C во времетраење од 1 и 2 часа покажаа дека при 1000°C нема појава на кристална фаза. Рендгено-структурните испитувања на пробите жарени на 1200°C покажуваат присуство на кристални фази, и тоа кристобалит и кварц. Кај пробата жарена на 1200°C во времетраење од 2 часа се забележува пораст на уделот на кристобалит во споредба со кварцот. Испитувањата SEM и TEM на дијатомеитот жарен на 1200°C за време од 2 часа покажуваат дека во пробите доаѓа до синтерување, проследено со пораст на зрната и намалување на порозитетот.