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STUDIES OF THE SILICON DIOXIDE-DOLOMITE SYSTEM BY THERMAL ANALYSIS

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ABSTRACT

A study of the processes occurring in the SiO_2-dolomite system at a temperature in the range 25-1500 °C was carried out with the use of thermoanalytical and high temperature X-ray diffraction methods. The purpose of this study was to reveal the effect of the composition on the transformation processes applied to similar mixtures which are frequently used in the silicate and glass industries.

INTRODUCTION

Most of the literature data on the SiO_2-dolomite system refer to the preparation of specific calcium magnesium silicates. The mechanisms of the processes occurring in the system under the influence of heat, and the composition of the formed phases and melts have not been elucidated. The information on these systems is based essentially on a study of heat-treated samples cooled to room temperature (1). The most detailed thermoanalytical description of the SiO_2-dolomite mixture has been furnished by Wilburn et.al. (2). These authors were unable to identify some of the peaks above 1000 °C but some other peaks were assumed to be originated from melt formation and due to the appearance of wollastonite.

In the present research the varied thermoanalytical tests at 25-1500 °C were complemented mainly by high temperature X-ray diffraction measurements in order to indentify the type of transformations and the new crystalline phases appearing at temperatures corresponding to the DTA peaks.

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EXPERIMENTAL

The thermoanalytical investigations were carried out on a Mettler-type instrument, in an air flow. The rate of heating was 6 ^{o}C/minute and a sintered Al_2O_3 crucible was used. The high temperature X-ray diffraction was carried out with a JEOL JDX type apparatus also at heating rate of 6 ^{o}C/min.

The samples used in this study were: SiO_2 p.a., with a grain size of 71 μm, and natural dolomite. The average oxide composition of the dolomite was: CaO 30.74 %, MgO 21.14 %, ignition loss 47.01 %.

RESULTS and DISCUSSION

Table 1 presents the results of the thermoanalysis. The DTA plots are shown in Figure 1. The results of XRD-measurements on the same samples at 25-1500 ^{o}C are given in Table 2. The table shows the temperature ranges in which the XRD-test indicated the appearance of a new phase or the disappearance of an existing phase in the sample. The crystalline phases of the mixtures in various ratios are compared in the plots taken at 1300 ^{o}C shown in Figure 2.

The first transformation recorded in the SiO_2-dolomite system is the alpha-beta transition of quartz (see the DTA plot with a peak temperature of 565 ^{o}C). The range of temperature of this transformation does not depend on the SiO_2/dolomite ratio of the mixture. The measured heat content values (ΔH) are scattered partly due to their low values; the average is 13.0 $\pm$ 4.0 Joule/g of quartz. (The literature gives a value of 12.1 J/g).

The processes of decarbonization start at around 570 ^{o}C and terminate at 800-860 ^{o}C (see DTA data and the XRD-data of the appearance of CaO). The DTG and DTA data readily indicate the lack of influence of the mixture ratio on the decomposition of the $MgCO_3$ content of the dolomite although it accelerates the decomposition of the $CaCO_3$ content. In the case of mixtures the average value is 1657 Joules/g dolomite. The scatter around the average value is $\pm$ 5 %; this proves the fact, also supported by X-ray measurements, that aside from decarbonization no other process may be expected below 1000 ^{o}C.

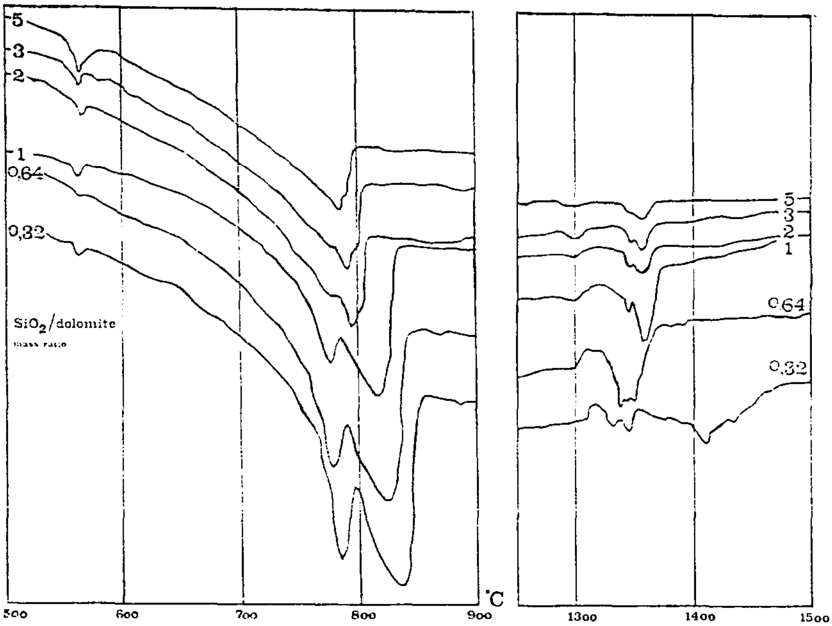
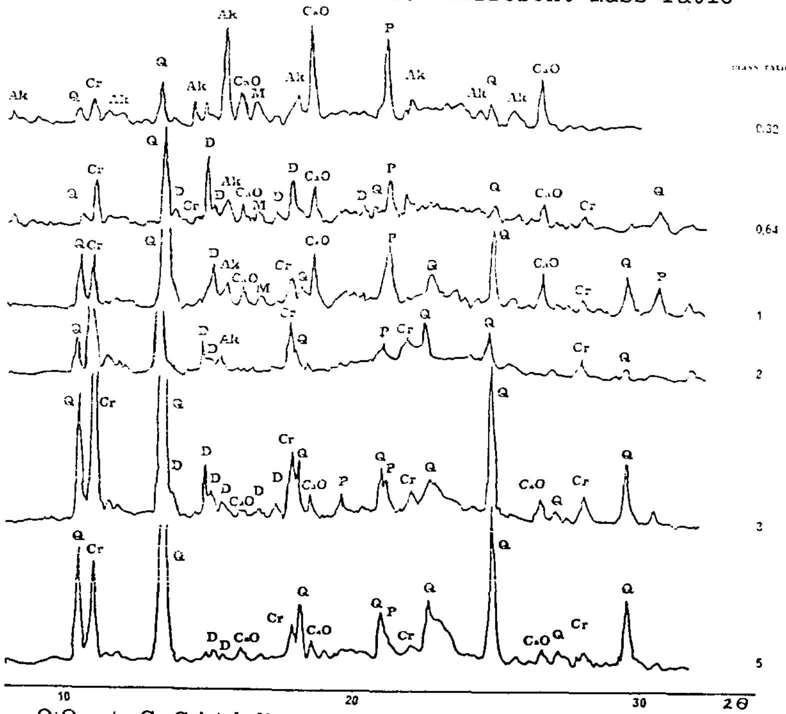


Fig.1. DTA curves of mixtures with different mass ratio



Q: Quartz, Cr: Cristobalite, Ak: Akermanite, M: Merwinite, D: Diopside

Fig.2. X-ray diffraction pattern of the crystalline phases at 1300℃

TABLE 1

Thermoanalytical investigations of SiO_2/dolomite mixtures at different ratios

Mass (mol) ratio of SiO_2/dolomite	Temperature ranges of DTA-peaks												Temp.rang. DTG-p.		
	α - β Quartz trans.				Decarbonization				Processes > 1000 °C				Decarbonization		
	Init. (°C)	Max. (°C)	Final (°C)	ΔH (J/g)	Init. (°C)	Max. (°C)	Final (°C)	ΔH (J/g)	Init. (°C)	Max. (°C)	Final (°C)	ΔH (J/g)	Init. (°C)	Max. (°C)	Final (°C)
Dolomite	-	-	-	-	640	776 838	860	1663	1364 1420	1368 1442	1375 1446	12,2 35,6	597	777 831	862
0,32 (1,0)	561	565	573	3,8	645	783 833	853	1231 (1632*)	1296	1310 ex	1329	-40,0	565	784 823	864
									1330	1335 1346	1353	37,0			
									1353	1410 1436	1461	271,4			
0,64 (2,0)	556	565	575	5,6	639	779 826	856	1051 (1736*)	1302	1311 ex 1322	1328	-40,3	617	779 817	854
									1328	1340 1351	1370	163,0			
1,0 (3,1)	554	565	575	7,5	631	779 818	843	844,5 (1609*)	1281	1303	1312	23,8	521	779 811	848
									1328	1349 1359	1373	158,7			
2,0 (6,3)	552	565	575	7,6	638	775 798	816	525,7 (1577*)	1270	1302	1310	17,8	573	774 795	823
									1328	1347 1358	1370	74,9			
3,0 (9,4)	556	565	573	6,7	609	775 793	812	419,9 (1679*)	1284	1300	1314	14,0	528	752 775 790	815
									1329	1347 1358	1370	53,1			
5,0 (15,7)	556	566	575	11,0	614	780	797	271 (1626*)	1283	1302	1314	9,3	571	768	809
									1335	1356	1372	27,4			

*: J/dolomite gramm

TABLE 2

High temperature X-ray diffraction measurements of SiO_2/dolomite mixtures at different ratios

Mass (mol) ratio of SiO_2/dolomite	Temperature ranges of phase changes (°C)									
	Disapp. of dolomite	CaO		MgO		Diopside		Akermanite		Disapp. of Quartz
		App.	Disapp.	App.	Disapp.	App.	Disapp.	App.	Disapp.	
Dolomite	660-680	570-590	> 1000	580-600	> 1000	-	-	-	-	-
0,3* (1,0)	650-670	570-590	1330-1360	620-640	> 1500	1120-1140	1310-1340	1130-1140	1410-1440	1330-1340
0,6* (2,0)	660-680	570-590	1310-1340	620-640	1310-1340	1120-1140	1310-1340	1120-1140	1310-1340	1320-1340
1,0* (3,1)	660-680	610-620	1310-1350	620-650	1310-1350	1060-1090	1310-1350	1170-1200	1310-1340	1370-1400
2,0 (6,3)	630-650	600-620	1300-1340	620-650	1360-1390	1110-1140	1360-1390	1210-1220	1360-1390	1420-1450
3,0 (9,4)	630-640	600-620	1310-1340	660-700	≈1500	1110-1140	≈1500	-	-	≈1500
5,0 (15,7)	610-620	600-630	≈1300	710-750	1410-1450	1170-1200	1390-1440	-	-	> 1500

Dolomite: $CaCO_3.MgCO_3$; Akermanite: $2CaO.MgO.2SiO_2$; Diopside: $CaO.MgO.2SiO_2$

*: Appearance of merwinite: $3CaO.MgO.2SiO_2$ (at the lower detection limit)

At temperatures above 1000 ^{o}C various processes of silicate formation are taking place, sintering and melt formations occur. For the given composition only a mixed calcium-magnesium silicate can be detected.

The most characteristic double endothermic peak of the DTA curve above 1000 ^{o}C, occurring at about 1350 ^{o}C, can definitely be assigned to melt formation. According to XRD measurements most crystalline phases (except SiO_2) vanish from the system at this point. According to the investigation of the melt phase content of the SiO_2/dolomite mixture heat-treated at 1350 ^{o}C the molar ratio of 2:1 mixture was found to melt the most readily; in parallel with decreasing dolomite content the melt formation is also reduced. This observation is also supported by the reduction in intensity of the DTA peaks around 1350 ^{o}C.

CONCLUSIONS

The quantitative composition of the SiO_2-dolomite mixture under the given experimental conditions has no effect on the temperature range of polymorphic transition (alpha-beta-quartz transition at about 560 ^{o}C), on the formation of calcium magnesium silicates and the melt phase (1100-1200 ^{o}C and 1300-1350 ^{o}C, respectively) and on the starting temperature of the decarbonization processes (570-620 ^{o}C).

The increased amount of SiO_2, however, accelerates the decarbonization of the $CaCO_3$ content of dolomite. The mixture ratio definitely determines the predominating calcium magnesium silicate phase (akermanite or diopside) and also the extent of formation of the melt phase.

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