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INVESTIGATIONS OF ELKEM MICRO SILICA BY THERMOSONIMETRY

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ABSTRACT

Elkem Micro Silica is an amorphous non-crystalline (glassy) material with a SiO_2-content of about 96 % SiO_2. This material has been investigated by thermosonimetry, TS. By this technique it has been possible for the first time to detect small amounts of cristobalite in the material. From semiquantitative determinations of the peak areas in the TS-diagrams of the transformation α-cristobalite to β-cristobalite at 260 °C, it has been possible to estimate the content of cristobalite in Elkem Micro Silica to be less than 0.3 weight%.

INTRODUCTION

Elkem Micro Silica is the name given to a product obtained through cleaning the fumes from electric arc furnaces. These furnaces usually contain quartz, coal and woodchips and are heated to 2000 °C. The fumes go through a unique condensing and filtering process, and the product obtained is a very finely divided silica. The mean particle size is 0.15 microns and the surface area is 22 m^2/g. The results of the chemical analysis of the micro silica used in this investigation are given in Table 1, and a microphotograph of the material is shown in Fig. 1. It has been known for some time that after micro silica has been heated to about 800-900 °C for 8-12 hours, cristobalite will start to grow and can be detected as such by X-ray analysis of the material. However, it has not been possible by any technique like X-ray or electron microscopy to show that traces of crystalline silica can also be present in the untreated material itself. Cristobalite has a phase transition at about 260°C with a volume expansion of 4 percent. The specific volumes involved are shown in Fig. 2. The transformation from α-cristobalite to β-cristobalite can also be detected very easily by using thermosonimetry. A TS-diagram for the transformation is shown on Fig. 3.

METHODS

Thermosonimetry (TS) is mainly a technique for detecting mechanical vibrations induced by volumetric changes, and changes in transport processes in

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TABLE 1.
Chemical analysis of Elkem Micro Silica Type FV 10/12 from Fiskaa Verk, Norway.

% SiO_2	96.4
SiC	0.57
Tot. C	1.88
H_2O	0.90
Fe	0.10
Al	0.13
Ca	0.11
Mg	0.11
K	0.54
Na	0.22
Ti	0.003
P	0.05
S	0.14
Mn	0.009
Ni	0.002
Co	0.001
Cd	0.001
Pb	0.009
Cu	0.006
Zn	0.011
Mo	0.005

TABLE 2.
X-ray data for α-cristobalite

$d_{obs.}$/Å	d_{ASTM} /Å
4.05	4.05
3.53	3.53
3.14	3.135
2.85	2.841
2.48	2.485
2.34	2.340
2.12	2.118
2.02	2.019
1.93	1.929
1.87	1.87
1.76	1.757
1.73	1.730
1.69	1.690
1.64	1.634
1.61	1.612
1.60	1.600
1.57	1.571
1.54	1.533
1.50	1.494

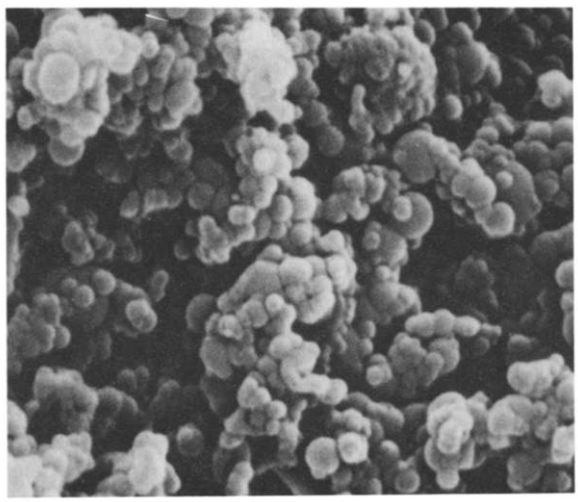


Fig. 1. Micro photograph (SEM) of Elkem Micro Silica.

solids. The basis of the experimental set-up is sketched in Fig. 4.

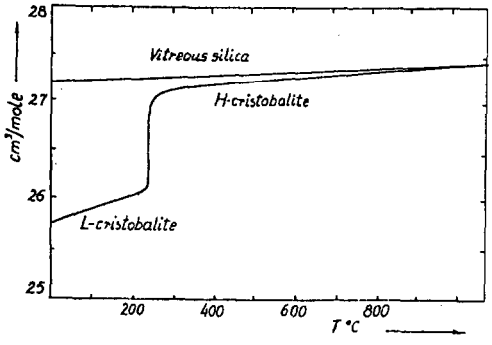


Fig. 2. Approximate specific volumes of vitreous silica and cristobalite.

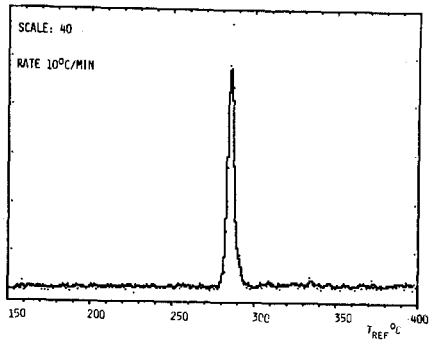
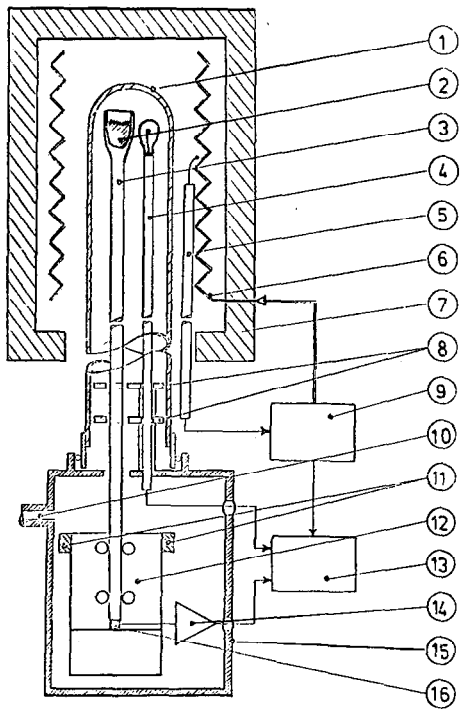


Fig. 3. TS-diagram for cristobalite in the temperature range 150-400 °C.



THE EXPERIMENTAL SET-UP.

1. PROTECTION TUBE OF ALUMINA.
2. SAMPLE.
3. STETHOSCOPE.
4. CHROMEL-ALUMEL THERMOCOUPLE
5. FURNACE THERMOCOUPLE.
6. HEATING ELEMENT KANTHAL A
7. FURNACE.
8. RADIATION SHIELDS.
9. TEMPERATURE CONTROL SYSTEM.
10. INLET FOR ATMOSPHERIC CONTROL.
11. SEISMIC MOUNT OF THE PICK-UP SYSTEM.
12. STETHOSCOPE MOUNTING AND CELL BASEMENT.
13. AMPLIFIER-SYSTEM.
14. PRE-AMPLIFIER.
15. VACUUM SEALED HOUSING OF THE PICK-UP SYSTEM.
16. PIEZOELECTRIC CELL.

Fig. 4. The experimental set-up.

The integral system of the sample on the top of the resonance stethoscope and the signal pick-up cell at the base, are entirely seismically mounted. The temperature was measured by a chromel-alumel thermocouple placed close to the sample. All experiments were carried out in air. The heating rate during the TS-investigation was 10 ^{o}C/min.

Sample preparation

Pure cristobalite was prepared by heating specpure silicon dioxide from Johnson Matthey Chemical Limited at 1470 ^{o}C for 6 hours. The material was examined both by X-ray and by DSC. The results from these examinations are given in Tables 2 and 3 together with literature values. As can be seen the results obtained agree very well with the corresponding data found in literature.

The micro silica samples were prepared by three different methods.
Series 1. Micro silica and pure cristobalite of particle size 0.2 µm were mixed mechanically as powder. The mixture was pressed to tablets, transferred to the termosonimeter stethoscope.
Series 2. Micro silica and cristobalite were mixed in water. The suspension was dried at 110 ^{o}C. The material was then pressed to tablets and transferred to the thermosonimeter stethoscope.
Series 3. Micro silica and cristobalite were mixed in acetone. The mixture was transferred directly to the stethoscope as a suspension and dried there.
In all the series the stethoscopes were weighed before and after the introduction of the sample. All contents are given in weight percent.

TABLE 3
The enthalpy of the transition $\alpha \rightarrow \beta$ cristobalite determined by DSC. (DSC-II from Perkin Elmer).

Literature	ΔH J/mol
JANAF (ref. 1)	1343 ± 251
A.J. Leadbetter and T.W. Smith (ref. 2)	1275
This work	1350 ± 26

RESULTS AND CONCLUSIONS

The TS-diagrams for some of the cristobalite micro silica mixtures are given in Figures 5-7. As can be seen from the figures, both the differential and the integral curve is plotted for each experiment. The differential curve shows qualitatively the TS-activity of the $\alpha \rightarrow \beta$ transformation in cristobalite at 260 ^{o}C. The integral curve on the other hand shows the *quantitative* respons to the same process.

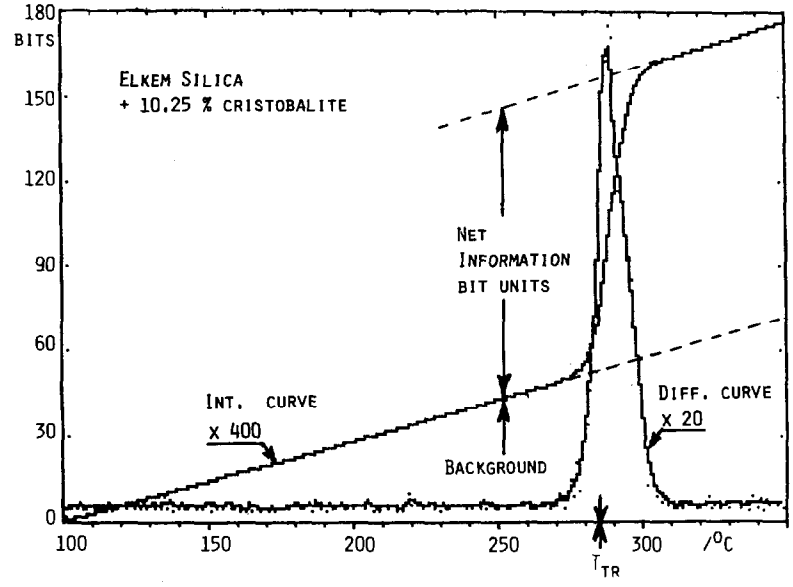


Fig. 5. TS-diagram for the mixture Elkem Micro Silica + 10.25 % cristobalite.

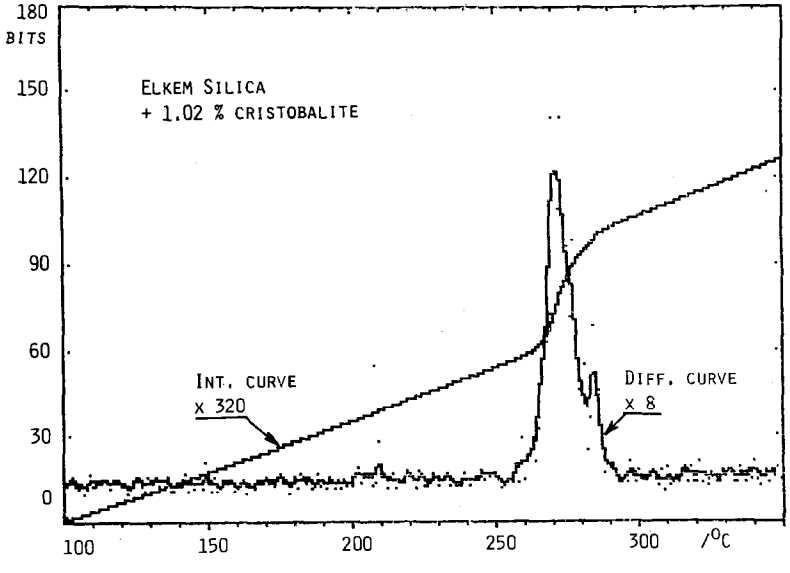


Fig. 6. TS-diagram for the mixture Elkem Micro Silica + 1.02 % cristobalite.

TABLE 4

Summary of the results after statistical treatment of the data.

X_G = graphically evaluated content of cristobalite.

X_A = analytically determined content of cristobalite.

Series No	X_G % crist.	X_A % crist.
1. (1. order)	0.153 ± 0.040	0.145 ± 0.030
1. (2. order)	0.123 ± 0.075	0.145 ± 0.019
2. (1. order)	0.194 ± 0.192	0.138 ± 0.074
1+2 (1. order)	0.167 ± 0.153	0.141 ± 0.049
3. (1. order)	0.291 ± 0.116	0.260 ± 0.060

Upper limit plus one standard error value for series 1 and 2:

$\overline{X}_G$ = 0.27 ± 0.05 % and $\overline{X}_A$ = 0.19 ± 0.01 %.

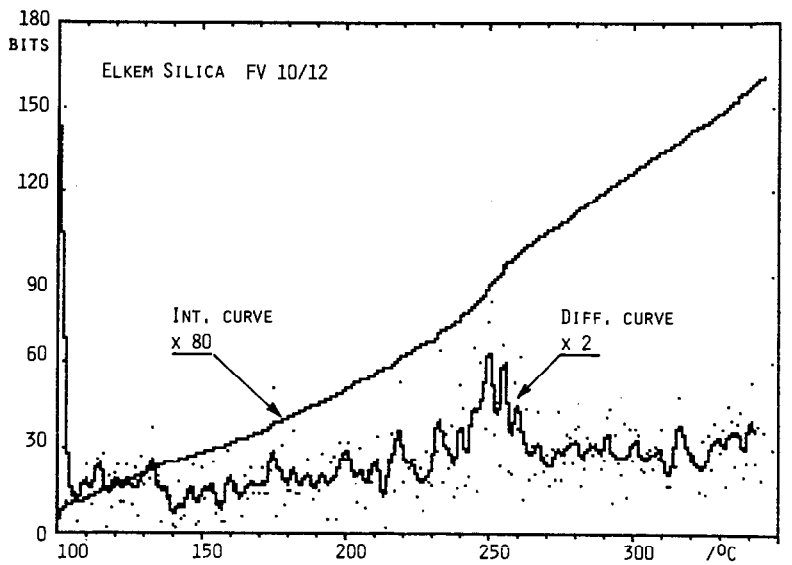


Fig. 7. TS-diagram for Elkem Micro Silica, type FV 10/12.

For calculation purposes the TS-information given in bits along the Y-axis, is assumed to be proportional to the amount of material that goes through a phase transformation at the temperature T_{tr}.

Table 4 presents a summary of the results after statistical treatment of the data, and these results are also given in Fig. 8. The regression line included

in the figure fits the expression

$$Y = 177.0\ Z + 34.7 = F(Z,X) \qquad (1)$$

Z = percent cristobalite added to the micro silica; Y = bits per mg mixture; X = the content of cristobalite in micro silica.

Extrapolation of the regression line to Y = 0 gives Z_o, the content of cristobalite in pure micro silica.

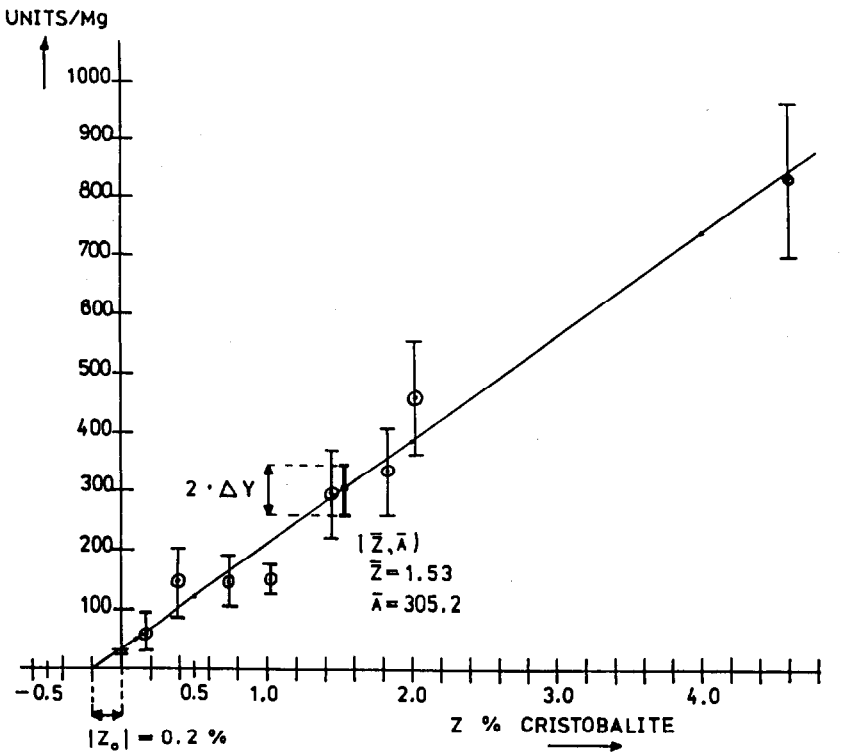


Fig. 8. Combined regression line drawn from the results of series 1 and 2.
Graphically evaluated content of cristobalite : X_G = 0.17 %;
Analytically determined content of cristobalite : X_A = 0.14 %.
Correlation coefficient : 0.988; standard error : ΔY = 40.95.

The conclusion of the investigation is that the content of cristobalite in this type of Elkem micro silica - FV 10/12 - is below 0.3 weight percent.

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ACKNOWLEDGEMENT

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