

the temperature the quicker the transformation took place. The DTA equipment used for the current work has a cooling rate of $10^{\circ}\text{Cmin}^{-1}$ from which one might expect to produce some metastable phase, or initially all metastable phase some of which has transformed to phase I by the time the sample reached room temperature (Table I). The reason that the pulled crystal X-ray powder photograph can be indexed solely on phase I presumably follows from a similar argument, namely that the crystal, which is cooling at a rate the order of $\frac{1}{2}^{\circ}\text{Cmin}^{-1}$, crystallizes in the metastable phase, but changes to phase I entirely during the cooling period which was at least 50h. This could explain the cracking phenomena, which did not apparently onset at any fixed temperature. If $\text{CaGa}_2\text{O}_4\text{I}$ is the stable phase, occurring during solidification, this would explain why no phase change was observed during the DTA heating cycle of phase I, the crystal being unable to revert to the meta phase once it had transformed to phase I. On cooling molten samples of crystal in the DTA unit, extensive supercooling was encountered and only one large exothermic peak was encountered about 200°C below the melting point. It is possible that under these conditions, crystallization and phase change occur simultaneously.

These results confirm the existence of the $3\text{CaO}\cdot\text{Ga}_2\text{O}_3$ and $\text{CaO}\cdot 2\text{Ga}_2\text{O}_3$ compounds, and show there are two other compounds in the region of the system studied, the first, CaGa_2O_4 existing in two polymorphs, one metastable at all temperatures, the other being designated $\text{CaGa}_2\text{O}_4\text{I}$ which is the phase obtained by Czochralski melt growth.

The second, a phase previously described as calcium gallate II has the formula $3\text{CaO}\cdot 2\text{Ga}_2\text{O}_3$ and bears no similarity to the garnet-like compound nominally $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$. This work also indicates that the growth of single CaGa_2O_4 from the melt will not be possible as a result of the nature of the phase diagram in the region around 50 mol% and the probability of a phase change on cooling causing internal strain and subsequent severe cracking.

Acknowledgements

The author would like to thank Mr M. R. Houlton for his work on the crystal growth of the material. Published by permission of the Controller, H.M.S.O., holder of Crown Copyright.

References

1. T. MOELLER and G. L. KING, *J. Amer. Chem. Soc.* 75 (1953) 6060.
2. H. J. DEISEROTH and Hk. MULLER-BUSCHBAUM *Z. Anorg. Allgen. Chem.* 396 (1973) 157.
3. J. JEEVARATNAM and F. P. GLASSER, *J. Amer. Ceram. Soc.* 44 (1961) 563.
4. J. JEEVARATNAM, F. P. GLASSER and L. S. DENT GLASSER, *Z. Krist. Bd.* 118 S (1963) 257.

Received 6 April
and accepted 11 May 1979

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Characterization of fused silica powders

Silica exists in several crystalline forms in nature. The most abundant forms are quartz sand and quartz crystals. Fused silica is an amorphous (non-crystalline) form of silica and can be prepared by arc fusion of quartz sand. The resulting fused silica retains some porosity, is translucent to opaque, and ranges in colour from off white to black.

Since 1956, a technique involving the process of slip casting and producing a rebounded form of fused silica [1] has been used. Some of the physical properties of the rebounded fused silica are

considerably different from the conventional fused silica while some, such as thermal expansion and specific heat are unchanged. The majority of the work with slip cast fused silica has been directed to aerospace applications, although rebounded fused silica has found applications in the refractory industry. This letter concerns some studies on the characterization of fused silica powders (C.E.C. France) produced by industrial arc fusion melting, which enter the composition of commercial slip cast silica refractories. Arc fusion of quartz sand is performed using graphite electrodes. After being melted and cooled down to room

temperature, the resulting fused silica is crushed into blocks of various sizes which are then ground and sieved into different grain sizes. For refractories applications black fused silica is usually discarded, only white powders are used for the production of the slips.

Our studies mainly deal with (a) an attempt to differentiate between white (W) and black (B) silica and (b) a comparison of the devitrification rates of silica to cristobalite for W and B powders as a function of grain sizes.

The high-quality quartz sand used as raw material for the fusion contained approximately 99.3 wt % SiO_2 ; 0.10 wt % Al_2O_3 ; 0.03 wt % TiO_2 ; 0.06 wt % Fe_2O_3 and various impurities in lower concentrations and showed an ignition loss of about 0.13%. After crushing the fused silica mass, various samples of W and B silica were collected as blocks.

A series of tests (X-ray diffraction, X-ray fluorescence, emission and absorption spectrography) performed on the W and B blocks produced inconclusive results for differentiating W and B silicas. Another series of tests using gas chromatography showed that the amount of carbon (from the graphite electrodes) in W and B silicas was very low (0.04% at the most) ruling out the hypothesis of the formation of large quantities of SiC in black silica.

It is known that the process of fusion with graphite electrodes may somehow introduce a certain degree of reduction [2, 3] in the fused materials. It was for this reason that we attempted to distinguish W and B silica blocks by ESCA using a Vacuum Generator Ltd ESCA I. Much care had to be taken in the preparation of suitable samples which were to be examined by ESCA. Indeed, preliminary results on samples shaped with carbide cutting tools had to be discarded because of some pollution effects occurring at the surface of the samples during the shaping operation. Suitable surface samples were obtained by fracture of W and B silica blocks, followed by an ultrasonic treatment in ethyl alcohol and washing in benzene. Then Si(2p), Si(2s), O(1s) and C(1s) photoelectron lines were recorded and analysed, the reference being the C(1s) line belonging to the carbon of the diffusion pump oil contaminating the surface. The spectra show that all peaks (W and B) offer an asymmetry in the lower binding energy side.

However, it was found that an important portion of this asymmetrical broadening could be attributed to some electrical effect which was an increasing function of the retarding potential applied between target and entrance slit. Such a negative charging effect, less common than the widely known positive effect [4], may appear in the case of an insulating sample of low photoelectron yield (as is the case in SiO_2 irradiated by $\text{AlK}\alpha$ rays) which are imbedded into a metallic matrix of high photoelectron yield [4, 5]. It must be also largely dependent on the specific geometry of the ionization chamber [6]. As binding energy shifts due to reduction are supposed to appear in the lower energy side from the Si(2p, 2s) peak, it was necessary to estimate the part of the asymmetry due to electrical effects in the total asymmetry of all peaks. This was attempted by considering the asymmetry of C(1s) as a reference in order to analyse Si(2p, 2s) lines. The C(1s) and the Si(2p, 2s) in W and B samples are presented in Fig. 1 and 2, respectively. The C(1s) line shown here was recorded at lower analyser energy than the Si lines so that its retarding potential was very near that of the Si(2s) line. It should be noted that the C(1s) asymmetry cannot result from carbonaceous impurity peaks as is ascertained by the aforementioned analysis. With respect to the Si(2p, 2s) lines, the important point is that in the range 0 to 2.3 eV (in the lower binding energy side from the top), the asymmetry of B silica is more important than that of W silica, unlike the situation encountered in the C(1s) spectrum (cf. Figs. 1 and

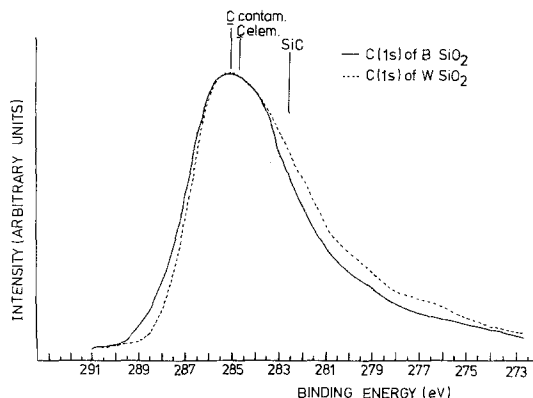


Figure 1 C(1s) photoelectron line of the pump oil film on the sample recorded with unmonochromatized $\text{AlK}\alpha$ radiation. (The energy position of C(1s) lines of graphite and silicon carbide are indicated in the upper part).

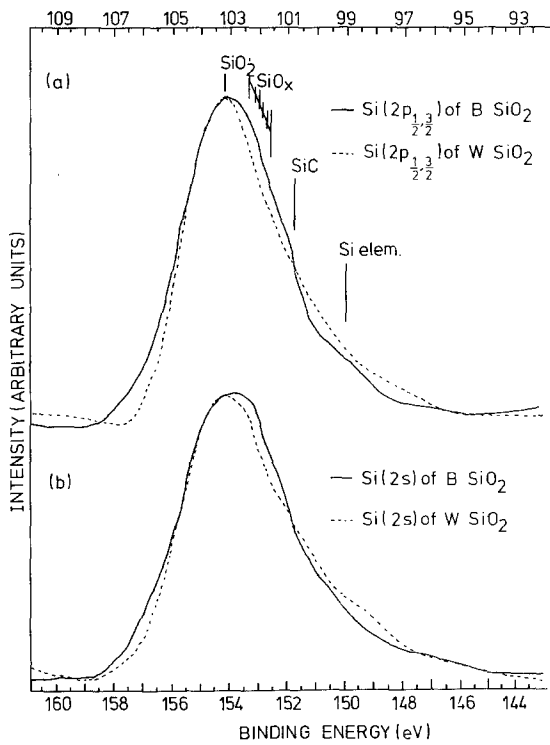


Figure 2 Si(2p, 2s) photoelectron lines of B(---) and W(—) silica (the energy position of Si lines in lower oxidation states are drawn in the upper part of the figure).

2). Such a behaviour may be a clue to the presence of a weak and broad peak around 1.5 eV (± 0.5 eV) in the lower energy side from Si(2p) and Si(2s) of B silica which corresponds to a shift of 2.6 (± 0.5 eV) with reference to Si(2p) and Si(2s) of silicon. This result roughly agrees with those of the literature concerning lower silicon oxides whose energy range is shown in Fig. 2 [7–9]. Thus it appears that B silica may differ from W silica by a certain amount of lower oxide SiO_X ($1 < X < 2$) (of the percent order) due to the use of graphite electrodes in the arc fusion process.

In order to make a distinction between W and B silica powders, devitrification tests were carried out on powders of W and B silicas of similar sizes. It is well known that silica changes into cristobalite at high temperatures. In Table I the grain sizes (sieving) as well as the specific areas (measured by BET) which were chosen for devitrification experiments, are given.

Devitrification tests have been performed in an electric furnace, using platinum crucibles at 1200°C, 1300°C, 1350°C, 1400°C for times

TABLE I Grain sizes (ϕ) of W and B silica powders used in devitrification tests

	ϕ_{inf} (μm)	ϕ_{max} (μm)	Specific area ($\text{m}^2 \text{g}^{-1}$)
G1	0	80	0.35
G2	40	200	0.12
G3	80	400	0.08
G4	200	707	0.015–0.022
G5	707	1200	0.010–0.015

varying from 15 min to 36 h. The amount of cristobalite formed as a function of temperature and time was recorded using an X-ray diffraction procedure described elsewhere [10] and is plotted in Fig. 3 for G1, G2, G3, G4 and G5. It should be noted that for each grain-size distribution and at all temperatures, the amount of devitrification in black silica powders is more important than in white silica powders. This difference is very marked at 1400°C and decreases with temperature.

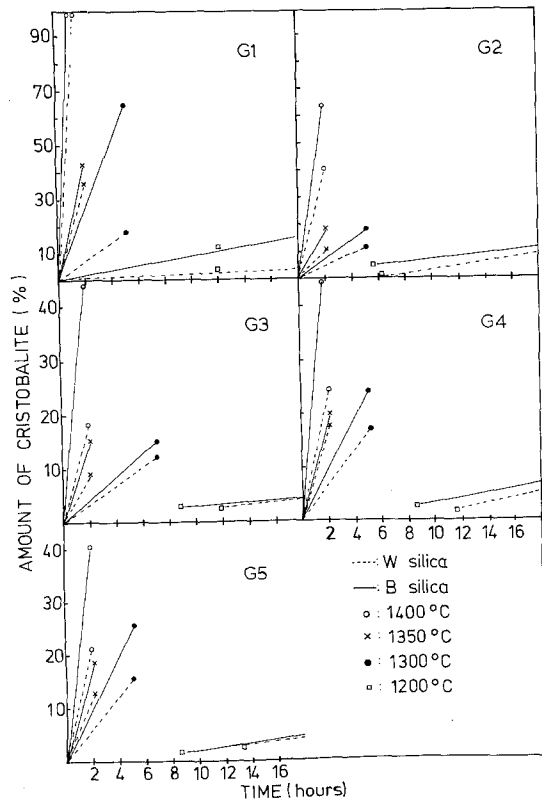


Figure 3 Amount of cristobalite formed as a function of time and temperature for G1, G2, G3, G4 and G5. (Devitrification curves are represented as straight lines for simplicity).

An attempt was also made to distinguish between surface and bulk devitrification by comparing the rates of devitrification as a function of grain sizes. A full account is given elsewhere [11, 12]. Briefly it can be said that:

(1) bulk devitrification is becoming more and more important when the grain sizes increase and/or temperatures decrease for a given grain-size distribution;

(2) the finer grain-size distribution G1 shows a rather different behaviour to the others. More chemical analyses were performed and it appeared that G1 contained approximately 0.345 Fe (ten times more than in the other grain sizes). This has been attributed to the crushing and grinding operations. Although all powders were submitted to a magnet for deironization it is thought that small iron particles remained stacked with the finer silica grains; the different devitrification behaviour of G1 being thus understood by an increased impurity content, as well as by the fineness of the grains.

Acknowledgements

This work is partially based on a B.Sc. Thesis (University of Mons) by P. Rousseau. The authors wish to thank Mr Lécrivain and Caruelle (C.E.C. France) for helpful discussions and for providing chemical analysis.

References

1. J. D. WALTON, *Ceram. Age* 77 (1961) 52.
2. A. M. ALPER, in "Ceramic Microstructures" (Wiley, New York, 1968) p. 763.

3. *Idem*, in "Refractory Materials", Vol. 5 (Academic Press, New York, London, 1970) p. 209.
4. T. A. CARLSON, "Photoelectron and Auger Spectroscopy" (Plenum Press, New York, 1975).
5. C. JOHANSSON, J. HEDMAN, A. BERNDTSSON, M. KLASSON and R. NILSSON, *J. Electron. Spectroscop.* 2 (1973) 295.
6. G. GRIMVALL, *Phys. Scripta* 9 (1974) 43.
7. G. HOLLINGER and TRAN HENCH DUC, 7th Conference on Amorphous and Liquid Semiconductors, Edinburgh, 27 June – 1 July (1977).
8. G. HOLLINGER, Y. JUGNET, P. PERTOSA, L. PARTE, TRAN HENCH DUC, 7th International Vacuum Congress and 3rd International Conference on Solid Surfaces, Vienna, 12–16 September (1977).
9. G. HOLLINGER, Y. JUGNET and TRAN HENCH DUC, *Solid Stat. Commun.* 22 (1977) 277.
10. J. N. HARRIS and E. A. WELSH, "Acceptance criteria for slip-cast fused silica radomes", Technical Report no. 3, June 1972, Georgia Institute of Technology, Atlanta, Georgia, USA.
11. P. ROUSSEAU, B.Sc. Thesis, University of Mons (Belgium) 1977.
12. C. LEBLUD, M. DELETERRE and M. R. ANSEAU, unpublished work.

Received 19 April
and accepted 17 May 1979

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