

Acknowledgement

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References

1. E. J. W. VERWEY, P. W. HAAIJMAN, and F. C. ROMEIJN, *Chem. Weekblad* **44** (1948) 705.
2. M. E. DRY and F. S. STONE, *Disc. Faraday Soc.* **28** (1959) 192.
3. N. P. KEIER and L. N. KUTSEVA, *Bull. Acad. Sci. USSR (Chem. Div.)* **5** (1959) 774.
4. A. BIELANSKI, J. DEREN, J. HABER, and J. SLOCZYNSKI, *Trans. Faraday Soc.* **58** (1962) 166.
5. E. R. S. WINTER, *J. Catalysis* **6** (1966) 35.
6. A. C. C. TSEUNG, B. S. HOBBS, and A. D. S. TANTRAM, *Electrochim. Acta* **15** (1970) 473.
7. G. EL SHOBAKY, P. C. GRAVELLE, and S. J. TEICHNER, *J. Catalysis* **14** (1969) 4.
8. A. C. C. TSEUNG and B. S. HOBBS, submitted to *J. Electrochem. Soc.*
9. R. M. GLAISTER, N. A. ALLEN, and N. J. HELLICAR, *Proc. Brit. Ceram. Soc.* **3** (1968) 229.
10. T. I. BARRY, R. K. BAYLISS, and L. A. LAY, *J. Mater. Sci.* **3** (1968) 229.
11. A. LANDSBERG and T. T. CAMPBELL, *Journal of Metals* (1965) 856.
12. F. J. SCHNETTLER, F. R. MONFORTE, and W. W. RHODES, "Science of Ceramics" edited by G. H. Steuart, **4** (British Ceramic Society, 1968) p. 79.
13. E. KOCH and C. WAGNER, *Zeits. fur phys. Chem. (B)* **38** (1937) 295.
14. S. BRUNAUER, P. H. EMMETT, and E. TELLER, *J. Am. Chem. Soc.* **60** (1938) 309.
15. R. W. GRIMSHAW, E. HEATON, and A. L. ROBERTS, *Trans. Brit. Ceram. Soc.* **44** (1945) 69.

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Letters

Rosette-like Precipitates of Silica

A rosette-like structure has often been observed in metallurgical slags. Whiteley and Hallimond [1] seem to be the first to have published in 1919 a micrograph of this structure, fig. 1, which they found in spoon samples withdrawn from acid slags with approximately the following composition: 55% SiO₂, 30% FeO, 15% MnO. From its appearance under the microscope, its refractive index and its response to various etching

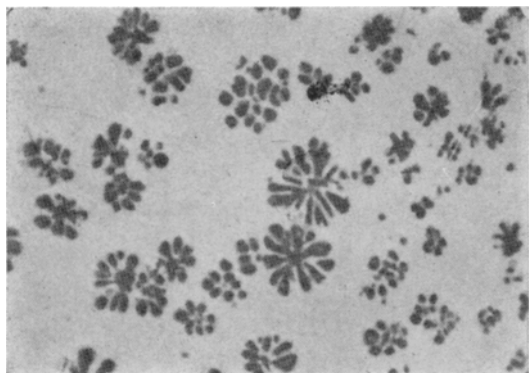


Figure 1 Rosette-like precipitate, observed by Whitley and Hallimont in acid slag ($\times 625$).

reagents, they concluded that it is a form of silica and suggested that it is cristobalite.

The same rosette-like structure was later observed in spherical inclusions found in solidified steel. Urban and Chipman [2] reported that these rosettes are glassy in appearance and have a refractive index that is near that of quenched cristobalite.

Later authors have accepted that the rosettes consist of cristobalite and Kiessling [3] in his 1968 review of non-metallic inclusions in steel states that cristobalite is easily recognised by its rosette morphology.

When investigating various glasses Greig [4] in 1927 noticed the separation of clusters of little "dots" which were occasionally seen to form a unit composed of rods radiating from a common centre. They were observed in the systems CaO-SiO₂ and MgO-SiO₂. From their appearance in the micrographs it seems certain that they are identical to the rosettes already discussed. Greig discussed whether they could consist of a second liquid, presumably very siliceous, formed in a two-liquid region but he finally concluded that they consist of cristobalite.

Barry, Clinton, Lay, Mercer, and Miller [5] recently reported on the same structure found in a glass of the following composition: 56% SiO₂, 23% Al₂O₃, 21% Li₂O. They suggest that it is a

hexagonal phase with a possible composition of LiAlO_2 and they explained the rosette-like shape by assuming that the crystals are polytwinned.

L. Hillert [6] has observed a number of examples of this structure in quenched melts containing SiO_2 and various amounts of fluorides and oxides of Mg, Ca, Sr and Ba. Fig. 2 shows

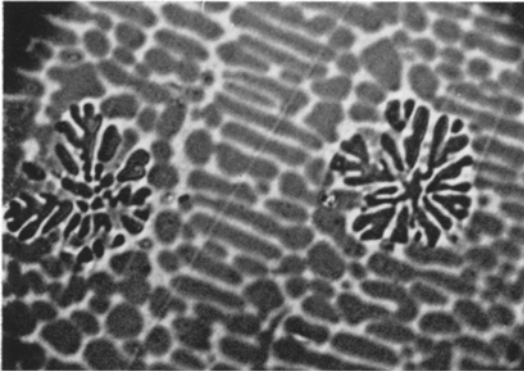


Figure 2 Star-like precipitate in a background of Sr dendrites, observed by L. Hillert in 68% SrF_2 , 32% SiO_2 ($\times 1180$).

an example which is very similar to one of the microstructures presented by Barry *et al.* Hillert described the shape as star-like and from the following observations he concluded that they should be regarded as a dendrite-related precipitate of vitreous silica.

(i) When the star-like precipitate was the only precipitate in a glassy matrix, the X-ray examination gave no indication of any crystalline phase. In fact, Barry *et al.* also observed that a specimen can contain large amounts of the star-like precipitate without the X-ray examination indicating any crystalline phase.

(ii) The star-like precipitate is formed when a melt is quenched into a two-liquid region where silica is one of the two co-existing liquids.

(iii) When a sample is quenched from a temperature where a two-liquid state is already established, the star-like precipitate will partly form as protuberances on the pre-existing liquid silica phase, fig. 3.

It may further be argued that the absence of any preferred growth direction in the star-like precipitate strongly indicates that neither of the two phases, matrix or precipitate, is crystalline. Furthermore, at least one of the non-crystalline phases must be very viscous. Otherwise, the sur-

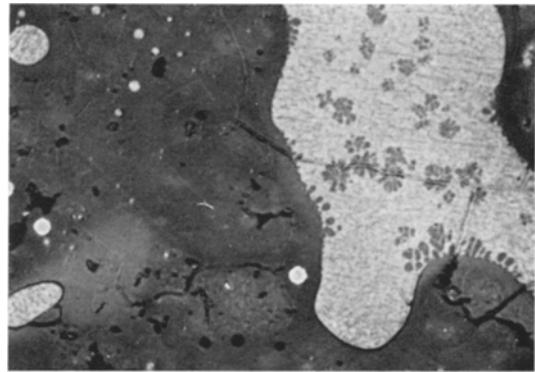


Figure 3 Star-like precipitate formed inside a SiO_2 -poor liquid (white region) and related protuberances formed in contact with a SiO_2 -rich liquid (grey region), observed by L. Hillert in 30% CaF_2 , 13% TiO_2 , 57% SiO_2 ($\times 228$).

face tension would soon make the shape spherical. The star-like morphology should thus be rather unique. Liquid silica goes through a glass transition in a temperature range at about 1500°C and liquid silica precipitated at or below this temperature range is thus sufficiently viscous to form as star-like dendrites and to retain this shape.

In view of the observations by L. Hillert it is now suggested that all the types of precipitate referred to in this note, the rosettes and the stars, are identical and consist of viscous silica. If found in new systems containing SiO_2 , the rosette morphology should be taken as a very strong indication that the particles consist of viscous silica. In fact, the rosette morphology has been found in a very different system. Zapffe and Sims [7] reported in 1943 a rosette-like precipitate formed directly in the metallic matrix of a

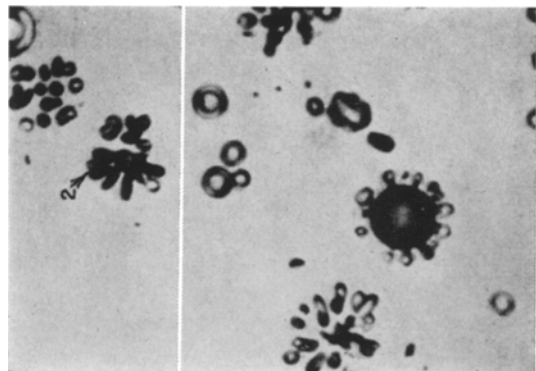


Figure 4 Raspberry-like precipitate, observed by Zapffe and Sims in the metallic matrix of a steel ($\times 1687$).

steel, fig. 4. They described the precipitates as glassy silica inclusions and from their discussion it is evident that they regard them as vitreous silica. This opinion seems to be shared by a number of authors who have later reported on this type of inclusion. It is sometimes referred to as raspberry-like [8].

Torszell [9] accepted the view that the raspberry-like precipitate in steel consists of vitreous silica and pointed out the importance of its high viscosity, as outlined above. However, he did not draw the conclusion that the same principles should hold for the case of precipitation of silica rosettes from the non-metallic matrix of slag inclusions in the steel. He still accepted them as cristobalite.

References

1. J. H. WHITELEY and A. F. HALLIMOND, *JISI* **99** (1919) 199.
2. S. F. URBAN and J. CHIPMAN, *Trans. ASM* **23** (1935) 93.

3. R. KIESSLING, "Non-metallic inclusions in steel, Part III" Report 115 (The Iron and Steel Inst., London, 1968) p. 50.
4. J. W. GREIG, *Am. J. Sci.* **213** (1927) 1.
5. T. I. BARRY, D. CLINTON, L. A. LAY, R. A. MERCER, and R. P. MILLER, *J. Mater. Sci.* **5** (1970) 117.
6. L. HILLERT, *Acta Polytechnica Scandinavica.* **90** (1970).
7. C. A. ZAPFFE and C. E. SIMS, *Trans. AIMME* **154** (1943) 192.
8. M. L. TURPIN and J. F. ELLIOTT, *JISI* **204** (1966) 217.
9. K. TORSZELL, *Jernkont. Ann.* **151** (1967) 890.

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A Fracture of Rubber in a State of Finite Torsional Shear

An interesting biaxial mode of failure has been observed in a solid rubber cylinder which had metal end plates bonded on to the flat ends.

Failure in torsion by a crack propagating perpendicular to the maximum tensile stress is well known for many materials, but biaxial failure in torsion has not, within the knowledge of the authors, been previously reported for a rubber.

The failure occurred during studies of the stress distribution necessary to maintain the rubber in a state of finite torsional shear. The rubber was an unfilled natural rubber, vulcanised for 30 min at 150° C using 5% by weight of dicumyl peroxide. The rubber cylinder was 4 in.* in diameter and 0.57 in. long.

It has been shown that the surface tractions necessary to maintain a right circular cylinder in a state of finite torsional shear correspond to two sets of stress components each acting only over the plane ends of the cylinder [1]. In addition to the distribution of tangential surface tractions providing the twisting couple, a distribution of normal surface tractions is required to maintain the cylinder at constant length. In the work

*1 in. = 2.54 cm.

described in this note the torsional shear was maintained by mounting the rubber unit vertically in such a manner as to allow the bottom plate to be twisted with respect to the top plate, while maintaining the length constant to an accuracy of better than 0.05% [2].

Fracture was observed in a particular rubber specimen when one end of the unit was twisted through 25° with respect to the other end. The failure was unintentional. Two distinct types of fracture surfaces were created, a primary surface and a secondary surface, and the nature of these surfaces has been studied. The directions of the fracture path have been examined in terms of the stress distribution through the rubber.

A limited number of attempts were made to reproduce the complete mode of failure by deliberately initiating a fracture in other specimens of rubber in a similar state of shear. Only one type of fracture surface was created, the nature and direction corresponding to the relatively smooth primary fracture surfaces discussed below.

When failure occurred the shear strain at the curved surface of the rubber cylinder was about 150% (i.e. a shear angle of about 56°). The deformation was then removed. The fracture path on the curved surface of the undeformed rubber