

Chrysotile asbestos can be dispersed essentially to the colloidal state when agitated at high speed in water in the presence of colloidal alumina. Presumably the coating of colloidal alumina, evidenced in Fig. 4, provides a strong positive repulsive charge which promotes separation of ultimate fibrils. Such dilute (0.5 to 2%) viscous translucent sols can be dried to semitransparent asbestos sheets in which the alumina plays the additional role of binder.

Kaolin and graphite, when coated with colloidal alumina, are adsorbed from dilute solution onto surfaces such as glass or cellulose and remain as a thin layer which is not easily rinsed off. An excess of colloidal alumina must be avoided in this case; only enough must be added to coat the clay or graphite,

since if more is present, the glass or cellulose will be covered preferentially with the free colloidal alumina to the exclusion of the larger alumina-coated particles.

The foregoing phenomena suggest means for depositing very uniform layers of alumina-coated particles of the order of 1μ in thickness on a variety of surfaces. Effects on lubricity, electrical conductivity, light transmission, and other phenomena might be expected, depending on the nature of the deposited material.

Acknowledgment

The writer wishes to acknowledge the cooperation of Vernon Keirstead in preparing the electron micrographs.

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Oxidation-Reduction Equilibria in Iron-Containing Glass

by W. D. JOHNSTON

Research and Engineering Center, Pittsburgh Corning Corporation, Pittsburgh, Pennsylvania

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The oxidation-reduction equilibrium between ferrous and ferric iron in $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glass melts was studied by equilibrating melts with various oxygen partial pressures. Exceedingly long equilibration times were required to obtain meaningful results. The reaction appears to be diffusion-controlled and may be expressed as $2\text{O}^{2-} + 4\text{Fe}^{3+} \rightleftharpoons 4\text{Fe}^{2+} + \text{O}_2$. Data are presented in which the valence of iron varies from predominantly +3 to predominantly +2.

I. Introduction

VERY little quantitative work has been done to elucidate oxidation-reduction equilibria of variable valence ions in glass melts. The state of knowledge has been reviewed by Tress,¹ who was forced to relate thermodynamic equilibria for pure oxide systems to what was presumed to be an oxidation-reduction sequence in glass obtained from the observation of glass colors. An attempt at a more quantitative study has since been made by Baak and Hornyak,² who measured the iron oxidation state in air as a function of temperature in glass melts containing small additions of iron oxide. In their work, the iron was almost completely trivalent. A more extensive investigation of the iron-oxygen equilibria in low-viscosity, high-iron silicate slags of metallurgical interest has been made by Turkdogan and Bills.³ In their work, the iron valence was varied from predominantly divalent to predominantly trivalent. A general review of the literature dealing with iron-containing glass has been made by Weyl.⁴

In no case has a systematic investigation of the iron oxidation-reduction equilibria been made on a high-viscosity glass melt in which the oxidation state of the iron was varied over a wide range. The purpose of the present work was to determine the conditions for the formation of the various valence states of iron and to permit an oxidation-reduction equation to be written describing this process.

II. Experimental Procedure

Glass melts containing small quantities of dissolved iron oxide were equilibrated in various atmospheres. The oxida-

tion state of iron in the melt was then determined by chemical analysis.

The glass used had the nominal composition $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 + \sim 2.5 \text{ wt}\% \text{ Fe}_2\text{O}_3$. Several master melts were prepared from reagent-grade Na_2CO_3 , SiO_2 , and Fe_2O_3 in a platinum crucible.

Small quantities of the master melts (2 or 3 g) were placed in 5- or 10-cm³ Morganite recrystallized alumina crucibles or in some cases, as mentioned later, in platinum crucibles. The crucible was lowered by a platinum or molybdenum wire into the hot zone of a vertical tube furnace under a controlled atmosphere. At the end of the experiment, the crucible was quenched by raising it out of the hot zone. Samples were repeatedly reground and refired for periods of at least 20 hours until a constant chemical analysis indicated that equilibrium had been attained. The furnace tube was constructed of mullite. The temperature of the furnace was controlled to within $\pm 1^\circ\text{C}$ as indicated by a Pt-Pt10Rh thermocouple encased in a mullite sheath suspended inside the furnace tube beside the sample. The temperatures used were 1100°, 1200°, 1270°, 1300°, and 1450°C.

Atmospheres used included oxygen, air, oxygen-free CO_2 , $\text{CO}-\text{CO}_2$ mixtures, CO in equilibrium with carbon (the crucible in this case), and H_2 saturated with H_2O at 0°C. The $\text{CO}-\text{CO}_2$ mixtures were metered using constant-head-type capillary

Received July 19, 1963; revised copy received November 8, 1963.

The writer is research chemist, Research and Engineering Center, Pittsburgh Corning Corporation.

¹ H. J. Tress, "Thermodynamic Approach to Redox Equilibria in Glasses," *Phys. Chem. Glasses*, 1 [6] 196-97 (1960); *Ceram. Abstr.*, 1961, October, p. 238i.

² T. Baak and E. J. Hornyak, Jr., "Iron-Oxygen Equilibrium in Glass: Effect of Platinum on $\text{Fe}^{2+}/\text{Fe}^{3+}$ Equilibrium," *J. Am. Ceram. Soc.*, 44 [11] 541-44 (1961).

³ E. T. Turkdogan and P. M. Bills, "Thermodynamic Study of $\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$, $\text{FeO}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$, and $\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5$ Molten Systems," *J. Iron Steel Inst. (London)*, 186, 329-39 (1957).

⁴ W. A. Weyl, *Coloured Glasses*. Dawsons of Pall Mall, London, 1959. 541 pp.

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