

Mechanism and kinetics of reduction of a FeO-Fe₂O₃-CaO-MgO aluminosilicate melt in a high-CO-activity environment

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ABSTRACT

Droplets of an iron-bearing calcia magnesia aluminosilicate (Fe-CMAS) melt were reacted under distinctly reducing conditions ($f_{\text{O}_2} = 2.4 \times 10^{-13}$ and 6.4×10^{-15} atm) at high temperature (~1400 °C) and ambient pressure. The low f_{O_2} environment was maintained by a flowing gas mixture of CO and CO₂, with a high content of CO. Molten metallic iron alloyed with silicon and carbon formed on the surface of the melt; no metal was observed in sample interiors. A color change from brown to pale blue confined to the outer layer of the melt indicated that essentially complete reduction of Fe³⁺ to Fe²⁺ had occurred in this region. Analysis of the reaction kinetics, particularly in comparison to melts of similar polymerization but free of CaO, reveals that the concentration of electron holes has decreased to such an extent that ionic transport in the melt is significantly slowed and the diffusion of CO as a neutral species becomes dominant and rate-limiting: molecular CO, initially incorporated into the melt as a physically dissolved species, subsequently reacts to form chemically dissolved (bonded into the melt structure) CO₃²⁻ anions, consuming electron holes in the process. The chemical diffusion coefficient for CO in the reduced melt at 1400 °C is estimated as $D_{\text{CO}} \approx 4 \times 10^{-4}$ cm²/s, consistent with that of other, similarly sized molecular species (e.g., H₂ and H₂O) for similarly polymerized melts, as reported by other investigators. Upon quenching, the droplet acts as a closed system. Internal redox couples see the reduction of the carbonate so as to form bubbles of CO, the composition of which are confirmed with Raman spectroscopy. The open-system reduction and closed-system quenching dynamics are analyzed following an Ellingham-diagram approach.

Keywords: Redox, silicate melts, carbon, diffusion, reactions, kinetics