Phase-Field Modeling of High-Temperature Oxidation Corrosion in Multi-Chemical Component Systems

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Abstract

For many materials, and particularly metals, corrosion is one of the most significant mechanisms regarding the chemical degradation of structural integrity. Therein, a chemical component diffuses to the surface of a structure and reacts with atmospheric elements to form a corrosive layer. The resulting products and their formation rates depend significantly on the material and atmospheric composition, as well as the operating temperature. Elevated temperatures accelerate this detrimental process, making it a key factor in estimating the lifespan of high-temperature electrolysis plants. In the "H2GIGA – HTEL" project, the influence and impact of corrosion are studied at temperature levels of up to 900 ◦C under dominant process atmospheres, such as those containing significant levels of hydrogen or high oxygen content.

Current state-of-the-art models allow the prediction of diffusion and reaction mechanisms using electrical or chemical potentials, see (1), but they are typically limited to solid or solid-liquid systems, where the system density remains nearly constant. Technological applications include ceramic filters used to purify molten steel by removing non-metallic inclusions, as in (2), or the reduction of iron oxide, see (3). To address oxidation processes involving changes in density due to reaction, diffusion, and phase transition mechanisms, a multi-phase, multi-component phase-field model is employed here, which is based on the work of Svendsen et al., cf. (4). This approach uses mixture theory to conserve the mass of all components in the system, as well as for the total mixture. The current mixture density is calculated using the molar mass and molar volume of each component. The chemical potential of each component contributes to the material point state, driving the diffusion in the sense of a generalized Cahn-Hilliard equation and enabling accurate modeling of mixing and separation processes via an Allen-Cahn framework. Following a phase-field approach, diffuse phase boundaries are implemented using spatial gradient terms in the free energy function, combined with contributions from components and phases. Reactions are defined by linear chemical equations and stoichiometric coefficients for all components according to (5). This work focuses on high-temperature oxidation processes in which chromium (Cr) plays a dominant role. Acting as a sacrificial anode, Cr oxidizes to form chromium(III) oxide (Cr2O3), protecting the underlying material until its concentration falls below a critical level, allowing other oxides to form. Experimental studies typically measure the weight change of specimens at discrete time intervals, even though cooling from high temperatures can cause

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mechanical stresses and delamination of the oxide layer. These factors complicate precise measurements. Another method involves microscopic imaging of cut specimens to directly evaluate layer thicknesses, capturing geometrical influences, such as variations in diffusion near corners. These spatially inhomogeneous effects are of high importance for the lifetime of a component and thus require an implementation of the model in a multi-dimensional framework, performed here in the finite element software Abaqus.

The proposed model simulates the reaction between chromium and oxygen to form Cr2O3 on the surface of a solid two-dimensional structure. To this end, the system comprises five components (Cr, O2, Cr2O3, air, and steel) and two phases (solid and gaseous). The reaction occurs at the interfaces, with the newly formed oxide adding to the solid phase, thereby expanding it. The model captures oxide layer growth on the surface and chromium depletion beneath it, while tracking phase interface movement due to Cr2O3 growth. Simulations also reveal differences in oxide formation at corners: outer corners are poorly supplied with chromium, resulting in thin oxide layers, whereas inner corners benefit from enhanced diffusion. Finally, we validated our model by comparing simulated results with experimental data, demonstrating its ability to replicate layer growth in real-world applications.

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