DIFFUSION IN HIGH-TEMPERATURE FERROCHROME ALLOY OXIDATION

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Simulation has been applied to the diffusion characteristics such as the effective component diffusion coefficients in Fe – 35 mass% Cr – (0.5-3.0) mass% Al bearing surface oxides at the time of peeling. The simulation results are in agreement with experimental data on the layerwise phase compositions of the oxides. The model is described for the diffusion in a three-layer oxide region. The research elucidates the formation mechanism for multilayer oxides, and also gives estimates of their effects on heat resistance.

Keywords: high-temperature oxidation, diffusion, ferrochrome alloy.

Alloys in the system Fe – 35 mass% Cr – (0.5-3.0) mass% Al are used as constructional materials (batchers) in forming mineral fibers. Multilayer oxides are formed on such alloys, which provide their high heat resistance at 1273-1673 K [1, 2]. The phase compositions of the oxides are based on Cr, Al, and Si.

The surface oxides were produced by high-temperature annealing of specimens 10 mm in diameter and height 20 mm at 1473 K for 20 h [2]. Powder x-ray diffraction (URS-55) patterns of the oxide layer revealed its composition. The phase composition of the outermost 3-5 µm layer had been established in [1] by the glancing incidence method (URS-002). The positions of the oxides were confirmed by electron-probe microanalysis of the component distributions over the oxide thickness.

The purpose of this study was to determine the effective diffusion coefficients for aluminum, silicon, and chromium in order to confirm the mechanism for the formation of multilayer oxides and the effects of them on the heat resistance.

The model was selected from the element distributions in the Me – MeO zone [3]. The effective diffusion coefficients for aluminum, chromium, and silicon were determined by using a one-dimensional model that describes the diffusion from an infinitely thin layer to bulk material [3]:

\[
C(x,t) = \frac{q}{2\sqrt{\pi D t}} \cdot \exp\left(\frac{-x^2}{4Dt}\right) + C_0. \tag{1}
\]

Here \(\tilde{D}\) is the diffusion coefficient in m²/sec, \(C\) the concentration (mass fraction in %), \(C_0\) the initial concentration level in %, \(x\) the linear coordinate in m, \(t\) time in sec, and \(q\) the output from the instant source at point \(x_0\) (Fig. 1).

The Al, Cr, and Si distribution curves have peaks at the points where the oxides of those elements are formed. These peaks correspond to the moments of oxide peeling (Figs. 1 and 2).

One determines the diffusion coefficient from equation derived from the correspondent transcendental equation (1) for \(t = 72000\) sec, \(q = 28.8\ \mu m\), \(x = 0\ \mu m\), \(C(x,t) = 3.6\%\), and \(C_0 = 0.4\%\):

\[
\tilde{D} = \frac{q}{2\sqrt{\pi D t}} \cdot \exp\left(\frac{-x^2}{4Dt}\right) - C(x,t) + C_0 = 0. \tag{2}
\]

The diffusion coefficient for aluminum was calculated from this model. Figure 3 shows the Al concentration distribution in the thickness.
The behavior of the function \( f(\tilde{D}) \) in the transcendental equation (2) was examined in the range of the argument from \( 10^{-10} \) to \( 10^{10} \) \( \mu \text{m}^2/\text{sec} \) by numerical methods (division into halves and secants). To check the solution to (2), the values of \( f(\tilde{D}) \) were displayed near its root (Fig. 4). The root of the transcendental equation was \( 7.1 \times 10^{-5} \) \( \mu \text{m}^2/\text{sec} = 7.1 \times 10^{-17} \text{m}^2/\text{sec} \). This is the effective diffusion coefficient for Al. The experimental data and the simulation results are in agreement (Fig. 5).

The same scheme was used to calculate the effective diffusion coefficients for Cr and Si (Figs. 6 and 7). The chromium distribution curve has three peaks. The effective diffusion coefficient was determined for each of these peaks: \( 2.2 \times 10^{-16}, 1.3 \times 10^{-16}, \) and \( 2.2 \times 10^{-16} \) \( \text{m}^2/\text{sec} \). To calculate \( \tilde{D} \), the distribution curve was split up into three segments: 88-116 \( \mu \text{m} \) from the origin as the first, 116-138 \( \mu \text{m} \) the second, and 138-166 \( \mu \text{m} \) the third. The experimental data and the simulation results correlate.

On the element curves, the accumulation of oxygen and metal vacancies corresponds to a fall in cation concentration. The valencies of the cations and anions correspond to the formation of the oxides.

With a content of 0.5% Al the oxides were formed at the surface of the alloy on the scheme Me \( \rightarrow \) \( \text{Al}_2\text{O}_3 \rightarrow \text{SiO}_2 \rightarrow \text{FeCr}_2\text{O}_4 \). The values obtained for \( \tilde{D}_{\text{Cr}}, \tilde{D}_{\text{Al}}, \) and \( \tilde{D}_{\text{Si}} \) were similar to but higher than the diffusion coefficients for the pure oxides [4]. This indicates that the oxides of these elements form substitutional solid solutions with one another:

\[
\begin{align*}
\text{FeO} + \text{Cr}_2\text{O}_3 & \rightarrow \text{FeCr}_2\text{O}_4, \\
3\text{FeCr}_2\text{O}_4 + 2\text{Cr} & \rightarrow 4\text{Cr}_2\text{O}_3 + \text{Fe}, \\
\text{Cr}_2\text{O}_3 + 2\text{Al} & \rightarrow \text{Al}_2\text{O}_4 + 2\text{Cr}, \\
2\text{Cr}_2\text{O}_3 + \text{Si} & \rightarrow 3\text{SiO}_2 + 4\text{Cr}.
\end{align*}
\]