A mass and charge balance (MCB) model that can simulate oxide growth and dissolution kinetics simultaneously during corrosion of an alloy has been recently developed. In this study, the MCB model was applied to the corrosion of the Co-Cr alloy Stellite-6. The construction of the model and the assignment of values to the rate parameters for the model are presented. The model simulation results are then compared with experimental corrosion data collected as a function of pH, temperature and polarization potential. The data include the current during potentiostatic polarization, the corrosion potential under open-circuit conditions, and post-test analyses of the oxide formed and the amount of metal dissolved. Excellent agreement between the model results and experimental data are found. This is evidence that the MCB model is a useful tool for predicting time-dependent corrosion while an oxide film is evolving.

The rate of a redox reaction in solution depends on the electric potential drop across the oxide film. However, the MCB model also takes into account the dependence of the potential drop across the oxide film on the rate of oxide formation and dissolution. The MCB model imposes mass and charge balance requirements on these rates, and chemical reaction and transport rate equations. The MCB model is based on mass and charge balance requirements on the rates of the electrochemical redox reaction and metal dissolution. The model takes into account the dependence of the rate of metal dissolution on the oxide film on the electric field present at the interface, the electrochemical potentials of the alloy, and the oxide film. The model is based on the assumption that the rate of metal dissolution is a function of the electrochemical potential, pH, and temperature. The MCB model considers the dependence of the potential drop across the oxide film on the rate of oxide formation and dissolution. The model is based on mass and charge balance requirements on the rates of the electrochemical redox reaction and metal dissolution. The model is based on the assumption that the rate of metal dissolution is a function of the electrochemical potential, pH, and temperature.

Alloys owe their corrosion resistance to protective oxide films formed on their surfaces. Corrosion involves surface redox reactions (metal oxidation coupled with solution reduction) and interfacial transfer of the charged species involved in the redox reactions. The presence of an oxide film hinders the interfacial charge transfer, slowing the rate of corrosion. Modeling oxide formation and growth as a function of the solution environment is an important component in predicting the corrosion behavior of an alloy.

Several corrosion models have been developed for predicting the rate of oxide growth and/or the rate of metal dissolution in the presence of an oxide film. To obtain the overall rate of corrosion, many of these models focus on solving the transport rate equations for individual charge carriers (interstitial cations and anions, cation and anion vacancies, and electrons and holes) across the oxide film, in addition to the rates of their creation at respective interfaces (e.g., chemical electrochemical redox reaction rates). These models assign rates to the transport of different charge carriers that are difficult to verify. Since the rate of interfacial charge transfer depends on the electric field present at the interface, the electrochemical potentials of the alloy, the oxide film, and solution phases are important parameters in determining the corrosion rate.

Many of the existing models acknowledge that the driving force for corrosion depends on the potential of the corroding system (the corrosion potential, \( E_{corr} \)); in an open circuit or the applied potential (\( E_{app} \)) during polarization. However, these models do not specifically quantify the driving force as a function of electrode potential and/or other quantifiable potentials such as the equilibrium potential of a redox pair involved in corrosion (\( E_{eq} \)). The electrode potential and the redox pair may change with time as corrosion progresses. The nature of oxide and the oxide film layer structure can also change with time as corrosion progresses even under potentiostatic polarization or constant solution conditions. The type of oxide that can form and its rate of formation depend on solution environmental parameters such as pH, temperature and the concentrations of redox active species. Few existing models specifically incorporate the solution environment in their model parameters and, even in those models that do so, the effects are formulated primarily based on empirical relationships. No existing models consider changes in oxide composition and layer structure as corrosion progresses. These shortcomings limit the predictive capabilities and the application ranges of these models.

Recently, we have developed a corrosion kinetics model that can simulate the metal oxidation rate (as a current), oxide film growth and metal dissolution as a function of electrode potential, pH and temperature. This Mass and Charge Balance (MCB) model considers the elementary processes that are included in other models: electrochemical redox reactions at the metal and oxide interfaces, the transport of charged species across the oxide film, and metal oxidation and dissolution. The rates of the individual elementary reactions/processes in the model are formulated using classical (electro-)chemical reaction rate equations and mass and charge flux equations. However, the MCB model imposes mass and charge balance requirements on these rates, and chemical reaction thermodynamic and kinetic constraints on the electrochemical redox reactions involved in corrosion. The mass and charge balance requirements involved in the MCB model dictate that the rate of metal oxidation must equal the rate of its coupled solution species reduction, and the rate of metal oxidation must equal the sum of the rates of oxide formation and metal dissolution. This allows us to avoid the need for detailed modeling of the transport of different charged species across the oxide film. Instead, the MCB model takes into account the dependence of the potential drop across the oxide film on the type and thickness of the oxide(s) that grow with time.

We have previously presented detailed descriptions of the fundamental physical and chemical properties and processes that underlie the MCB model, and a few model calculation results that show its capability of simulating corrosion. In this paper we expand on the capabilities of the MCB model and its construction for an application to the corrosion of a Co-Cr alloy, Stellite-6. Model simulation results are compared with experimental measurements of current, potential, oxide composition and layer structure, and dissolved metal concentrations at various pHs, temperatures and polarization potentials.

**Overview of the MCB Model**

Detail descriptions of the fundamental physical and chemical processes that underlie the MCB model and the general formulation of the flux equations included in the model can be found elsewhere. Only a brief description of the MCB model is provided here. The MCB model takes into account the dependence of the potential drop across an oxide film on the type and thickness of the oxide(s) that grow with time. Thus, the MCB model contains only three flux equations for metal oxidation (\( J_{Mox} (r) |_{ox} \)), oxide growth (\( J_{Mind} (r) |_{oxide} \)) and metal dissolution (\( J_{Mred} (r) |_{sol} \)) and these of only two fluxes are independent of each other, see schematic in Figure 1. The mathematical formulae of these fluxes are given in Table 1. Table 1 also provides formula for the model output of experimentally measured parameters, current, oxide thickness and dissolved amount of metal ions.
Butler–Volmer equation due to the use of an effective overpotential, terms, the effective overpotential (Formula 1 in Table I). This equation is referred to as a “modified” Butler–Volmer equation due to the use of an effective overpotential, \( \eta_{\text{eff}}(t) \). As described later the effective overpotential takes into account the potential drop across the oxide layer that is not available for an electrochemical reaction. The oxidized metal either participates in oxide formation or dissolves into solution. The MCB model formulates the fluxes of both oxide growth and dissolution to have first-order rate constants, \( k_{\text{MO}}(t) \) and \( k_{\text{diss}}(t) \), respectively.

The flux equations in the MCB model contain time-dependent terms, the effective overpotential (\( \eta_{\text{eff}}(t) \)) in the oxidation flux and the first-order rate constant for oxide dissolution flux \( k_{\text{diss}}(t) \) in the oxide growth flux. These kinetic parameters are further defined as listed in Formulas 4 to 7 in Table I. Irrespective of the type of oxide that forms and the rate of its formation, oxide formation is an electrochemical reaction and is constrained by reaction thermodynamics. The thermodynamic constraints invoked in the MCB model include a requirement that the driving force for metal oxidation (coupled with solution reduction) leading to formation of a specific oxide is the difference in the equilibrium potentials of the two coupled half-reactions for that redox reaction \( (E_{\text{eq}} - E_{\text{re}}) \). The MCB model distributes this thermodynamic driving force between the \( \text{m} | \text{o} \) and \( \text{o} | \text{sol} \) interfaces and the oxide layer. The potential drop in the oxide \( (\Delta V_{\text{oxide}}(t)) \) is assumed to be linearly dependent on the oxide thickness \( (L_{\text{MO}}(t)) \), see the schematic in Fig. 1b. This increase in \( \Delta V_{\text{oxide}}(t) \) with \( L_{\text{MO}}(t) \) decreases the effective overpotentials for the redox half-reactions at the two interfaces. This allows the flux of metal oxidation to be formulated using a Butler–Volmer equation but with an effective overpotential. The effective overpotential for a specific metal oxidation reaction can then be defined as a function of the thickness of the oxide that is growing, as presented in Formula 4 and Formula 5 in Table I, respectively. It should be noted that a space charge layer can add an additional Coulombic potential barrier. The potential drop due to a space charge will depend on the nature of the semi-conducting oxide and the solution redox environment. This value will be constant.

### Table I. Mathematical formulae of the fluxes in the MCB model.

| Formula | Flux Equations used in the Model | Model Output | Time Dependent Terms in the Flux Equations | Model Parameters |
|---------|---------------------------------|--------------|------------------------------------------|------------------|
| 1       | \( J_{\text{MO}}(t)|_{\text{m}} = J_{\text{MO}}^{\text{eq}} \cdot \exp(\frac{\alpha_{M} E_{\text{re}}}{R T} \cdot \eta_{\text{eff}}(t)) \) when \( \eta_{\text{eff}}(t) > 0 \) \( J_{\text{MO}}(t)|_{\text{m}} = 0 \) when \( \eta_{\text{eff}}(t) \leq 0 \) \( J_{\text{MO}}(t)|_{\text{oxide}} = \left( k_{\text{MO}}(t) \cdot \eta_{\text{MO}}(t) \right) \cdot J_{\text{MO}}(t)|_{\text{m}} \) | Current (t) \( i_{\text{ox}}(t) = i_{\text{MO}}(t)|_{\text{m}} \) | \( \eta_{\text{MO}}(t) = E_{\text{eq}} - E_{\text{re}} \cdot \Delta V_{\text{oxide}}(t) \) \( \Delta V_{\text{oxide}}(t) = \Delta V_{\text{oxide}}(0) + \varepsilon_{\text{MO}} \cdot L_{\text{MO}}(t) \) \( \Delta E_{\text{MO}}(0) = \Delta E_{\text{MO}}(0) + \varepsilon_{\text{MO}} \cdot L_{\text{MO}}(t) \) \( k_{\text{MO}}(t) = k_{\text{MO}}(0) \cdot \exp \left( \frac{-\varepsilon_{\text{MO}} (t) \cdot \Delta V_{\text{oxide}}(t)}{RT} \right) \) | \( E_{\text{re}} \cdot \Delta V_{\text{oxide}}(0) \) \( \varepsilon_{\text{MO}} \) \( \Delta E_{\text{MO}}(0) \) \( k_{\text{MO}}(0), k_{\text{diss}}(t) \) |
independent of oxide thickness on a pure-phase oxide layer and can be easily incorporated in the model. The oxide that grows during corrosion of an alloy will have a concentration gradient of metal cations or oxygen anions. In this case, the potential drop over a space charge layer is not significant compared to that over the oxide layer that is growing on the alloy and hence it is not explicitly modelled in this study.

The potential drop across a growing oxide layer depends on oxide thickness, and the oxide thickness depends on the rate for 1-D oxide growth that can change with time. The MCB model assumes that the rate of oxide growth has a first-order dependence on the oxidation flux, the oxide growth rate constant \(k_{MO}(t)\) has an Arrhenius dependence on the activation energy, and the oxide layer is an activation energy barrier for the formation of a metal-oxygen bond that adds to the growing oxide crystal. Because the activation energy increases with an increase in \(\Delta V_{\text{oxide}}(t)\) (Formula 6 in Table I), the rate constant for oxide formation decreases exponentially with an increase in oxide thickness (Formula 7 in Table I). In contrast to the changing oxide growth rate with oxide thickness, the rate constant for metal dissolution at the oxide/sol interface is generally assumed to be independent of oxide thickness. It is recognized as being dependent on the type of dissolving oxide and the metal cation dissolution properties of the contacting solution (pH, temperature, flow, metal ion solubility, etc.).

It should be emphasized that the linear dependence of potential drop over an oxide layer does not mean a linear growth of the oxide layer. This model does not assume that an oxide layer grows at a specific, predetermined rate, such as a linear or logarithmic. Instead the MCB model calculates the growth of a specific oxide based on the competition between metal-oxygen bond formation and surface hydration/hydrolysis of oxidized metal cations. In the MCB model the fraction of the metal oxidation flux going to the oxide growth flux is determined by the relative rates of metal oxide formation and metal ion dissolution. The model simulation results show that the growth of an oxide layer on the alloy follows a logarithmic growth rate once an oxide establishes a layer thicker than a few angstroms.\(^{11}\) At short times, the logarithmic growth rate can be approximated as a linear growth rate. Because the MCB model assumes that the rate constant of the metal-oxygen bond formation decreases as the oxide grows, at sufficiently long times the oxide eventually stops growing and the metal oxidation rate becomes equal to the metal dissolution rate.

Alloys may contain more than one redox-active element that can form an oxide or hydroxide of a single metal element. As well, an alloy can support the formation of a mixed oxide/hydroxide that contains more than one metal element. In addition, transition metals can exist in more than one oxidation state and this, combined with the possibility of forming several different stable oxides and hydroxides, leads to the possible formation of many different layers of oxides/hydroxides on a metal surface. The MCB model recognizes that different metal oxides can form and that the oxide composition and structure may change as corrosion progresses. The result can be a complex and shifting set of oxides that form and grow as a function of time.\(^{10,13-17}\) The MCB model applies the three flux equations to each metal oxidation reaction leading to the formation of a specific oxide and the dissolution of the different metal ions. For each oxidation reaction, the MCB model imposes the mass and charge balance requirements and the reaction thermodynamic and kinetic constraints on each metal oxidation process. The MCB model formulates the specific (per unit thickness) potential drop across an oxide layer to depend on the type of oxide and temperature but not on the solution pH or electrode potential. The model allows the type and the thickness of the oxide layer to evolve with time according to the flux equations. This in turn allows for changes in the overall potential drop across the oxide layer as corrosion progresses.

### Table II. Elemental composition of Stellite-6 in both weight percentage (wt%) and atomic percentage (at.%).

|        | Co | Cr | C | W | Ni | Fe | Si | Mo |
|--------|----|----|---|---|----|----|----|----|
| wt.%  | 57 | 27 | 1.4 | 4.1 | 2.6 | 2.9 | 1.1 | 0.4 |
| at.%  | 54.7 | 29.4 | 6.6 | 1.3 | 2.5 | 2.9 | 2.2 | 0.2 |

formulated in the model. The model simulations results are presented in section Model simulation results.

**Alloy composition.**—The alloy composition of Stellite-6 is provided in Table II. The morphology of the alloy surface shows two distinct phases, a Cr-carbide network (darker areas in the SEM images) distributed in a Cr-Co solidus solution, Figure 2. For the model simulations presented here, we assumed that the surface activity of Cr or Co is proportional to its atomic fraction in the alloy. Hence, the oxidation flux of each metal element is the oxidation flux determined by the modified Butler-Volmer equation (Formula 1 in Table I) multiplied by its atomic fraction. The implicit assumption is that the surface electrochemical reactions of the individual elements do not interact synergistically. Oxidation reactions of all other minor elements were ignored for simplicity (not due to a model limitation). The model included all of the possible oxidation reactions of the two main alloy elements that can occur within the reaction thermodynamic constraints. Different rates of oxide growth on different alloy phases may be possible, but the model simulation presented in this paper did not separate the rate equations occurring over different phases. This again made the model simpler and it also reflects our lack of verifiable experimental data for separate corrosion rates on the two phases.

**Redox reactions and their equilibrium potentials.**—The oxidation flux \(J_{MO^+}(t)|_{\text{ox}}\) for a specific metal oxidation reaction \((\text{ox#})\) is determined by the modified Butler-Volmer equation, Formula 1 in Table I:

\[
J_{MO^+}(t)|_{\text{ox}} = J_{d_{\text{diss}}}^q \cdot \exp \left( \frac{0.5nF}{RT} \cdot \eta_{\text{ox#}}^{\text{eff}}(t) \right)
\]

where \(J_{d_{\text{diss}}}^q\) is the forward rate overpotential, and \(J_{d_{\text{diss}}}^q\) is the forward and reverse rates of the redox reaction at equilibrium and is equivalent to the exchange current, \(i_{\text{diss}}\).

![Figure 2. SEM of a freshly polished surface of Stellite-6 showing two alloy phases.](image)

The MCB Model for Stellite-6 Corrosion

In this section we show how the MCB model (i.e., elementary corrosion reactions and the corresponding flux equations) is constructed for Stellite-6, and how the rate parameters and boundary conditions are...
Table III. The metal oxidation reactions considered in the simulation of Stellite-6 corrosion and the corresponding equilibrium reactions and equilibrium potentials.

| M**+ | Metal Oxidation Reaction | Corresponding Equilibrium Reaction | $E_{eq}$ at pH 10.6 (SCE) |
|------|--------------------------|-----------------------------------|--------------------------|
| 1    | $\text{Cr} \rightarrow \text{Cr}_2\text{O}_3/\text{Cr(OH)}_3$ | $2 \text{Cr} + 3 \text{H}_2\text{O} = \text{Cr}_2\text{O}_3 + 3 \text{H}^+$ | $-1.4$ |
| 2    | $\text{Co} + \text{Cr}_2\text{O}_3 \rightarrow \text{CoCr}_2\text{O}_4$ | $\text{Co} + \text{Cr}_2\text{O}_3 + \text{H}_2\text{O} = \text{CoCr}_2\text{O}_4 + \text{H}^+$ | $-1.1$ |
| 3    | $\text{Co} \rightarrow \text{CoO}/\text{Co(OH)}_2$ | $\text{Co} + 2 \text{H}_2\text{O} = \text{Co(OH)}_2 + \text{H}_2$ | $-0.7$ |
| 4    | $\text{Co}^{III} \rightarrow \text{CoO}_x$ | $3 \text{Co(OH)}_2 = \text{Co}_2\text{O}_4 + \text{H}_2 + 2 \text{H}_2\text{O}$ | $0.07$ |
| 5    | $\text{Co}^{III} \rightarrow \text{CoOOH}$ | $2 \text{Co(OH)}_2 = 2 \text{CoOOH} + \text{H}^+$ | $0.10$ |
| 6    | $\text{Cr}^{III} \rightarrow \text{Cr}^{VI}$ | $2 \text{Cr(OH)}_2 + \text{H}_2\text{O} = \text{Cr}_2\text{O}_7^{2-} + 3 \text{H}^+ + 2 \text{H}^+$ | $0.06$ |

* All of the metal oxide surfaces in contact with water will be hydrated and hydrolyzed and hence the oxide phase will be in equilibrium with the hydroxide phase, see discussion in the text.

The oxidation flux equation contains two rate parameters, $\eta_{red}^f(t)$ and $\eta_{ox}^f$. The MCB model defines $\eta_{red}^f(t)$ as a function of the system potential (created by corrosion or external polarization) ($E_{elec}(t)$), the equilibrium potential ($E_{eq}^f$) for reaction $\alpha \#$, and the potential drop across a growing oxide layer(s) ($\Delta V_{oxide}(t)$) (Formula 4 in Table I):

$$\eta_{red}^f(t) = E_{elec}(t) - E_{eq}^f - \Delta V_{oxide}(t)$$

where $E_{elec}(t)$ and $\Delta V_{oxide}(t)$ may change with time. Even for constant $E_{elec}(t)$, the effective overpotential can change due to a change in $\Delta V_{oxide}(t)$ as corrosion progresses and the oxide layer changes.

The exchange-current equivalent parameter, $J_{eq}^f$, is the forward or reverse rate of a redox reaction at equilibrium (e.g., $\text{Co}^{III} \rightleftharpoons \text{Co}^{II}$). It is a kinetic parameter and, unlike a thermodynamic parameter, is not a state function. It cannot be extracted from an arithmetic combination of the properties of different chemical states but has to be measured for a given chemical system under a given condition. The exchange current is a fundamental parameter that is specific to a specific metal oxidation in a given corrosion environment. The MCB model recognizes this. For example, the exchange current for the cobalt oxidation of $\text{Co}^{II}$ is not available (reaction 3 of Table III). Similarly, any $\text{CoCr}_2\text{O}_4$ or $\text{CoOOH}$ in contact with water can be hydrated and hydrolyzed, leading to either formation and growth of solid $\text{Co(OH)}_2$, or dissolution of the hydrated $\text{Cr}^{VI}$ ions into the solution. In contrast, the equilibrium potential used for the oxidation of $\text{Co}$ to $\text{Co}^{III}$ is that of $\text{Cr}$ forming $\text{Cr}_2\text{O}_3$. The $\text{Cr}_2\text{O}_3$ that is in contact with water can be hydrated and hydrolyzed ($\text{Cr}_2\text{O}_3 + \text{H}_2\text{O} \rightleftharpoons 2 \text{Cr(OH)}_2^{x}$, $x = 0,1,2,3,4$ leading to either formation of solid $\text{Cr(OH)}_2$, or dissolution of the hydrated $\text{Cr}^{VI}$ ions into the solution. Any solid $\text{Co(OH)}_2$ that forms can build up and be slowly dehydrated to form solid CrO. The surface hydration and hydrolysis of metal cations and the solid-state conversion of the oxide/hydroxide phases do not generate a net current, but they do influence oxide growth and dissolution of metal. The $\text{Co}^{III}$ or $\text{Cr}^{VI}$ species that are present on the surface are also allowed to undergo further oxidation at sufficiently oxidizing conditions to form $\text{Co}_2\text{O}_4$ and $\text{CoOOH}$ (reactions 4 and 5 of Table III), and to form $\text{Cr}_2\text{O}_7^{2-}$ (Cr(VI)) (reaction 6 of Table III), respectively. However, as discussed later, these reactions do not take place at any substantial rates in the potential ranges ($\leq 0.1$ V vs. SCE) that were simulated here.

The oxide layer formed on an alloy may be passive for ion or oxide vacancy transport but not for electron and hole transport.32 Thus, while the presence of an oxide layer may suppress further metal oxidation, under potentiostatic polarization the reduction reaction of $\text{Co}^{III}$ overpotential for that oxidation. For example, reaction 1 of Table III occurs in the presence of $\text{Cr}_2\text{O}_3$ on a Stellite-6 surface and hence the equilibrium potential for the oxidation of $\text{Cr}$ to $\text{Cr}^{III}$ is that of $\text{Cr}$ forming $\text{Cr}_2\text{O}_3$. The $\text{Cr}_2\text{O}_3$ that is in contact with water can be hydrated and hydrolyzed ($\text{Cr}_2\text{O}_3 + \text{H}_2\text{O} \rightleftharpoons 2 \text{Cr(OH)}_2^{x}$, $x = 0,1,2,3,4$ leading to either formation of solid $\text{Cr(OH)}_2$, or dissolution of the hydrated $\text{Cr}^{VI}$ ions into the solution. In contrast, the equilibrium potential used for the oxidation of $\text{Co}$ to $\text{Co}^{III}$ is the value that leads to the formation of $\text{Co}_2\text{O}_4$ by combining with $\text{Cr}_2\text{O}_3$ on the surface (reaction 2 of Table III), or the formation of $\text{Co(OH)}_2$ when $\text{Co}_2\text{O}_3$ is not available (reaction 3 of Table III). Similarly, any $\text{CoCr}_2\text{O}_4$ or $\text{CoOOH}$ in contact with water can be hydrated and hydrolyzed, leading to either formation and growth of solid $\text{Co(OH)}_2$, or dissolution of the hydrated $\text{Co}^{III}$ ions into the solution. Any solid $\text{Co(OH)}_2$ that forms can build up and be slowly dehydrated to form solid CrO. The surface hydration and hydrolysis of metal cations and the solid-state conversion of the oxide/hydroxide phases do not generate a net current, but they do influence oxide growth and dissolution of metal. The $\text{Co}^{III}$ or $\text{Cr}^{VI}$ species that are present on the surface are also allowed to undergo further oxidation at sufficiently oxidizing conditions to form $\text{Co}_2\text{O}_4$ and $\text{CoOOH}$ (reactions 4 and 5 of Table III), and to form $\text{Cr}_2\text{O}_7^{2-}$ (Cr(VI)) (reaction 6 of Table III), respectively. However, as discussed later, these reactions do not take place at any substantial rates in the potential ranges ($\leq 0.1$ V vs. SCE) that were simulated here.

**Figure 3.** Equilibrium potentials for the redox reactions that can occur on Stellite-6. The potential regions of stability of different oxides are indicated on top as bars with Roman numerals. The arrows indicate dissolution pathways of $\text{Co}^{III}$. 
Table IV. The parameters derived for use in the MCB model for corrosion of Stellite-6.

| T (°C) | pH  | Cr2O3 | CoCr2O4 | Co(OH)2 | Cr2O3 | CoCr2O4 | Co(OH)2 | Cr | CrIII | Co | Co3O4 | O2 |OH− | H2 | H2O |
|--------|-----|-------|---------|---------|-------|---------|---------|----|-------|----|-------|----|-----|----|-----|
| 25     | 8.4 | 0.967 | 0.533   | 0.400   | 3.2   | 5.2     | 1.0     | 50 | 1     | 0.1| 2 × 10^-6 | 0.1 | -10^-4 | -0.1 |
| 10.6   | 9.95 | 0.704 | 0.282   | 3.0     | 4.4   | 0.1     |         |     |       |    |        |    |      |    |
| 80     | 10.6 | 0.967 | 0.526   | 0.421   | 3.0   | 4.4     | 0.1     |     |       |    |        |    |      |    |

a solution species that is not coupled with metal oxidation but is coupled with the oxidation of another solution species on the counter electrode, can continue to occur. For example, reduction of H2O or dissolved O2 at an impurity level can occur on a ‘non-corroding’ potential barrier for electron transfer for solution redox reactions and where

where the working electrode coupled with oxidation of H2 or H2O on the counter electrode:

| 2H2O + 2 e− → H2 + 2 OH− | on WE |
|--------------------------|------|
| H2 + 2 OH− → 2 H2O + 2 e− | on CE |

and/or

| O2 + 2 H2O + 4 e− → 4 OH− | on WE |
|---------------------------|------|
| 4 OH− → O2 + 2 H2O + 4 e− | on CE |

These solution redox reactions do not contribute to either a metal oxidation flux or an oxide growth flux (on a passive alloy), but they do contribute to the net current that is being monitored during polarization. To compare the results of model calculations with the experimentally measured net current, the contribution of any such solution reactions on the WE must be taken into account. To do this we considered a solution reduction reaction on the working electrode as a separate independent redox reaction with its own equilibrium potential (or the difference of the equilibrium potentials of the two half-reactions of aqueous reduction and aqueous oxidation).

The solution reduction flux was modeled the same way as the metal oxidation flux, i.e., using the modified Butler-Volmer equation with an effective overpotential:

\[ J_{\text{red}} (t) \approx J_{\text{red}}^0 \exp \left( \frac{0.5nFE}{RT} \right) \]

where \( n \) is the number of electrons involved and \( F \) is Faraday’s constant.

Potential drop across a growing oxide layer.—Solving the oxidation flux equation requires formulation of \( \Delta V_{\text{oxide}} (t) \) as corrosion progresses and the oxide layer changes. In the MCB model the potential drop is formulated as:

\[ \Delta V_{\text{oxide}} (t) = \sum \varepsilon_{\text{MO}} \cdot L_{\text{MO}} (t) \]

where \( \varepsilon_{\text{MO}} \) is the thickness of the layer of oxide, MO#, at time t, \( L_{\text{MO}} \) is the specific potential drop per unit thickness, or field strength of the MO# layer, and the summation is over all of the different types of oxides that comprise the oxide layer. The specific potential drop is characteristic of the oxide and should be independent of solution pH and the polarization potential but dependent upon temperature. The metal oxides that can form on Stellite-6 within the studied potential range (−0.4 V_{SCE} to 0.1 V_{SCE}) are Cr2O3, CoCr2O4, Co(OH)2, Co3O4, and CoOOH. The Cr2O3 oxide is highly soluble and hence will not form a solid oxide layer in our solution volumes. The values for the specific potential drops across these oxides are not available. As for the exchange currents (section Redox reactions and their equilibrium potentials), we determined values for the specific potential drops by comparing the results of model calculations with trial values against the oxide depth profile data obtained as a function of potential at a given temperature (section Potentiotstatic polarization experiments). Recursion was used to obtain ‘best’ fit values. The values that were determined this way are listed in Table IV and are within the range of the values found for transition metal oxides (10^5 to 10^7 V cm^-1).11,18–29

Note that although the formation of CoO2 and CoOOH is allowed to occur their formation is negligible at the studied potentials (≤ 0.1 V_{SCE}) and hence any model parameters associated with these oxides are not listed in Table IV.

In the simulations of Stellite-6 corrosion, the surface was assumed to be initially covered with a 2-nm thick layer of chromium oxide (Cr2O3). It has been well established that alloys containing more than 12% Cr display corrosion resistance and this resistance is attributed to the presence of a thin protective layer of air-formed Cr2O3 on the surface. Mott has shown that the thickness of the oxide on the surface of self-passivating metals like chromium after long exposure to air at room temperature can be 5 nm thick at maximum.27 The oxide thickness used in the simulations is within this limit.

Our studies on oxide formation and growth on a range of Cr-containing alloys have shown that the pre-formed chromium oxide can be converted to chromite under conditions where oxide growth is favored over dissolution, e.g., at a high pH.10,16,17 On Stellite-6 the redox reaction for this conversion is:

\[ \text{Co}^2+ + \text{Cr}_2\text{O}_3 + \text{H}_2\text{O} = \text{CoCr}_2\text{O}_4 + \text{H}_2 \]

As corrosion progresses the oxide film changes from a chromium oxide layer to a more chromite-like layer.26,17 While this occurs there is a slow change in the electric field across the oxide layer. As the oxide changes two layers will become present, chromium oxide and chromite. The boundary between the layers will not be sharp, but we can treat them as distinct layers for mathematical formulation of the potential drop across the mixed oxide film. The oxidation of chromium (albeit very slowly) will increase, while its conversion into chromite will decrease the thickness of the chromium oxide layer with time:

\[ L_{\text{CrO}_2} (t) = L_0 - f(t) \cdot L_{\text{CrO}_2} (t) + \frac{dL_{\text{CrO}_2} (t)}{dt} \cdot \Delta t \]

where \( L_{\text{CrO}_2} (t) \) and \( L_{\text{CrO}_2} (t) \) are the thicknesses of the chromium oxide and chromite layers, and \( L_0 \) is the initial air-formed chromium oxide thickness. The factor \( f(t) \) accounts for the thickness change associated with the different lattice constants of the Cr2O3 and CoCr2O4. For the purpose of our initial simulations we have set \( f(t) = 1 \).

As noted above, the linear dependence of potential drop over an oxide layer does not mean that there is a linear growth of the oxide layer. This model does not assume that an oxide layer grows at a specific, predetermined rate, such as a linear or logarithmic growth.
rate. Instead the MCB model calculates the growth rate of a specific oxide based on the competition between oxide growth and dissolution of oxidized metal ions where the fraction of the metal oxidation flux going to the oxide growth flux is determined by the relative rate constants of metal oxide bond formation and metal ion dissolution.

The oxidative conversion of Co0 to Co3+ is assumed to occur only in the presence of Cr2O3. Thus, when all of the oxide growth flux is going to the oxide growth flux, formation will compete with dissolution for the metal cations produced during Cr oxidation of Cr0 to form Cr2O3. For an alloy in de-oxygenated water solution, the rate of formation of CoCr2O4 is limited by the rate of oxide formation.

The fractions are independent of the polarization potential and dependent upon pH and temperature because of their impact on the activation energy, \( \Delta E_{\text{MO}} \), which is the pre-exponential factor for the oxide formation; they are assumed to be constant with time.

The rate constants at time 0, \( k_{\text{MO}(0)} \) and \( k_{\text{diss}} \), and the activation energy, \( \Delta E_{\text{MO}(0)} \), can be independently measured. However, these values as a function of solution pH and temperature are not available for the cobalt and chromium oxides. In the model simulations, the individual values of \( k_{\text{MO}(0)} \) and \( k_{\text{diss}} \) are not needed but only their fractional contributions because mass balance requires the metal oxidation flux to be the same as the sum of the oxide formation flux and dissolution flux. The initial oxide-flux fraction of the metal oxidation flux at time 0, \( f_{\text{k-MO}(0)} \), is defined as:

\[
f_{\text{k-MO}(0)} = \left( \frac{k_{\text{MO}(0)}}{k_{\text{MO}(0)} + k_{\text{diss}}} \right)
\]

The fractions are independent of the polarization potential and dependent upon pH and temperature because of their impact on \( k_{\text{diss}} \). As for the exchange currents and specific potential drops across oxides (section Redox reactions and their equilibrium potentials and section Potential drops across a growing oxides layer), we determined values for the initial oxide-flux fractions in the same manner using the potentiostatic polarization data obtained as a function of potential and pH at a given temperature (section Potentiostatic polarization experiments).

Recursion was used to obtain ‘best’ fit values.

The oxide-flux fraction, \( f_{\text{k-MO}(t)} \), changes with time because \( k_{\text{MO}(t)} \) changes with oxide thickness according to Eq. 9. The value for the proportionality constant, \( c_{\text{MO}} \), was also the best fit of potentiostatic polarization data and was independent of potential and pH but dependent on oxide type and temperature. The values used in the simulations are listed in section Model simulation results.

**Model output of experimental quantities.**—In order to compare the model simulation results with experimental data, the different fluxes calculated in the model were converted to the experimentally measured quantities (e.g., oxide thickness, dissolved metal quantities).

**Current.**—The current monitored as a function of time is the sum of the anodic current arising from the oxidation fluxes, \( J_{\text{MO}^+}(t) \), of all the cobalt and chromium reactions listed in Table III, and the cathodic current arising from the reduction flux of solution species at the working electrode (reactions 3a and 4a):

\[
i_{\text{tot}}(t) = i_{\text{c}}(t) + i_{\text{e}}(t)
\]

\[
i_{\text{c}}(t) = nF \sum_i f_{\text{k-MO}(t)} \cdot J_{\text{MO}^+}(t)_{\text{inj}}
\]

\[
i_{\text{e}}(t) = -nF \int_{t_{\text{ref}}}^{t_{\text{tot}}} J_{\text{MO}^+}(t)_{\text{sol}} \, dt
\]

**Oxide composition and thickness.**—The oxide growth flux, \( J_{\text{MO}^+}(t)_{\text{oxide}} \), is related to the thickness of the oxide, MO#:
literature are 24, 45 and 12 cm$^3$·mol$^{-1}$, respectively, and these values are used in the simulations.

Amount of dissolved metal.—The dissolution flux, $J_{\text{diss}}(t)|_{\text{sol}}$, is the rate of dissolution of metal cation $M^{n+}$ per unit surface area exposed to solution:

$$J_{\text{diss}}(t)|_{\text{sol}} = \frac{dm_{\text{diss}}(t)}{dt}$$  \hspace{1cm} [19a]

$$m_{\text{diss}}(t) = \frac{MW_M A_{\text{int}}}{V_{\text{sol}}} \int_0^t \left(J_{\text{diss}}(t)|_{\text{sol}} \cdot dt\right)$$  \hspace{1cm} [19b]

where $m_{\text{diss}}(t)$ represents the amount of dissolved $M^{n+}$ over time $t$ in units of g·L$^{-1}$, $MW_M$ is the molar mass of metal M (g·mol$^{-1}$), $J_{\text{diss}}(t)|_{\text{sol}}$ is in units of mol·cm$^{-2}$·s$^{-1}$, $A_{\text{int}}$ is the interfacial surface area (cm$^2$) and $V_{\text{sol}}$ is the volume of solution (L). The molar masses of Co and Cr are 59 and 52 g·mol$^{-1}$, respectively.

Model Simulation Results

Description of the simulated experiments.—The model simulations were carried out for the experiments performed at relatively low temperatures (room temperature and 80°C) and at basic pHs (8.4 and 10.6). At a given pH and temperature, three different experiments were performed:16,17 (1) time-dependent current during, and surface analyses include morphology and elemental depth profiles using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) with Ar$^+$ sputtering. The coupon exposure experiments were performed in sealed quartz vials and the dissolved cobalt and chromium concentrations in the solutions were determined using inductively coupled plasma – mass spectrometry (ICP-MS). Some of these studies have been published and the details of the experiments can be found elsewhere.16,17 The AES depth-profile data from those studies were reanalyzed to enable comparison of the experimental results with model calculations. This AES data reanalysis is summarized in Appendix.

The MCB model calculations were performed for the experiments on Stellite-6 at two different pHs (10.6 and 8.4) and two different temperatures (25 and 80°C). The low temperatures and basic pHs were chosen for this first MCB model application study because under these conditions thermal processes, such as solid-state conversion between different oxide phases, do not occur at any substantial rates. In addition, thermal properties such as the solvation properties of water do not change much over the studied temperature and pH conditions. For example, surface hydration/dehydration of transition metal cations is base-catalyzed and does not control the overall dissolution rate of metal cation. However, the hydration is much slower in neutral or acidic pHs than in basic solutions. Hence, the surface hydration/dehydration rate can contribute significantly to the rate determining step for dissolution. In this case, detailed modeling of the rate equations of the individual elementary processes involved in dissolution (such as surface hydration/dehydration, migration and diffusion, saturation) is required. The experimental results obtained at low temperatures and at basic pHs provide information that tests the formulations of the electrochemical oxidation flux and consequently, the oxide and dissolution fluxes, without the complication of thermal conversion of an oxide. Once the MCB model has proven to simulate the experiments under these conditions, the contribution of such thermal processes and the dependence of the elementary processes involved in dissolution on temperature, pH and flow conditions can be included in the MCB model. This will enable the model to simulate experiments performed over a wider range of conditions. The application of the MCB model to lower pHs and higher temperatures will be reported in near future.

The model calculation results of potentiostatic polarization experiments as a function of potential are presented in section Potentiostatic polarization experiments, the corrosion potential measurements in section Corrosion potentials in deaerated solutions and the coupon exposure tests in section Oxide formation and dissolution in 3-d corrosion tests. The values of the rate parameters used in the model calculations are listed in Table IV. It should be emphasized that at a given pH and temperature all of the model parameters are independent of the electrode potential (corrosion potential or polarization potential), and that at a given temperature, the only model parameter that depends on pH is the initial oxide-flux fraction ($f_{\text{OX}}(0)$). The temperature affects $f_{\text{OX}}(0)$ and the specific potential drop ($\epsilon_{\text{MOR}}$).

Potentiostatic polarization experiments.—The model calculation results are compared with the data from potentiostatic polarization experiments in three figures. The time-dependent behavior of current is shown in Figure 4, the layer structure and thickness of the oxide formed at the end of each polarization test are shown in Figure 5, and the composition of the oxide in the top 3 nm layer is shown in Figure 6 (oxidized cobalt (Co$^{ii}$ and Co$^{iii}$) and metallic cobalt (Co$^{0}$)). The oxide-layer structure presented in Figure 5 was determined by analyzing the elemental depth profiles obtained by AES with Ar$^+$ sputtering, as described in reference10 and summarized in the Appendix. The experimental data for the fraction of oxidized cobalt were obtained from deconvolution of high resolution XPS O$-$1s, Co$-$2p and Cr$-$2p bands.10,17 Note that the analysis depth of the XPS instrument for a chromium oxide and cobalt oxide covered surface is not well defined and hence the XPS results are compared with the calculated fraction of oxidized cobalt in only the outer 3 nm of the oxide layer. The results obtained at only three potentials are shown for brevity in Figures 4 to 6. The model also simulates the results obtained at other potentials (ranging from 0.4 to 0.1 V$\text{SCE}$) very well (the results not shown for brevity).

The model predicts the observed oxide layer structure consisting of Cr$_2$O$_3$, CoCr$_2$O$_4$ and CoO/Co(OH)$_2$, and the changes in their thicknesses as a function of polarization potential very well. The outer most layer of CoO/Co(OH)$_2$ increases most rapidly with increasing polarization potential while the inner cobalt oxide (CoCr$_2$O$_4$) increases to a smaller extent, at the expense of the inner most layer of Cr$_2$O$_3$. It should be noted that although it is difficult to clearly separate Co$^{ii}$ oxides (CoO/Co(OH)$_2$) from the mixed Co$^{ii}$/Co$^{iii}$ oxide (Co$_x$O$_y$) or the Co$^{iii}$ oxides (CoOOH and Co$_2$O$_3$), the surface analysis results indicate that, if present, the fraction of Co$^{iii}$ in the oxide layer formed over the 5-h polarization at temperatures lower than 80°C is very small. If Cr$^{vi}$ oxides had formed, they would not have been detected by the AES or XPS due to the high solubility of the Cr$^{vi}$ ions. As described earlier, the model allows further oxidation of Cr$^{iii}$ and Cr$^{ii}$ species to Co$_2$O$_4$ and CoOOH and to Cr$_2$O$_7^{2-}$ (Cr$_2$O$_7^{2-}$), respectively. Nevertheless, the model predicts that these reactions do not take place at any substantial rates at potentials below 0.1 V$\text{SCE}$, consistent with the observations.

Corrosion potentials in deaerated solutions.—Under potentiostatic polarization the potential on the working electrode is controlled and any oxidation or reduction occurring on the working electrode is coupled with a redox reaction on the counter electrode. Under naturally corroding or open-circuit conditions, both half-reactions occur on the same (macroscopic) surface. In this case, the sum of all of the oxidation fluxes (the anodic current) must be the same as the sum of all of the reduction fluxes (the cathodic current) due to the charge and mass balance requirements, and these requirements dictate the corrosion potential:

$$\sum i_a = \sum |i_c| \text{ at corrosion potential}$$  \hspace{1cm} [20]

This is a necessary condition for the time evolution of the corrosion potential.

The MCB model determination of $E_{\text{cor}}$ on Stellite-6 in deaerated water was carried out as follows. The flux equations and the values of the rate parameters used for the $E_{\text{cor}}$ simulations were those
Figure 4. Experimental data (solid lines) and model calculations (broken lines) of current density as a function of time during potentiostatic polarization. Data were obtained at three different potentials, +0.1, −0.1 and −0.4 V_{SCE}, at pH 8.4 and 10.6, and at 25°C and 80°C.

Figure 5. Comparison of the MCB model calculations with experimentally determined oxide-layer structures on Stellite-6 electrodes polarized for 5 h at different potentials at pH 10.6 and 80°C. The numbers on the top of the graph indicate the polarization potentials.

determined by fits to the potentiostatic polarization data. For the solution reduction flux, Eqs. 5 and 6 were used. There is no data available for the exchange current density on Co-Cr alloys, so we set the exchange current density for water reduction (reaction 3a) on the surface of Stellite-6 at 10^{-7} A/cm^2 (Table IV). This value is in the range reported for the water reduction exchange current densities on the transitional metals. Hydrogen (H_2) is produced by corrosion and quickly reaches a saturation level at room temperature of 5 \times 10^{-5} atm. This value was used to calculate the equilibrium potential for water reduction, E_{eq}^{\text{H}_2\text{O}/\text{H}_2} = -0.74 V_{SCE} at pH 10.6. Since the test solutions were Ar-purged the partial pressure of oxygen is very low, on the order of 10^{-6} atm. This value was used to calculate the equilibrium potential for the oxygen reduction reaction, E_{eq}^{\text{OH}^-/\text{O}_2} = 0.2 V_{SCE} at pH 10.6. The equilibrium potential for oxygen reduction is greater than the corrosion potential measured on Stellite-6 under all conditions studied. Hence we assume that the rate of oxygen reduction is limited by the rate of aqueous diffusion of O_2 to the surface and not by the rate of the reduction at the surface. It is possible to calculate a diffusion-controlled current density for the O_2 reduction if the value for the dissolved O_2 concentration in the Ar-purged solution is known. We could not measure this O_2 concentration with our instruments. For a dissolved O_2 concentration of 10 ppb the diffusion-controlled current...
density is about $-10^{-10}$ A/cm². This value was used as the limiting current density of oxygen reduction on the Stellite-6 surface.

The model calculation starts at $-1.1$ V$_{SCE}$ (the potential used for cathodic cleaning for 5-min prior to the E$_{corr}$ measurement). At the end of cathodic cleaning the surface is covered with a thin layer of chromium oxide formed by air oxidation that cannot be removed by this cathodic cleaning. The anodic current density from the sum of cobalt and chromium oxidation fluxes and the total cathodic current density from the sum of solution reduction fluxes were calculated according to Eqs. 1 and 5. Current density calculations were carried out over a potential range from $-1.1$ V$_{SCE}$ to the solution oxidation potential of 0.2 V$_{SCE}$. The upper limit was established by measuring the open-circuit potential using a platinum working electrode. The potential for the calculations was stepped by 0.1 mV and the potential at which the difference between the anodic and cathodic current densities was less than 1% was taken as the corrosion potential.

Figure 7 compares the calculated and experimental corrosion potentials as a function of time for a few selected conditions. The MCB model calculation results are in excellent agreement with the data. The MCB model simulates both the type of oxide and its thickness.

Oxide formation and dissolution in 3-d corrosion tests.—We have also performed MCB model simulations of the 3-d corrosion tests for Stellite-6 coupons. The same set of kinetic parameters derived from the potentiostatic polarization data were used for these calculations. The model results are compared with the experimental data for oxide formation and metal ion dissolution in Figures 8 and 9. The MCB model simulates the corrosion tests very well. The model predicts correctly the effect of pH and temperature on not only the layer structure and thickness of the oxide formed but also the amounts of Co and Cr dissolved. The rate parameters used in the modeling of the corrosion tests were the same as those used for the other model calculations.

As for the simulation of the 5-h potentiostatic polarization experiments, the model correctly simulates an oxide layer structure and the overall metal oxidation rate becomes equal to the metal dissolution rate. The E$_{corr}$ at long times is thus determined by the solution redox condition (deaerated in this study) and the type and thickness of the oxides that have grown. The rapid changes in E$_{corr}$ at early times in constant solution environments are the consequences of rapid changes (conversion and growth) in the oxide layer. The changes in the oxide layer are also reflected in the rapid changes in current during potentiostatic polarization (Figure 4). These changes at early stages of corrosion can alter the oxidation pathways thereby dictating the type and the thickness of the final oxide and hence the metal dissolution rate at long times, as can be seen from the surface and solution analysis results of the corrosion tests discussed below.

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Consistency with experimental observations.—The model simulations are in good agreement with experimental results obtained for Co-Cr alloys. Figure 9 compares the model predictions with experimental measurements of the amounts of dissolved Co and Cr ions at pH 10.6 and 80°C. The model correctly predicts the observed increases in the thickness of the Co(OH)\(_2\) layer with increasing pH at room temperature and with increasing temperature at pH 10.6. The model somewhat overestimates the thickness of the Cr\(_2\)O\(_3\) layer, while it underestimates the thickness of the outermost Co(OH)\(_2\) layer. As described in section Potential drop across a growing oxide layer, in the model simulations the surface was assumed to be initially covered with a 2-nm thick layer of chromium oxide (Cr\(_2\)O\(_3\)) taken from an estimated value reported in Ref. 34. The experimentally determined AES depth profiles (Figure 8) indicate that this Cr\(_2\)O\(_3\) layer may have been thinner. The oxidation of Co to Co\(^{III}\) oxides (reactions 2 and 3 of Table III) would be faster with a thinner Cr\(_2\)O\(_3\) layer due to a smaller potential drop across the layer. The effect of the thickness of the initial Cr\(_2\)O\(_3\) layer on cobalt oxidation would diminish with an increasing potential.

It should be noted that the current version of the MCB model is a 1-D oxide growth model and the role of surface variation has not been taken into consideration. As a result, the gradients in the oxide layers are not modelled. As described in section Alloy composition Stellite-6 has two alloy phases, a Cr-carbide network distributed in a Cr-Co solidus solution. The rate of oxide growth will be different on the different alloy phases, but the model simulation presented here did not separate the rate equations occurring on the different phases. This made the calculations simpler. Additionally, verifiable experimental data for separate corrosion rates on the two phases are lacking. The next step in the MCB model development is to convert the 1-D model to a 3-D model using the COMSOL Multiphysics code. This work is underway.

Improvements in the MCB model capabilities.—The MCB model predicts the changes in oxide growth and dissolution rates as a function of time during corrosion and their dependences on pH, temperature and electrode potential. Particularly important is the predictability of oxide growth and dissolution simultaneously at early times when the rates of these processes change fast. These changes at early stages of corrosion can alter the oxidation pathway, thereby dictating the type and the thickness of the final oxide and hence the metal dissolution rate at long times. Other important features of the MCB model are its ability to model corrosion of multi-element alloys and its ability to model the growth of a multi-layered oxide structure.

The current MCB model, however, does not explicitly consider thermal processes such as solid-state conversion between different oxide phases or solution transport processes. For example, at high temperatures thermal conversion between different oxides can be fast and the solution may be quickly saturated with metal cations in a small solution volume. Under these conditions the rate equations for these processes must be modelled in detail. The experimental results obtained at low temperatures and at basic pHs provide information that tests the formulations of the electrochemical oxidation flux and consequently, the oxide and dissolution fluxes, without complication of thermal oxide conversion during oxide growth and/or solution transport limited corrosion. This study has demonstrated that the MCB model can simulate the experiments under these conditions. The next version of the MCB model will incorporate the rate or flux equations for the thermal oxide conversion processes and the elementary dissolution processes (surface hydration/hydrolysis, migration/diffusion, saturation) as a function of temperature, pH and solution conditions. This will enable the MCB model to simulate experiments performed over a wider range of pH and temperature and geometrical conditions.

Conclusions

We have applied the mass and charge balance (MCB) model to simulate corrosion tests and electrochemical experiments performed on the Co-Cr alloy, Stellite-6. We have shown how the rate or flux equations for metal oxidation, oxide growth and dissolution are constructed and how the values of the rate parameters in the model can be derived. Most of the model parameters are fundamental thermodynamic and reaction properties of the chemical elements involved in the corrosion reactions. Of these parameters the rate constants for metal oxide growth and metal ion dissolution are the only ones that are sensitive to temperature and solution pH.

The model simulation results are in excellent agreement with the data obtained from different sets of experiments (electrochemical and corrosion tests) at two different pHs and at two different temperatures. The data compare include the time-evolution of current during polarization as a function of potential, the layer structure and thickness of oxide formed, and the amounts of Co and Cr ions dissolved in the solutions.

This study demonstrates that the MCB model can simulate the oxide growth and metal ion dissolution simultaneously during corrosion, even for an alloy with multiple oxidizing elements, and predict the effects of different solution environmental conditions on the overall corrosion rate.

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Appendix: AES Depth Profile Analysis

Auger electron spectroscopy (AES) combined with argon-ion sputtering can provide a depth profile of the chemical composition of a surface oxide. The AES depth profiles on Stellite-6 reported in this study were obtained using a Physical Electronics Model PHI 660 instrument with an excitation energy of 5 keV. The AES scans for Co, Cr, C, Ni and O were performed as a function of sputtering time. The AES intensities were calibrated and converted into mole fractions, and the sputtering time was converted into depth. The sputter depths were calibrated using standard samples under the same sputtering conditions.

An example of the AES depth profiles obtained for Stellite-6 corroded at 80°C, pH = 10.6, E_{corr} = -0.4 V_{SCF} are shown in Fig. A1. Due to the presence of multiple metal elements in the alloy the nature of the oxide as a function of depth is difficult to decipher from the atomic fractions. To identify the degree of oxidation of the metal elements and their relative abundances in the oxide, the AES data were analyzed as ratios of each metal element (M = Co or Cr) to their sum (M/(Co + Cr)) and the ratio O/(Co + 1.5 Cr) (Fig. A2). An O/(Co + 1.5 Cr) ratio of 1.0 corresponds to an oxide where both Co and Cr have been oxidized to their lowest stable oxidation states, Co\(^{III}\) and Cr\(^{III}\). A ratio less than 1.0 corresponds to a layer in which a fraction of the metal atoms has not been oxidized, and a ratio more than 1.0 corresponds to a layer in which some of the
metal atoms are present in higher oxidation states or as hydroxides. The abundances of Co and Cr (expressed as M(Co + Cr)) have different depth profiles in the oxide (Fig. A2) indicating that the oxide layer has a multi-layered structure with different oxides dominating at different depths.

To determine the dominant oxide at a given depth, another analysis methodology has been developed. ‘Theoretical’ depth profiles are calculated assuming that all of the measured metal present at a particular depth is present solely as a particular metal oxide or mixed metal oxide. Using this theoretical depth profile a corresponding O at.% profile can be calculated. For example, a theoretical Cr$_2$O$_3$ yields the O profile that one would expect to see if all of the Cr at a given depth was present as Cr$_2$O$_3$. Any Co present is assumed to be in metallic state Co. Similar profiles can be constructed for the other possible oxides. In the case of a mixed oxide like CoCr$_2$O$_4$, one assumes that the metal with the lowest concentration (e.g., Cr) is present as an oxide along with the requisite Co and any excess Co would be present as CoO. Using this methodology a series of theoretical O depth profiles can be calculated. If the measured O profile is greater than the theoretical O profile determined for all of the possible oxides, it indicates that there is a metal hydroxide present, mostly Co(OH)$_2$ for Stellite-6.

The theoretical O depth profiles calculated for one case are shown in Fig. A2 and compared with the actual measured O depth profile. The theoretical lines do not follow the observed O profile, but intersect with the observed profile at different depths. The order in which the different theoretical oxide lines intersect the observed O profile is for the oxides formed on all of Stellite-6 coupons tested. This order follows the order of the equilibrium potentials of the redox reactions of cobalt and chromium that can occur on a Co-Cr alloy (see Fig. 3 in the main text).

The ordered intersection of the theoretical O profiles with the measured O profile indicates that the oxide grows in a multi-layered structure with the order of oxides, from the innermost to outermost layer being:

$$\text{Cr}_2\text{O}_3 + \text{CoCr}_2\text{O}_4 + \text{CoO}/\text{Co(OH)}_2$$

We can use the locations of the intersections of the O profiles to establish the depth span in the oxide layer where a particular oxide species is dominant. The depth where the O profile derived from a theoretical Cr$_2$O$_3$ profile intersects the observed O profile corresponds to the point at which the oxide is present predominantly as Cr$_2$O$_3$. Similarly, the depth where a theoretical CoCr$_2$O$_4$ profile intersects the observed O profile corresponds to the point at which the oxide is present predominantly as CoCr$_2$O$_4$. In the range between these two points the oxide composition changes from predominantly CoCr$_2$O$_4$ to predominantly CoCr$_2$O$_3$.

A schematic of the oxide-layer structure determined from this analysis using ‘theoretical’ O profiles is shown in Fig. A2. The concentration gradient of the oxide between two points where the profiles intersect is not known and is assumed to be linear. This leads to the triangularly shaped oxide zones shown in Fig. A2.

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**Figure A1.** Elemental depth profiles derived from AES analysis with Ar$^+$ sputtering for a Stellite-6 electrode polarized at $-0.4 \text{ V}_{\text{SCE}}$ at pH 10.6 and 80°C.

**Figure A2.** Oxide layer structure analysis of the AES data shown in Figure A1: (a) depth profiles of O/(Co + 1.5 Cr) and (b) observed (thick black line) and theoretical (colored lines) O at.% depth profiles. The depths marked by the vertical lines where the O profiles intersect in the middle graph indicate the boundaries of regions where a particular oxide is dominant. These regions are shown in the bar chart below the graphs.
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