Localised corrosion of heat-treated alloys
Part II – Predicting grain boundary microchemistry and its effect on repassivation potential

A. Anderko*1, N. Sridhar2 and G. Tormoen3

A methodology has been developed for predicting the effect of thermal aging on the repassivation potential of austenitic alloys. The methodology combines two models, a grain boundary microchemistry model for calculating the chromium and molybdenum depletion profiles in the vicinity of grain boundaries and an electrochemical model that relates the repassivation potential to the microchemistry and environmental conditions, including temperature and solution chemistry. The grain boundary microchemistry model incorporates a thermodynamic paraequilibrium treatment of the formation of carbides and a kinetic treatment of the diffusion of Cr and Mo. With this model, experimental Cr and Mo depletion profiles can be reproduced for sensitised alloys 600, 825 and 316L. The repassivation potential model accounts for the effects of solution chemistry and temperature by considering competitive dissolution, adsorption and oxide formation processes at the interface between the metal and the occluded site solution. Using a previously developed relationship between the repassivation potential and bulk alloy composition, a procedure has been established for calculating the observable repassivation potential of thermally aged alloys by integrating the local $E_{rp}$ values that correspond to the alloy microchemistry in the depletion zone. The predicted repassivation potentials agree with experimental data for thermally aged alloys 600 and 825 in chloride solutions. Additionally, the model has been applied to estimate the repassivation potential of welded samples in which segregation of alloying elements is observed.

Keywords: Localised corrosion, Alloys 600, 825 and 22, Repassivation potential, Thermal aging

Introduction

Localised corrosion of engineering alloys is a complex function of metallurgical factors and environmental conditions. Among metallurgical factors, effects of thermal instabilities are of interest for assessing the performance and expected service life of industrial components fabricated from nominally corrosion-resistant stainless steels and nickel-based alloys. Fabrication processes such as heat treatment and welding are known to introduce microstructural changes that may affect both the mechanical and corrosion performance of an alloy. In particular, thermal instability of stainless steels and nickel-based alloys may lead to the formation of complex metal carbides of the type $M_3C_2$, $M_7C_3$, $M_6C$ or $M_{23}C_6$ in which the metallic component $M$ represents Cr, Mo, W and Fe. The carbide is chromium- or molybdenum-rich depending on the carbide type, which in turn depends on the alloy composition and temperature. In addition, chromium-rich intermetallic phases such as the $\sigma$, $\chi$, $R$ and $\mu$ phases can form in many alloys. Precipitation of such phases may occur at temperatures ranging from 500 to 900°C depending on alloy composition. Formation of grain boundary carbides often results in the depletion of chromium and possibly, molybdenum in the vicinity of the grain boundary because of the slow diffusion of substitutional elements such as chromium relative to the interstitial carbon. Similarly, the corrosion resistance of welded components may be affected by the segregation of alloying elements and precipitation of intermetallic phases, carbides or nitrides in the solidified weld and unmixed zones as well as the precipitation of carbides and other phases in the heat-affected zone adjacent to the weld.

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corrosion cracking (IGSCC) has been extensively modelled in the literature. Much less effort has been devoted to pitting and crevice corrosion of thermally aged and fabricated alloys. Most of the studies of localised corrosion of thermally aged or welded stainless steels and Ni-based alloys have been focused on developing comparative performance data in specific environments, for example, critical crevice temperatures in ferric chloride solutions. Recent localised corrosion studies have been focused on characterising the dependence of localised corrosion parameters in certain environments on thermal aging of Ni-based alloys, i.e. alloy 825 and alloy 22. In the first part of this study, the authors investigated the localised corrosion of alloy 600. However, no generalised treatment has been proposed so far to rationalise and predict the effects of heat treatment on the susceptibility of Fe–Ni–Cr–Mo alloys to pitting or crevice corrosion.

In the authors’ previous papers, a computational methodology has been proposed to predict the tendency of base metals to undergo localised corrosion. This methodology is based on the computation of two characteristic parameters as functions of aqueous environment composition and temperature, i.e. the corrosion potential \( E_{\text{corr}} \) and the repassivation potential \( E_{\text{rp}} \), also called the protection potential. The repassivation potential provides a threshold condition below which stable pitting or crevice corrosion does not occur. \( E_{\text{rp}} \) is amenable to modelling because it is relatively insensitive to surface finish and coincides for pitting and crevice corrosion as long as propagation exceeds a certain minimum value. The values of \( E_{\text{rp}} \) and \( E_{\text{corr}} \), calculated as a function of environmental conditions, can be then compared to determine the susceptibility of an alloy to localised corrosion. To predict the repassivation potential as a function of environmental conditions, a mechanistic model was developed in a previous paper. This model was shown to reproduce \( E_{\text{rp}} \) for a number of alloys in laboratory solutions and in complex chemical process environments. The repassivation potential model can be used as a predictive tool for alloys in multicomponent industrial environments because its parameters are expressed as functions of aqueous solution chemistry. Moreover, the \( E_{\text{rp}} \) model parameters have been correlated with the composition of Fe–Ni–Cr–Mo–W–N alloys, thus making it possible to predict the effect of compositional variations in an alloy on \( E_{\text{rp}} \).

The objective of this study is to find a quantitative relationship between the repassivation potential and the microstructural changes that are associated with thermal instabilities. For this purpose, the authors establish a new model for predicting the chromium and molybdenum depletion profiles that develop at grain boundaries as a result of sensitisation. Then, the authors combine the new grain boundary chemistry model with the previously developed repassivation potential model to predict \( E_{\text{rp}} \) of thermally aged alloys or alloys with compositional changes due to element segregation during solidification. This allows us to establish a link between the microstructural variations in alloy composition and the observable, macroscopic values of the repassivation potential, thus providing a threshold condition for localised corrosion. Furthermore, the predictions are verified using previously obtained repassivation potential data for thermally aged alloys 600 and 825 and welded alloy 22.

**Experimental**

The modelling studies reported here rely on the previous experimental results of Tormoen et al. and Pan et al. for the repassivation potential of heat-treated alloys 600 and 825 respectively. In addition, the authors use the repassivation potential data reported by Dunn et al. for welded samples of alloy 22. The nominal compositions of the alloys studied here are summarised in Table 1. In addition to the repassivation potential data, depletion profile data for alloys 600, 825 and 316L are used to verify the grain boundary composition model. The sources of these data are listed in Table 2.

**Computational model**

The computational model developed in this study consists of three parts, i.e.

(i) a grain boundary microchemistry model for predicting the chromium and molybdenum depletion in the vicinity of grain boundaries as a result of carbide formation;

(ii) an electrochemical model for calculating the repassivation potential of Fe–Ni–Cr–Mo–W alloys as a function of alloy composition and environmental conditions including temperature and concentrations of aqueous solution species;

(iii) a procedure for calculating the observable repassivation potential that corresponds to macroscopic localised corrosion by applying the electrochemical model to the depletion profiles and performing suitable integration.

**Grain boundary microchemistry model**

*Review of literature models*

In the last four decades, several computational models have been developed to predict the redistribution of alloying elements in the vicinity of grain boundaries. The motivation for these studies was to be able to understand and quantitatively predict IGA and IGSCC, which are controlled by the depletion of chromium in a region adjacent to the grain boundary. The models developed in the literature can be roughly divided into two classes, i.e.

(i) models that combine a thermodynamic equilibrium formalism for metal carbide formation with a kinetic treatment of the redistribution of Cr and other elements as a function of the distance from the grain boundary;

(ii) models that rely on a kinetic treatment of the evolution of grain boundary chromium

**Table 1 Nominal compositions of alloys studied**

<table>
<thead>
<tr>
<th>Nominal composition, wt-%</th>
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<tr>
<td>Alloy</td>
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</tr>
<tr>
<td>600</td>
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<tr>
<td>825</td>
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<tr>
<td>C-22*</td>
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concentration without explicitly invoking thermodynamic relationships for the local equilibrium associated with carbide formation.\textsuperscript{13,29,31} Such an approach can be used to facilitate separating the stages of chromium depletion and self-healing\textsuperscript{29} or to introduce a detailed, three-dimensional treatment of the growth kinetics of carbides.\textsuperscript{31}

The literature models have been successful in predicting the Cr depletion profiles\textsuperscript{10,11,13,29} and the critical conditions of sensitisation as investigated using electrochemical potentiokinetic reactivation\textsuperscript{28} and IGA/IGCC susceptibility data.\textsuperscript{11,13} Much less attention has been devoted to molybdenum depletion, primarily because Mo depletion data are much less abundant in the literature. However, the computation of Mo depletion profiles is of great interest here because of the importance of Mo in localised corrosion.

Requirements for microchemistry model

In this study, the authors develop a grain boundary microchemistry model that serves as a foundation for predicting the effect of heat treatment on localised corrosion. While the concepts introduced in the combined thermodynamic/kinetic models mentioned above are utilised, the authors construct the model in a way that is particularly suitable for applications to localised corrosion prediction. For this purpose, the model is designed to satisfy the following requirements:

(i) it should be applicable to the prediction of Mo depletion as well as Cr depletion as a function of temperature and time of heat exposure
(ii) it should make it possible to predict the effects of variations in bulk alloy composition and, in particular, the alloy’s carbon content rather than merely fit the depletion profiles for individual alloys. This requirement necessitates the use of a thermodynamic model for the alloy phase
(iii) the model parameters should be limited to quantities that have a well-defined physical meaning, can be obtained from independent experimental data or reasonably estimated and are readily transferable to similar alloys. This requirement effectively limits the model to the use of thermodynamic functions of formation of carbides, thermodynamic parameters for activity coefficients in solid solutions, diffusion coefficients and the average grain size
(iv) the computations should be reasonably fast because they need to be performed numerous times. This means that the authors endeavour to develop analytical expressions, whenever possible, rather than numerically solving the pertinent diffusion equations. Therefore, multi-component diffusion effects\textsuperscript{6} are not taken into account and diffusion equations are written in terms of concentrations of individual alloy components.

Compared with the models described in the open literature, the key new features of the proposed model are

(i) computation of the full time evolution of alloying element depletion (including healing) using easily solvable algebraic equations that incorporate the thermodynamic, diffusion and mass balance aspects of the phenomenon (rather than having to solve differential equations numerically)
(ii) a simple, yet accurate method for predicting Mo depletion together with Cr depletion. This will be achieved without using any empirical parameters beyond those specified in requirement (iii) above.

Assumptions for modelling grain boundary chemistry

To develop a simple model for calculating the depletion profiles as a function of temperature and time of heat exposure and bulk alloy composition, the authors adopt the following assumptions:

(i) the precipitating carbides can be treated as if they form a grain boundary film of equivalent, averaged thickness and consequently, the diffusion in the matrix can be treated as one-dimensional. Grain boundary diffusion can be assumed to be sufficiently rapid to establish equilibrium along the grain boundaries between carbide particles and the adjacent region of the matrix. In reality, grain boundary precipitates are

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
\textbf{Parameters for carbides} & & & & & & & \\
\textbf{Diffusion coefficients} & & & & & & & \\
\hline
\textbf{Alloy} & \textbf{Stoichiometry} & \textbf{Mo/Cr ratio} & \textbf{A}_i & \textbf{B} & \textbf{Q}_\text{Cr} & \textbf{D}_{\text{Cr}}^0 & \textbf{D}_{\text{Mo}}^0 & \textbf{Q}_{\text{Mo}} \textbf{kJ mol}^{-1} \textbf{m}^{-2} \textbf{s}^{-1} \textbf{kJ mol}^{-1} \\
\hline
600 & M_{3}C_{3} & 0 & -405.2 & -25.77 & 4.40 \times 10^{-4} & -243 & n/a & 123 \text{ sample} & 0.0052 & 10 \\
825 & M_{23}C_{6} & 0.078 & 465.7 & -1400 & 1.68 \times 10^{-4} & -287 & 7.93 \times 10^{-6} & 274 & 160 \text{ sample} & 0.0127 & 14 \\
316L & M_{23}C_{6} & 0.165 & 41.22 & -966 & 1.68 \times 10^{-4} & -289 & 7.93 \times 10^{-6} & 274 & 253 \text{ sample} & 0.0139 (Cr) & 45 \text{ sample} & 0.0009 (Mo) & 0.0071 & 46, Krupp sample \\
& & & & & & & & & 30 & 0.0055 & 46, Creusot–Loire sample \\
& & & & & & & & & 30 & 0.0055 (Cr) & 7 \\n\hline
\end{tabular}
\end{table}

\*The average deviation is defined as \( \text{AAD} = \frac{1}{N} \sum_{j=1}^{N} |x^\text{exp} - x^\text{mod}| \) where \( N \) is the number of experimental points and \( x \) are the mole fractions of Cr or Mo.
often discontinuous, a fact that is used in measuring grain boundary depletion profiles without interference from the carbides. However, for model simplification, the authors assume that these discontinuous particles can be treated as if they coat the grain boundaries uniformly (ii) since the interstitial diffusion of carbon is several orders of magnitude faster than the diffusion of substitutional elements (i.e. Cr, Mo, Ni and Fe), carbon activity can be assumed to be equal throughout the material (iii) at the carbide/matrix interface, local thermodynamic equilibrium (or paraequilibrium) is assumed. This equilibrium is determined by the local activity of Cr and Mo and the global activity of C (iv) at a sufficiently long distance from the grain boundary, the concentrations of substitutional elements are the same as those in the bulk alloy because the amount of these elements precipitated as carbides is small compared to their original amounts. On the other hand, the concentration of carbon decreases appreciably as the process of carbide formation advances (v) the carbides may be of the form $M_7C_3$ or $M_{23}C_6$ and contain only Cr and, if applicable, Mo in addition to carbon. While the authors do not consider other carbide phase compositions in this study, an extension of the model to other stoichiometries would be straightforward (vi) carbide nucleation and incubation time are neglected, and the model deals only with the growth of the carbides (vii) carbide growth is controlled by the diffusion of the metallic component of the carbide. The diffusion coefficients are independent of concentration (viii) the moving boundary at the carbide/matrix interface is ignored in diffusion calculations. This implies that the thickness of the carbide is negligible in comparison to the grain diameter.

For simplicity, the authors first describe the computation of chromium depletion profiles and then present its extension to treat molybdenum depletion.

**Derivation of semi-analytical model of Cr depletion**

Figure 1 defines the variables used in the microchemistry model and presents a scheme of material balances for Cr and C in the carbide and alloy phases. The essential features of this scheme were first introduced by Zener and have been generally adopted in physical metallurgy. The authors assume that the concentrations of Cr in the bulk alloy and in the carbide phase $β$ are $C_0^ϕ$ and $C_ϕ^β$ respectively. As in the previously published models it can be assumed that the bulk concentration $C_0^β$ remains practically unchanged. This assumption can be easily verified by calculating the maximum possible drop in bulk Cr concentration that would be obtained in the hypothetical case if all carbon in the alloy was incorporated into the carbide phase. For the alloys listed in Table 1, such a calculation yields a drop of the order of 1%, which is within the uncertainty of depletion profile measurements. The concentration of Cr at the matrix (γ)/carbide (β) interface is given by $C_γ^β$ and results from the paraequilibrium between the carbide phase and chromium and carbon from the matrix. At a given instant of time $t$, the carbide thickness is $r$ and the concentration of Cr in the matrix is a function of the distance from the grain boundary $z$ and is given by the function $C_γ^β(z)$. The area of the rectangle $U$ represents the accumulation of Cr in the carbide at a given instant of time. The consumption of chromium as a result of carbide growth is balanced by the diffusion of Cr from the bulk, which results in a Cr concentration gradient as given by $C_γ^β(z)$. Thus, the area $U$ is always equal to the chromium content that has been withdrawn from the depleted zone $V$. The mass balance for chromium (Fig. 1, upper diagram) is inextricably linked with the mass balance for carbon (Fig. 1, lower diagram). Simultaneously with the accumulation of Cr within the carbide, carbon is progressively consumed,
and its concentration drops throughout the grain. While the activity of carbon remains constant within the grain, its concentration develops a certain profile in the vicinity of the grain boundary as a function of $z$ (cf. $C_C(z)$ in Fig. 1, lower diagram) because the activity coefficient of carbon varies with the changing concentration of Cr and other elements. The drop in the matrix concentration of carbon (i.e. from the original concentration of $C^0_C$ to $C_C$) entails a drop in the interface concentration to $C_C^\beta$ until the matrix carbon concentration reaches the solubility limit. The interface concentrations of carbon $C_C^\beta$ and chromium $C_{Cr}^\beta$ are linked through the thermodynamic equilibrium of carbide formation

$$\nu_{Cr}C + \nu_{Cr}C = Cr_{cb}C_{Cr}$$  \hspace{1cm} (1)

where $\nu_{Cr}$ and $\nu_{Cr}$ are the stoichiometric coefficients of chromium and carbon within the carbide respectively.

Thus, the growth of the carbide and the corresponding evolution of the concentration profiles are controlled by the flow of carbon as well as chromium to the interface. Since the available amount of carbon is finite within a grain, the depletion profile will depend on the grain size, which determines the available volume from which carbon can be withdrawn to form the carbide. The conservation of mass requires that the areas $Y$ and $Z$ in Fig. 1 (lower diagram) be equal to each other because the carbon content in the carbide is equal to the amount of carbon withdrawn from the matrix $Z$. The model must simultaneously satisfy the two mass balance conditions, i.e. $U = V$ and $Y = Z$.

Since the mass is assumed to be one-dimensional, the chromium concentration profile can be obtained from Fick’s second law, i.e.

$$\frac{\partial C_C}{\partial t} = D_C \frac{\partial^2 C_C}{\partial z^2}$$  \hspace{1cm} (2)

where $D_C$ is the diffusion coefficient of Cr. The concentration profile can be expressed as a function of time $t$ and distance from the grain boundary $z$ using the error function solution\textsuperscript{13,34}

$$C_{C1}^\beta(z,t) = C_C^\beta + (C_C^0 - C_C^\beta)erf\left[\frac{z}{2(D_C\tau)^{1/2}}\right]$$  \hspace{1cm} (3)

where the superscripts denote the phases and have been explained in Fig. 1. Since the concentration of component $i$ $C_i$ is related to its mole fraction $x_i$ and molar volume of the matrix $V_{m}$ by

$$C_i = \frac{x_{im}}{V_m} \text{ (i = Cr, Fe, Ni, C, ...)}$$  \hspace{1cm} (4)

Equation (2) can be rewritten in a more convenient form by using mole fractions, i.e.

$$x_{C1}^\beta(z,t) = x_C^\beta(0) + (x_C^0 - x_C^\beta)erf\left[\frac{z}{2(D_C\tau)^{1/2}}\right]$$  \hspace{1cm} (5)

The accumulation of Cr in the carbide phase, as depicted by area $U$ in Fig. 1, is given by

$$\Delta n_{Cr} = \rho_{Cr} \bar{r}$$  \hspace{1cm} (6)

where $\bar{r}$ is the average thickness of the carbide phase along the $z$ axis. The parameter $\bar{r}$ should be regarded as a statistical average and, in actuality, reflects the total volume of the carbide phase (when multiplied by $S$). Therefore, it does not necessarily represent the actual dimension of the carbide and is equally applicable to continuous and discontinuous intergranular carbides. It is introduced in order to calculate the mass balances of Cr and C because the same volume of the carbide phase is available to both Cr and C. The total depletion of Cr in the grain can be calculated by integrating the local depletion over the entire grain, i.e.

$$\Delta n_{Cr} = S \int_0^\infty \left[ C_{Cr}^0 - C_{Cr}^\beta(z,t) \right] dz$$  \hspace{1cm} (7)

In equation (7), the integral is calculated from 0 to infinity even though the size of the grain is finite. However, this is justified by the fact that the size of the depletion zone is much smaller than the size of the grain because the local concentration of Cr rapidly approaches the original concentration ($C_C^0$) at a sufficiently large distance from the depletion zone. By substituting equations (4) and (5) into equation (7), the following can be obtained

$$\Delta n_{Cr} = \frac{S}{V_{m}} \int_0^\infty \frac{\tau}{(\pi)^{1/2}} erf\left[\frac{z}{2(D_C\tau)^{1/2}}\right] dz$$  \hspace{1cm} (8)

Considering that the definite integral of the complementary error function erf is

$$\int_0^\infty erf(x)dx = \frac{1}{(\pi)^{1/2}}$$  \hspace{1cm} (9)

equation (8) becomes

$$\Delta n_{Cr} = \frac{S}{V_{m}} \frac{\tau}{(\pi)^{1/2}}$$  \hspace{1cm} (10)

The mass balance of Cr requires that

$$\Delta n_{Cr} = \Delta n_{Cr}$$  \hspace{1cm} (11)

By substituting equations (6) and (10) into equation (11) and utilising equation (4), a condition for the quantity $\bar{r}$ is obtained

$$\tau = \frac{V_{m}}{\rho_{Cr}} \left( x_{C1}^0 - x_C^\beta(0) \right) (2(D_C\tau)^{1/2})$$  \hspace{1cm} (12)

The accumulation of carbon in the carbide phase is given by an equation analogous to equation (6)

$$\Delta n_{C} = (C_C^0 - C_C)S\bar{r}$$  \hspace{1cm} (13)

where $C_C^0$ and $C_C$ are the concentrations of carbon in the carbide phase and in the original alloy respectively (cf. Fig. 1, lower diagram). The quantity $C_C^0$ (and hence, $x_C^0$) results directly from the assumed stoichiometry of the carbide. The total depletion of C in the grain can be calculated as

$$\Delta n_{C} = (C_C^0 - \overline{C_C})Sd$$  \hspace{1cm} (14)

where $\overline{C_C}$ is the average concentration of carbon in the grain and $d$ is the average distance over which carbon
can be withdrawn. In equation (14), the average concentration $\overline{C}_C$ is used instead of integrating the carbon concentration $C_C$ throughout the grain. This approximation introduces a negligible error because the concentration of carbon shows a certain gradient only in the vicinity of the grain boundary (cf. Fig. 1), due to the change in the activity coefficient of carbon with the change in the concentration of substitutional elements. However, the size of the depletion zone is substantially smaller than the size of the grain. Hence, the distance over which the carbon concentration changes is much smaller than the distance over which it is effectively constant. Thus, the average concentration $\overline{C}_C$ is essentially equivalent to the concentration of carbon at sufficiently large distances from the grain boundary, at which the gradients of concentrations become effectively zero.

The mass balance for carbon requires that

$$\Delta n_C^\beta = \Delta n_C$$

Substituting equations (13) and (14) into equation (15) and utilising the expression for $f$ given by equation (12), the authors obtain an expression for the carbon mole fraction in the grain

$$\overline{x}_C = \frac{x_C^\beta}{x_C^0} = \frac{2(D_C t)^{1/2}}{d} \frac{x_C^0 - x_C}{x_C^0 - x_C^b} \left(x_C^b - \overline{x}_C^b\right)$$

Equation (16) is not an explicit expression for $\overline{x}_C$ because the right-hand side of equation (16) depends on the carbon concentration $x_C^b$ through the paraequilibrium at the $\gamma/\beta$ interface. The paraequilibrium condition for the reaction of carbide formation (equation 1) takes the form

$$K = \frac{1}{(a_C^\beta)^{2/3}(a_C^b)^{2/3}}$$

where $K$ is the equilibrium constant, and the activities of Cr and C at the interface are denoted by $a_C^\beta$ and $a_C^b$ respectively. In equation (17), the activity of the carbide is equal to 1 because the carbide forms a separate phase. Equation (17) can be written in a more convenient form by relating the equilibrium constant $K$ to the Gibbs energy of formation $\Delta G_f$, i.e.

$$\Delta G_f^0 = -RT \ln K$$

which can be expressed as a function of temperature as

$$\Delta G_f^0 = A + BT$$

Equation (19) embodies the reasonable assumption that the enthalpy and entropy of formation are independent of temperature and is used to represent experimental Gibbs energy of formation data.35 Rearrangement of equations (17) and (18) gives an expression for the activity of Cr at the grain boundary

$$\ln a_C^\beta = \frac{1}{V_{Cr}} \left(\frac{\Delta G_f^0}{RT} - v_C \ln a_C^\beta\right)$$

Equation (20) can be further rewritten by decomposing the activity into mole fractions and activity coefficients, i.e.

$$\ln x_C^{\beta,\gamma} = \frac{1}{v_C} \left(\frac{\Delta G_f^0}{RT} - v_C \ln a_C^\beta\right)$$

where the activity coefficients are functions of the vector of composition $x$ and temperature $T$. In addition to the thermodynamic equilibrium condition (21), the equality of carbon activities at the grain boundary and outside of the depletion zone (i.e. $a^\beta_C = a_C$) provides another condition.

$$x_C^{\beta,\gamma}(x^\beta, T) = \frac{\overline{x}_C^\beta(x^\gamma, T)}{\overline{x}_C^\gamma(x^\gamma, T)}$$

To apply equations (21) and (22), it is necessary to calculate the activity coefficients in the Cr–Ni–Fe–C system as a function of $x$ and $T$. For this purpose, the authors use the activity coefficient formulation developed by Babu et al.36 for Fe–Ni–Cr–Mo–C–N alloys on the basis of the models of Hertzman,37,38 Hertzman and Jarl39 and Andersson and Lange.40 Conditions (21) and (22) are supplemented by the normalisation condition for mole fractions

$$\sum_i x_i^\beta = 1$$

and the requirement that the molar ratio of the alloy components that do not participate in carbide formation be constant in the grain

$$\frac{x_{Cr}^\beta}{x_{Ni}^\beta} = \frac{x_{Cr}^0}{x_{Ni}^0}$$

Equations (16) and (21)–(24) constitute a set of five equations, which can be solved numerically with respect to the four mole fractions at the interface $x_i^\gamma (i=Cr, Ni, Fe, C)$ and the carbon mole fraction of carbon in the matrix outside of the depletion zone $\overline{x}_C$. The remaining mole fractions in the matrix outside of the depletion zone (i.e. $x_i^\gamma$ for $i=Cr, Ni, Fe$) are essentially the same as those in the original alloy ($x_i^0$) except for a slight renormalisation to accommodate the changes in the matrix carbon concentration $\overline{x}_C$ in each iteration. In a practical implementation, the two linear constraints (equations (23) and (24)) are used to eliminate two variables $x_C^b$ and $x_C^0$, which leaves three non-linear equations (equations (16), (21) and (22)) to be solved numerically. For optimum numerical stability, Equations (21) and (22) are then solved with respect to $x_C^\beta$ and $x_C^\gamma$ for a given value of $\overline{x}_C$ in an inner loop, and equation (16) is converged with respect to $\overline{x}_C$ in an outer loop.

Once the value of $\overline{x}_C$ is found for a given temperature and time of exposure, the Cr concentration profile $x_C(z,t)$ is calculated from equation (5) as a function of the distance $z$ from the grain boundary and time. The corresponding concentration profiles of the other elements are then found from equations that are analogous to equations (23)–(24) but in which the local concentrations in the matrix $x_i(z,t)$ ($i=\text{Ni, Fe}$) are substituted instead of the grain boundary concentrations $x_i^\beta$. It should be noted that the thermodynamic model of carbide formation implies that the minimum chromium concentration is achieved at the very beginning of the heat exposure ($t=0$) because carbon concentration is
then at its highest value. It is known, however, that the
time to reach the minimum Cr concentration is finite
rather than zero. Various approaches to account for this
observation have been proposed in the literature. Here,
the authors adopt the approach of Sourmail et al. who
explained the delay in reaching the minimum of Cr depletion by considering the average
composition that is measured rather than the exact
predicted interface composition. Sourmail et al. argued
that the measurements are likely to overestimate the
actual interface composition because of strong concentra-
tion gradients in the vicinity of the grain boundary,
which cause the measured values to reflect an averaged
effect due to beam spreading. Because of this effect,
coupled with the problems of relative orientation of the
grain boundary and the beam, SOURMAIL et al. proposed to calculate the measurable concentration as
the average over a finite range in a direction perpendi-
cular to the boundary. At distances \( z \) close to the
boundary, such an averaged value is significantly differ-
ent from the local value when the concentration gradient is steep. As the authors move farther from the
boundary, the average value rapidly approaches the
local value. Thus, the averaged, measurable concentra-
tion at a distance \( z \) from the grain boundary is calculated as

\[
\overline{x}(z) = \frac{1}{\Delta_z} \int_{z-\Delta_z/2}^{z+\Delta_z/2} x(z) dz
\]

(25)

where \( \Delta_z \) is assumed to be 20 nm. The averaged value can be then compared with the results of experimental
measurements. At distances close to the grain boundary,
the averaged concentration naturally decreases as a
function of time in a relatively short time interval, then
reaches a minimum and finally increases.

This approach to calculating the measurable local
concentration is sufficient for the study of localised
corrosion because the authors are not concerned here with the detailed calculation of time evolution in the
initial stages of chromium depletion. The accurate prediction of depletion profiles over a larger interval of
time is much more important.

As discussed above, the growth of the carbide strongly depends on the volume (i.e. \( V = Sd \)) from which carbon is
withdrawn. If the available distance \( d \) is small, the carbon concentration rapidly drops to the solubility limit,
and self-healing starts after a short amount of time. Conversely, if \( d \) is infinite, self-healing will never occur because the carbon concentration will remain at its
bulk value. Following SOURMAIL et al., the authors assume that \( d \) is equal to one-sixth of the average size of the
grain, i.e.

\[
d = \frac{g}{6}
\]

(26)

where \( g \) is the average grain size. Equation (6) was postulated by the sensitisation of Fe–Ni–Cr–C alloys
by arguing that, since soft-impingement is a three-
dimensional phenomenon, it is appropriate to attribute to the calculation volume a sixth of the grain given that,
if a cubic model is used to represent the grain, six faces
will actually draw the carbon from the same volume.

In total, the chromium depletion model contains the
following parameters:

(i) parameters \( A \) and \( B \) for calculating the Gibbs
energy of formation of the carbide as a function of
temperature (equation (19))

(ii) parameters \( D^0_i \) and \( Q_i \) for calculating the
diffusion coefficient of Cr as a function of
temperature according to the general relation

\[
D_i = D^0_i \exp \left( \frac{Q_i}{RT} \right) \quad (i = Cr)
\]

(27)

(iii) the average grain size \( g \)

In principle, all these parameters can be obtained from
independent experimental data, but they may be adjusted in practice to match concentration profile data.

Extension of model to Mo depletion

Assuming that multicomponent diffusion effects can be
neglected, the molybdenum concentration profile can be
calculated from equations analogous to equations (2)–
(5). The mole fraction of Mo as a function of time and
distance from the grain boundary is then given by

\[
x_{\text{Mo}}(z,t) = x_{\text{Mo}}^0 + (x_{\text{Mo}}^0 - x_{\text{Mo}}^b) \text{erf} \left( \frac{z}{2(D_{\text{Mo}})^{1/2}} \right)
\]

(28)

The accumulation of Mo in the carbide phase can be
obtained from an equation analogous to equation (6)

\[
\Delta n_{\text{Mo}} = \frac{S(x_{\text{Mo}}^0 - x_{\text{Mo}}^b)}{V_m} 2(D_{\text{Mo}})^{1/2} \quad \left( \frac{\pi}{6} \right)^{1/2}
\]

(30)

Using the mass balance constraint for Mo, i.e.

\[
\Delta n^b_{\text{Mo}} = \Delta n_{\text{Mo}}
\]

(31)

an equation for the average dimension of the carbide
along the \( z \) axis can be obtained

\[
r = \frac{V^b_{\text{Mo}}}{V_m} \left( x_{\text{Mo}}^0 - x_{\text{Mo}}^b \right) 2(D_{\text{Mo}})^{1/2} \quad \left( \frac{\pi}{6} \right)^{1/2}
\]

(32)

Since the quantity \( r \) obtained from equation (32) must be
the same as that obtained from equation (12), a
relationship between the mole fractions of Mo and Cr at
the \( \gamma/\beta \) boundary is obtained

\[
x_{\text{Mo}}^b = x_{\text{Mo}}^0 - \left( \frac{x_{\text{Cr}} - x_{\text{Cr}}^b}{x_{\text{Cr}}^b - x_{\text{Cr}}^0} \right) \frac{x_{\text{Mo}}^0 - x_{\text{Mo}}^b}{x_{\text{Cr}}^b - x_{\text{Cr}}^0} \left( \frac{D_{\text{Cr}}}{D_{\text{Mo}}} \right)^{1/2}
\]

(33)

To apply equation (33), it is necessary to know the mole
fractions in the carbide phase, \( x_{\text{Mo}}^b \) and \( x_{\text{Cr}}^b \). For this
purpose, the authors assume the overall metal carbide
stoichiometry \( M_{\text{Mo}}(\text{C}) \), where the typical values of \( \gamma_M \)
and \( \text{VC} \) are 23 and 6 or 7 and 3 respectively. Then, the
following equation can be written

\[
\frac{x_{\text{Mo}}^b}{x_{\text{Cr}}^b} = \frac{\gamma_M}{\text{VC}}
\]

(34)

In addition, it is necessary to specify the ratio of the
to Mo and Cr in the carbide phase, i.e.
The main advantage of this decomposition is the fact that equation (43) is algebraically equivalent to equation (20) or (21). Equations (16) and (22)–(24) remain unchanged for systems containing Mo. Thus, the system is described by seven equations, i.e. equations (16), (22)–(24), (33) and (43), equation (44) may be used for testing the consistency of the solution as long as $\Delta G^f_i(MO_{x_{Mo}}C_{Cr})$ can be estimated with sufficient accuracy.

Using this approach, calculation of depletion profiles for molybdenum-containing systems requires two additional parameters in addition to those used for computing the Cr depletion profiles as described above, i.e. (iv) the diffusion coefficient of Mo, which is calculated from the standard equation (27) where $i=Mo$ (v) the Mo/Cr molar ratio in the carbide (equation (35)), which can be obtained from experimental data or adjusted based on Mo depletion profiles.

Effective size of depletion zone

The effective size of the depletion zone provides information on the width of the depletion zone in a direction perpendicular to the grain boundary. The depletion profile does not automatically define the size of the depletion zone because it asymptotically approaches the bulk concentration of Cr (cf. Fig. 1, upper diagram). Therefore, to evaluate the effective size of the depletion zone $z_{eff}$, the authors can approximate the chromium depletion zone by a triangle with the vertices defined by $C_{Cr}^b$ and $C_{Cr}^a$ along the concentration axis (cf. Fig. 1) and $z_{eff}$ along the $z$ axis. Then, the total depletion of chromium $\Delta n_{Cr}$ calculated from the triangular approximation, should be equal to that obtained by rigorous integration from zero to infinity (equation 10). From simple geometrical considerations, the total depletion calculated using the approximate triangle is equal to

$$\Delta n_{Cr} = S(C_{Cr}^b - C_{Cr}^a)\frac{z_{eff}}{2} = \frac{1}{2}\frac{S}{\pi r_m^2}(x^b_{Cr} - x^a_{Cr})z_{eff}$$

By equating $\Delta n_{Cr}$ calculated from equations (10) and (45), the following equation can be obtained

$$z_{eff} = \frac{4(D_{Cr}r)^{1/2}}{(\pi)^{1/2}}$$

Repassivation potential model

In a previous paper,19 a comprehensive model was developed to calculate the repassivation potential of bulk alloys as a function of environment chemistry and temperature. Since the details of this model were described previously,19 only its essential features are summarised here. The model was derived by considering the dissolution of a metal in a localised corrosion environment in the limit of repassivation. The model envisages the dissolution of the metal (M) underneath a layer of a concentrated metal halide solution MX. In the process of repassivation, a thin layer of oxide is assumed to form at the interface between the metal and the hydrous metal halide. The model represents the formation of the oxide layer using a partial coverage approach. The partial coverage fraction increases as repassivation is approached. The dissolution rate of the metal under the oxide is lower than at the metal/halide interface and corresponds to the passive dissolution rate. Thus, as the repassivation potential is approached, the dissolution rate tends towards the passive dissolution
rate. The model includes the effects of multiple aggressive and non-aggressive or inhibitive species, which are assumed to undergo competitive adsorption. The aggressive species form metal complexes, which dissolve in the active state. The inhibitive species and water contribute to the formation of oxides, which induce passivity. The formalism that describes these phenomena leads to a closed-form equation in the limit of repassivation, i.e. when the current density reaches a predetermined low value \( i_{0p} \) (assumed to be \( i_{0p} = 10^{-2} \text{ A m}^{-2} \)) and the fluxes of metal ions become small and comparable to those for passive dissolution. Most importantly, for the study of thermally aged alloys, the parameters of the model have been generalised in terms of alloy composition for Fe–Ni–Cr–Mo–W–N alloys. This generalisation was based on experimental \( E_{rp} \) data for 13 base (typically mill-annealed) stainless steels and nickel-based alloys, supplemented by those for Fe and Ni. The Appendix summarises the final working equations for the \( E_{rp} \) model, defines the model parameters and provides the equations for calculating the parameters as functions of alloy composition. Thus, Appendix contains a complete recipe for predicting the repassivation potential as a function of alloy composition, aqueous environment temperature and chloride activity. This model will be used further in this study to predict the repassivation potentials of heat-treated alloys.

**Effective repassivation potential of sensitised alloys**

The two models described above (i.e. the local Cr/Mo depletion model and the \( E_{rp} \) model) make it possible to calculate the hypothetical ‘local’ repassivation potential at each microscopic point on the alloy surface. However, a question arises as to how the macroscopically measured repassivation potential is related to local microchemistry. Specifically, does the localised corrosion sense the minimum in the depletion profile or some kind of average? A somewhat similar problem has been investigated for sensitised alloys in environments that cause uniform, passive corrosion except in the presence of grain boundary depletion. Such phenomena can be investigated using electrochemical potentiodynamic reactivation (EPR) tests. In particular, Gaudett and Scully examined the distribution of grain boundary Cr depletion and its effect on the degree of sensitisation as measured by EPR tests. They found that IGSCC failure occurs when the boundary Cr concentration is depleted to below a certain critical level, and also, more than a certain fraction of grain boundaries must be depleted to the critical level to observe macroscopic IGSCC. Jiang et al. also examined the effect of Cr-rich and depleted zones in duplex stainless steels due to the \( \chi' \) phase in sulphuric acid using the EPR technique. They established a correlation between reactivation kinetics and the percentage of atomic layers that have Cr less than a threshold level. In contrast to intergranular corrosion or IGSCC, the repassivation potential of sensitised samples is not merely a reflection of Cr depletion below a certain threshold level. In contrast to intergranular dissolution, which occurs primarily in the Cr-depleted regions, pitting/crevice corrosion can occur in both Cr-depleted and non-depleted areas. Further, the rate of dissolution inside a pit or active crevice region is not likely to be dramatically different between a Cr-depleted and non-depleted material because localised corrosion occurs in a completely active state in a highly aggressive environment. In repassivation potential tests, the potential at which the rate of oxide film formation exceeds the active dissolution rate is measured as a function of heat treatment. This process is expected to be different between the Cr-depleted and non-depleted areas, leading to a different potential at which the oxide film is stabilised as a function of local alloy composition.

The repassivation potential model described above can be directly used to predict local values of \( E_{rp} \) on the basis of the local Cr (and Mo) concentration as a function of the distance from the grain boundary. However, local values of \( E_{rp} \) are not experimentally accessible. This is due to the fact that the measured repassivation potential is a macroscopic property, i.e. it reflects the repassivation of several pits with dimensions ranging from several hundred micrometres to a millimetre. These dimensions are much larger than the depletion zone sizes, and therefore, each pit can be imagined to contain several depleted grain boundaries at the bottom of the pit. In principle, it would be possible to calculate the average repassivation potential if the geometry of the pit was exactly known and the composition of the alloy that is exposed to the pit environment could be exactly ascertained. However, information about the pit geometry and alloy composition at the bottom of the pit is not available in practice and even if it were available, prediction of \( E_{rp} \) based on detailed measurements of individual pits would be of little predictive value for corroding structures. Instead, it is necessary to establish a procedure for estimating the average repassivation potential for statistically distributed pits. Such a procedure is made possible by the fact that plentiful experimental information is available about the dependence of the repassivation potential on the composition of bulk Fe–Ni–Cr–Mo–W–N alloys. Furthermore, this information is embodied in a computational model. To calculate \( E_{rp} \) of thermally aged samples, it is reasonable to make the following assumptions:

(i) the measured \( E_{rp} \) primarily reflects the localised corrosion of the Cr-depleted regions rather than...
of the nominal alloy composition. This is due to the fact that a pit stabilises more easily in an area that is more susceptible to localised corrosion because of chromium (or molybdenum) depletion. The experimentally observed localised corrosion occurred predominantly in the grain boundary area. Even if some localised corrosion occurs outside of the depleted zones, the repassivation potential calculated over the depletion zone should provide a conservative (i.e. lower) estimate, which is desirable in engineering practice. Thus, the average repassivation potential should be calculated by integrating the $E_{rp}$ over the depleted zone

(ii) a pit needs to achieve a certain minimum size to be stabilised in an $E_{rp}$ measurement. Therefore, in the case of a narrow Cr depletion zones, the averaging should extend beyond the depletion zone to ensure that a certain minimum area of the alloy contributes to the measurable $E_{rp}$.

Following assumption (i), the average repassivation potential $E_{rp}$ can be obtained by integration of the local repassivation potential, $E_{rp}(z)$, as follows

$$
E_{rp} = \frac{\int_{0}^{L} w(z)E_{rp}(z)dz}{\int_{0}^{L} w(z)dz}
$$

where $L$ is the distance from the grain boundary over which the integration is performed and $w(z)$ is a weighting factor, which reflects, in principle, the uneven contribution of the depleted zone surface to the observable repassivation potential. In view of assumption (i), the distance for integration $L$ can be identified with the effective size of the depletion zone $z_{eff}$ (equation (46)). However, this value should be adjusted in agreement with assumption (ii) to ensure that the repassivation potential is integrated over at least a certain reasonable minimum distance from the grain boundary. Thus, the distance for integration can be estimated as

$$
L = z_{eff} + 2\Delta z
$$

where $z_{eff}$ is calculated from equation (46), and $2\Delta z$ is the minimum size for stabilisation of localised corrosion. For simplicity, $\Delta z$ is set at the same value as that used to calculate the observable depletion profiles (equation (25)). The expression for $z_{eff}$ obtained from equation (46) is somewhat arbitrary because a different value could be obtained, for example, on the basis of the molybdenum depletion profile. However, the precise definition of the effective size is not crucial for integrating the repassivation potential over the depletion zone. With equation (48), the repassivation potential is effectively integrated over the depletion zone when the zone is reasonably wide. When it is very narrow, the integration is effectively performed over the minimum distance.

The weighting factor $w(z)$ for the integration should recognise that the contribution of the depleted areas with Cr concentration below a threshold value (e.g. $x_{Cr}^c = 0.12$) should be greater than the contribution of the areas in which Cr is less severely depleted. For this purpose, the authors define $w(z)$ as follows

$$
w(z) = 1 + \eta \max \left( \frac{\chi_{z} - \chi_{0}(z)}{\chi_{Cr}}, 0 \right)
$$

In equation (49), the term in parentheses ensures that the weighting factor is equal to 1 for all chromium concentrations above the threshold value (i.e. when $x_{Cr}(z) > x_{Cr}^c$) and becomes progressively enhanced as the Cr concentration drops below $x_{Cr}^c$. The enhancement factor $\eta$ is assumed to be equal to 100, which is the order of magnitude of the elevation of dissolution rates in Cr-depleted areas in standard tests in acidic solutions. While equation (49) is arbitrary, it provides a reasonable enhancement of the weighting factor for the Cr compositions that fall below $x_{Cr}^c$. The minimum value of $w(z)$ is 1, while the maximum value is $1 + \eta$. Thus, the averaged repassivation potential for heat-treated samples can be obtained from equations (47)–(49), where the local value of the repassivation potential $E_{rp}(z)$ is calculated from the generalised repassivation potential model (as described in Appendix) using the local alloy compositions obtained from the Cr and Mo depletion profiles as a function of the distance from the grain boundary.

This method of averaging can be compared with the computation of $E_{rp}$ directly at the grain boundary, where the Cr concentration is at its minimum and therefore, the repassivation potential reaches its lowest value. It can be expected that the method of averaging should give reasonable predictions if a critical size needs to be accounted for as discussed above. On the other hand, the $E_{rp}$ value calculated at the grain boundary will reflect a different hypothetical scenario, in which, in the process of repassivation, most of the surface is already repassivated and the only remaining activity is in little grooves at the grain boundaries. In such a situation, the measured $E_{rp}$ value should correspond to the local boundary concentration of Cr/Mo. These two scenarios will be tested against experimental data below.

Results

In this section, the authors first verify the grain boundary microchemistry model by comparing the calculated depletion profiles with experimental data. Then, the authors calculate the repassivation potentials of thermally aged and welded alloys using the procedures described above.

Depletion profiles

The grain boundary microchemistry model has been verified using experimental data for alloys 600, 825 and 316L. The model parameters for these alloys and the sources of experimental data are summarised in Table 2. The parameters $A$ and $B$ were determined by regressing depletion data simultaneously for various samples of a given alloy. As shown in Table 2, the only sample-specific parameter is the average grain size, and the remaining parameters are general for a given alloy. However, the predicted depletion profiles are rather less sensitive to the grain size than to the remaining parameters, and the effect of grain size manifests itself only at relatively advanced stages of healing because the grain size determines the available supply of carbon. In addition, Table 2 gives the average deviations between the calculated and experimental concentrations of Cr and Mo.
In the case of alloy 600, experimental data are available from three sources. These three data sets are in reasonably good agreement with each other. Model calculations are compared with selected experimental data in Fig. 2. The two diagrams in Fig. 2 illustrate the progressive self-healing (i.e. the increase in the minimum Cr concentration and the concomitant widening of the depletion profiles) for sensitised samples aged at 973 K (Fig. 2a) and 923 K (Fig. 2b) as a function of aging time. For comparison, depletion profiles are also shown for lower aging temperature and longer aging time (873 K, 250 h) and higher temperature and shorter time (1073 K, 0-42 h). Good agreement has been obtained with all data sets, in particular with the data of Was and Kruger. However, molybdenum depletion profiles are not available for this alloy so that a comparison cannot be made.

On the other hand, some experimental Mo depletion profiles are available for type 316L stainless steel. In this case, experimental Cr depletion data are particularly abundant as shown in Table 2. Selected results of calculations are shown for this alloy in Fig. 4. Figure 4a shows the time evolution of depletion profiles for a relatively low aging temperature (823 K) and long times. Figure 4b illustrates the Cr depletion profiles for a fixed aging time (1000 h) and temperatures varying from 873 to 1023 K. The widening of the profiles and the increase in the minimum Cr concentration as a function of aging temperature at constant aging time are correctly reproduced. Figure 4c shows the molybdenum depletion profile at the conditions that correspond to the Cr profiles in Fig. 4a. For type 316L stainless steel, the Mo/Cr ratio was adjusted to reproduce the depletion profiles and is listed in Table 2 together with the remaining...
parameters. Thus, the model simultaneously reproduces the Cr and Mo depletion profiles generally within the uncertainty of experimental data.

Repassivation potential of thermally aged samples

Figures 5 and 6 show the results of modelling the repassivation potential for alloy 600. Figure 5 summarises the dependence of the repassivation potential of mill-annealed samples on temperature and the activity of chloride ions. The lines in Fig. 5 have been obtained from the correlation described in Appendix. Over most of the chloride range, \( E_{rp} \) shows the standard semi-logarithmic dependence on chloride activity. This dependence provides a baseline for calculating \( E_{rp} \) of thermally aged samples.

Figure 6 shows the difference between the repassivation potentials of solution annealed and thermally aged samples and those of mill-annealed samples, i.e.

\[
\Delta E_{rp} = E_{rp} - E_{rp,\text{mill-annealed}}
\]  

The experimental \( E_{rp} \) data have been reported in a previous paper for samples aged at 700°C as a function of time. The repassivation potentials have been measured at 60°C in 0.001, 0.005 and 0.04M NaCl solutions. The measurements have been performed on alloy 600 with 0.02%C at all conditions and on samples with 0.04%C in 0.001 and 0.04M NaCl solutions.

The calculations have been performed using the averaging procedure described above and by assuming the alloy composition at the grain boundary. In Fig. 6, the thick lines show the averaged repassivation potentials predicted according to equations (48)–(50). The thin lines represent the minimum value of the repassivation potential, which corresponds to the minimum predicted concentration of chromium at the grain boundary. Additionally, the dotted line in the middle diagram in Fig. 6 (i.e. the one for 0.005M solutions) shows the results obtained using the averaging procedure without the weighting factor (equation (49)). The experimental data are plotted with error bars of ±50 mV, which is a reasonable estimate for the uncertainty of \( E_{rp} \) measurements. Comparison between the calculated and experimental values reveals that the predictions obtained using the weighted averaging procedure agree, in general, with the data for the 0.02%C alloy within the experimental
scattering range. Although the scattering of the data is substantial, both the data and the calculated curves show the same trends. For the 0.04%C alloy, the agreement is poorer in 0.001M solutions, since the experimental data indicate an increase in $E_{rp}$ over the values for mill-annealed samples, whereas the model predictions do not show such an effect. The predictions obtained using only the grain boundary composition (thin lines) are, in general, lower than the data and provide a reasonable estimate of the lower limit of the repassivation potential. Predictions obtained using the unweighted averaging procedure are somewhat too high. While the weighted averaging procedure (thick lines) shows the best results, the predictions obtained from the alternative approaches are too close to draw unequivocal conclusions as to which procedure reflects the

4 a, b Calculated and experimental chromium and c molybdenum depletion profiles for heat-treated type 316 stainless steel. The data are from Sahlaoui et al.44 (a, c) and Tekin et al.45 (b)

5 Effect of chloride activity (molality-based) and temperature on the repassivation potential of mill-annealed alloy 600
actual mechanism of localised corrosion stabilisation in alloy 600.

The repassivation potential initially drops fairly rapidly as a function of aging time and then slowly recovers towards the $E_{rp}$ value of the annealed sample (which is indicated by the horizontal line in Fig. 6). This behaviour parallels the evolution of chromium depletion as a function of aging time. Although the calculated $E_{rp}$ values can never exceed the repassivation potential of the bulk alloy, some of the experimental data lie above the horizontal line for $\Delta E_{rp}=0$. This apparently unphysical behaviour may be due to an incomplete homogenisation of the annealed samples, which may later proceed to completion as a result of the self-healing process. If the experimental points that lie above the $\Delta E_{rp}=0$ line are neglected, the lines calculated using the weighted averaging procedure are in reasonably good agreement with experimental data.

The depression of $E_{rp}$ as a function of aging time is slightly deeper for the 0.04%C alloy compared with the 0.02% alloy, which reflects a lower concentration of chromium in the depleted zone of the alloy with a higher carbon content. This is illustrated in Fig. 7, which compares the predicted depletion profiles after 2.5 and 96 h of thermal aging for the 0.02 and 0.04%C lots. Furthermore, the higher carbon content has a substantial effect on the predicted recovery of the repassivation potential as a function of aging time, i.e. the recovery is notably slower for the alloy with a higher carbon content.

Results of calculations for alloy 825 are summarised in Figs. 8 and 9. In contrast to alloy 600, alloy 825
contains an appreciable amount of molybdenum. Therefore, the predicted repassivation potential depends on the molybdenum profile in addition to the chromium profile. To calculate molybdenum depletion, it has been assumed that the molar Mo/Cr ratio in the carbide (equation (35)) is the same as in the bulk alloy. This is consistent with measurements of grain boundary carbide compositions reported by Pan et al.\textsuperscript{14}

The baseline results for the repassivation potential of mill-annealed alloy 825 are shown in Fig. 8 as a function of chloride ion activity and temperature.\textsuperscript{19,46} The plot of $E_{rp}$ versus chloride activity exhibits a change in slope, which is consistent with the repassivation potential model.\textsuperscript{19} While the slope is low and similar to that observed for alloy 600 at higher chloride concentrations, it becomes much steeper in dilute solutions. This
The repassivation potential is sensitive to environmental conditions. The calculated and experimental depression in the repassivation potential $\Delta E_{rp}$ is shown in Fig. 10 for samples aged for 15 and 100 h as a function of aging temperature. As with alloy 600, the calculations were performed using the averaging procedure (thick lines) and the grain boundary composition hypothesis (thin lines). In the case of alloy 825, the weighting factor $w(z)$ is always equal to 1 because the grain boundary concentration is always greater than the threshold concentration $x_C^z = 0.12$. Thus, the weighted averaging is equivalent to unweighted averaging here.

In contrast to alloy 600, the predicted minimum values of $E_{rp}$ (thin lines) are much lower than the averaged values (thick lines). The predicted averaged values are in excellent agreement with experimental data for samples aged for 15 h (circles in Fig. 9). The comparison of the results obtained using both approaches provides a strong indication that the averaging procedure more accurately reflects the mechanism of localised corrosion stabilisation, which underscores the importance of a critical size. For the samples aged for 100 h, the agreement is good for lower aging temperatures, but the $E_{rp}$ depression is underestimated for higher temperatures. However, the predicted $\Delta E_{rp}$ is consistent with the observed self-healing at higher temperatures after 100 h, which is indicated by the depletion profiles. Therefore, these deviations may be due to the incomplete self-healing of the samples used in the $E_{rp}$ measurements.

Another indirect confirmation of the proposed methodology of averaging $E_{rp}$ is provided by the cyclic potentiodynamic polarisation scans and potential staircase tests for sensitised samples of alloy 600. These results indicate that there is no distinct two-stage repassivation behaviour observed for sensitised alloys in either test. A hypothetical two-stage behaviour would support the notion that the repassivation of unsensitised areas is followed by the repassivation of the sensitised areas, which would reflect the minimum Cr/Mo composition. The fact that such behaviour is not observed is consistent with the assumption that the measured repassivation potential is an average over a relatively large area compared to the depletion zone. The measurements are likely to reflect the repassivation of a large pit that spans the grain boundary region, including some matrix.

**Estimation of $E_{rp}$ for welded Ni-based alloys**

Modelling the alloy microchemistry in welded alloys is outside of the scope of this paper. However, the approach developed here for thermally aged alloys can be applied to welded alloys if the local composition of alloy components is available from experimental data or can be estimated. Then, the repassivation potential of welded samples can be estimated using the local composition information on the basis of the previously accepted assumption that $E_{rp}$ primarily reflects the localised corrosion of the chromium and/or molybdenum-depleted regions.

It is known that solidification of nickel-based alloy welds leads to segregation patterns associated with dendrite formation. The segregation leads to Ni depletion and solute (Cr, Mo, W) enrichment in interdendritic volumes. At the same time, the dendrite cores are somewhat depleted with respect to the solute components. Therefore, it is possible to estimate the repassivation potential on the basis of the dendrite core compositions. It should be noted that such an estimation does not explicitly take into account the effect of other phases that form as a result of solidification, in particular the topologically close-packed phases such as $\mu$, $\sigma$ and $P$. Although these phases are Mo-rich, it can be expected that the solute depletion is primarily due to segregation.

Figure 9 shows the calculated and experimental repassivation potentials for mill-annealed and welded alloy 22. In both cases, $E_{rp}$ was calculated from the correlation described in Appendix as a function of chloride activity. For the welded alloy, the composition of the dendrite core as reported by Cieslak et al. has been assumed (i.e. Ni–20Cr–10Mo–2.7W–3.1Fe–0.06C–Ni). As shown in Fig. 9, the repassivation potential predicted for the welded sample is only slightly lower than that for the bulk alloy. These predictions are consistent with experimental data within their scattering range. Also, Fig. 9 includes the $E_{rp}$ values that have been predicted for thermally aged welded samples using the procedures described above.

**Discussion of model features**

The microchemistry model described above is one-dimensional and assumes, in analogy with a number of previously published theories, an effectively uniform carbide layer at the grain boundary. In reality, the continuity of the carbides depends on the aging treatment and may vary from continuous to widely spaced. A detailed treatment of discontinuous carbides would necessitate the use of a two-dimensional model, such as the collector plate model, in which the size of carbides is explicitly taken into account and carbide growth is assumed to consist of volume diffusion.
to the grain boundary, transport along the grain boundary to the precipitate and interfacial diffusion and deposition at the surface of the growing carbide. The collector plate model successfully reproduces the growth (i.e., lengthening and thickening) of grain boundary carbides\textsuperscript{22,51} and has been applied, in conjunction with a finite difference numerical algorithm, to calculate two-dimensional Cr depletion profiles in the presence of discrete carbides.\textsuperscript{27} However, the use of a two-dimensional microchemistry model was deemed unnecessary in the present study. First, the available experimental studies typically do not reveal a change in Cr content along the grain boundaries between discrete carbides, which is due to the much faster rate of grain boundary diffusion than the corresponding rate of bulk diffusion and indicates that the whole grain boundary acts as a collector plate to supply the precipitates with Cr.\textsuperscript{54} In such cases, the Cr concentration is constant along the grain boundary, and the one-dimensional solution of Fick’s law applies as described above even though the precipitates are discontinuous. In some partially sensitised grain boundaries, the carbides may be so widely spaced that the Cr diffusion fields around them may not overlap\textsuperscript{27} and a two-dimensional model is necessary to fully reproduce the depletion profiles.\textsuperscript{25} However, a one-dimensional model is still adequate in such cases to represent the Cr depletion in local areas around the carbides even though the distance over which carbon is withdrawn (equation (26)) may be then underestimated. Since localised corrosion is most likely to stabilise in the most susceptible, Cr-depleted areas, such a locally valid representation of Cr depletion should remain useful for estimating the repassivation potential (even though it may be less accurate for simulating intergranular corrosion). The second reason for not using a two-dimensional model here is due to the fact that it requires information about the spacing of carbides, which may change and is difficult to predict a priori. Third, a two-dimensional model is much more computationally demanding because it requires the numerical solution of differential equations rather than the semi-analytical solution derived here, which would make it cumbersome especially for repetitive calculations that are needed to evaluate \( \Delta E_{rp} \). Thus, the one-dimensional model developed here can be expected to be sufficiently accurate for the purpose of modelling localised corrosion.

Additionally, it should be noted that a certain dispersion of results is expected to occur because of differences between various boundaries. The types of experiments that have been performed\textsuperscript{14,18} to examine the effect of sensitisation on localised corrosion do not lend themselves to the examination of boundary-to-boundary differences. The scanning electrochemical techniques may be used to determine whether there are boundary-to-boundary differences in the electrochemical response, but these techniques are not useful for examining repassivation of pits along grain boundaries. It may be worthwhile to conduct, in the future, some studies on the effect of grain boundary mismatch on sensitisation and localised corrosion. Such studies would not negate the modelling approach that the dissolution rate at the bottom of pits is a function of local alloy chemistry: they would just add further complexity.

The model presented here does not take into account the effect of possible intragranular carbides. The formation of intragranular carbides would affect the mass balance of carbon and therefore, the depletion profiles would be changed primarily in the advanced healing regime. However, for the alloys considered here, there were few, if any, intragranular carbides for the aging treatments studied.\textsuperscript{14} It is possible that under extreme aging conditions, intragranular precipitates may be observed, for example, on slip planes. Nevertheless, the approach presented here can be expected to remain valid even in the presence of some limited amount of intragranular carbides, since the mass balances are then not severely affected.

It is also of interest to examine how the results are affected by the carbon mass balance assumptions that have been made in the derivation of the depletion model. The assumption of the equality of carbon activity within the grain is unequivocally supported in the literature. This is due to the large difference between the diffusion coefficients of carbon and chromium or other substituional elements. For example, the diffusion coefficient of C in austenite at 700°C \textsuperscript{55} is \( 2.2 \times 10^{-13} \text{ m}^2 \text{ s}^{-1} \) whereas that of Cr is \( 6.8 \times 10^{-20} \text{ m}^2 \text{ s}^{-1} \) in type 304 stainless steel\textsuperscript{56} or 1.2 \( \times \) \( 10^{-19} \text{ m}^2 \text{ s}^{-1} \) in alloy 800.\textsuperscript{57} Since the diffusion coefficients of C are about six orders of magnitude larger than those of Cr, the diffusion gradient of C is negligible compared to that of Cr at the same conditions. While the equality of carbon activity is generally accepted, the average distance \( d \) over which carbon can be withdrawn (equation (26)) is based on simple geometrical considerations\textsuperscript{30} and requires an estimate of the average grain size. The healing of grain boundary depletion is affected by the parameter \( d \). The healing occurs simultaneously with the gradual, thermodynamically driven depletion of carbon in the grain until carbon solubility is reached as described previously.\textsuperscript{10} While the model described here qualitatively follows the grain carbon content evolution described by Was and Kruger.\textsuperscript{10} Fig. 11 quantitatively illustrates the effect of the assumed grain size (equation (26)) on the depletion profiles. In Figure 11, calculations have been made for alloy 600 heat treated at 973 K for 1 and 100 h, assuming that the grain size varies in a very wide range from 30 to 500 μm. This range is wider than the commonly encountered range for nickel-based alloys. For short heat treatment times, the effect of the grain size is insignificant. On the other hand, it becomes important at long exposure times (e.g. 100 h in Fig. 11) for which healing plays a dominant role. As expected, healing occurs faster in small grains, in which carbon can be withdrawn rapidly from a small volume. It should be noted that the optimum grain sizes that provide the best representation of depletion profiles (Table 2) are reasonably close to experimental grain size estimates, when such estimates are available. This provides empirical support for the validity of equation (26). It is interesting to note that the grain size has a relatively limited effect on the calculated repassivation potential. This is due to the fact that, at the temperature–time conditions at which the grain size has a strong effect on depletion profiles (i.e. in the healing regime), the depletion profiles are relatively flat and, therefore, do not strongly contribute to the \( E_{rp} \) depression (which is most strongly affected by the lowest Cr/Mo concentrations). For example, the \( E_{rp} \) depression for alloy 600
thermally aged at 973 K and 100 h (cf. Fig. 11) and exposed to 0.04 M NaCl solutions at 333 K ranges from 0.070 to 0.096 V for assumed grain sizes varying in a realistic range from 30 to 200 μm respectively. Finally, it should be noted that the $E_{rp}$ depression of austenitic alloys (both calculated and experimental) is relatively modest. Much larger depressions are observed for duplex alloys. However, the mechanism of chromium depletion in duplex alloys is different and is outside of the scope of this study.

Conclusions

1. A general procedure has been developed for predicting the effect of thermal aging on the repassivation potential of austenitic alloys. The procedure combines two mechanistic models, a grain boundary microchemistry model for calculating the chromium and molybdenum depletion profiles in the vicinity of grain boundaries and an electrochemical model that relates the repassivation potential to alloy composition as well as temperature and solution chemistry.

2. The grain boundary microchemistry model combines a thermodynamic treatment of the paraequilibrium between grain boundary carbides and alloy matrix components with a closed-form solution for the diffusion of chromium and molybdenum. It accurately reproduces the experimental Cr and Mo depletion profiles for sensitised alloys 600, 825 and 316L. In addition to activity coefficients for the solid solution, the model utilises parameters that have a well-defined physical meaning, i.e. the composition and Gibbs energy of formation of the carbide phase, diffusion coefficients of Cr and Mo and average grain size. Thus, the model is applicable to alloys with different compositions, e.g. with different carbon contents.

3. Using the previously developed $E_{rp}$ model, a methodology has been established to calculate the observable repassivation potential by integrating the $E_{rp}$ values that correspond to the local alloy chemistry in the depletion zone. Such averaged values are in satisfactory agreement with experimental $E_{rp}$ data that have been measured in chloride solutions for thermally aged samples of alloys 600 and 825.

4. In addition to the computation of the repassivation potential of thermally aged alloys, the model is applicable to alloys whose microchemistry has been altered by fabrication procedures. This has been demonstrated by estimating the repassivation potential of welded alloy 22.

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References

Appendix

Generalised correlation for predicting the repassivation potential

The $E_{rp}$ model has been described in detail and validated against experimental data in previous papers\cite{19,24} and therefore, only the final equations are summarised here. In general, a case of a system containing NA aggressive ions and NI inhibitive ions, the repassivation potential $E_{rp}$ is obtained by solving an equation given by

$$1 + \sum_{i}^{\text{NI}} \left( \left( \frac{i_{rp}}{i_{p}} - 1 \right) \frac{\dot{\theta}_{i}}{\dot{\theta}_{p}} \right)^{\theta_{i}} \exp \left( \frac{\Phi_{i} E_{rp}}{RT} \right) = \sum_{j}^{\text{NA}} \left( \frac{\dot{\theta}_{j}}{\dot{\theta}_{p}} \right)^{\theta_{j}} \exp \left( \frac{\Phi_{j} E_{rp}}{RT} \right)$$

(51)

where $i_{p}$ is the passive current density, $i_{rp}$ is the current density threshold that defines repassivation ($i_{rp}=10^{-2}\text{ A m}^{-2}$), $\theta_{i}$ is the partial surface coverage fraction by solution species $j$, $T$ is the temperature, $R$ is the gas constant, $F$ is the Faraday constant and $\Phi_{i}$, $\Phi_{j}$, $\theta_{i}$, $\theta_{j}$, $\gamma_{i}$ and $\gamma_{j}$ are electrochemical kinetic parameters as defined below. The summation on the right-hand side of equation (51) is performed over all aggressive species ($j=1, 2, ..., \text{NA}$), and the summation on the left-hand side pertains to inhibitive species ($k=1, 2, ..., \text{NI}$). The $\text{H}_2\text{O}$ molecules are treated as inhibitive species because they contribute to the formation of the oxide layer. The electrochemical parameters of the model are defined as follows:

(i) The quantity $k_{j}^{\ast}$ is the reaction rate constant for alloy dissolution mediated by the adsorption of aggressive species $j$. This constant is used in a scaled form (i.e. as $k_{j}=k_{j}^{\ast}/I_{rp}$) and is expressed using a scaled Gibbs energy of activation $\Delta g_{A,j}^{\ast}$

$$k_{j} = k_{j}^{\ast} I_{rp}^{\ast} = \exp \left( \frac{-\Delta g_{A,j}^{\ast}}{RT} \right)$$

(52)

(ii) the quantity $k_{i}^{\ast}$ is the reaction rate constant for the formation of oxide mediated by the adsorption of inhibitive species $k$. It is also used in a scaled form, i.e. as

$$I_{k} = \left( \frac{i_{rp}}{i_{p}} - 1 \right) \frac{\dot{\theta}_{i}}{\dot{\theta}_{p}}$$

and is expressed using a scaled Gibbs energy of activation $\Delta g_{A,k}^{\ast}$

$$I_{k} = \left( \frac{i_{rp}}{i_{p}} - 1 \right) \frac{\dot{\theta}_{i}}{\dot{\theta}_{p}} = \exp \left( \frac{-\Delta g_{A,k}^{\ast}}{RT} \right)$$

(53)

(iii) The quantities $n_{i}$ and $n_{k}$ are the reaction rate orders with respect to the aggressive species $j$ and inhibitive species $k$ respectively

(iv) The parameters $\gamma_{j}$ and $\gamma_{k}$ are the electrochemical transfer coefficients for the reactions involving the aggressive species $j$ and inhibitive species $k$ respectively. The parameter $\gamma_{j}$ has been assumed to be equal to one for simplicity.

Since the model has a limiting character, it has been shown\cite{15} that the partial surface coverage fraction of a species $j$
can be related to the activity of this species in the bulk solution through an adsorption isotherm, i.e.

$$\theta_j = \frac{r_{j0}}{1 + \sum_k n_k a_k}$$

where the adsorption coefficient is defined using the Gibbs energy of adsorption $\Delta G_{ads,i}$, i.e.

$$r_j = \exp\left(-\frac{\Delta G_{ads,i}}{RT}\right)$$

For $H_2O$ in aqueous solutions, $\theta_{H2O}$ is assumed to be equal to one for simplicity. For calculating the temperature dependence of the kinetic parameters, the scaled Gibbs energies of activation are further related to temperature as

$$\frac{\Delta g_{J}^{*}}{T} = \frac{\Delta g_{J}^{*}(T_{ref})}{T_{ref}} + \Delta h_{J}^{*}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)$$

for aggressive ions and

$$\frac{\Delta g_{I,J}^{*}}{T} = \frac{\Delta g_{I,J}^{*}(T_{ref})}{T_{ref}} + \Delta h_{I,J}^{*}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)$$

for water and inhibitive species. In equations (56) and (57), the parameters $\Delta g_{J}^{*}(T_{ref})$ and $\Delta g_{I,J}^{*}(T_{ref})$ are the scaled Gibbs energies of activation at reference temperature $T_{ref} = 298$ K for the reactions mediated by the adsorption of aggressive and inhibitive ions respectively. The quantities $\Delta h_{J}^{*}$ and $\Delta h_{I,J}^{*}$ are the corresponding enthalpies of activation.

The environments considered in this study are limited to one kind of aggressive species (i.e. the $Cl^{-}$ ions) and one kind of inhibitive species (i.e. the $H_2O$ molecules). In such a case, the repassivation potential is characterised, in the most general case, by seven parameters, i.e. $\Delta g_{A,Cl}^{*}(T_{ref})$, $\Delta g_{A,Cl}(T_{ref})$, $\Delta g_{A,Cl}(T_{ref})$, $\Delta g_{A,Cl}(T_{ref})$, $\Delta g_{A,Cl}(T_{ref})$, $\Delta g_{A,Cl}(T_{ref})$, $\Delta g_{A,Cl}(T_{ref})$, and $\Delta g_{A,Cl}(T_{ref})$. In a previous study, 24 generalised expressions for these parameters have been developed. Specifically, the Gibbs energy of adsorption of ions $\Delta G_{ads,Cr}$, the electrochemical transfer coefficient for the formation of passive oxide as a result of a reaction with water $\xi_{H_2O}$ and the reaction order with respect to $Cl^{-}$ ions $n_{A,Cl}$ have been set equal to common values, i.e.

$$\Delta G_{ads,Cr}/(kJ/mol) = 10$$

$$\xi_{H_2O} = 0.8$$

$$n_{A,Cl} = 1-1$$

The enthalpies of activation $\Delta h_{A,Cl}^{*}$ and $\Delta h_{I,H_2O}^{*}$ (in kJ mol$^{-1}$) have been found to be linearly related to the respective Gibbs energies of activation $\Delta g_{A,Cl}^{*}(T_{ref})$ and $\Delta g_{I,H_2O}^{*}(T_{ref})$, i.e.

$$\Delta h_{A,Cl}^{*} = 55 + 2\Delta g_{A,Cl}^{*}(T_{ref})$$

$$\Delta h_{I,H_2O}^{*} = -15 + 32\Delta g_{I,H_2O}^{*}(T_{ref})$$

Finally, the two Gibbs energies of activation $\Delta g_{A,Cl}^{*}(T_{ref})$ and $\Delta g_{I,H_2O}^{*}(T_{ref})$ have been expressed in terms of alloy composition for Fe–Ni–Cr–Mo–W–N alloys. The Gibbs energy of activation (in kJ mol$^{-1}$) for dissolution mediated by adsorption of aggressive species $\left[\Delta g_{A,Cl}^{*}(T_{ref})\right]$ is calculated as a sum of four contributions, i.e.

$$\Delta g_{A,Cl}^{*}(T_{ref}) = \Delta g_{A,Cl}^{*}(Cr,Fe,Ni) + \Delta g_{A,Cl}^{*}(Mo,W) + \Delta g_{A,Cl}^{*}(N) + \Delta g_{A,Cl}^{*}(misc)$$

where $\Delta g_{A,Cl}^{*}(Cr,Fe,Ni)$ is the baseline contribution for Fe–Ni–Cr alloys, $\Delta g_{A,Cl}^{*}(Mo,W)$ is an increment due to the effect of Mo and W, $\Delta g_{A,Cl}^{*}(N)$ is an increment due to N and $\Delta g_{A,Cl}^{*}(misc)$ is a miscellaneous contribution of other elements. The baseline contribution for Fe–Ni–Cr alloys is given by

$$\Delta g_{A,Cl}^{*}(Cr,Fe,Ni) = \Delta g_{A,Cl}^{*}(Fe)_{w_{Fe}} + \Delta g_{A,Cl}^{*}(Ni)_{w_{Ni}} + 398:5w_{Cr}w_{Fe}^{0.7} + 555:9w_{Cr}w_{Fe}^{0.7} - \frac{335:4w_{Cr}}{}$$

where $\Delta g_{A,Cl}^{*}(Fe) = -74:1$ and $\Delta g_{A,Cl}^{*}(Ni) = -18:7$ are the Gibbs energies of activation for iron (or, for practical purposes, carbon steel) and nickel respectively. The remaining contributions are calculated as

$$\Delta g_{A,Cl}(Mo,W) = w_{Cr}(w_{Mo} + w_{W})^{0.7}(985:9w_{Ni}^{0.7} - 839:0w_{Fe}^{0.7})$$

$$\Delta g_{A,Cl}(N) = w_{Ni}^{0.5}w_{Cr}^{0.3}(1 - 293:65w_{Fe}^{0.2} + 1:451e5w_{Ni}^{0.2})$$

$$\Delta g_{A,Cl}(misc) = -1764w_{Ni}w_{Cr}$$

With the current database, the $\Delta g_{A,Cl}^{*}(misc)$ term is limited to the effect of Nb and should be treated as tentative. An expression similar to equation (63) has been adopted for the Gibbs energy of activation for the formation of oxide mediated by adsorption of $H_2O$, i.e.

$$\Delta g_{I,H_2O}^{*}(T_{ref}) = \Delta g_{I,H_2O}^{*}(Cr,Fe,Ni) + \Delta g_{I,H_2O}^{*}(Mo,W) + \Delta g_{I,H_2O}^{*}(N) + \Delta g_{I,H_2O}^{*}(misc)$$

where

$$\Delta g_{I,H_2O}^{*}(Cr,Fe,Ni) = 18:14w_{Fe} + 169:6w_{Ni} + 1983w_{Cr}^{1.1}$$

$$\Delta g_{I,H_2O}^{*}(Mo,W) = -2422\left[(w_{Mo} + w_{W})^{0.4} + w_{Fe}^{0.6}(w_{Fe} + 1:49w_{Ni})\right] + 2024\left[(w_{Mo} + w_{W})^{0.4} + w_{Fe}^{0.6}\right]$$

$$\Delta g_{I,H_2O}^{*}(N) = w_{Ni}^{0.5}w_{Cr}^{0.3}\left[-2:607d5w_{Fe}^{0.2} + 2:384e5w_{Ni}^{0.2}\right]$$

$$\Delta g_{I,H_2O}^{*}(misc) = -4950w_{Mo}w_{Ni}w_{Cr}$$

Equations (51)–(72) constitute a generalised correlation for predicting $E_{sp}$ of Fe–Ni–Cr–Mo–W–N alloys as a function of composition. The overall average deviation between the calculated results and experimental data for all alloys is 67 mV. 24 The effect of ions other than $Cl^{-}$ can be also included as discussed in a previous study, 24 but such ions are outside of the scope of this work.