

# 30. Thermal Aging and Variations in Alloy Composition

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## Overview

In this tour we will show examples of simulating the effects of thermal aging on Fe-Ni-Cr-Mo-W-C-N alloys (i.e., stainless steels and nickel-base alloys). Specifically, we show how to predict:

- Chromium and molybdenum depletion profiles in the vicinity of grain boundaries, which result from heat treatment of austenitic alloys;
- Depletion parameters for sensitized austenitic alloys, which provide an indicator of whether the alloy is susceptible to intergranular corrosion
- Effect of thermal aging on the repassivation potential of austenitic alloys, which provides a threshold condition for localized corrosion (pitting or crevice corrosion)
- The repassivation potential of alloys with compositional variations that may or may not result from thermal aging. This facility can also be used for bulk alloys that are not in the database or to hypothetical or experimental alloys as long as they belong to the Fe-Ni-Cr-Mo-W-C-N family. An example will be given for a duplex alloy, either annealed or thermally treated.

At this point you should be very familiar with entering data into OLI Studio. Also, you need to know the foundations of the use of the repassivation potential to predict the occurrence of localized corrosion (Anderko et al., 2004 and papers cited therein).

## Example 1: Thermal aging of alloy 600

We will be studying the behavior of thermally aged alloy 600 in a dilute aqueous solution of sodium chloride. Therefore, click on **Add Stream** and start by creating a stream with the following conditions:

Temperature	60	°C
Pressure	1	Atmospheres
H2O	55.5082	moles
NaCl	0.04	moles

The definition grid of the stream should look similar to the following figure:

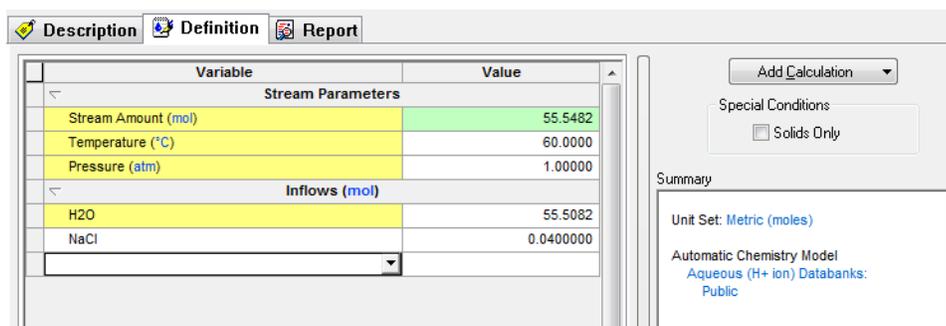


Figure 30-1: The stream definition.

With the above stream selected in the tree view, double-click on the **Add Corrosion Rates** icon in the **Actions/Explorer** pane. Even though the thermal aging simulation facilities do not predict corrosion rates per se, they belong to the category of corrosion kinetics and, therefore, they are included in the Corrosion Rates section of the Corrosion Analyzer.

Then, click on the **Definition** tab.

## Setting up the calculation

We will be simulating how the time of thermal aging affects *alloy 600* at a fixed thermal aging temperature of 700 °C. For this purpose:

Select *Alloy 600* from the drop-down **Contact Surface** menu.

In the **Calc Parameters** section, replace the default value for the **Thermal Aging Temperature** with 700 °C.

Note that the default value for the **Thermal Aging Temperature** is 399 °C, which is a low value so that, in the default case, no effects of thermal aging will be calculated.

Then, from the **Survey By** button select Thermal Aging Time.

The definition grid for the Corrosion Rates should look similar to the following figure. The key specifications are highlighted using red squares:

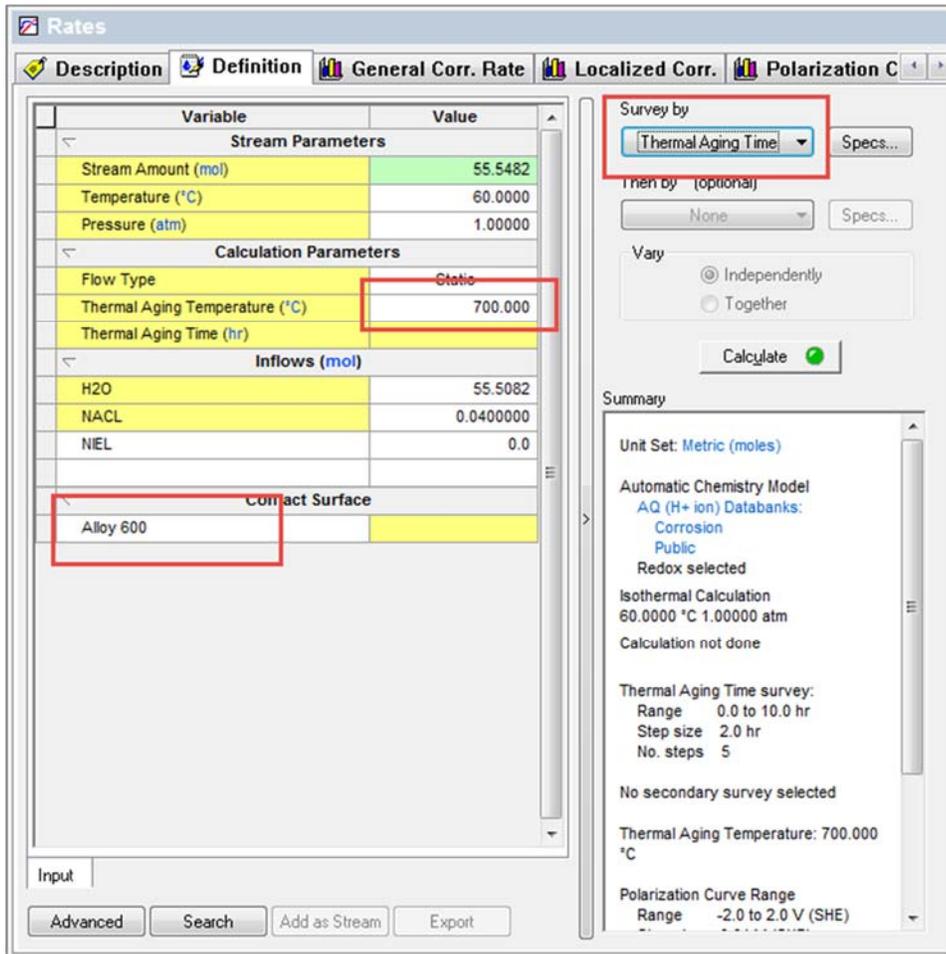


Figure 30-2 Specifying contact surface, thermal aging temperature and type of calculations.

Now, click on the **Specs...** button. **The Survey Range** category allows you to specify the range for the thermal aging time survey. Change the range from 0 to 10 hours with a step of 2.0 hours.

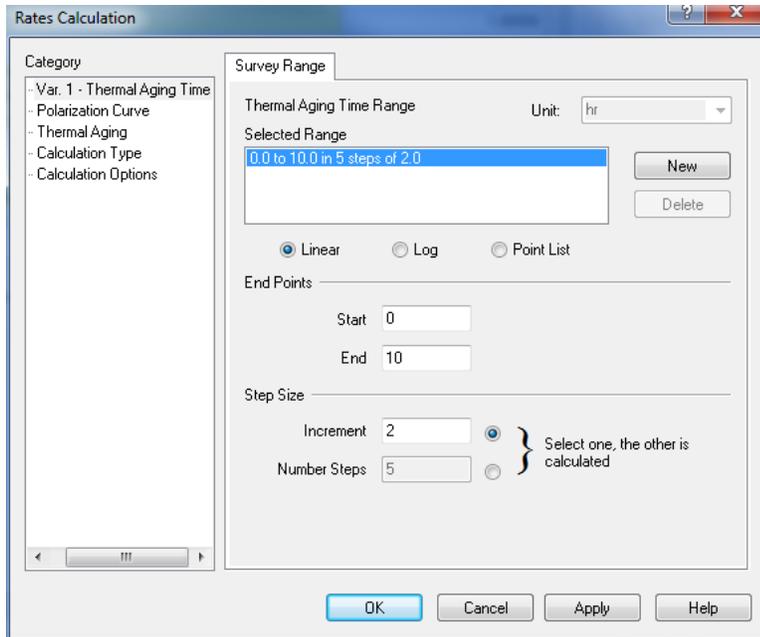


Figure 30-3 Default Thermal Aging Survey Range

Then, click on the **Thermal Aging** category.

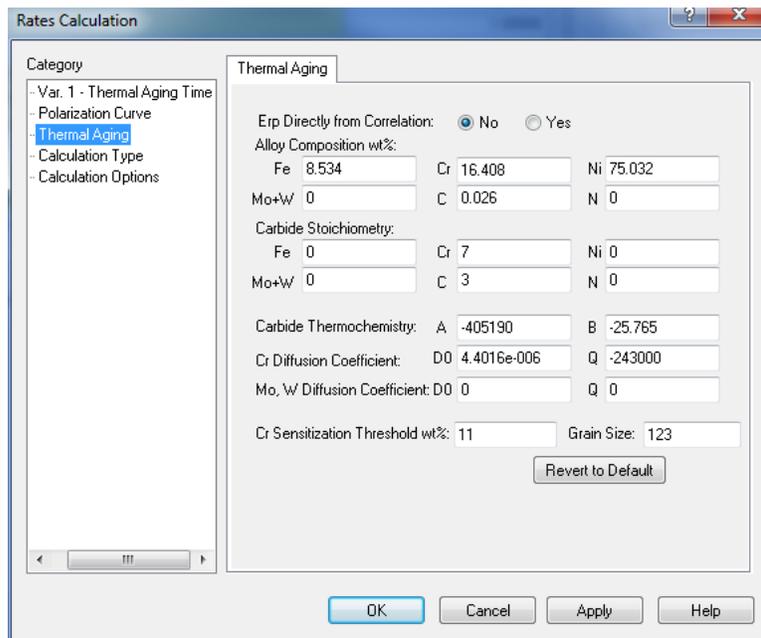


Figure 30-4 Thermal Aging Parameters

In this category, you can change all parameters that are necessary for calculating chromium and (if applicable) molybdenum depletion profiles. You can change:

- The alloy composition (for example, to analyze the effect of a different carbon content);
- The stoichiometry of the carbide phase that may form at the grain boundary; the typical carbide stoichiometry is  $M_7C_3$  or  $M_{23}C_6$  (where  $M = Cr, Mo$ ) but can be adjusted

- The parameters that define the equilibrium constant for the formation of the carbide
- The diffusion coefficient of Cr and, if applicable, Mo
- The threshold concentration of Cr for sensitization. This threshold concentration is used for calculating the depletion parameter.
- The average grain size, which affects the process of healing of chromium depletion as a function of time

Also, you can indicate whether the repassivation potential ( $E_{rp}$ ) should be calculated directly from the correlation developed by Anderko et al. (2008), which expresses  $E_{rp}$  as a function of alloy composition or not. If it is not calculated directly, then the repassivation potential is calculated first using the alloy-specific parameters for the alloy of interest and only the decrement of  $E_{rp}$  (i.e.,  $E_{rp, \text{thermally aged}} - E_{rp, \text{bulk alloy}}$ ) is obtained from the correlation. This decrement is then added to the alloy-specific  $E_{rp}$  value. This option is set by default to “No” because this maximizes the accuracy of calculations for alloys that are already in the database.

For now, we will accept the default settings but we will return to them later in the tour. Therefore, click **OK** to close this window.

Then click the **Calculate** button.

## Analyzing the results

When the calculations are finished, click on the **Depletion Profile** tab<sup>47</sup>. You will see a plot of concentrations of chromium and molybdenum within a grain as a function of the distance from the grain boundary (in  $\mu\text{m}$ ). You will see that, for each condition, there are four lines:

Cr weight % : concentration of Cr in weight %

Mo+W weight % : sum of the concentrations of molybdenum and tungsten in weight %

Corrected Cr weight % - concentration of Cr corrected for beam scattering and related effects so that it can be directly compared with experimental results. The procedure for calculating the correction is described by Anderko et al. (2009).

Corrected Mo+W weight % sum of the concentrations of Mo and W corrected in the same way as those for Cr.

Since alloy 600 does not contain any molybdenum, the molybdenum curves will always be equal to zero. The plot will look similar to the following one:

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<sup>47</sup> Remember to use the scroll-arrows if necessary

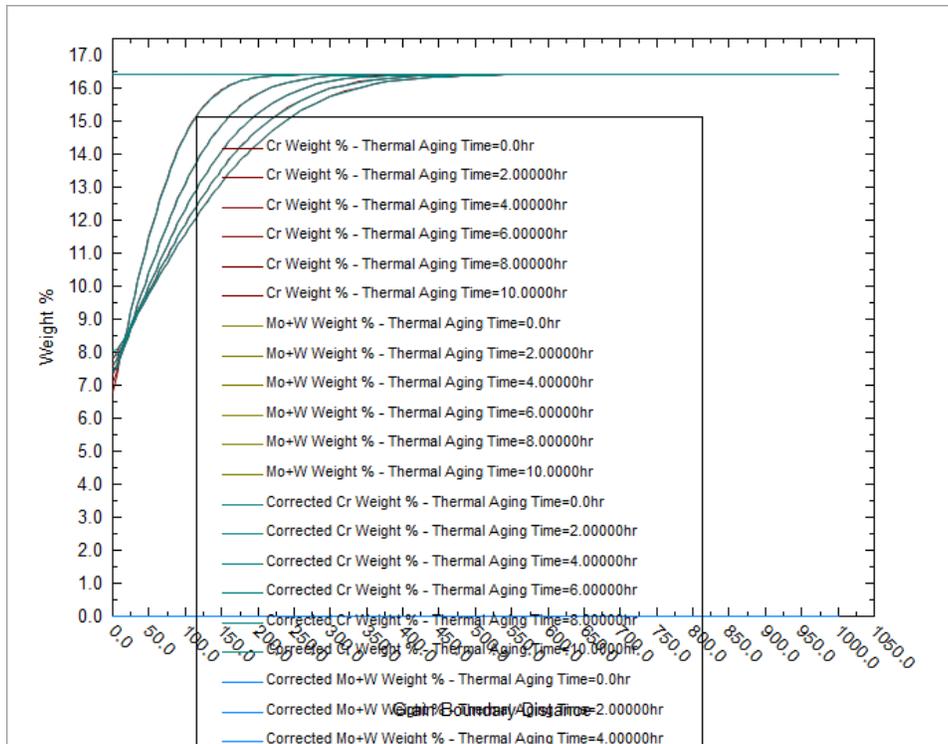


Figure 30-5 The plot of predicted depletion profiles for alloy 600 thermally aged at 700 °C as a function of time.

Let us customize the plot now by clicking on the **Options** button.

Since alloy 600 does not contain Mo or W, let us eliminate the Mo+W curves. To do this, select the **Curves** category from the left-hand side pane (**NOTE: this is not the same as the Curves Button!**)

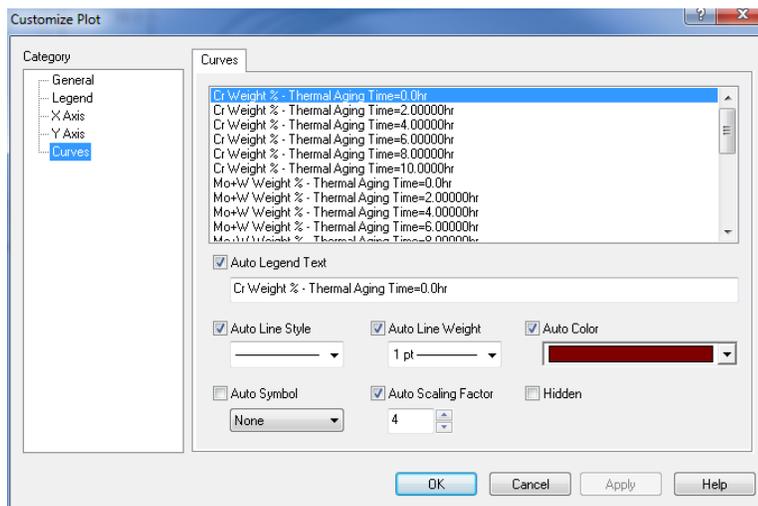


Figure 30-6 Plot Options | Curves Category

Then, highlight the Mo+W weight % curves by pressing the Shift key and moving the cursor. After highlighting these curves, check the **Hidden** button. The **Customize Plot** portion of the screen will look as follows:

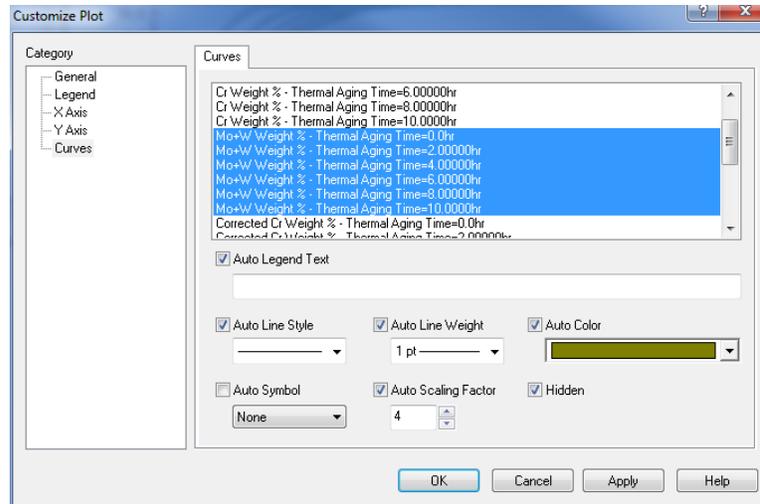


Figure 30-7 The window for customizing the display of depletion profiles.

After *hiding* the Mo+W weight % curves, do the same for the Corrected Mo+W weight % curves. Then, press OK. The plot will look as follows:

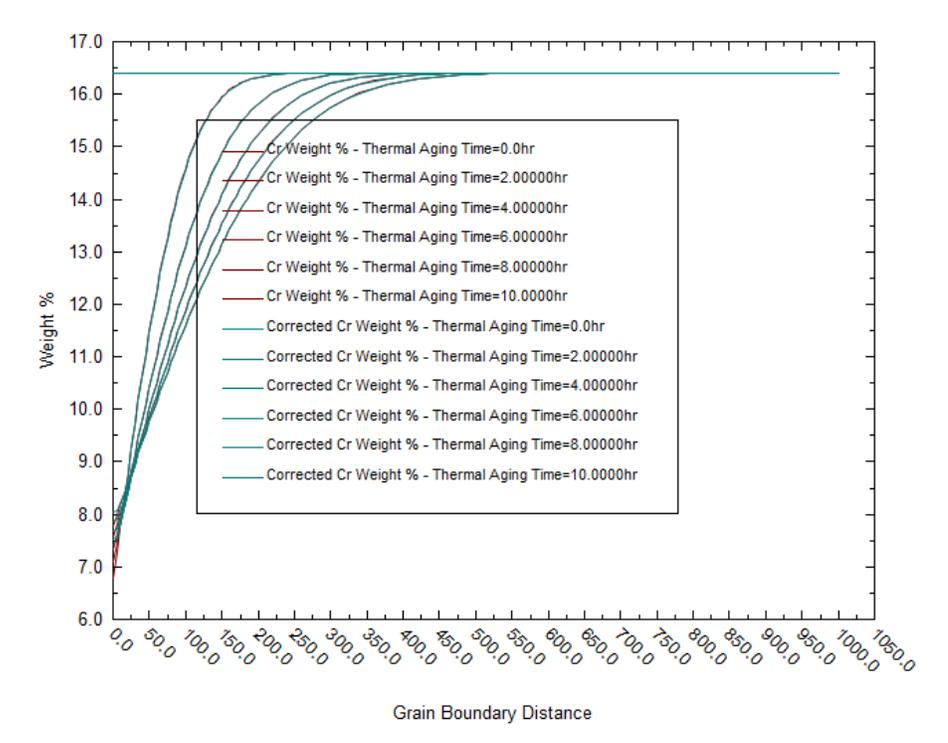


Figure 30-8 A customized depletion profile plot that shows only Cr depletion profiles

Now, let us focus on the differences between the uncorrected and corrected depletion profiles. To have a clear picture of the difference between them, let us focus on only one depletion profile – for 2 hours. For this purpose, click on **Options** again, then select the **Curves** category. Highlight all curves except the ones labeled

Cr Weight % - Thermal Aging Time = 2.00000 hr, and

Corrected Cr Weight % - Thermal Aging Time = 2.00000 hr

Check the Hidden box. Then, you will see a plot that looks like the following one:

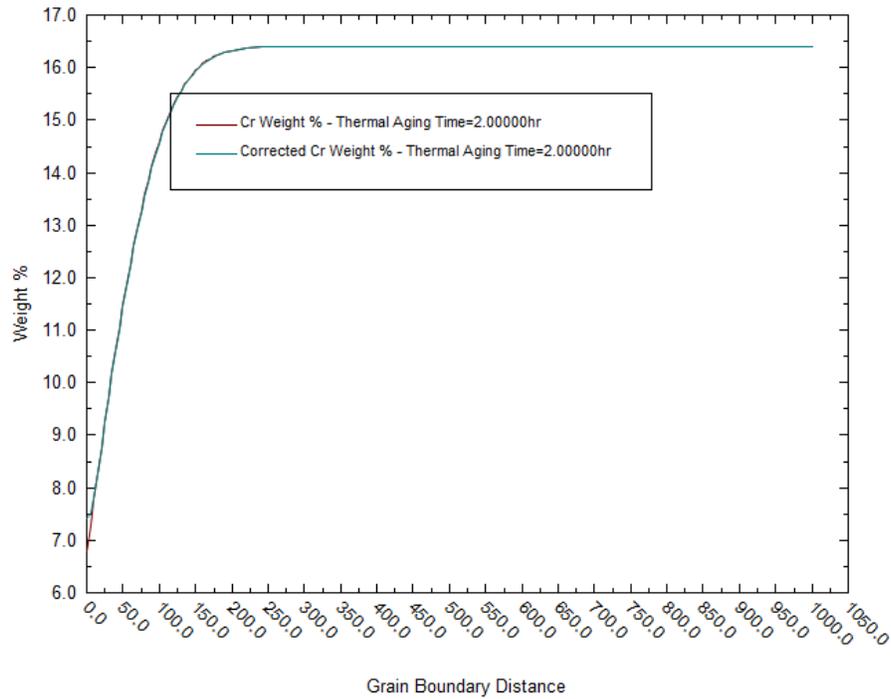


Figure 30-9 A customized depletion profile plot that shows uncorrected and corrected Cr depletion profiles only for 2 hours of thermal aging

In the obtained plot, you can see the difference between the two curves for small distances from the grain boundary (roughly below 30  $\mu\text{m}$ ). The corrected concentration is much more rounded in the vicinity of the minimum because instrumental measurement effects. At larger distances from the grain boundary, there is no difference between the two curves.

After analyzing the depletion profiles, let us focus on the effects of Cr depletion on corrosion. We will do it by analyzing two parameters – the depletion parameter and the repassivation potential.

To have more meaningful results, let us expand the range of thermal aging time and reduce the interval for calculations. To do it, go back to the **Definition** tab and click on **Specs**. In the **Thermal Aging Time** category, change the **End** to 60 hours and the **Increment** to 1 hour. The screen should look like the following one:

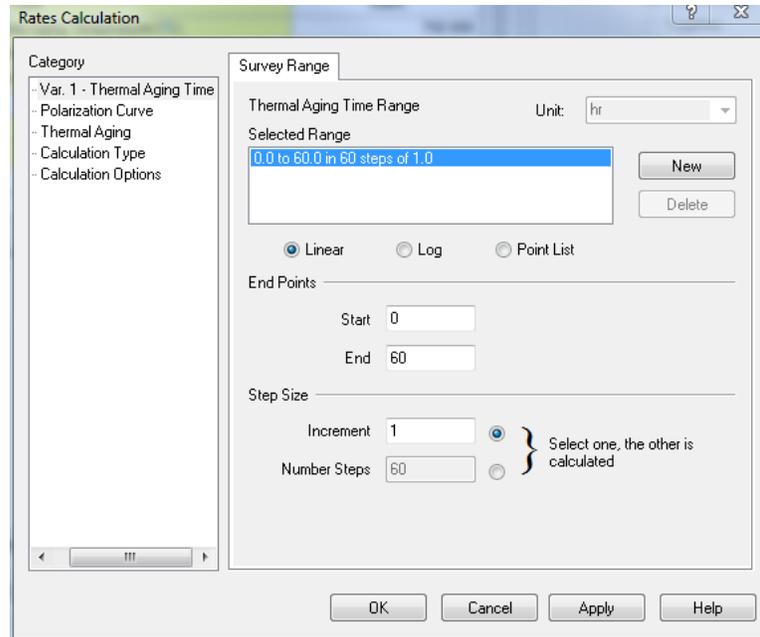


Figure 30-10 Changing the survey range for thermal aging.

After making the change, click **OK**.

Then, click **Calculate**.

After the calculations are complete, click on the **Localized Corr.** tab. By default, this tab will show a plot of the corrosion potential and repassivation potential.

Let us add a new parameter – the depletion parameter to the plot. To do this, click on **Curves**. A new window titled “Select Data to Plot” will appear. Under **Corrosion Values** in the left-hand side pane, highlight **Depletion Parameter** and click on the >> button under **Y2 Axis**. The screen will look like:

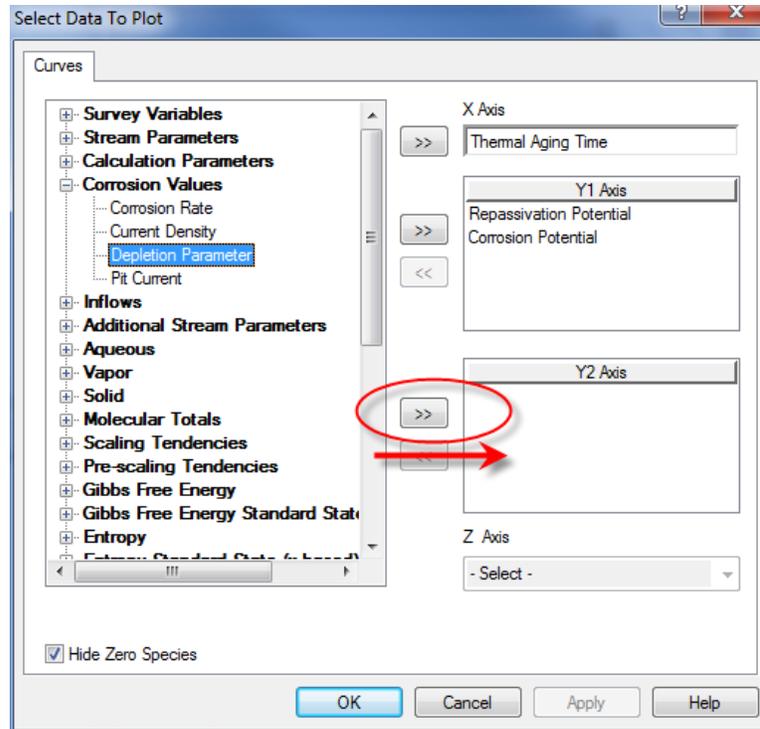


Figure 30-11 Including the depletion parameter in the plot on the Y2 axis.

Click **OK**. You will see a plot that should look like:

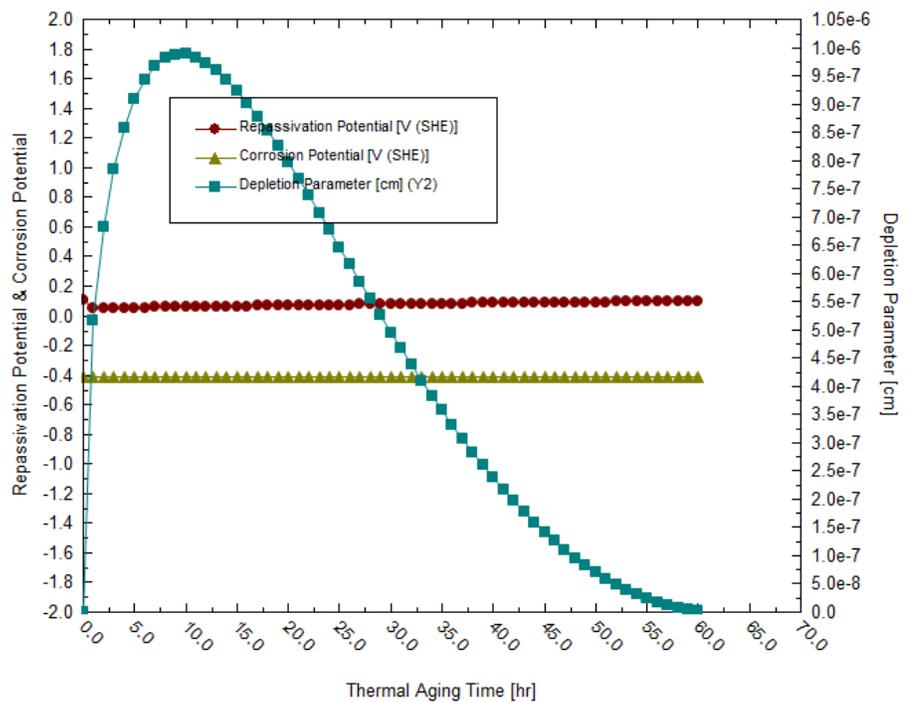


Figure 30-12 A plot of the repassivation potential and depletion parameter for thermally aged alloy 600 as a function of aging time.

It is clear that the depletion parameter reaches a maximum for aging time of about 10 hours. Since the depletion parameter is a measure of the susceptibility of an alloy to intergranular corrosion, we can expect that the alloy will be most susceptible to intergranular corrosion at intermediate aging times. When the depletion parameter is zero, intergranular corrosion or intergranular stress corrosion cracking are unlikely. The decrease of the depletion parameter as a function of time is a manifestation of the phenomenon of healing of Cr depletion.

The repassivation potential shows a minimum as a function of aging time. This indicates that the tendency of the alloy to undergo localized corrosion is enhanced as a result of thermal aging. However, the effect of thermal aging on the repassivation potential of alloy 600 is small (cf. Tormoen et al., 2009, Anderko et al., 2009). The repassivation potential shows a minimum at low aging times (ca. 1-2 hours). Therefore, the susceptibility to localized corrosion is enhanced the most for these aging times. It is noteworthy that the maximum in the depletion parameter does not coincide with the minimum in the repassivation potential. This is due to the fact that intergranular corrosion (which is related to the depletion parameter) and localized corrosion (which is controlled by the repassivation potential) are subject to different mechanisms. A general discussion of these differences is given by Tormoen et al. (2008).

In general, the alloy will be susceptible to localized corrosion if the corrosion potential exceeds the repassivation potential. In the above example, the corrosion potential is low because we have no oxidizing agents in the system. Therefore, the alloy will not undergo localized corrosion at the conditions of this example. However, a rise in the corrosion potential due to the presence of oxidizing agents may cause localized corrosion. We will return to this topic later in this chapter.

## Example 2: Thermal aging of alloy 825

In the second example, we will be studying the behavior of thermally aged alloy 825. Alloy 825 is appreciably different from alloy 600 because it contains molybdenum and, also, substantially more chromium in addition to other alloying elements. To make this simulation, click on **Add Stream** and create a stream with the following conditions:

<b>Temperature</b>	<b>95</b>	<b>°C</b>
<b>Pressure</b>	<b>1</b>	<b>Atmospheres</b>
<b>H2O</b>	<b>55.5082</b>	<b>moles</b>
<b>NaCl</b>	<b>2.846e-3</b>	<b>moles</b>

The definition grid of the stream should look similar to the following figure:

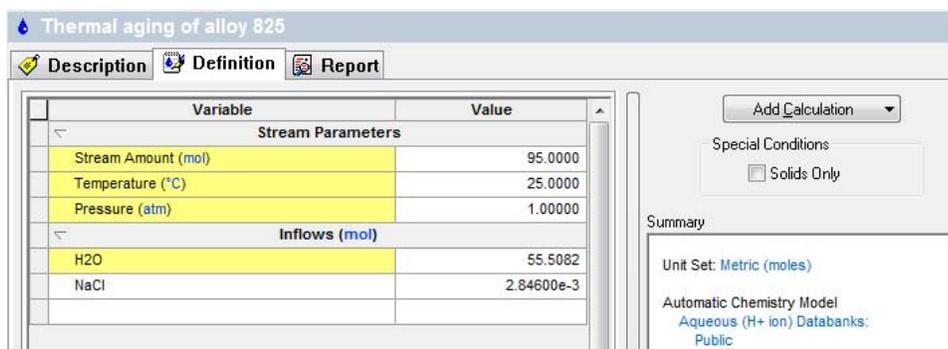


Figure 30-13 Stream definition for studying the effect of thermal aging on alloy 825.

Double-click on the **Add Corrosion Rates** icon in the **Actions/Explorer** pane.

Then, click on the **Definition** tab.

## Setting up the calculation

In this example, we will simulate how the temperature of thermal aging affects alloy 825 at a fixed thermal aging time of 15 hours. For this purpose:

Select **alloy 825** from the drop-down **Contact Surface** menu.

In the **Calc Parameters** section, replace the default value for the **Thermal Aging Time** with 15 h.

Note that the default value for the **Thermal Aging Temperature** is 0, which means that no thermal aging is considered by default.

Then, from the Type of rates calculation drop-down menu, select **Thermal Aging Temperature**.

The definition grid for the Corrosion Rates should look similar to the following figure. The key specifications are highlighted using red ovals:

Variable	Value
<b>Stream Parameters</b>	
Stream Amount (mol)	95.0000
Temperature (°C)	25.0000
Pressure (atm)	1.00000
<b>Calculation Parameters</b>	
Flow Type	Static
Thermal Aging Temperature (°C)	200.000
Thermal Aging Time (hr)	15.0000
Ignore Influence of Scales	<input type="checkbox"/>
<b>Inflows (mol)</b>	
H2O	55.5082
NaCl	2.84600e-3
Ni	0.0
<b>Contact Surface</b>	
Alloy 825	

Survey by: Thermal Aging Temp. [Specs...]

Then by (optional): None [Specs...]

Vary:  Independently  Together

Calculate [OK]

Summary

Unit Set: Metric (moles)

Automatic Chemistry Model  
Aqueous (H+ ion) Databanks:  
Corrosion  
Public  
Redox selected

Stream amount overridden:  
95.0000 mol

Isothermal Calculation  
25.0000 °C 1.00000 atm  
Calculation not done

Thermal Aging Temp. survey:  
Range 700.0 to 900.0 °C  
Step size 50.0 °C  
No. steps 4

No secondary survey selected

Thermal Aging Time: 15.0000 hr

Figure 30-14 Specifying the type of calculation, thermal aging time, and contact surface.

Then, click on **Specs** to define the survey range.

In the **Thermal Aging Temp.** category, specify the start of the survey as **550 °C**, the end of the survey as **900 °C**, and the increment as **50 °C**. The **Rates Definition** screen should look as follows:

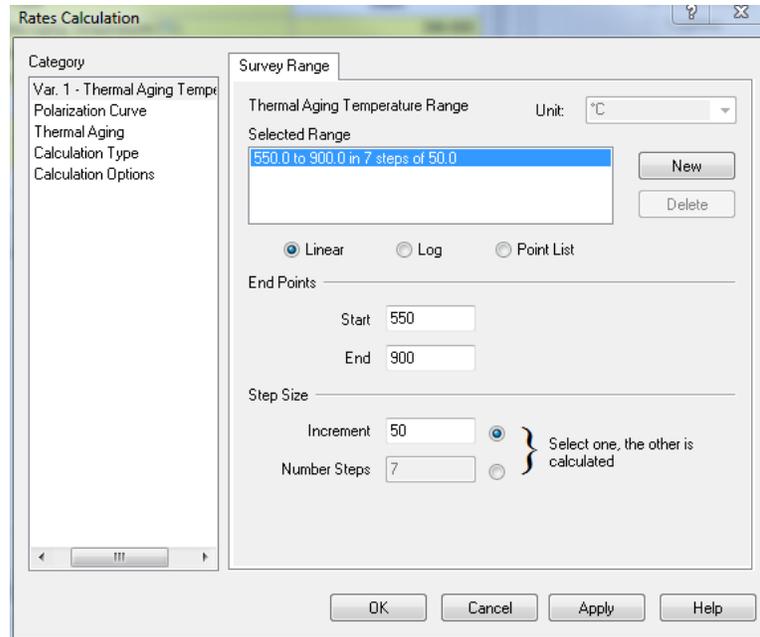


Figure 30-15 Defining the range for a thermal aging temperature survey.

Click **OK** to close this window. We will keep the other parameters at their default values. Then, click **Calculate**.

## Analyzing the results

When the calculations are finished, click on the **Depletion Profile** tab.

Since alloy 825 contains Mo in addition to Cr, you will see the depletion profiles for both Cr and Mo. For clarity, customize the plot by removing the corrected depletion profiles and leaving only the uncorrected (or directly calculated) ones.

For this purpose, click on **Options**, select the **Curves** category, highlight the Corrected curves and check the hidden box as described in the previous example. The resulting plot should look similar to the following one:

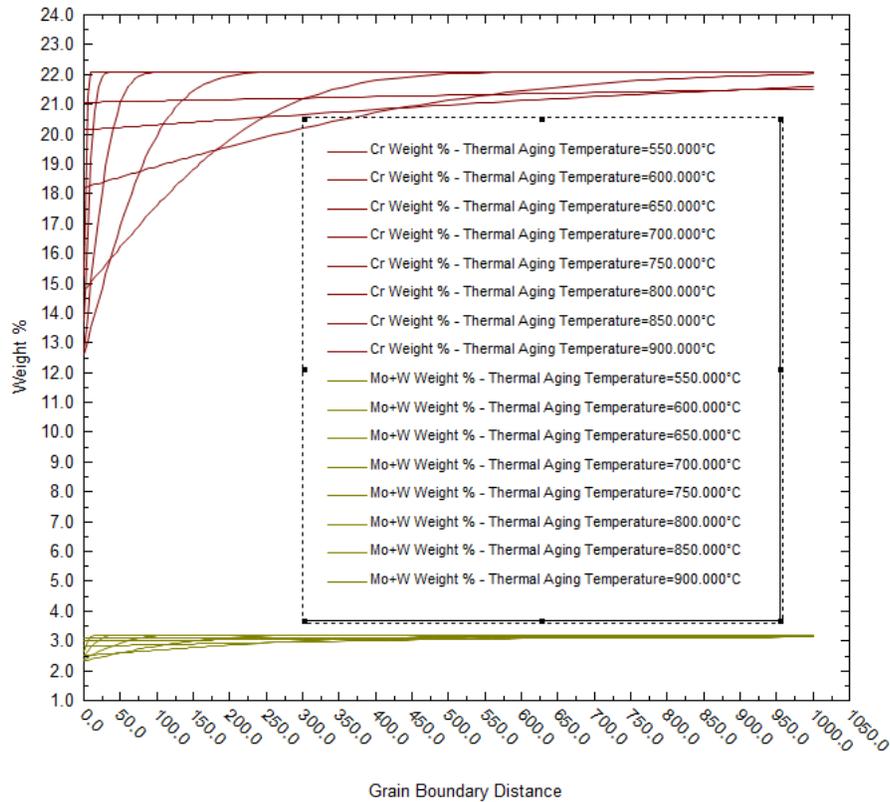


Figure 30-16 Predicted Cr and Mo depletion profiles for alloy 825 as a function of thermal aging temperature.

As shown in this plot, the depletion profile is very narrow at the lowest temperature, i.e., 550 °C. On the other hand, it becomes flat at high temperatures and it has a high minimum. The high minimum value is particularly important because it indicates that the local depletion of Cr and Mo is much less severe at high temperatures (due to much faster diffusion of substitutional elements and subsequent healing).

It should be noted that the Mo profile qualitatively parallels the Cr profile but has somewhat different slopes because of differences in diffusion coefficients of Cr and Mo.

To look at the effect of Cr and Mo depletion on corrosion, click on the **Localized Corrosion** tab and add the **Depletion Parameter** to the plot as described in the previous example. The plot should look similar to the following one:

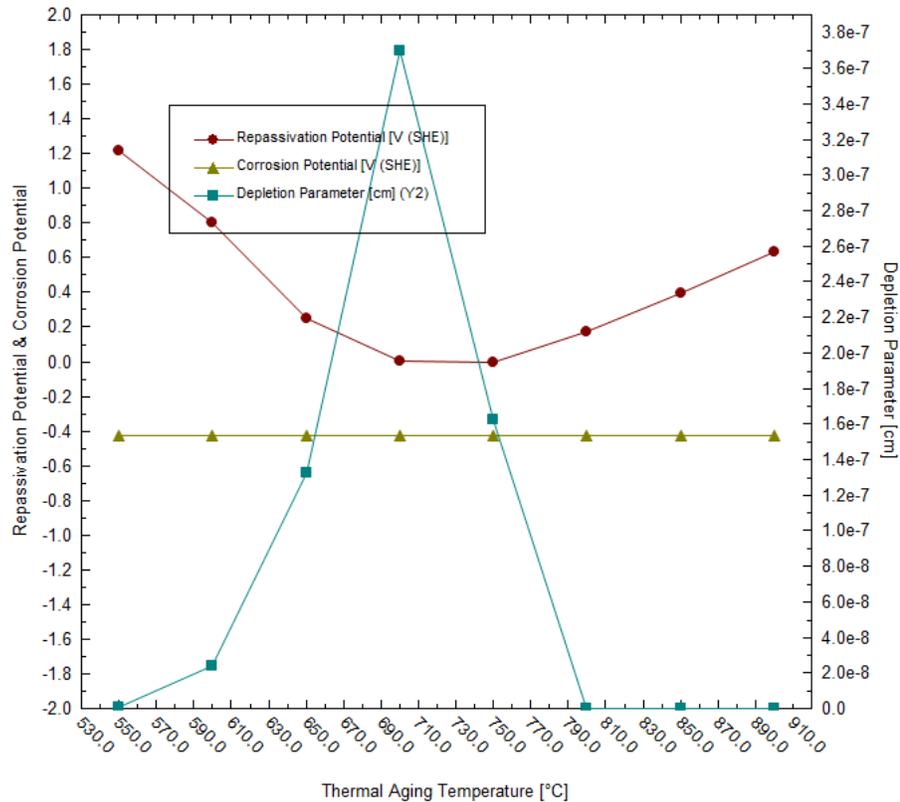


Figure 30-17 Calculated repassivation potential and depletion parameter for alloy 825 as a function of thermal aging temperature.

It is evident that both the depletion parameter and repassivation potential show their extreme values at intermediate temperatures of thermal aging. In the case of the depletion parameter, it is a maximum and, in the case of the repassivation potential, it is a minimum. This is in agreement with experimental data (Anderko et al., 2009). Non-zero values of the depletion parameter indicate the possibility of intergranular corrosion. A depression in the repassivation potential indicates an increased tendency for localized corrosion.

### Example 3: Localized corrosion of annealed and thermally aged duplex alloy 2205

In the first and second tour, we used the Corrosion Analyzer’s capabilities to predict the Cr and Mo depletion profiles for austenitic stainless steels and nickel-base alloys. However, we are not limited to such calculations. We can also use the Corrosion Analyzer to predict the localized corrosion behavior of other alloys and other phases, including those that are not stored in the database. This facility is based on a generalized correlation for predicting the repassivation potential of Fe-Ni-Cr-Mo-W-N alloys as a function of alloy composition (Anderko et al., 2008). This correlation can be applied to both bulk alloys that are not in the database and to phases that may result from thermal aging.

In this example, we will make two simulations:

- First, we will predict the tendency for localized corrosion for the duplex alloy 2205 in an aerated chloride solution. Alloy 2205 is not in the database, so the repassivation potential will be calculated from the generalized correlation (Anderko et al., 2008). The corrosion potential will be calculated for a similar alloy because the corrosion potential does not differ much for many Fe-Cr-Ni-Mo alloys in the passive state in neutral solutions.
- Second, we will predict the localized corrosion tendency for alloy 2205 after thermal aging. Thermal aging of duplex steels in the temperature range of 900°C to 600°C leads to the formation of various phases -  $\chi$ ,  $\sigma$ ,  $M_{23}C_6$ -type carbide, and secondary austenite ( $\gamma_2$ ). The secondary austenite phase is primarily responsible for the increased tendency of the alloy for localized corrosion. This is due to a very significant depletion of chromium in the secondary austenite over relatively wide spatial areas (Sridhar et al., 2009). Since the composition of the secondary austenite cannot be predicted at present, we will use experimental microstructural data (Sridhar et al., 2009) in conjunction with the generalized correlation for the repassivation potential.

Click on **Add Stream** and create a stream with the following conditions:

<b>Temperature</b>	<b>60</b>	<b>°C</b>
<b>Pressure</b>	<b>1</b>	<b>Atmospheres</b>
<b>H2O</b>	<b>55.5082</b>	<b>moles</b>
<b>NaCl</b>	<b>0</b>	<b>moles</b>
<b>Oxygen</b>	<b>0.02</b>	<b>moles</b>
<b>Nitrogen</b>	<b>0.08</b>	<b>moles</b>

The oxygen and nitrogen have been added to simulate the presence of air.

The definition grid of the stream should look similar to the following figure:

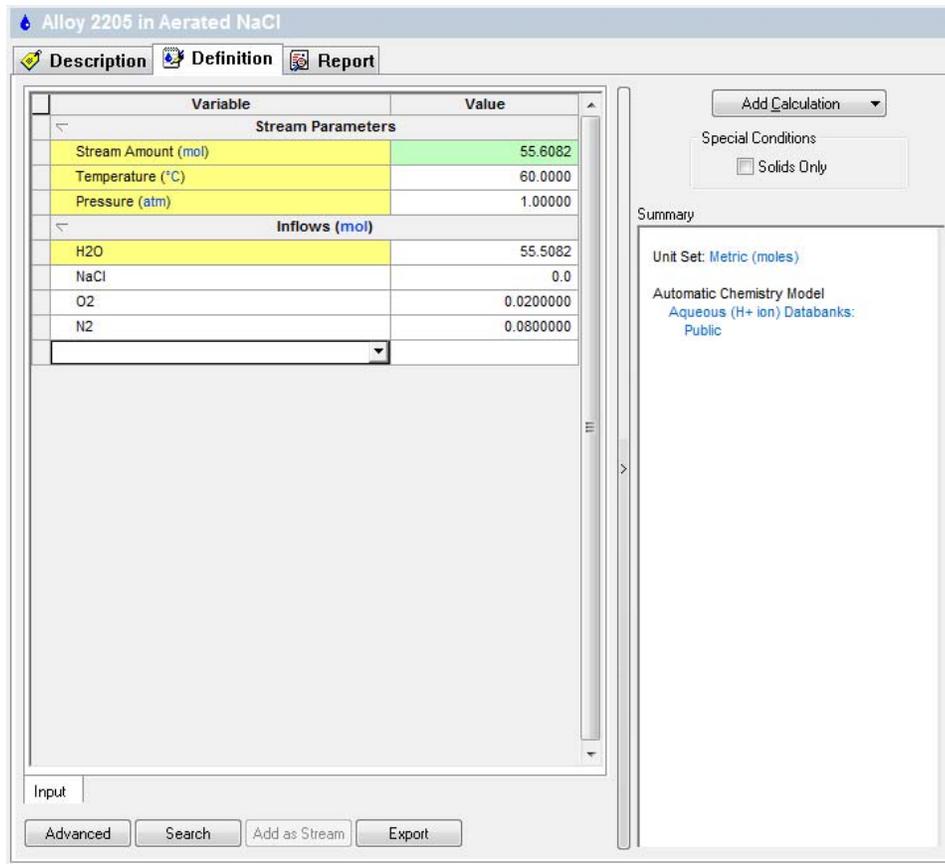


Figure 30-18 Stream composition for simulating localized corrosion of alloy 2205.

Double-click on the **Add Corrosion Rates** icon in the **Actions/Explorer** pane.

Then, click on the **Definition** tab.

## Setting up the calculation

Since alloy 2205 is not available in the database, we will select stainless steel 316 as the contact surface. This will ensure that the predicted corrosion potential is very similar to that for alloy 2205.

Select **316 Stainless Steel** from the drop-down **Contact Surface** menu.

Unlike in the previous examples, do not make any changes in the **Calc Parameters** section. We will not make Cr depletion calculations; rather, we will be specifying the compositions of the phases.

From the Type of rates calculation drop-down menu, select **Composition**.

The definition grid for the Corrosion Rates should look similar to the following figure. The key specifications are highlighted using red ovals:

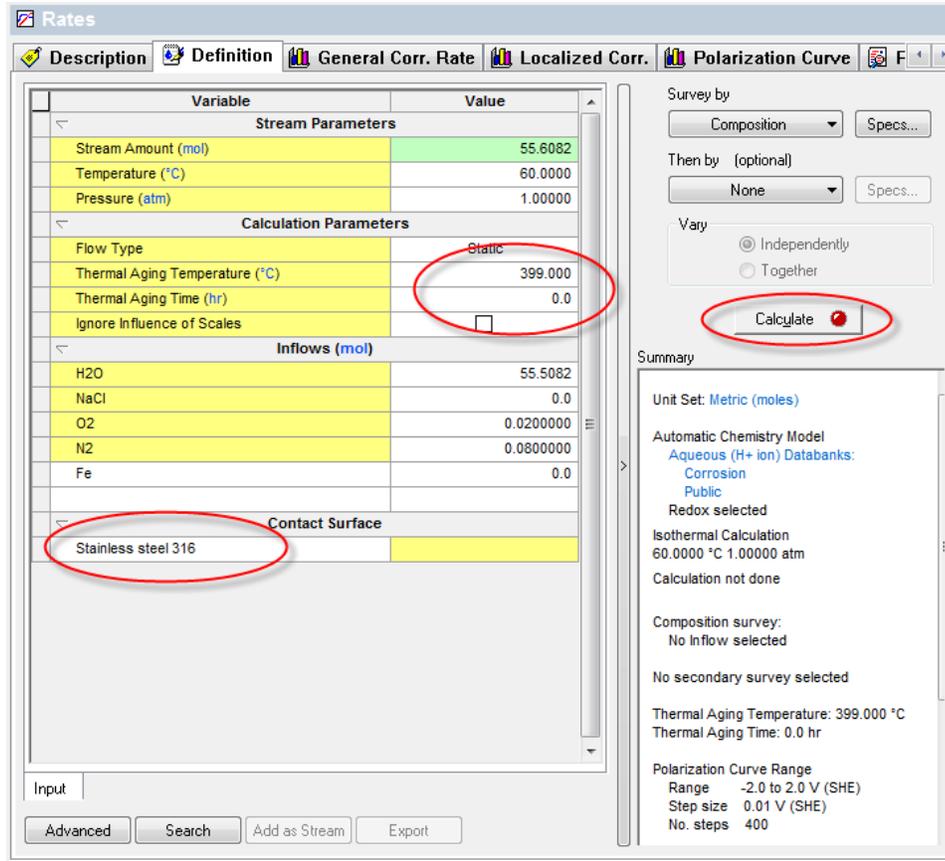


Figure 30-19 Selection of contact surface and survey type.

We will be running a composition survey to see how the concentration of NaCl affects the propensity for localized corrosion. To define the survey type, click on **Specs.**

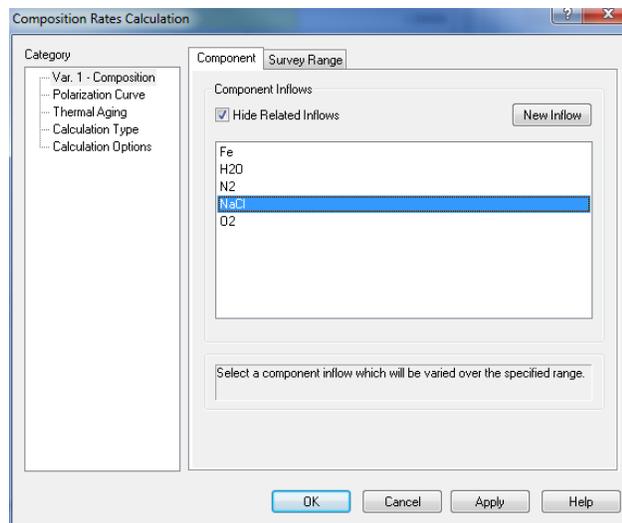


Figure 30-20 Selecting the component for the survey (NaCl)

In the **Var. 1 – Composition** category, select **Sodium Chloride** in the **Component** tab.

Then, click on the **Survey Range** tab and enter:

**Start 0.0001**  
**End 6**  
**Number of steps 20**  
**Click the “Log” radio button**

The screen should look similar to:

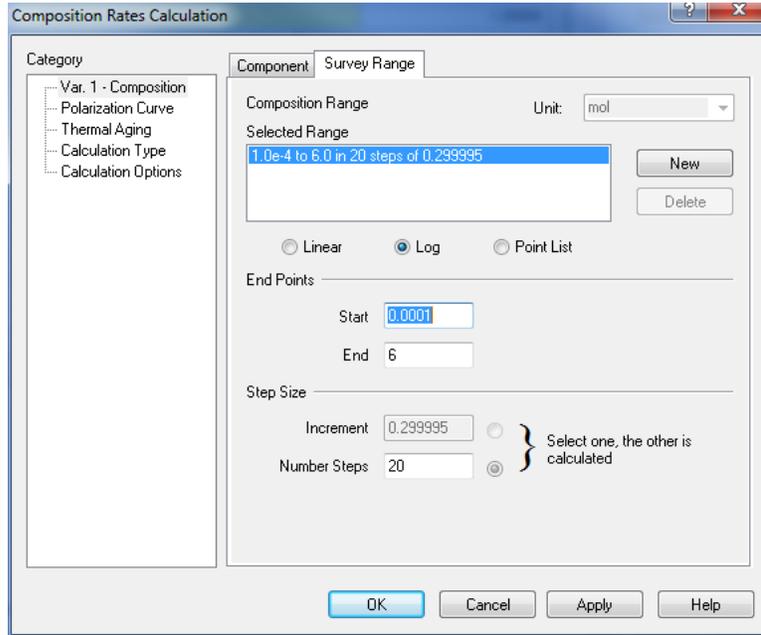


Figure 30-21 Defining the survey range for the NaCl concentration survey.

Then, click on the **Thermal Aging** category on the left-hand side pane. The screen will be populated with default parameters for type 316 stainless steel.

First, click on the **Yes** button next to **Erp directly from correlation**.

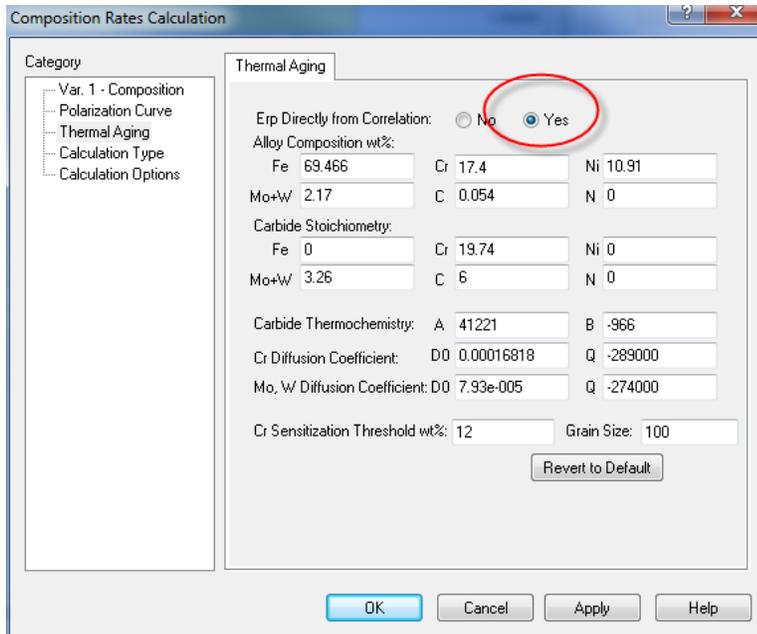


Figure 30-22 Thermal Aging Parameters

This is necessary because no parameters for alloy 2205 are stored in the databank and we have to rely exclusively on the correlation to predict the repassivation potential.

Then, enter the composition of alloy 2205 by replacing the default values for alloy 316.

Enter the following composition of alloy 2205:

Fe	68.319	wt. %	(which is the balance that includes many minor elements)
Cr	22.5	wt. %	
Ni	5.8	wt. %	
Mo+W	3.2	wt. %	
C	0.017	wt. %	
N	0.164	wt. %	

The remaining parameters in the Thermal Aging screen can remain the same because we will not be using them in this example (i.e., we will not be calculating any depletion profiles). After entering the values, the screen should look as follows:

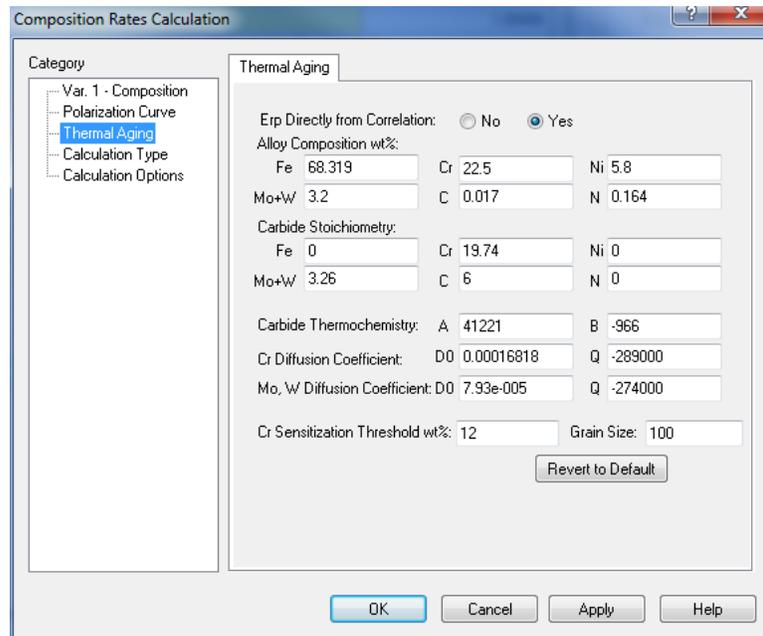


Figure 30-23 Defining the composition of alloy 2205 and specifying the direct use of the correlation for predicting the repassivation potential.

Click **OK** to accept the changes.

Then, click **Calculate**.

## Analyzing the results

When the calculations are finished, click on the **Localized Corrosion** tab.

The same results can be also viewed in a numerical form by clicking on the **Report** tab. You will see a plot of the corrosion and repassivation potentials as a function of

NaCl concentration. To visualize the results better, change the horizontal axis to a logarithmic scale.

For this purpose, click on **Options**, select the **X Axis** category, check the **Logarithmic Scale** box and click **OK**. Then, the plot should look similar to the following one:

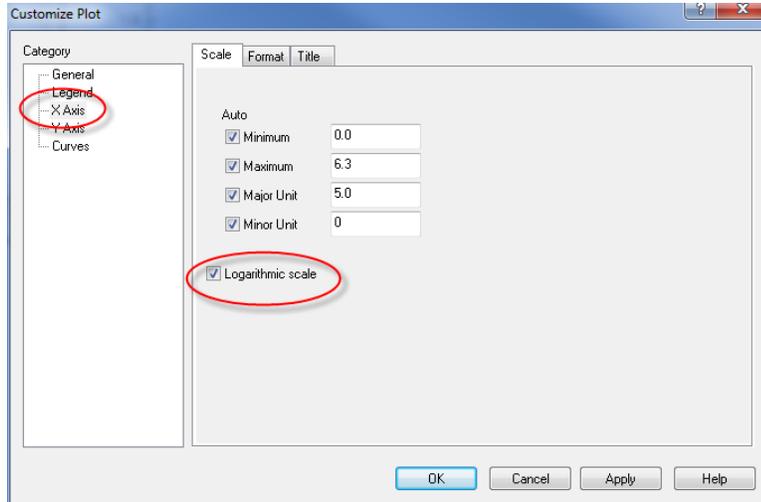


Figure 30-24 Changing the X-Axis to Log

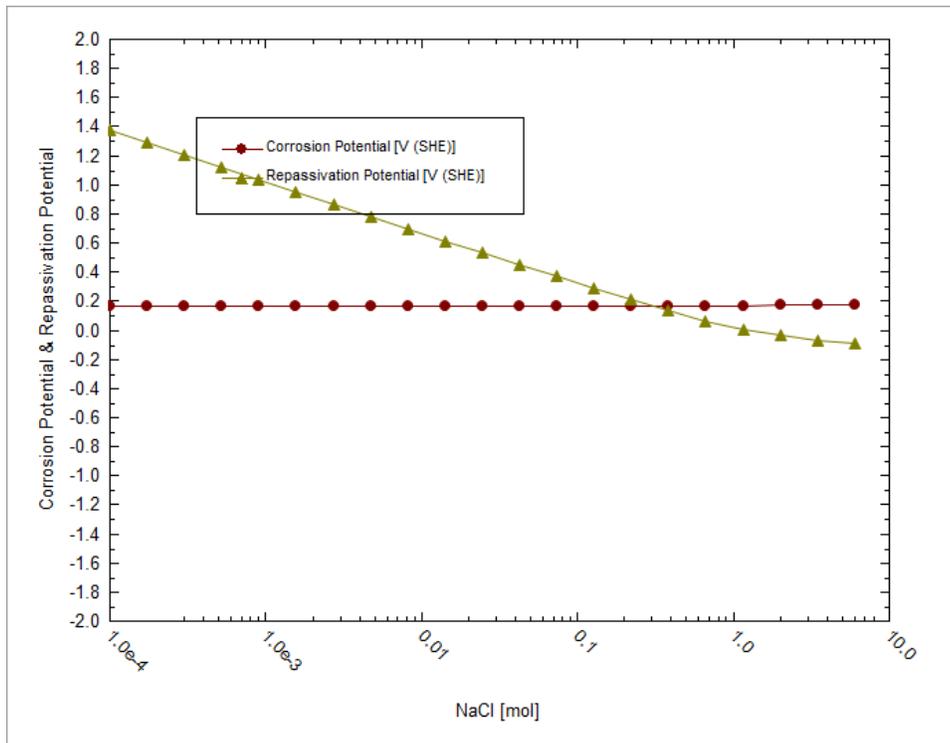


Figure 30-25 Predicted repassivation potential and corrosion potential for alloy 2205.

The plot indicates that alloy 2205 is susceptible to localized corrosion in aerated solutions when the chloride concentration exceeds ca. 0.3 molal. Above this concentration, the repassivation potential drops below the corrosion potential and, therefore, localized corrosion can be stabilized at these conditions.

## Setting up the calculation

Now, we will perform the same calculations for thermally aged alloy 2205. We will use the experimental data of Sridhar et al. (2009), which show that the formation of a chromium-depleted secondary austenite phase is responsible for a much increased tendency for localized corrosion. This phase was identified after aging at 700 °C for 24 hours.

To make this simulation, click on the stream name that you used in the previous simulation. Then, double-click on the **Add Corrosion Rates** icon in the **Actions/Explorer** pane and click on the **Definition** tab.

As in the previous simulation, select **316 Stainless Steel** from the drop-down **Contact Surface** menu.

We will run the same concentration survey as in the previous case so that we can compare the results for bulk alloy 2205 with those for a heat-treated sample. To define the survey type, click on **Specs**. In the **Var. 1 – Composition** category, select **Sodium Chloride** in the **Component** tab. Then, click on the **Survey Range** tab and enter:

Start	0.0001
End	6
Number of steps	20

The screen should look similar to Figure 30-20 Selecting the component for the survey (NACL)

Then, click on the **Thermal Aging** category on the left-hand side pane. The screen will be populated with default parameters for type 316 stainless steel.

Click on the **Yes** button next to **Erp directly from correlation** because we will be running calculations for a completely new phase.

Then, enter the composition of the secondary austenite phase by replacing the default values for alloy 316. For more details how these compositions were determined, see the paper of Sridhar et al. (2009). Enter the following values:

Fe	80.774 wt.% (which is the balance that includes many minor elements)
Cr	12.512 wt.%
Ni	5.134 wt.%
Mo+W	1.399 wt.%
C	0.017 wt.%
N	0.164 wt.%

After entering the values, the screen should look as follows:

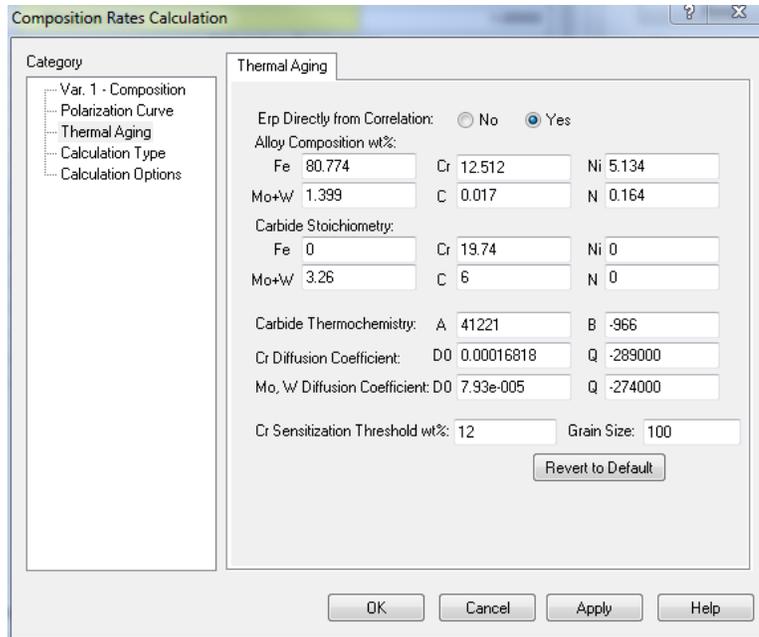


Figure 30-26 Entering the composition of secondary austenite phase in a heat-treated sample of alloy 2205.

Click **OK** to save this information.

Then, click **Calculate**.

## Analyzing the results

When the calculations are finished, click on the **Localized Corrosion** tab. You will see a plot of the corrosion and repassivation potentials as a function of NaCl concentration. As in the previous example, change the horizontal axis to a logarithmic scale. For this purpose, click on **Options**, select the **X Axis** category, check the **Logarithmic Scale** box and click **OK**. Then, the plot should look similar to the following one:

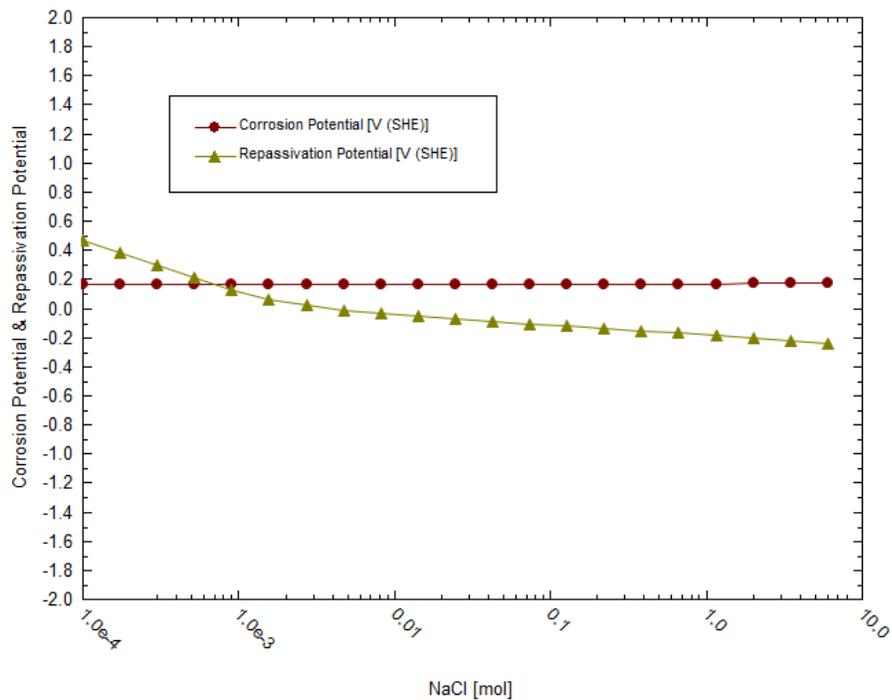


Figure 30-27 Predicted repassivation potential and corrosion potential for thermally aged alloy 2205. The calculations were made using the composition of the secondary austenite phase.

The obtained plot shows that the repassivation potential is much lower than that for bulk alloy 2205 (cf. Figure 30-25). Because of the strong depression of the repassivation potential, the corrosion potential exceeds the repassivation potential at chloride concentrations of ca. 0.0007 m. Thus, localized corrosion is predicted to be possible at concentrations above 0.0007 m. This indicates a very strong increase in the propensity for localized corrosion compared with bulk alloy 2205, for which the predicted threshold is ca. 0.3m.

In general, you can use this facility to predict the repassivation potential for any alloys, including unknown and experimental ones, as long as they belong to the Fe-Ni-Cr-Mo-W-N-C family.

You can download a worked example of this chapter from the [OLI Wiki Page](#)

