

# 29. Thermal Aging and Variations in Alloy Composition Introduction

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## What can be simulated?

Localized 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-base 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-base 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. Also, various chromium-rich intermetallic 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.

Sensitization of Fe-Ni-Cr-Mo alloys and its effects on intergranular attack and intergranular stress corrosion cracking is the most directly observed effect of Cr depletion. It may result in intergranular attack and intergranular stress corrosion cracking. Localized corrosion can be also affected by Cr and Mo depletion.

Corrosion Analyzer contains the following technology that can help address these issues:

- (1) A grain boundary microchemistry model for predicting the chromium and molybdenum depletion in the vicinity of grain boundaries as a result of carbide formation;
- (2) 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;

- (3) A procedure for calculating the observable repassivation potential that corresponds to macroscopic localized corrosion by applying the electrochemical model to the depletion profiles and performing suitable integration.

More details about this technology are described by Anderko et al. (2008), Tormoen et al. (2009), Anderko et al. (2009), and Sridhar et al. (2009).

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## Alloy Chemistry

Simulations can be performed, in general, for alloys that belong to the Fe-Ni-Cr-Mo-W-N-C family (i.e., for stainless steels and nickel-base alloys).

Depletion profiles in the vicinity of grain boundaries and depletion parameters can be obtained for austenitic alloys (including stainless steels and Ni-base alloys). Also, the effect of Cr and Mo depletion on localized corrosion can be calculated. This effect can be examined using the repassivation potential, which provides a threshold potential for the stabilization of localized corrosion (Anderko et al., 2009).

For other alloys from the Fe-Ni-Cr-Mo-W-N-C family, the repassivation potential can be calculated if the alloy composition is known. This also includes experimental alloys and separate phases that may be formed as a result of various forms of heat treatment (Sridhar et al., 2009).

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## Calculation types

Thermal aging is an additional phenomenon that can be simulated within the framework of corrosion kinetics. All calculations types and, in particular, survey types, that are supported for corrosion kinetics are also supported in conjunction with the study of thermal aging.

If it is desired to make calculations on a thermally aged sample, the thermal aging temperature and time need to be specified in the **Calc Parameters** section in the **Definition** tab. The default values are 399 °C for the thermal aging temperature and 0.0 hours for the thermal aging time. If either of these default values is used, no thermal aging effects will be predicted. Thus, by default, Corrosion Analyzer performs calculations on samples that have not been thermally aged.

### ***Thermal Aging Temperature Survey***

This calculation makes it possible to vary the thermal aging temperature within a certain range. A fixed value of thermal aging time is assumed as specified by the user. Typically, the temperatures for which thermal aging effects can be observed range from ~500 °C to ~900 °C, with the effects being most pronounced in the middle of this range.

### ***Thermal Aging Time Survey***

This calculation can be used to examine the effect of aging time at a fixed thermal aging temperature.

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## Output specific to thermal aging

The following output can be generated:

- (1) Chromium and molybdenum depletion profiles, i.e., the variation of Cr and Mo concentration within the grain as a function of grain boundary
- (2) The depletion parameter, which provides compact information on the extent to which the depletion process reduces the grain boundary concentration below a certain critical value of, which can be defined by well-known criteria for maintaining passivity (e.g.  $x_{Cr}^* = 0.11$  or  $0.12$ ). This parameter can be calculated as the area of the depletion profile below the threshold concentration  $x_{Cr}^*$ , divided by bulk Cr concentration,  $x_{Cr}^0$  :

$$\delta(x_{Cr}^*) = \frac{1}{x_{Cr}^0} \int_0^{z^*} (x_{Cr}^* - x_{Cr}(z)) dz$$

where  $z^*$  is the distance from the grain boundary that corresponds to the threshold concentration  $x_{Cr}^*$ .

- (3) The repassivation potential, which is a key parameter for determining whether localized corrosion can occur, may be affected by thermal aging in a rather complex way.

