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Research

On Water Induced Sensitization of Ni (Fe,Cr) alloys towards Stress Corrosion Cracking in LWR Piping from 1st Principles Modelling

2021:02

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SSM perspective

Background

In Swedish Light Water Reactors (LWR), stress corrosion cracking of reactor components and welds occurs from time to time. As the nuclear power plants are ageing, it is essential to study and further understand the mechanism for environmentally induced sensitization. Natural cracking is a phenomenon that is difficult to predict and very hard to study since it occurs suddenly and often unexpectedly. In order to study the crack initiation and growth, the crack is traditionally experimentally provoked and it is not known to what degree these experimental cracks correspond to those that occur naturally. The environment in an LWR contributes to material ageing through chemical reactions with the environment. An in-depth examination has shown that the microstructures of oxide films changes along the crack path and the oxide film in the crack tip is significantly different from what one detects at the crack opening. In this study, 1st principles modelling is used to articulate an environment induced sensitization mechanism for stress corrosion cracking of Ni(Fe,Cr) alloys in LWR conditions.

Results

Density functional theory (DFT) has been used to theoretically describe the processes that occur along a crack in LWR environment. The working hypothesis of the present study takes environmentally sensitized stress corrosion cracking (ES SCC) to be owing to internal oxidation of chromium along alloy grain boundaries. This scenario implies random cracking to be repeatedly healed by outward diffusion of chromium to the crack tip, where sealing becomes subsequently achieved by chromia formation. The water chemistry including the impact of dissolved hydrogen in the reactor coolant, becomes decisive for oxide scale composition, its coherence as well as its adherence to the supporting alloy. The resulting passive layer is understood to control the effective permeability of the water equivalents, i.e., the oxidising agents, along oxide grain boundary interfaces from the water/oxide interface to the crack tip. In cases of limiting chromium mobility in the alloy grain boundaries, the sluggish outward diffusion of Cr risks being overtaken by the inward diffusion of oxygen. Impact of carbide, nitride or hydride precipitates along alloy grain boundaries was taken to have dual detrimental effect. Thus, the precipitates would render Cr locally enriched while also mitigating the Cr mobility along the oxygen activity gradient. Internal oxidation of stationary Cr rich precipitates would render the precipitating additives dissolved. The increased activity of the additives would in turn stabilize corresponding precipitates further away from the sensitization front possibly also intercepting any outward diffusing chromium. Thus, the internal oxidation driven dissolution-precipitation process has chromium carbides, nitrides or hydrides acting guides for the sensitization. Were this understanding to be valid then the ES SCC would fundamentally be owing to oxygen competing with carbon, nitrogen, or hydrogen for the chromium in the alloy. It would apparently be resolved by increasing the relative Cr content in the Ni(Fe,Cr) alloys.

However, employing water as oxygen carrier adds the possibility of chromium activity loss beyond the crack tip owing to formation of transient hydride precipitates. Indeed, the DFT study showed how water may be conveyed along chromia and nickel-decorated chromia grain boundaries, to support the oxidation mediated hydrogen pick-up beyond the crack tip. Thus, while any carbon in the alloy would originate from the manufacturing process, the hydrogen uptake would originate from the oxidation process. And while the carbon content would stay constant, the increasing hydrogen content in the alloy with time, in spite of a small pick-up fraction, would cause increased environment sensitization by supporting inward oxidation along the alloy grain boundaries.

Relevance

The method of using 1st principles electronic structure calculations by means of density functional theory (DFT) is a new approach towards understanding possible mechanisms for environmentally sensitized stress corrosion cracking in load bearing structures in LWR environment. The results obtained in this study show that DFT calculations combined with experimental research can offer important information that provides better understanding of ageing mechanisms in LWR environments.

Need for further research

This study was a first step towards understanding if 1st principles electronic structure calculations by means of density functional theory could be employed to formulate and test possible mechanisms for environmentally sensitized stress corrosion cracking (ES SCC) in load bearing structures. The method has been proved to be useful. It can be further developed and used to explain, for example, the effect of hydrogen pick-up on the enrichment of chromium at the alloy grain boundaries in LWR environments, and how Li^+ from the coolant becomes enriched at the crack tip by acting H^+ equivalent at the oxide grain boundaries. The purpose of the 1st principles electrochemical approach to ES SCC is to offer chemical rates for the various sensitization processes, these time scales in turn serving phenomenological structural mechanics' based predictive modelling tool.

Project information

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This report concerns a study which has been conducted for the Swedish Radiation Safety Authority, SSM. The conclusions and viewpoints presented in the report are those of the author/authors and do not necessarily coincide with those of the SSM.

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Sammanfattning

Vår åldrande svenska kärnkraftspark gör det allt mer angeläget att beakta ökade risker för spänningsinducerad sprickutveckling i lastbärande strukturer. Naturlig sprickbildning är ett fenomen som är svårt att förutsäga och än mindre studera, eftersom det uppkommer plötsligt och ofta oväntat. Experimentellt, framprovoceras sprickbildningen, så att detta förlopp sen kan studeras. Stora frågetecken kvarstår dock kring i vad mån dessa konstgjorda sprickor överensstämmer med de som uppstår naturligt. I en aggressiv miljö – som exempelvis vatten vid förhöjda temperaturer inuti ett kärnkraftverk utgör – gentemot Ni(Fe,Cr) legeringar, så föregås sprickbildningen av ett kemiskt åldrande orsakat av omvandlingar i legeringen men även av kemiska reaktioner med omgivningen. Vi har intresserat oss för det senare och då hur känslighet för sprickutveckling skulle kunna byggas upp som ett resultat av att en Ni(Fe,Cr) legering oxideras med vatten. Vårt tillvägagångssätt är rent teoretiskt. Vår metodik för att bidra med sådan komplementär kunskap, som annars endast med stor svårighet kan erhållas från experiment, baserar sig på kvantmekanikens grundläggande ekvation – Schrödingerekvationen. Ur denna kan i sin tur den vedertagna täthetsfunktionalteorin (TFT) härledas. Utgående från TFT-beräkningar diskuterar vi hur den önskade utdiffusionen av krom – för att täta sprickor genom kromoxidbildning vid gränssnittet legering/oxid vid sprickspetsen – hålls tillbaka av kromkarbid- och kromhydridutfällningar i legeringskorngränserna. Den inåtdiffunderande oxidanten utgörs av vattenekvivalenter, det vill säga hydroxidjoner och vätejoner, som klär oxidkorngränser (kromoxid och nickelkromoxidspinell). Den är komplementär mot utdiffusionen av krom. Således orsakar oxidation av kromkarbid och kromhydrid vid legeringskorngränserna dessa att lösas upp för att återbildas längs legeringskorngränserna i riktning bort från sprickspetsen. Detta föreslås orsaka sensibilisering för sprickbildning i legeringen bortanför sprickspetsen. Vi påvisar ett gångbart sätt för väte att, i samverkan med den vatteninducerade oxidationen, tas upp i legeringen. Något som skulle vara av avgörande betydelse för den åtföljande tänkta sprickutvecklingen. Vikten av detta möjliga scenario understryks i det att medan exempelvis kromkarbiderna är en rest från tillverkningsprocessen, så sker kromhydridbildningen under drift och som resultat av oxidationen orsakad av vatten. Således kan inverkan av karbider undertryckas genom att tillföra krom i överskott i legeringen eller genom användning av legeringar med låg kolhalt. Emellertid, i motsats till karbiderna så kan nämnda väteupptag i samband med inväxande oxid orsakad av vatten inte undvikas. Det senare är något vi tidigare funnit för zirkonia på Zircaloy, för alumina på FeCrAl (RE) och nu så också för kromia- och NiCr-spinell på Ni(Fe,Cr). Denna mekanism för väteanrikning i legeringen innebär en med tiden ökande sensibilisering av legeringen mot väteassisterad spänningsinducerad sprickbildning.

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1. Introduction

In Swedish Light Water Reactors (LWR), stress corrosion cracking of reactor components and welds occurs from time to time. A more recent example is the cracking found in Alloy 182 welds of core shroud support legs in Forsmark Boiling Water Reactor (BWR) Unit 1¹. An in-depth examination has shown that the microstructures of oxide films changes along the crack path and the oxide film in the crack tip is significantly different from what one detects at the crack opening². The susceptibility for cracking of Ni based alloys has often been reported to exhibit a maximum at hydrogen levels normally used in primary water of Pressurized Water Reactor (see Figure 1), while the time to initiation shows a minimum in the similar hydrogen region³⁻⁷. Based on these studies an optimized Dissolved Hydrogen (DH) level, either very low or very high, has been suggested. A similar study was performed on DH dependence of crack growth rates of Alloy 600 material from 5 to 75 cc H₂/kg H₂O in simulated PWR coolant⁸, but making very different observations. In these tests, the oxide films at crack tip were found to experience a large structural transformation from rock salt to spinel crystal structure in the DH range from 5 to ≥16 cc H₂/Kg H₂O. These experimental evidences highlight the need to understand the dependence of oxide film structure on corrosion environments in the crack tip region.

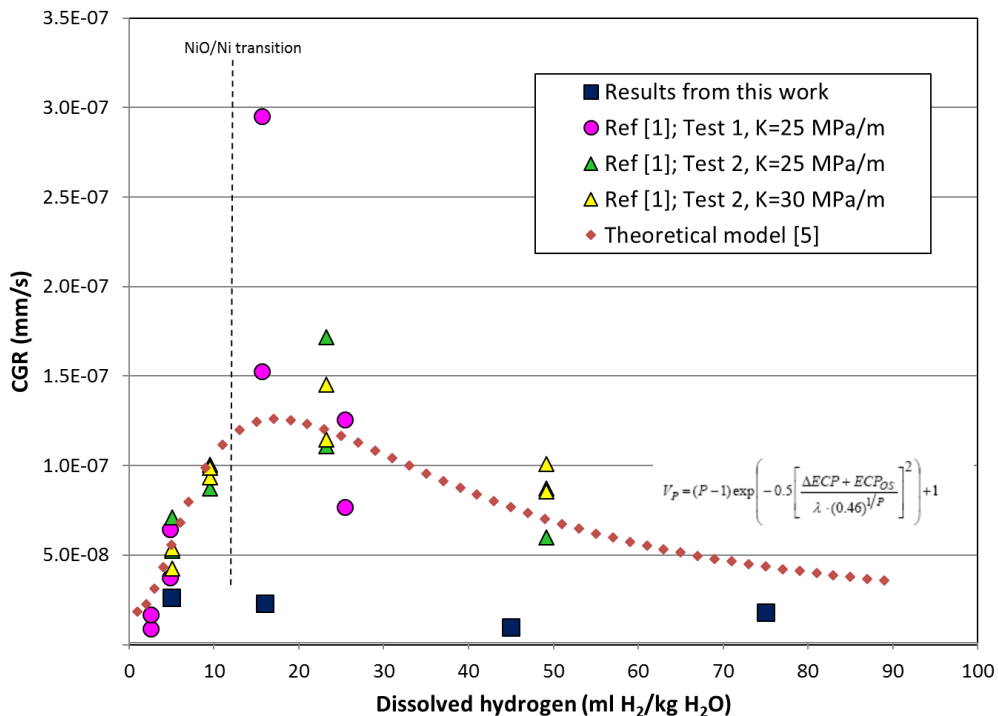
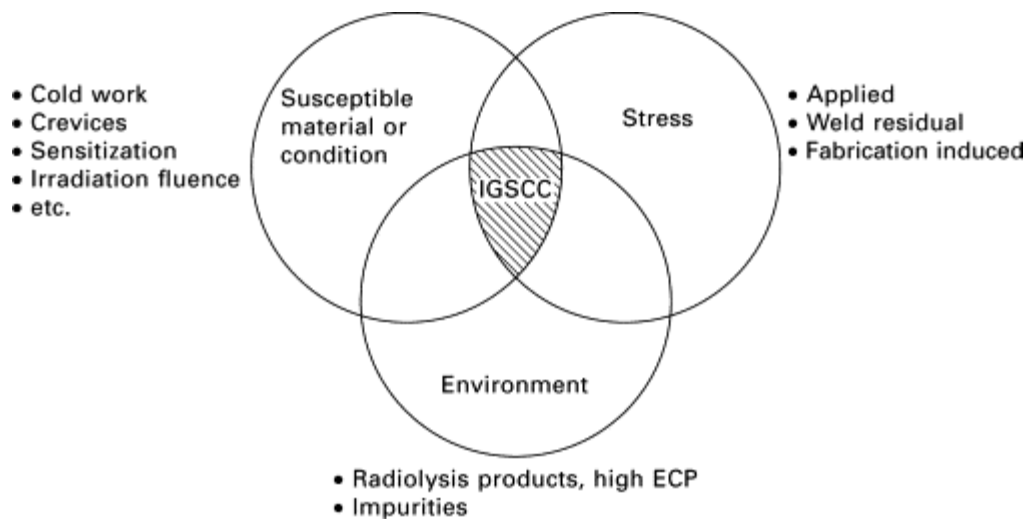


Figure 1. Dependence of CGR on DH obtained from the present work where all data are normalized to K=30 MPa√m, assuming a K^{1.16} dependency. Some data from ref. [3, 7] are also shown

Resilience towards mechanical and chemical stresses are central traits decisive for the durable integrity of functional alloys. Ability to resist plastic deformation is commonly achieved by dedicated thermo-mechanical treatments that produce a

wanted crystalline texture or submicron size precipitates from a supersaturated solid solution. Alternatively, enhanced strength may be achieved by introducing oxide dispersions (OD) dedicated to the mitigation of dislocations movements. Moreover, oxide scale formers and complementary tailored additives are introduced to the base metal in order to facilitate the scaling⁹⁻¹⁰ but also to suppress scale growth¹⁰⁻¹³, thereby allowing the component to withstand commonly harsh chemical environments as decided by the particular application. But while additives are introduced to improve some properties, not seldom as a consequence, others may suffer. The interplay of water and dispersions of reactive elements oxides (REO) in case of FeCrAl(RE) alumina formers was recently addressed experimentally and by modelling¹⁰, in case of which e.g. small REO particles were found to be beneficial and large REOs detrimental.

The present study sets the stage for the use of density functional theory to formulate and test possible mechanisms for environmentally sensitized stress corrosion cracking (ES SCC) in load bearing structures. Commonly, the factors which influence the stress corrosion cracking are distinguished according to their metallurgical and environmental origins, and the applied stress, compare Scheme 1.



Scheme 1: illustration of the interplay between environment, inherent material characteristics and applied or residual stress resulting in inter-granular stress corrosion cracking, here ES SCC. Figure from ¹⁴.

Indeed, the integrity and durability of an alloy is determined jointly by the interplay between the materials and environment. Characteristics relevant to ES SCC include grain size, grain boundary GB microstructure; cold work; bubbles at GBs from creep or gas (e.g. CH₄); precipitates in GB (hydride, carbide, nitride, oxide) in quasi-equilibrium with the corresponding atoms dissolved in the alloy or permeating through the passive layer; local loss of protection owing to catalytic process etc., see Figure 2.

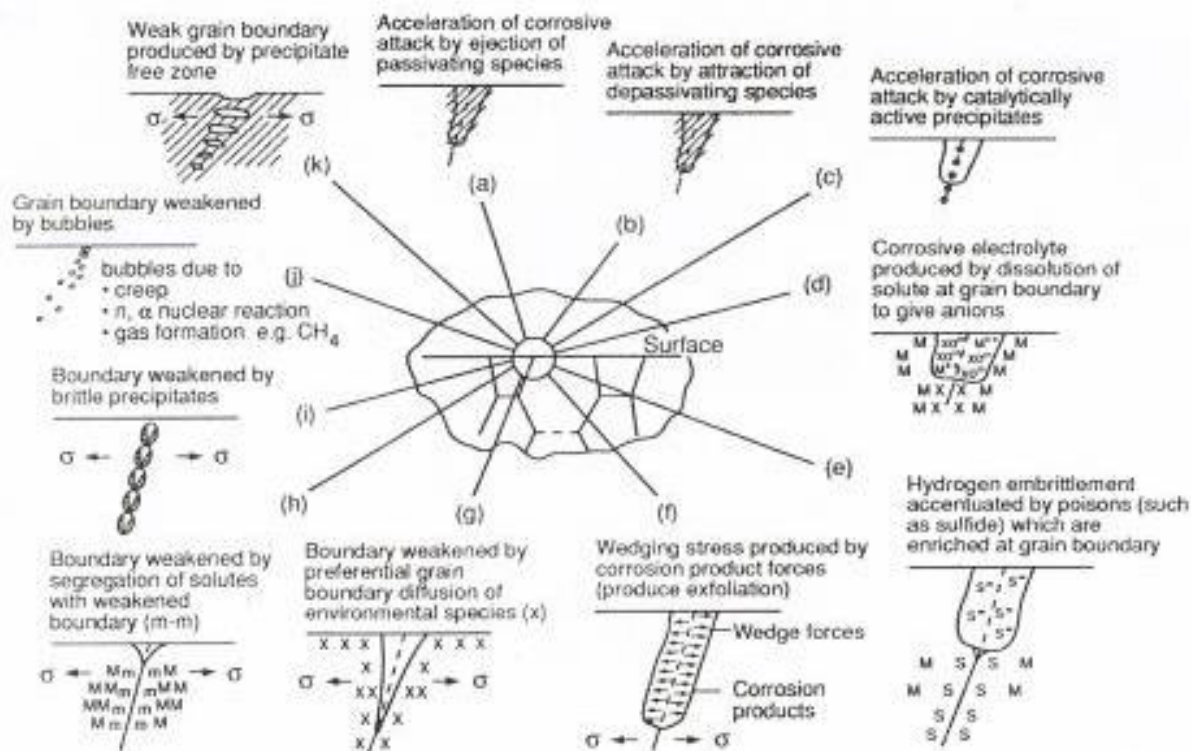


Figure 2. The processes starting from (a) to (k) range from the mostly chemical to the mostly mechanical ¹².

Two time-domains have been identified for ES SCC: (i) the incubation time for a smooth surface to develop a crack, and (ii) the crack propagation time. In paper ¹³ the authors claim that there is no proven mechanism or equation that predicts or even explains how material and environmental parameters interact to generate the cracking. Still, several interesting mechanisms are reviewed including the theory of Galvele involving atomic displacement and vacancy capture at the crack tip¹⁵⁻¹⁶. Also relevant for the present study is the mechanism for intergranular embrittlement caused by internal oxidation beyond the crack tip, i.e. diffusion of oxygen in the alloy constituting the essential component causing formation of Cr_2O_3 or gas bubbles owing to oxidation of intergranular carbides to form $CO(g)$ or $CO_2(g)$ ¹⁷. After long-term exposure to high-temperature water, cavity formations at grain boundaries in proximity to carbides mainly in carbon steel was inferred to result from condensation of vacancies. These cavities were shown to form 10 times faster in carbon steel than in thermally treated alloy 690 and in milling annealed alloy 600¹⁸.

Our approach to the modeling of ES SCC, is based on a series of studies that jointly may be taken to offer complementary perspective on the ES SCC. These applications include the impact of water on chromium oxidation and vaporization from chromia scales¹⁹⁻²⁰; zircaloy oxidation by water including permeation of zirconia by H^+ and H^- of $H_2O(l)$ origins, hydrogen pick-up in the alloy and co-dissolution of oxygen²¹⁻²³; interplay of water and reactive elements (RE) in oxide scale formation on FeCrAl(RE) including RE assisted permeation of alumina by H^+ & H^- of $H_2O(g)$ origin^{11, 24}, disentangling the RE effects in alumina formers¹⁰ and 3rd element effect⁹; permeation of chromia by N^{3-} of $N_2(g)/H_2O(g)$ origin, driven by oxidation of Al in FeCrAl and resulting in internal AlN formation in the alloy matrix²⁵; permeation of iron oxide scales by Cl^- of KCl/HCl origins and as driven by inward oxide growth²⁶, and impact of grain boundary density on oxide scaling rates²⁷.

In this spirit, we tackle the SCC problem focusing on two specific questions: (1) How presence of carbon, nitrogen and hydrogen impurities in the alloy may impact the SCC process, and (2) what would be a viable mechanism for hydrogen pick-up during oxidation by water causing sensitization towards SCC of the chromia forming stainless steels.

In what follows, internal consistency of a possible understanding is explored where the actual sensitization becomes a phenomenon akin to internal oxidation¹⁷. This working hypothesis takes oxide precipitation-dissolution at alloy grain boundaries to precede crack initiation. Once a crack is formed, sensitization beyond the crack tip occurs along the grain boundary network, causing the intergranular crack propagation. Moreover, in as much as the oxygen activity in the alloy is taken to reflect the equilibrium dissociation pressure of the oxide, there is little *a priori* reason for spontaneous chromia precipitation at alloy grain boundaries. Indeed, once chromia is formed at the alloy grain boundaries that would require the equilibrium oxygen activity in the alloy to be instantaneously recovered by the dissociation of chromia at the outer alloy/oxide interface. Else, the chromia precipitate would again dissolve. In this scenario, sensitization is ascribed to non-equilibrium processes (i) oxygen activity fluctuations in the vicinity of alloy grain boundaries in the bulk, (ii) the oxygen activity gradient beyond the crack tip, or (iii) oxygen assisted enrichment of chromium at the alloy grain boundaries. It is noted that were internal chromia formation to be spontaneous, it would be slowed down by the reaction volume required for the chromia precipitation. Indeed, sensitization owing to “internal oxidation”, guiding crack propagation, is countered by the outward diffusion of chromium to the crack tip rendering it to heal. Thus, oxide being present all the way into the crack tip is an essential element in crack evolution as well as in alloy resilience to cracking.

This overall understanding provides the foundation for the present study, where new insight regarding the potentially detrimental impacts of carbide, nitride as well as hydride precipitates at the alloy grain boundaries are sought. Assuming that internal oxidation of alloy grain boundaries actually precedes alloy cracking, and this actually comprising the critical component in the ES SCC, two questions arise:

- (1) can there be synergy between said internal oxidation and pre-formed hydrides, carbides or nitrides in the alloy grain boundaries where the latter pave the way for the former by resisting outward diffusion of Cr and thus any ability to crack healing?
- (2) and in case of hydrides in particular, if these were indeed to render outward diffusion of Cr sluggish, is hydrogen pick-up from the coolant possible?

2. Modelling considerations

DFT – Fundamentals

Density functional theory is a misleading term. Rather, the fundamental theory that provides the basis of our understanding of the materials world today is Quantum Mechanics. In as much as our interest is in chemistry and solid state physics, the properties we seek can be extracted from solutions to the Schrödinger equation. These solutions come in the form of wave functions. Before even trying to solve the Schrödinger equation, we make the simple observation that it is impossible to solve exactly for relevant systems, and that this is due to the complexity of the interacting many-particle-system. Here enters DFT. Rather than a theory, DFT expresses that all properties of a quantum mechanical system, in its ground state, and in particular its total energy, may be extracted from the electron density of the system. Exactly. Thus, there is a 1:1 mapping of the electronic density onto a non-degenerate ground state wave function. The electron density uniquely determines the positions of the nuclei, the latter providing “external” potential, which acts on the former. There exists a universal density functional that relates the potential energy of the complex correlated many-electron system to the corresponding electron density. But how to compute the true electron density? In order to do this, we make the observation that the true electron density – resulting from interacting electrons experiencing the external potential – that the very same electron density may be arrived at for non-interacting electrons subject to a so-called exchange-correlation potential which includes the kinetic energy discrepancy between the interacting and non-interacting electrons. It is that coupled Schrödinger equation for non-interacting electrons, the so-called Kohn-Sham equations, which constitutes the bulk of the DFT calculations performed in any DFT study. The solutions of the Kohn-Sham equations are the Kohn-Sham orbitals such that the sum of squared occupied orbitals add up to the electron density that determines the energy of the system. The latter can be subject to minimization by optimizing the atomic structure of the system. In order to simplify matters further, the occupied orbitals on each atom are said to be either inert or belong to the valence. While the latter are the main focus of the Kohn-Sham equations, the former impact on the system jointly with the nucleus in the form of an effective core potential. In DFT the size of the calculations grows at least quadratically with the number of electrons. In order to make macroscopic calculations accessible, periodic boundary conditions are commonly employed. In the solid state this amounts to assuming that the systems at hand are crystalline. Crystal orbitals are produced by coupling intra-unit cell orbitals non-locally, in k-space, that result in bands via the so-called k-space sampling. Disordered systems are treated as if ordered but with a large enough unit cell so that the impact of the periodicity does not affect the result. Added benefit is that thereby dangling bonds are avoided.

Computational details

All the DFT results presented in this report were obtained using the CASTEP program package within the Material Studio 2017 R2 framework²⁸. The PBE on-the-fly ultrasoft pseudopotential²⁹ with 571.4 eV cut-off energy was employed for all the spin polarized calculations. The k-point sampling of the Brillouin zone was made by means of the Monkhorst–Pack³⁰⁻³¹ scheme each time with a proper k-points mesh suitable for the crystal system under investigation. All the crystal structures were fully optimized using the BFGS algorithm³² from a starting geometry (when existing) taken from the Springer Materials database.

For what concerns more in specific the calculations the results presented, the dimensions in the **ab** plane of the fundamental unit cell of chromia (corundum structure) could be maintained because the stacking fault is considered in the 0001 direction, while the total energy for H₂O and H₂ molecules utilize large enough unit cells, so as to disallow direct interaction between the molecules. The chromia grain-boundary GB is modelled according to earlier work on alumina, where two 1.5 nm thick lamella are fused together at the 0001 planes either by water (forming hydrogen bonds across the two chromia interfaces), see Figure 3a or by the inclusion of an M-O layer where if M=Cr, a nominal stacking fault is introduced into the supercell, see Figure 3b. This low energy interface offers an upper bound to the grain-boundary reaction energies of interest. Where NiO incorporation into grain-boundaries has been studied, two different Ni concentrations have been modelled, 75 % Ni decoration i.e. two cation vacancies with corresponding oxygen vacancies and 100% Ni decoration i.e. a monolayer of NiO, see Figure 4.

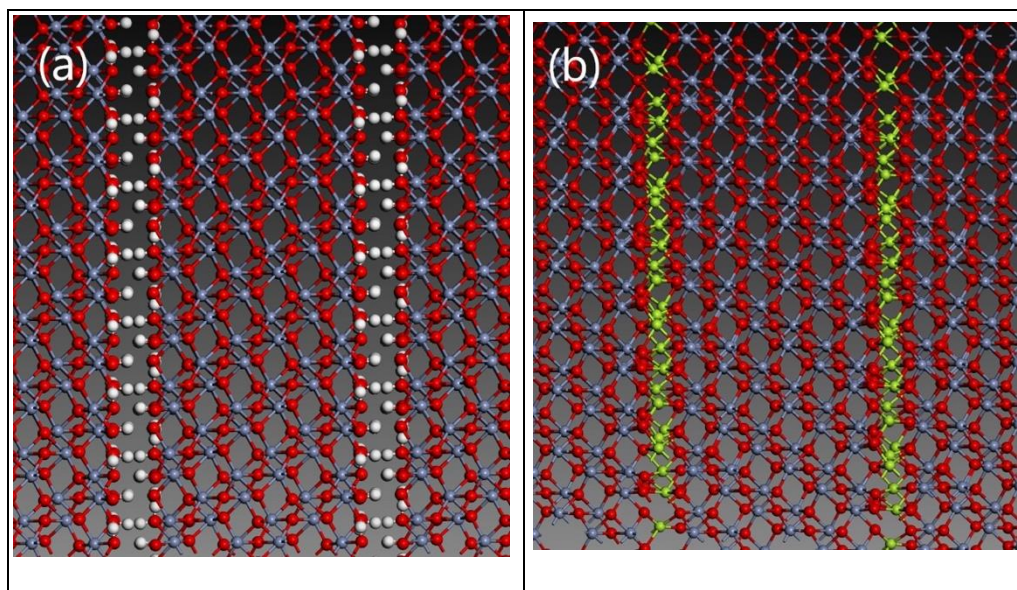


Figure 3. Structure of the 1.5 nm thick chromia lamella that are fused together along the 0001 plane by (a) water in the form of hydroxides and (b) an inserted M-O layer, where M=Cr represents a stacking fault. Color scheme: Cr – gray, O – red, H – white, inserted M at the fusion zone – green.

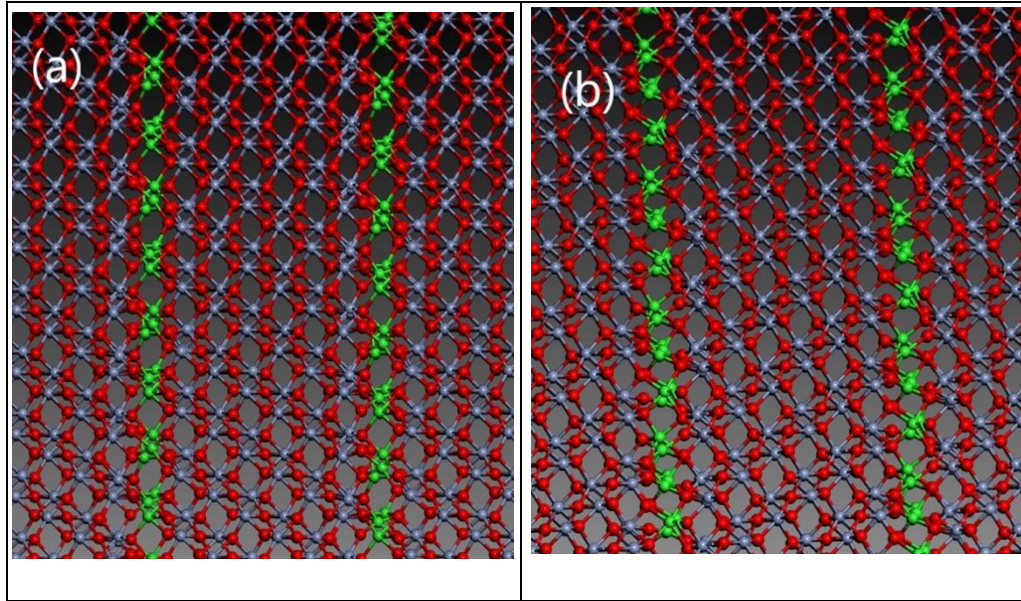
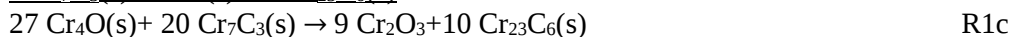


Figure 4. Structure of 1.5 nm thick chromia lamella that are fused together along the 0001 plane by (a) NiO corresponding to a 75 % coverage and (b) NiO corresponding to 100% coverage. Color scheme: Cr – gray, O – red, H – white, Ni – green.

3. C, N and H as guides of crack tip

In this paragraph we offer a first attempt at testing the working hypothesis of ES SCC, i.e. to result from synergy between internal oxidation and corresponding dissolution and reprecipitation of any inherent carbides, nitrides and hydrides residing in the alloy grain boundaries. Mechanistic insight into the ES SCC in nickel base alloys is sought from 1st principles DFT, where the aim is to make contact between theory and the experimental observations. The proposed ES SCC process is subdivided into (i) oxygen dissolution into the alloy – as decided by the dissociation pressure of the outer chromium oxide away from the crack, and (ii) co-enrichment of oxygen and chromium in the alloy grain boundaries driving the dissolution of pre-existing (Fe,Cr,Ni) carbides, nitrides or hydrides in the grain boundaries that in turn end up reprecipitating in the grain boundary deeper into the alloy.

Here, a scenario is provided where inherent carbides, nitrides as well as accumulating hydrides support SCC sensitization by internal oxidation beyond the crack tip. In doing so, we propose and validate the notion that interconversions between different hydrides, carbides, and nitrides may cause apparent supersaturation of oxygen in the alloy. Thus, loss of oxygen activity during non-equilibrium oxygen enrichment at the alloy grain boundaries is replaced by a corresponding carbon activity, i.e. chromia is driven by hydrides, carbides or nitrides acting sink for alloy constituents released by the oxide disproportionation



The mechanism is summarized in Figure 5 (compare also Figure 6 in the following text).

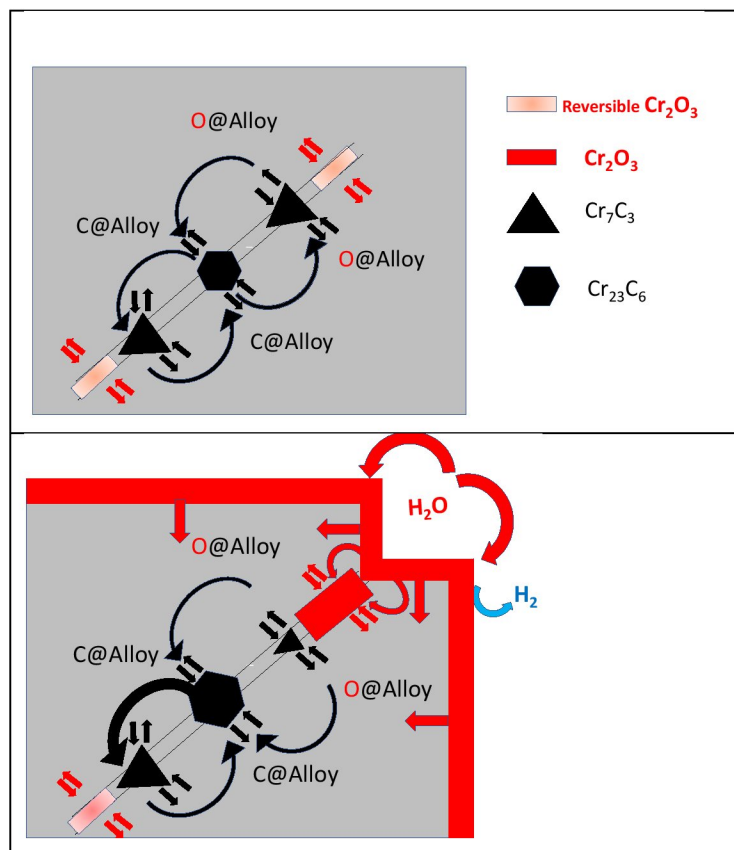
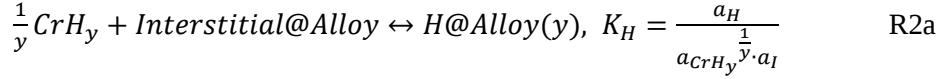


Figure 5 Top: A grain boundary in the alloy away from the outer oxide scale. Coupled equilibria between (i) oxygen at the chromia dissociation pressure and chromia formation and (ii) carbon dissolved in alloy, Cr_7C_3 and Cr_{23}C_6 , rendering the grain boundary sensitized towards stress corrosion cracking. Bottom: Cr_7C_3 decomposing while Cr_{23}C_6 precipitates grow, causing supersaturation of O in then alloy and precipitation of chromia beyond the crack tip or initiating the crack.

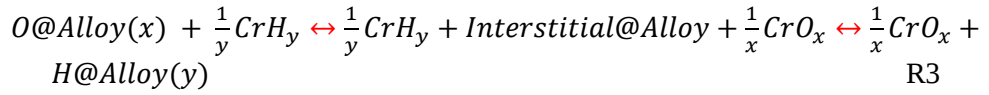
It should be pointed out that in this study Cr is employed for evaluating on the one hand the stabilities of hydrides, carbides, nitrides and oxides and on the other hand Cr to model the alloy, as it becomes a first effort to test the concepts of the emerging understanding. To make contact with real systems, ternary and even quaternary carbide systems must be considered³³. This working hypothesis would imply absence of inherent $(\text{Fe,Cr,Ni})_7\text{C}_3(\text{s})$ to slow down the ES SCC. Indeed, this is consistent with what is observed for Ni base alloys 600 and 690: The former possesses intergranular $(\text{Cr,Ni})_7\text{C}_3$ in conjunction with coexisting intragranular $(\text{Fe,Cr,Ni})_7\text{C}_3$ and $(\text{Fe,Cr,Ni})_{23}\text{C}_6$, while the latter only exhibits $(\text{Fe,Cr,Ni})_{23}\text{C}_6$ precipitation however, indications for an intermediate M_7C_3 phase have been formulated³⁴⁻³⁵. Hence, Ni-base alloy 600 is taken to support the internal oxidation mechanism for ES SCC more readily than does alloy 690.

It may be worthwhile to reiterate that corrosion processes in general and ES SCC in particular, comprise non-equilibrium processes. Time and time again however, it has been found useful to employ thermodynamic concepts when discussing these phenomena. Here the present approach is reiterated to underline in particular the impact of hydrogen enrichments in grain boundaries offering a manifestation of environmental sensitization. In order to clarify the generalized sensitization process further, one should consider the two equilibria related to chromium hydride and chromium oxide dissolution/precipitation. Moreover, one should take the dissolution to comprise accommodation of either oxygen or hydrogen in interstitial sites in the nickel base alloy.

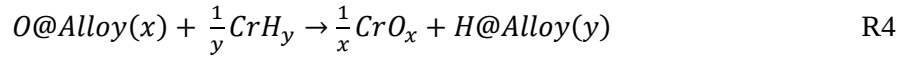


If decoupled, any increased activity of interstitial sites drives each of the reactions forward. Thus, in response, dissolution of oxides and hydrides would result, thereby increasing the activities of oxygen and hydrogen in the alloy in order to maintain the equilibria.

Now, let the two processes be coupled owing to competition for interstitial sites. In as much as accommodation of these sites contributes configurational entropy, the competition for the interstitial sites in the alloy ensures $\Delta S_r \approx 0$, in the Gibbs free energy of reactions,



Thus, ΔG_r associated with the total reaction



$$\Delta G_r = RT \ln \frac{a_H \cdot a_{CrO_x}^{\frac{1}{x}}}{a_O \cdot a_{CrH_y}^{\frac{1}{y}}}$$

becomes dominated by the enthalpy change ΔH_r . This conceptual understanding holds for as long as *a priori* hydrogen and chromium coprecipitate in the alloy GB, and there is dissolved oxygen in the alloy. For the corresponding energetics, see Figures 6, and 7.

Moreover, here the alloy is replaced by pure chromium. In order to track a possible path for increased oxygen enrichment in chromium, we employ iron carbide line-phases as an Ariadne's thread for tracing the transient chromium suboxides ending up at the most stable chromium oxide, i.e. chromia. In contrast to e.g. CrO and Cr₂O₃, the corresponding carbides are significantly less stable. This in turn lends stability to e.g. M₂₃C₆ and M₇C₃ where neither M₂₃O₆ nor M₇O₃ has been reported owing to the drive to form M₂O₃ in case of the latter. The fundamental assumption of the present study is that the structures of said carbides (see Figure 6) are representative for the oxygen enrichment path, i.e. their stabilities are representative of the corresponding transient oxides, building on the fact that the carbides are stable to the extent that they are observable while the corresponding oxides are metastable intermediates that have not been observed directly due to the sub-dissociation pressure regime of chromia. Thus the Ariadne's thread. Consistency in the employed strategy to unravel the drive for oxygen enrichment initiating a pre-crack process beyond the crack tip is validated by including the corresponding path for the carbides and nitrides, see Figure 7 and Figure 8.

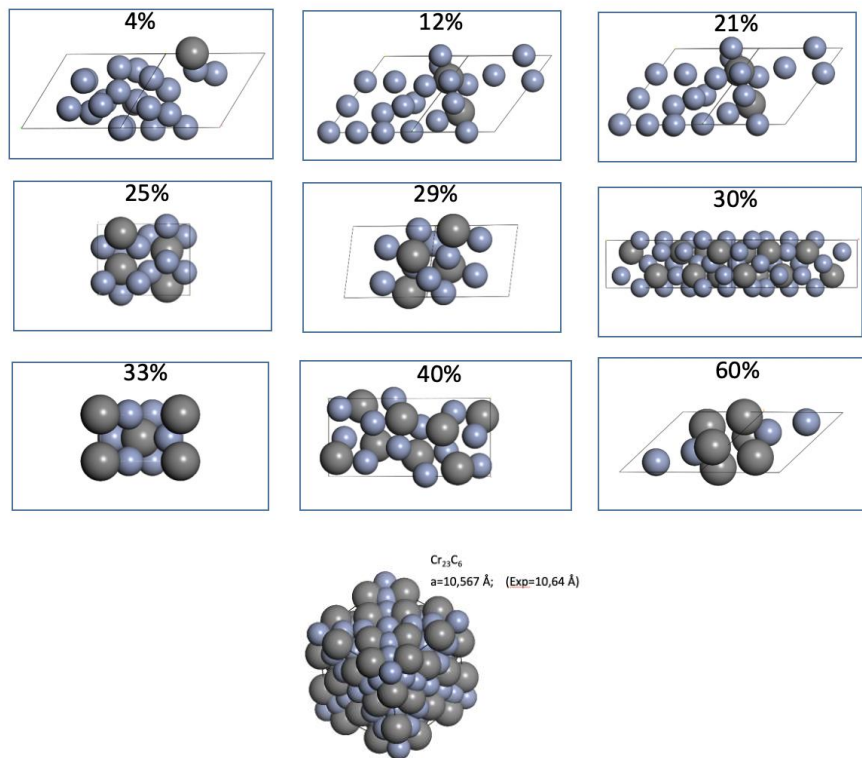


Figure 6. The iron carbide structures employed to map out the “Ariadne’s thread” path for oxygen as well as nitrogen and hydrogen enrichment. Color code: light blue, chromium; grey, carbon.

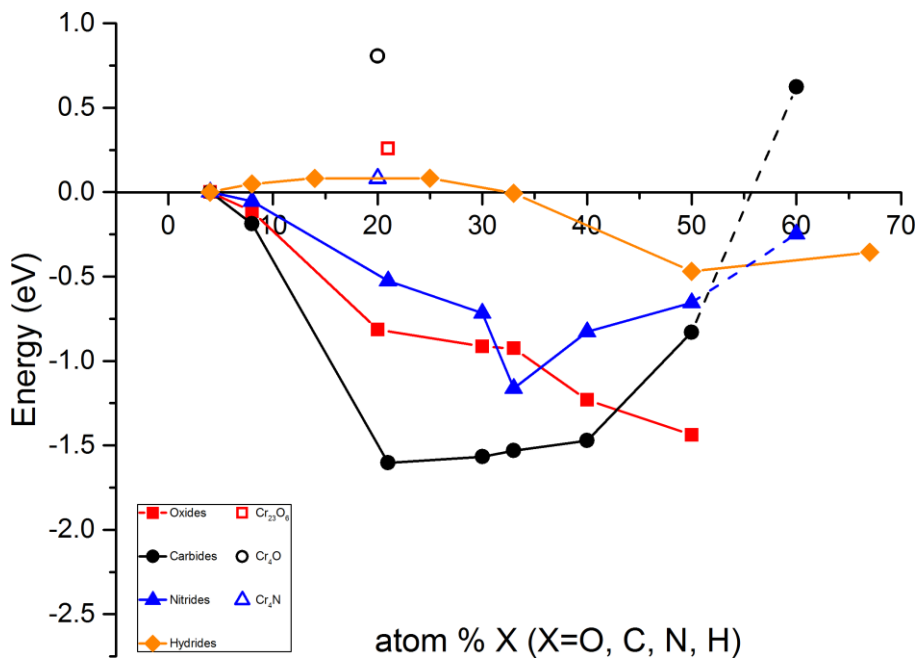


Figure 7. Disproportionation energies for carbon, nitrogen, hydrogen and oxygen according to the reaction: $Cr_aX \rightarrow Cr_bX(s) + (a-b)Cr(s)$. We note that $Cr_{23}X_6$ is viable for C, N but only barely for O, while Cr_4X is viable for O but not for C and barely for N.

Thus, it is gratifying to note how the nitride stabilities are similar to the oxides’ at low concentrations while connecting more to the carbide stabilities at higher concentrations. The central flat region in the stability-concentration diagram for the

carbides at intermediate concentrations around $\text{Cr}_{23}\text{C}_6 - \text{Cr}_7\text{C}_3$ is taken to reflect ability of Cr_7C_3 to absorb Cr. Similarly, destabilization beyond $\text{Cr}_2\text{N}-\text{Cr}_{3/2}\text{N}-\text{CrN}$ tell of the ability of CrN to act Cr absorber. In case of the hydrides, the flat region in vicinity of the $\text{Cr}_2\text{H} - \text{Cr}_3\text{H}$ couple is deemed relevant here. The reaction energies for bare oxygen enrichment owing to disproportionation are found in Table 1, and plotted in Figure 6. The consecutive oxygen enrichment reactions balanced by the corresponding carbide, nitride and hydride dissolution reactions, i.e. $2\text{Cr}_7\text{C}_3+9\text{Cr} \rightarrow \text{Cr}_{23}\text{C}_6$, $2\text{CrN}+\text{Cr} \rightarrow \text{Cr}_3\text{N}_2$ and $\text{Cr}_2\text{H}+\text{Cr} \rightarrow \text{Cr}_3\text{H}$, respectively, are also included in Table 1 and Figure 8. Thus, all three buffer systems, the carbide, nitride and hydride couples, may be understood to assist the internal oxidation process.

Table 1. Energetics for the consecutive oxygen enrichment process, bare and coupled to the corresponding dilution of carbon, nitrogen and hydrogen by the reactions $2\text{Cr}_7\text{C}_3+9\text{Cr} \rightarrow \text{Cr}_{23}\text{C}_6$, $2\text{CrN}+\text{Cr} \rightarrow \text{Cr}_3\text{N}_2$, and $\text{Cr}_2\text{H}+\text{Cr} \rightarrow \text{Cr}_3\text{H}$, respectively.

Oxygen enrichment	Bare disproportionation		Reaction energy eV
	Carbon dilution (reaction energies)		
	Nitrogen dilution (reaction energies)		
$\text{Cr}_{24}\text{O} \rightarrow \text{Cr}_{12}\text{O} + 12\text{Cr}$	-		-0.115
$\text{Cr}_{12}\text{O} \rightarrow \text{Cr}_4\text{O} + 8\text{Cr}$	-		-0.699
	$8/9[2\text{Cr}_7\text{C}_3+9\text{Cr} \rightarrow \text{Cr}_{23}\text{C}_6]$	(-0.196 eV)	-0.895
	$8[2\text{CrN}+\text{Cr} \rightarrow \text{Cr}_3\text{N}_2]$	(-2.75 eV)	-3.45
	$\text{Cr}_2\text{H}+\text{Cr} \rightarrow \text{Cr}_3\text{H}$	(-0.05 eV)	-0.749
$\text{Cr}_4\text{O} \rightarrow \text{Cr}_{7/3} + 5/3\text{Cr}$	-		-0.102
	$5/27[2\text{Cr}_7\text{C}_3+9\text{Cr} \rightarrow \text{Cr}_{23}\text{C}_6]$	(-0.04 eV)	-0.142
	$5/3[2\text{CrN}+\text{Cr} \rightarrow \text{Cr}_3\text{N}_2]$	(-0.573 eV)	-0.675
	$5/3[\text{Cr}_2\text{H}+\text{Cr} \rightarrow \text{Cr}_3\text{H}]$	(-0.083 eV)	-0.185
$\text{Cr}_{7/3}\text{O} \rightarrow \text{Cr}_2\text{O} + 1/3\text{Cr}$	-		0.010
	$1/27[2\text{Cr}_7\text{C}_3+9\text{Cr} \rightarrow \text{Cr}_{23}\text{C}_6]$	(-0.008 eV)	-0.018
	$1/3[2\text{CrN}+\text{Cr} \rightarrow \text{Cr}_3\text{N}_2]$	(-0.115 eV)	-0.105
	$1/3[\text{Cr}_2\text{H}+\text{Cr} \rightarrow \text{Cr}_3\text{H}]$	(-0.017 eV)	-0.007
$\text{Cr}_2\text{O} \rightarrow \text{Cr}_{3/2}\text{O} + 1/2\text{Cr}$	-		-0.305
	$1/18[2\text{Cr}_7\text{C}_3+9\text{Cr} \rightarrow \text{Cr}_{23}\text{C}_6]$	(-0.01 eV)	-0.315
	$1/2[2\text{CrN}+\text{Cr} \rightarrow \text{Cr}_3\text{N}_2]$	(-0.172 eV)	-0.477
	$1/2[\text{Cr}_2\text{H}+\text{Cr} \rightarrow \text{Cr}_3\text{H}]$	(-0.025 eV)	-0.33
$\text{Cr}_{3/2}\text{O} \rightarrow \text{CrO} + 1/2\text{Cr}$	-		-0.205
	$1/18[2\text{Cr}_7\text{C}_3+9\text{Cr} \rightarrow \text{Cr}_{23}\text{C}_6]$	(-0.01 eV)	-0.215
	$1/2[2\text{CrN}+\text{Cr} \rightarrow \text{Cr}_3\text{N}_2]$	(-0.172 eV)	-0.377
	$1/2[\text{Cr}_2\text{H}+\text{Cr} \rightarrow \text{Cr}_3\text{H}]$	(-0.025 eV)	-0.23
$\text{CrO} \rightarrow \text{Cr}_{2/3}\text{O} + 1/3\text{Cr}$	-		-1.03
	$1/27[2\text{Cr}_7\text{C}_3+9\text{Cr} \rightarrow \text{Cr}_{23}\text{C}_6]$	(-0.008 eV)	-1.038
	$1/3[2\text{CrN}+\text{Cr} \rightarrow \text{Cr}_3\text{N}_2]$	(-0.115 eV)	-1.14
	$1/3[\text{Cr}_2\text{H}+\text{Cr} \rightarrow \text{Cr}_3\text{H}]$	(-0.017 eV)	-1.047

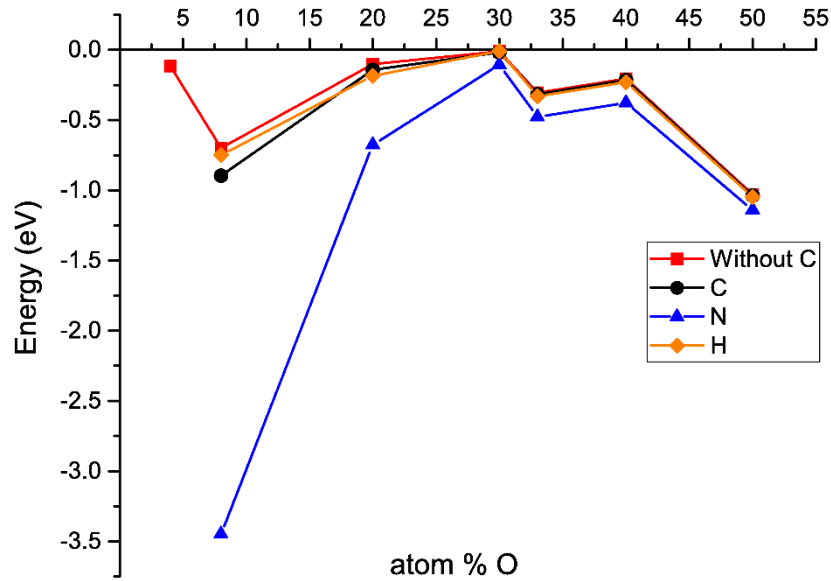


Figure 8. Energetics for the consecutive oxygen enrichment process, bare and coupled to the corresponding dilution of hydrogen, carbon and nitrogen by the reactions $2\text{Cr}_7\text{C}_3 + 9\text{Cr} \rightarrow \text{Cr}_{23}\text{C}_6$, $2\text{CrN} + \text{Cr} \rightarrow \text{Cr}_3\text{N}_2$ and $\text{Cr}_2\text{H} + \text{Cr} \rightarrow \text{Cr}_3\text{H}$, respectively (cf. Table 1).

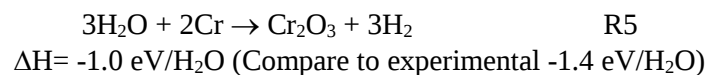
It is emphasized that the present study has only taken reaction enthalpies explicitly into account. Moreover, it is noted that the bare internal oxidation process will become increasingly more difficult at elevated temperatures owing to the entropy effect which counters the corresponding oxygen enrichment processes. Thus, temperature will increase the impact of the internal oxidation mechanism for ES SCC as the entropy loss owing to the dressing of the bare O enrichment is countered by the corresponding entropy gain resulting from dissolution of hydrides, carbides or nitrides, by e.g. $\text{Cr}_2\text{H} + \text{Cr} \rightarrow \text{Cr}_3\text{H}$, $2\text{M}_7\text{C}_3(\text{s}) + 9\text{M}(\text{s}) \rightarrow \text{M}_{23}\text{C}_6(\text{s})$ and $2\text{CrN} + \text{Cr} \rightarrow \text{Cr}_3\text{N}_2$, respectively.

4. On hydrogen pick-up during Ni(Fe,Cr) alloy oxidation by water

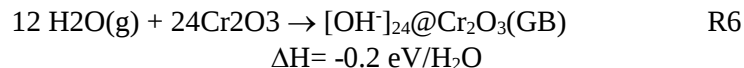
In the previous section, a viable mechanism for guiding a crack tip – involving dissolution and reprecipitation of carbides, nitrides or hydrides along the grain boundaries of a chromia forming alloy – was proposed and substantiated. Thus, carbides, nitrides and hydrides understood to suppress the outward diffusion of chromium also encourage inward diffusion of oxygen, i.e. consecutive dissolution-reprecipitation of the former facilitate inward migration of the latter. Scenarios that predict SCC owing to any carbon remnant from the alloy manufacturing process follow naturally. In order for hydrogen to reach the relevant activity to cause SCC, however, a viable mechanism for the hydrogen pick-up must exist allowing the environment inflicted sensitization. Consequently, the topic of the present study concerns possible oxidation assisted hydrogen permeation of the oxide scale taken to form on alloy 690. The alloy becomes oxidized by water-equivalents, effectively comprising hydroxide moieties diffusing along chromia grains interfaces, see Figure 1a. Clearly, in as much as all oxide formed during oxidation of the alloy must originate from water, to the same extent any hydrogen picked up by the alloy too must originate from water.

Possible oxidation of Cr by water while incorporating H in oxygen vacancies

First it is noted that chromium oxidation by water to form Cr_2O_3 is highly exothermic, and yet it is underestimated by GGA functional



This underestimation, however, is well understood as it originates from the self-interaction error of the GGA PBE functional. Cancellation of errors is achieved when electronically similar systems are compared. This applies as well to the hydroxylation of interfaces and grain-boundaries. It is gratifying to note that the formation of our generic hydroxylated grain boundary model comes out slightly exothermic, that is



Here, the hydroxylation energy also includes interface formation thus underestimating the hydroxylation energy of a pre-existing grain boundary. In as much as the dehydrated grain boundary model is designed to include a stacking fault, this defect *per se* offering a lower bound to the necessary water conveying grain boundaries, offsetting the hydroxylation enthalpy by the stacking fault formation energy the drive to maintain the grain boundary hydroxylated is captured.

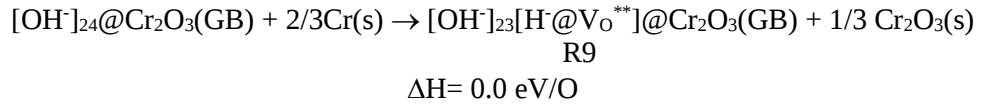


$$\Delta H = -1.1 \text{ eV/H}_2\text{O}$$

The further oxidation of Cr by water results from the hydration and dehydration of said stacking fault. Interestingly, while this favors the hydration of the grain boundary, it will render the further oxidation of Cr more difficult. Now we arrive at a central point of the present project. Indeed, upon subsequent oxidation of chromium by the hydroxylated grain boundary model, a necessary prerequisite for any hydrogen incorporation that could potentially support ES-SCC is to provide alternative means to deposit the resulting hydride ions, i.e., other than the hydrogen evolution reaction recombining H^- with H^+ to form H_2 . Incorporation of H^- transients in charged oxygen vacancies resulting from the oxidation process and forming $\text{H}^-@V_{\text{O}}^{**}$ would be such a possibility, i.e.



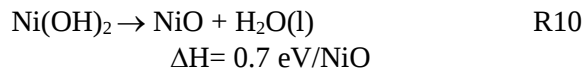
The relevance of this possibility was explored by quantifying the enthalpy change for the reaction



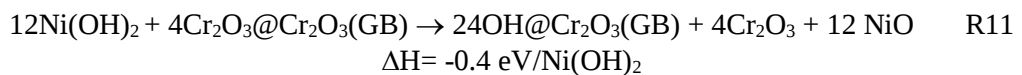
Taking again the underestimation of the GGA PBE oxide formation energy into account, after correction, a net drive of -0.4 eV/O is obtained. Having thus shown that it is indeed possible to incorporate hydrogen in the oxide as hydride ions, the next step would be to study how hydrogen accumulation at the alloy/oxide interface could take place, e.g. via build-up of and transport in hydride decorated oxide pores²¹.

Ni(OH)₂ – possible hydrating agent toward chromia grain boundaries

Having shown that water is able to hydrate the employed generic chromia grain boundary model and that the resulting hydroxylated grain boundaries are in turn able to oxidize chromium while incorporating hydrogen in oxygen vacancies, we may ask if Ni(OH)₂ may act as a hydrating agent toward chromia grain boundaries as well. From experiment we have



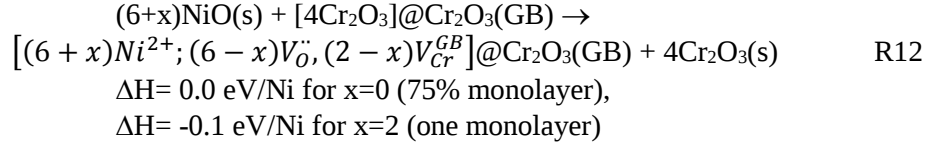
This implies that



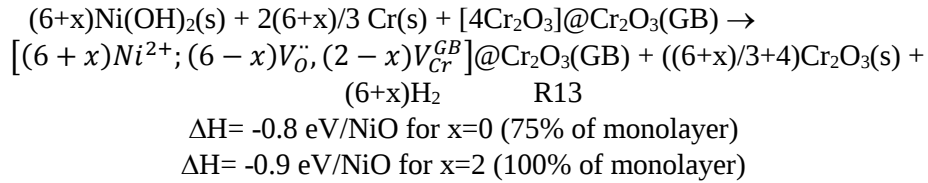
Thus, if formation of Ni(OH)₂ is spontaneous, then a viable channel for hydroxylation of the model chromia grain boundary would utilize Ni(OH)₂ as a water source. By virtue of R9, it follows that H uptake becomes again possible, and this time as a result of Cr oxidation by Ni(OH)₂.

Possible NiO decoration of Cr₂O₃ grain boundaries

While NiO indeed may act to convey water to the chromia grain boundaries adjacent to the oxide/metal interface, it may as a result also become incorporated in said grain boundary. Consider the marginal exothermic reaction



Thus, compatibility of Cr₂O₃ and NiO is arrived at, and indeed to the extent that the latter acquires enhanced stability. Still, it is concluded that were such NiO decoration to form spontaneously, then it must have been driven by the oxidation process itself, i.e. by employing water from the dehydration reaction $\text{Ni(OH)}_2 \rightarrow \text{NiO} + \text{H}_2\text{O}$, as oxygen carrier. Clearly, that net reaction comes out exothermic owing to the oxidation of Cr(s)



Active as well as passive oxygen vacancies for hydrogen in NiO decorated chromia grain boundaries

On general grounds, once NiO decorated chromia grain boundaries are formed, segregation into NiO precipitates and Cr₂O₃ grains is expected to ensue. This drive to minimize the interfaces between NiO and Cr₂O₃ implies that the $\text{NiO} + \text{H}_2\text{O} \rightarrow \text{Ni(OH)}_2$ mechanism may indeed be utilized as a viable water transport channel to the scale/alloy interface. Thus conveyed, water in the form of Ni(OH)₂, subsequently acts oxidant towards chromium while allowing formation of transient chromium oxy-hydroxy-hydride grain boundaries.

Having said this, it is noted that the NiO decorated chromia grain boundaries are highly defect rich, e.g. for every two Ni(II) there is one Vo^{**} to preserve charge neutrality. And while such oxygen vacancies are ubiquitous in the NiO decorated chromia grain boundaries, these are not accessible for accommodation of hydrogen. It is so because the Ni(II) associated Vo^{**} sites are unable to reduce H⁺ as this requires oxidation of two Ni(II) into Ni(III), which the crystal field is unable to support according to our calculations. The only way to produce neutral V_O sites is by utilizing grain boundary hydroxides, i.e. upon oxidizing Cr by hydroxide associated oxygen in the hydroxylated chromia grain boundaries, H⁺ can be accommodated in the resulting Vo site, thereby achieving the requested H⁺@Vo^{**}. Thus, it is implied that, in contrast to Ni(II), two nominal Cr(II) ions adjacent to a Vo^{**} are indeed able to reduce H⁺ to H⁻@Vo^{**} while converting into Cr(III). This too was validated by our calculations.

5. Summary and Conclusions

Relevant for the piping in light water nuclear reactors, an environment induced sensitization mechanism for stress corrosion cracking of Ni(Fe,Cr) alloys owing to water was articulated and substantiated by means of 1st principles modelling

The working hypothesis of the present study takes ES SCC to be owing to internal oxidation of chromium along alloy grain boundaries. This scenario implies random cracking to be repeatedly healed by outward diffusion of chromium to the crack tip, where sealing becomes subsequently achieved by chromia formation. The water chemistry including the impact of dissolved hydrogen in the reactor coolant, becomes decisive for oxide scale composition, its coherence as well as its adherence to the supporting alloy. The resulting passive layer is understood to control the effective permeability of the water equivalents, i.e., the oxidising agents, along oxide grain boundary interfaces from the water/oxide interface to the crack tip. In cases of limiting chromium mobility in the alloy grain boundaries, the sluggish outward diffusion of Cr risks being overtaken by the inward diffusion of oxygen. Impact of carbide, nitride or hydride precipitates along alloy grain boundaries was taken to have dual detrimental effect. Thus, the precipitates would render Cr locally enriched while also mitigating the Cr mobility along the oxygen activity gradient. Internal oxidation of stationary Cr rich precipitates would render the precipitating additives dissolved. The increased activity of the additives would in turn stabilize corresponding precipitates further away from the sensitization front possibly also intercepting any outward diffusing chromium. Thus, the internal oxidation driven dissolution-precipitation process has chromium carbides, nitrides or hydrides acting guides for the sensitization. Were this understanding to be valid then the ES SCC would fundamentally be owing to oxygen competing with carbon, nitrogen, or hydrogen for the chromium in the alloy. It would apparently be resolved by increasing the relative Cr content in the Ni(Fe,Cr) alloys.

This is how we understand the superior performance of Ni(Fe,Cr) alloys 690 and compared to e.g. alloy 600, and also the beneficial effects of the low-carbon alloys. However, employing water as oxygen carrier adds the possibility of chromium activity loss beyond the crack tip owing to formation of transient hydride precipitates. Indeed, while any carbon in the alloy would originate from the manufacturing process, hydrogen uptake would originate from the oxidation process. And while the carbon content would stay constant, the increasing hydrogen content in the alloy with time, in spite of a small pick-up fraction, would cause increased environment sensitization by supporting the oxidation process.

Hence, 1st principles electronic structure calculations by means of density functional theory was employed to

1. validate the central assumption that internal oxidation of chromium carbides, nitrides and hydrides resulting in corresponding dissolution of C, N, and H in the alloy, constitute spontaneous processes.
2. demonstrate a viable route for hydrogen to effectively permeate the mixed Cr₂O₃ and NiO/Ni(OH)₂ oxide scale to access an inner cathode, following hydrolysis and effective co-diffusion of protons and hydroxide ions.

In (2), the $\text{Cr}_2\text{O}_3/\text{NiO}/\text{Ni}(\text{OH})_2$ mix is experimentally observed and it is taken to reflect the non-equilibrium process of cracking. The viable steady-state mechanism validated in the present study involves

- a. water conveyed by the mixed oxide, being subject to hydrolysis according to $\text{NiO} + \text{H}_2\text{O} \rightarrow \text{Ni}(\text{OH})_2$;
- b. $\text{Ni}(\text{OH})_2(\text{s})$ as well as nickel hydroxide decorated chromia grain boundaries that effectively oxidize Cr to form Cr_2O_3 and NiO, or alternatively, $\text{Ni}(\text{OH})_2(\text{s})$ may first hydroxylate chromia grain boundaries, which in turn may again oxidize Cr to form Cr_2O_3 and NiO;
- c. crucially, the residual hydrogen may evolve as $\text{H}_2(\text{g})$ or become deposited in the chromia lattice as hydroxide ions and hydride ions, a fraction of which to be picked up in the alloy.

In conclusion, accelerated stress corrosion cracking of Ni(Fe,Cr) alloys under LWR conditions owing to environmental sensitization at late stages – as a consequence of hydrogen pick-up and subsequent transient hydrides formation beyond the crack tip rendering Cr mobility increasingly sluggish, and thus promoting internal oxidation sensitization towards stress corrosion cracking by guiding the crack tip – cannot be excluded.

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The Swedish Radiation Safety Authority has a comprehensive responsibility to ensure that society is safe from the effects of radiation. The Authority works from the effects of radiation. The Authority works to achieve radiation safety in a number of areas: nuclear power, medical care as well as commercial products and services. The Authority also works to achieve protection from natural radiation and to increase the level of radiation safety internationally.

The Swedish Radiation Safety Authority works proactively and preventively to protect people and the environment from the harmful effects of radiation, now and in the future. The Authority issues regulations and supervises compliance, while also supporting research, providing training and information, and issuing advice. Often, activities involving radiation require licences issued by the Authority. The Swedish Radiation Safety Authority maintains emergency preparedness around the clock with the aim of limiting the aftermath of radiation accidents and the unintentional spreading of radioactive substances. The Authority participates in international co-operation in order to promote radiation safety and finances projects aiming to raise the level of radiation safety in certain Eastern European countries.

The Authority reports to the Ministry of the Environment and has around 300 employees with competencies in the fields of engineering, natural and behavioral sciences, law, economics and communications. We have received quality, environmental and working environment certification.

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