Thermodynamic Study on the Surface of Nickel-base Alloys in Hydrogenated Water

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1. Introduction

Nickel-base alloys such as alloy 600 (Ni-16Cr-9Fe) are known to exhibit intergranular stress corrosion cracking (IGSCC) at pressurized water reactor (PWR) primary water environments, Primary water stress corrosion cracking (PWSCC) of alloy 600 and related 82 and 182 weld metal has become an increasing concern, because cracks and leaks have been discovered at numerous PWR pressure boundary and it has been a threat to the safety of nuclear reactor systems.

A number of past studies on PWSCC has shown that stress corrosion cracking growth rate (SCCGR) of nickel-base alloys in primary water is affected by dissolved hydrogen and exhibit a maximum susceptibility in the proximity of the nickel/nickel oxide (Ni/NiO) phase transition when the dissolved hydrogen concentrations($C_{aq,H2}$) is varied. From this point of view, it is reasonable to hypothesize the crack growth mechanism is affected by oxide stability on nickel-base alloys.

In this paper, thermodynamics of the oxide scale on pure nickel, which is the major alloying elements, is analyzed because a peak in the crack growth rate is near the electrochemical corrosion potential (ECP) of nickel/nickel-oxide phase equilibrium.

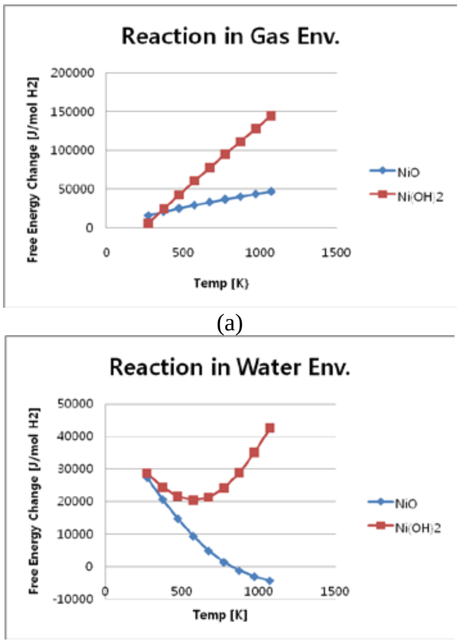
2. Thermodynamic modeling of nickel-base alloys surface

In thermodynamic modeling of nickel-base alloys, two different case of reaction can be considered. First one is the oxidation in high temperature steam environments (($Ni+H_2O(g) = NiO+H_2(g)$) and another one is the oxidation in water environments ($Ni+H_2O(l) = NiO+H_2(g)$). Due to the difficulty of experiments in high temperature and high pressure environments, lots of experimental studies on oxidation nickel or nickel-base alloys have been conducted by controlling the oxygen partial pressure instead of liquid water autoclave test. And it is believed that similar IGSCC behavior is observed between water test environments and steam test environments.

Thermodynamic equation ($Ni+H_2O$(gas or liquid) = $NiO+H_2(g)$) is used for modeling of the nickel and nickel oxide phase transition. As the Gibbs free energy change is zero at equilibrium, Nernst equation of Ni/NiO phase equilibrium can be expressed in Eq.(1). Hydrogen fugacity at equilibrium is determined when thermodynamic free energy of formation is determined.

$$\Delta G^0 = -RT\ln\frac{a_{NiO}a_{H_2}}{a_{Ni}a_{H_2O}} = -RT\ln f_{H_2} \qquad (1)$$

As the nickel hydro-oxide can be formed on nickel surface as well, thermodynamic equation ($Ni+2H_2O$(gas or liquid) = $Ni(OH)_2+H_2(g)$) is also considered as an possible surface reaction on nickel. As shown in Fig.1(a) and Fig.1(b), free energy in gas environments and water environments shows very different aspects and much attention should be paid on using thermodynamic data. Free energy change data in water environments is mainly used in this study.



(a)

Fig.1. Free energy change of nickel oxidation in gas environments (a) and water environments (b).

Capell conducted tests of nickel oxidation in a steam environments [1] and Attanasio and Morton performed contact electric resistance (CER) experiments in primary water environments [2]. In their research, theoretical prediction showed discrepancy with their experimentally determined data. To clarify the cause of this error, Henrys' law coefficient of hydrogen is developed using solubility data and new method was developed.

3. Determination of Henry's Law Coefficient

In this thermodynamic model, Henry's law coefficient (k_H) of hydrogen, the ratio of partial pressure of hydrogen in atmosphere to the aqueous hydrogen concentration, is identified as a key parameter that should be verified at temperature and pressure of interest to assure reliable results.

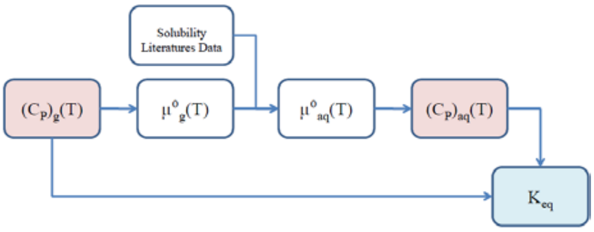


Fig.2. Flow chart to determine the equilibrium constant

Fig.2 shows the flow chart to determine the equilibrium constant of reaction, $(H_2)_g=(H_2)_{aq}$ to obtain the Henry's constant (See Eq.(2)). Detail procedure is explained in previous study.

$$(H_2)_g=(H_2)_{aq}, \quad K_{eq}=\frac{[\gamma\cdot c_{aq}]}{[\phi\cdot P_{H_2}]}=\frac{[H_2]_{aq}}{[H_2]_g}=\frac{1}{k_H}\left(\frac{\gamma}{\phi}\right) \qquad (2)$$

Developed Henry's constant, Eq.(3), is compared with other published correlation as shown in Fig.3 [3].

$$k_H=\frac{\exp\left[\begin{array}{l}110.554-\dfrac{4849.98}{T}+0.00553731\cdot T\\ -5.2428\times10^{-6}\cdot T^2\\ +3.27109\times10^{-9}\cdot T^3-9.00745\times10^{-13}\cdot T^4\end{array}\right]}{22390\cdot T^{15.5137}} \qquad (3)$$

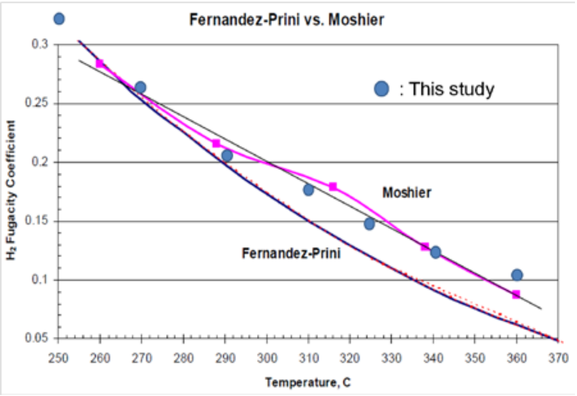


Fig.3. Comparison of Henry's constant with the Fernández-Prini's work.

4. Equilibrium dissolved hydrogen concentration for Ni/NiO phase transition

With the developed Henry's constant and the equilibrium fugacity which can be obtained from thermodynamic free energy data in water environments, equilibrium concentration of dissolved hydrogen in primary water to form the NiO and $Ni(OH)_2$ phase on nickel surface was determined as shown in Fig.4. The NiO equilibrium line shows a discrepancy with the equilibrium NiO line of Attanasio and Morton's contact electric resistance (CER) test.

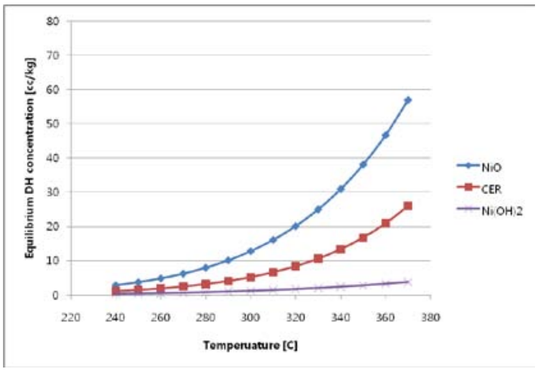


Fig.4. Calculated equilibrium dissolved hydrogen concentration and comparison with the Morton's equilibrium

. The discrepancy comes from the inaccuracy of thermodynamic data because most of the thermodynamic data at high temperature and high pressure was extrapolated from the experimentally observed data of low temperature range and atmosphere. However, the discrepancy between thermodynamic equilibrium line and CER experimental line is reduced by using the new Henry's constant and analyze the reaction including the notion of non-linear free energy change.

5. Conclusion

Thermodynamic data for free energy change is compared with the experimental free energy of formation equation and gives a confidence in using the data from HSC Chemistry®. Henry's law coefficient was developed and used to determine the equilibrium NiO and $Ni(OH)_2$ phase transition line. For a future work, ab-initio study is going on to explain the discrepancy between thermodynamic results and experimental results.

REFERENCES

[1] Capell, B.M. and G.S. Was, *Selective Internal Oxidation as a Mechanism for Intergranular Stress Corrosion Cracking of Ni-Cr-Fe Alloys.* Metallurgical and Materials Transactions A, 2007. **38**(6): p. 1244-1259.

[2] Attanasio, S.A. and D.S. Morton, *Measurement of the Nickel/Nickel Oxide Transition in Ni-Cr-Fe Alloys and Updated Data and Correlations to Quantify the Effect of Aqueous Hydrogen on Primary Water SCC.* Proc. 11th Int. Conf. Environmental Degradation of Materials in Nuclear Systems, Stevenson, WA, Aug. 10-14, 2003, 2003.

[3] Fernández-Prini, R., J.L. Alvarez, and A.H. Harvey, *Henry's constants and vapor-liquid distribution constants for gaseous solutes in H2O and D2O at high temperatures.* Journal of Physical and Chemical Reference Data, 2003. **32**(2): p. 903-916.