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Preliminary Observations of the
Thermodynamic Predictions of Fe-Cr-Ni
Alloys in Coal Gasifier Environments

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Abstract

The construction of thermodynamic stability diagrams for the Fe-Cr-Ni systems is discussed. The constructed diagrams are used to predict materials behavior at coal gasifier oxygen and sulfur potentials. Some preliminary experiments are run to compare predicted results with experimental observations. Powder mixtures of FeS, NiS, and Cr_2O_3 are used to observe the formation of the iron-chromia and nickel-chromia spinels at 871°C . Only the iron-chromia spinel was observed. No spinels were observed on 310 stainless steel samples exposed to the same environment.

Key words: thermodynamics, stability diagrams, spinels, Fe-Cr-Ni, corrosion

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As discussed previously¹, the construction of thermodynamic stability diagrams for the Fe-Cr-Al alloy systems is straightforward, given accurate and reliable thermodynamic data. The alloy system of interest, depending on the particular alloy composition, can be either an Al_2O_3 or a Cr_2O_3 former. Alloys that form protective Al_2O_3 or Cr_2O_3 layers generally show good corrosion resistance. This is particularly crucial in the construction and operation of coal gasifiers since the raw synthesis gas from a gasifier contains sufficient oxygen and sulfur to attack iron-base alloys at high temperatures¹.

In this brief report, the calculated diagrams for the Fe-Cr-Ni systems at 871°C and 982°C will be presented. This system is of practical interest because it forms the basis for the 300 series stainless steels. Some preliminary experimental observations will be presented and the results compared with the phases predicted by the diagrams.

The construction and use of stability diagrams is detailed elsewhere¹ and only those features which are peculiar to the Fe-Cr-Ni system will be discussed.

The most significant difference is that at both 871°C and 982°C, the nickel sulfides are liquid. The formation of a liquid phase is of concern because it can severely affect the adherence of a protective Cr_2O_3 scale. It is also of concern in the construction of the stability diagrams. Sufficient nickel may be dissolved in the liquid nickel sulfide phase to make the phase non-stoichiometric. This makes the calculation of the dissociation pressure of the sulfide inexact. Data have been taken from Rosenqvist² and are a direct measure of the vapor pressure of sulfur over liquid nickel sulfide. Such data are unrelated to the stoichiometry of the sulfide so the equilibrium between NiO and $\text{NiS}(\ell)$ remains inexact. This implies that the slope of the line dividing the two phases (see Figures 1

and 2) is imprecise and is drawn assuming a reaction of the form

Two spinels, FeCr_2O_4 and NiCr_2O_4 are of interest in this system. Oxides of iron higher than FeO have not been considered so the nickel-iron spinel, NiFe_2O_4 , also is not considered.

The Gibbs free energy data were obtained from a variety of sources, shown in Table 1. Data for FeCr_2O_4 were taken from Jacob³ and for NiCr_2O_4 from Tretjakow *et al*⁴. Other values were compiled as required⁵⁻⁸.

Figures 1 and 2 represent the completed diagrams for the Fe-Cr-Ni system at 871°C and 982°C. These temperatures represent the mean and maximum operating temperatures of coal gasifiers. The rectangle in the center of each diagram represents the P_{O_2} and P_{S_2} ranges for coal gasifiers and the "x" in the center of the rectangle represents the values of P_{O_2} and P_{S_2} at which experimental data were taken. These regions are of practical interest and have been enlarged in Figure 4.

At high values of P_{O_2} five phases are possible: FeO , NiO , Cr_2O_3 , FeCr_2O_4 , and NiCr_2O_4 . From stoichiometric considerations a maximum of three phases can coexist. This is illustrated in Figure 3 and has been explained previously¹.

In these diagrams the metal activities are taken to be unity. The effect of decreasing the metal activity is to stabilize the alloy with respect to oxidation and sulfidation, but it is a small effect^{1, 9}.

At the test conditions the predicted product phases from Figures 1, 2 and 3b are $\text{NiS}(\ell)$, FeCr_2O_4 , and Cr_2O_3 . This assumes that there is sufficient chromium present to permit the formation of a protective Cr_2O_3 scale.

Two alloys from the Fe-Cr-Ni system were used - a commercial 310

stainless steel and a laboratory-melted pure 310 stainless steel. Both are Fe-25Cr-20Ni steels. The commercial samples contained about 2% manganese and 1.5% silicon while the pure 310 did not.

Powder mixtures of 60 wt % FeS + 40 wt % Cr₂O₃ and 60 wt % NiS + 40 wt % Cr₂O₃ were selected to determine whether the spinels can form in a gas having the oxygen and sulfur potentials of a coal gasifier according to the reactions

The furnace operating conditions have been described previously¹. These preliminary observations are confined to exposures at 871°C.

X-ray diffraction of the powder mixtures showed no evidence of NiCr₂O₄ formation but did show considerable FeCr₂O₄. The formation of FeCr₂O₄ was also observed at 982°C. Both of the 310 stainless steels showed only the formation of a thin, adherent Cr₂O₃ layer.

The diagrams do accurately predict that under the experimental conditions, NiCr₂O₄ will not be formed according to equation 3 and the FeCr₂O₄ will be formed according to equation 2.

The alloys developed only Cr₂O₃ scales and did not form spinels. Because they contain sufficient chromium to form protective oxide scales, sulfur must migrate through the oxide to form either FeS or NiS. Once the sulfur gets through the scale, it should react to form the more stable chromium-rich sulfides (see Figures 1 and 2) at the scale-alloy interface. Chromium may therefore serve as a getter for sulfur and longer exposures may be required to form FeCr₂O₄ via equation 2.

Since NiS is stable with respect to the formation of NiCr₂O₄, it was

expected and observed that no spinel would form in the powder mixtures. It is possible that at higher oxygen partial pressures, the spinel could form under the same constraints as the formation of the FeCr_2O_4 spinel. Further experiments will be done to test this hypothesis.

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TABLE 1

PHASE	ΔG_{871}^0 (Kcal/mole)	ΔG_{982}^0 (Kcal/mole)	Ref.
CrS	- 28.5	- 26.9	5
Cr ₂ S ₃	- 77.2	- 72.4	5
Cr ₂ O ₃	-198.1	-191.5	6
FeO	- 45.4	- 43.6	7
FeS	- 21.4	- 20.0	7
NiO	- 33.0	- 30.8	8
NiS(l)	log P _{S₂} = -8.11	log P _{S₂} = -7.13	2
FeCr ₂ O ₄	-253.9	-245.4	3
NiCr ₂ O ₄	-257.1	-228.3	4

Figure 1. Thermodynamic stability diagram for the Fe-Cr-Ni system represented at 871°C (1600°F). The arrows indicate P_{O_2} and P_{S_2} lines at which the specific phase becomes stable. Where arrows overlap, the indicated oxide or sulfide phases are simultaneously stable. For instance, at $P_{O_2} = 10^{-20}$ and $P_{S_2} = 10^{-12}$ atmosphere, the stable phases are $FeCr_2O_4$, Cr_2O_3 , and Ni. The rectangular region indicates P_{O_2} and P_{S_2} ranges of typical coal gasifiers corrected for temperature. All metal activities are taken to be equal to 1.

KEY: _____ phase boundaries involving Fe.
 ----- phase boundaries involving Ni.
 _____ Phase boundaries involving only Cr.

XBL78I-4446

Fig. 1

Figure 2. Thermodynamic stability diagram for the Fe-Cr-Ni system represented at 982° (1800°F). The arrows indicate P_{O_2} and P_{S_2} lines at which the specific oxide or sulfide becomes stable. The rectangular region indicates P_{O_2} and P_{S_2} ranges of typical coal gasifiers corrected for temperature. All metal activities are taken to be equal to 1.

Key: ————— phase boundaries involving Fe.
----- phase boundaries involving Ni.
————— phase boundaries involving only Cr.

XBL 781-4447

Fig. 2

Figure 3.

Triangular diagrams showing how the stoichiometry determines which phases are actually present when the stability diagram indicates that more than 3 phases are possible. The scales represent compositions on a per gram-atom of metal basis. A point within a region on the diagrams indicates a mixture of the three phases at the corners of the region. A point on a line indicates a mixture of the two phases at the ends of the line.

- a) This figure applies to the regions of the diagram where NiO (or NiS) is stable, where the stability diagram predicts five phases are possible.
- b) This figure applies to the region of the diagram where Ni (or NiS) is stable, where the stability diagram predicts four phases were possible.
- c) This figure applies to the region of the diagram where Ni (or NiS) and Fe (or FeS) are stable, where the stability diagram predicts three phases are possible.

XBL 781-4444

Fig. 3

Figure 4. This represents the rectangular region from Figures 1 and 2: the P_{S_2} and P_{O_2} ranges in which typical coal gasifiers operate. Note that although the temperature shift changes the P_{O_2} range by two orders of magnitude and the P_{S_2} range by one order of magnitude, the shift of the phase boundaries relative to the enclosed rectangle is much less than that.

a) Fe-Cr-Ni system at 871°C.

b) Fe-Cr-Ni system at 982°C.

XBL 78I-4445

Fig. 4

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