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Thermodynamic Predictions of the Behavior of Fe-Cr-Al
Alloys in Coal Gasifier Environments

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Abstract

The construction of thermodynamic stability diagrams for the Fe-Cr-Al system is discussed. The constructed diagrams are used to predict materials behavior at coal gasifier oxygen and sulfur potentials. Experiments are run to compare predicted results with experimental observations. Powder mixtures of FeS, Cr₂O₃, and Al₂O₃ are used to observe the formation of the iron-chromia and iron-alumina spinels. The spinels are observed at both 871° and 982°C. The formation of an alumina spinel is observed only on the Fe-10Al alloy whereas no iron-chromia spinel is found on the Fe-Al-Cr alloys.

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INTRODUCTION

One critical problem in the production of synthetic natural gas (SNG) from coal is the development of non-corrosive alloys for gasifier internal components. Since these components must operate in high pressure (1000-1500 psig) and high temperature (700-1000°C) environments, the materials selected must have good resistance to corrosion as well as erosion from solid particle impingement. The environment in a gasifier consists of a reactive gas mixture containing hydrogen, water, carbon dioxide, carbon monoxide, methane, and hydrogen sulfide (see Table 1). As a result, formation of oxide and sulfide scales on the surfaces of the gasifier internals can be anticipated. Since the operating temperatures are high, some of the sulfide scales, particularly those containing high concentrations of nickel, may be liquid. This will presumably hamper the adherence of any protective oxide scale. The major solid reactant in the gasification process is coal char, so gasifier materials should be capable of withstanding high temperature erosion.

Prediction of the corrosion scales formed under specified coal gasification environments is a necessary initial stage in the design of effective corrosion tests. The thermodynamic stability diagram is a graphical model which has been used by several investigators for such predictions.^(1,2) The diagram depicts, for a given temperature, the phases formed as a function of gas phase partial pressures. For a coal gasifier the major active corroding species are oxygen and sulfur. The ordinate of the stability diagram is the log of the

sulfur partial pressure and the abscissa is the log of the oxygen partial pressure.

In this work, the stability diagrams for the Fe-Cr-Al ternary will be presented. This alloy system is of interest because it offers a promising combination of corrosion resistance and high temperature strength.

The calculated diagrams for the various systems at 871°C (1600°F) and 982°C (1800°F) will be presented. These temperatures represent the mean and maximum expected operating temperatures for commercial gasifiers. The diagrams predictive value for conditions prevalent in typical coal-gasification systems will be discussed. Experimental results will be presented, and the observed product phases compared with those predicted by the diagrams.

STABILITY DIAGRAMS FOR THE Fe-Cr-Al SYSTEM

The thermodynamic stability diagram is a plot of the thermodynamically stable phases as a function of gas composition. The primary requisite in constructing such a diagram is having reliable and consistent thermodynamic data. For simple oxides and sulfides such as Al_2O_3 and FeS such thermodynamic data are available in the JANAF tables.⁽³⁾ For complex phases such as FeCr_2O_4 and FeAl_2O_4 , the data have been taken from Jacob⁽⁴⁾ and Chan et al.⁽⁵⁾ Although the existence of several chromium sulfides is reported only CrS and Cr_2S_3 , whose existence and stabilities are well-documented, were used.⁽⁶⁾ Other isolated values were compiled as required⁽⁷⁻⁸⁾ (see Table 2).

In a thermodynamic stability diagram, the vertical axis represents the sulfur partial pressure (P_{S_2}) and the horizontal axis the oxygen partial pressure (P_{O_2}) . A vertical line in the diagram represents metal-oxide or oxide-oxide equilibria and a horizontal line represents metal-sulfide or sulfide-sulfide equilibria. Lines representing equilibria between phases containing oxygen and/or sulfur will have a slope between zero and infinity in these diagrams.

For example, in Figure 1 the Fe-Cr-Al system is represented at 871°C. If the sulfur potential is 10^{-16} , no sulfide is stable and one can consider what happens as the oxygen potential is varied. If the P_{O_2} is less than 10^{-26} , only Al_2O_3 is stable. If the P_{O_2} is above $10^{-25.2}$, Cr_2O_3 is also thermodynamically stable. Above $10^{-21.3}$, $FeCr_2O_4$ becomes stable. As the oxygen potential continues to increase, the system moves into regions where $FeAl_2O_4$ and FeO become stable. In these diagrams the formation of iron oxides higher than FeO have not been considered.

Now consider what happens with increasing P_{S_2} . If the P_{O_2} is 10^{-41} and the P_{S_2} is allowed to vary, the alloy is stable until the P_{S_2} is about $10^{-15.4}$, where Al_2S_3 becomes a stable phase. As the P_{S_2} increases, CrS becomes stable above $10^{-10.8}$, FeS is stable above $10^{-8.2}$ and Cr_2S_3 replaces CrS above $10^{-7.7}$.

The free energies of formation of $FeAl_2O_4$ and $FeCr_2O_4$ have been obtained from Jacob and Alcock⁽⁴⁾ and Chan et al.⁽⁵⁾ The specific reactions are:

At high values of P_{O_2} five phases can exist: FeO , FeAl_2O_4 , FeCr_2O_4 , Cr_2O_3 , and Al_2O_3 (see Figures 1 and 2). Figure 3 illustrates from stoichiometric considerations that a maximum of three phases can coexist since two of the five possible phases are combinations of the other three. In a region where all five phases are possible, Figure 3a shows that if there is a stoichiometric excess of FeO (or FeS), then the only phases that will coexist will be FeO (or FeS), FeAl_2O_4 , and FeCr_2O_4 . If there is not enough iron, then the phases may be Al_2O_3 , FeAl_2O_4 , and FeCr_2O_4 . However, if there is an excess of chromium, then FeCr_2O_4 , Al_2O_3 , and Cr_2O_3 will be the only phases possible. As P_{O_2} decreases into a region where FeAl_2O_4 is not stable, then Figure 3b will apply. Here Fe and Cr_2O_3 cannot coexist, and which one is present depends on whether there is an excess of iron or chromium. If the P_{O_2} continues to decrease into a region where neither FeAl_2O_4 nor FeCr_2O_4 is stable, then Figure 3c will apply. This is merely a non-interacting mixture of the stable forms of the three metals.

The Fe-Cr-Al system is of practical interest because Al_2O_3 is quite stable (see Figures 1 and 2). It is a rapidly growing, low-defect structure scale. Alloys which form stable Al_2O_3 layers generally exhibit good corrosion resistance. Cr_2O_3 layers also exhibit good corrosion resistance but as shown in Figures 1 and 2, Cr_2O_3 does not have as negative a free energy as Al_2O_3 . This is reflected in the fact that Al_2O_3 is formed at a much lower P_{O_2} than Cr_2O_3 . However, FeCr_2O_4 forms at a lower P_{O_2} than FeAl_2O_4 .

The effect of metal activity on the structure of the diagram is indicated in Figure 4 wherein the Fe-Cr-Al system is presented at 982°C for an iron activity of 0.1. Note that the overall effect is to stabilize the alloy with respect to oxidation and sulfidation. It is a small effect, and as yet has not been correlated with experiment. (1)

PREDICTED PRODUCT PHASES

Typical coal gasifier gas compositions are presented in Table 1. There are large amounts of CO , CO_2 , H_2O , and H_2S . (9) Thermodynamically these imply a range of P_{O_2} 's and P_{S_2} 's. At 982°C, the P_{O_2} ranges from 10^{-14} to 10^{-16} atmosphere and the P_{S_2} from 10^{-4} to 10^{-8} atmosphere. At 871°C, the range for the P_{O_2} is 10^{-16} to 10^{-18} atmosphere and for the P_{S_2} from 10^{-5} to 10^{-9} atmosphere. These regions are included as the rectangular regions in Figures 1 and 2, and an expanded picture of these is shown in Figure 5. The "x" in the center of each rectangular region is the experimental value of P_{O_2} and P_{S_2} .

at which the samples were exposed. From Figures 1, 2, and 3a, the predicted phases are (assuming sufficient Al to form an Al_2O_3 phase) FeAl_2O_4 , FeCr_2O_4 and Al_2O_3 . This should hold at both 871°C and 982°C but it should be noted that at 871°C, the experimental conditions are very close to the FeAl_2O_4 - FeCr_2O_4 border. Experimental deviations in the gas-phase partial pressures may move the system into a region where FeCr_2O_4 is the only stable spinel.

EXPERIMENTAL

Alloys from the Fe-Cr-Al system selected for the corrosion studies are listed in Table 3. All alloys are expected to develop Al_2O_3 barrier scales in oxidizing environments.

Powder mixtures of 60 wt.% FeS + 40 wt.% Cr_2O_3 and 60 wt.% FeS + 40 wt.% Al_2O_3 were also selected to find out whether the oxide spinels can form in a gas having the oxygen and sulfur potentials of a coal gasifier according to reactions (5) and (6).

A vertical tube corrosion furnace 91.5 cm long 6.5 cm I.D. was used to carry out the experiments. The specimens, hung individually on the hooks of an Al_2O_3 holder, were loaded from the top into the middle of the constant temperature zone. The gases were introduced into the furnace from the bottom to insure thermal equilibration prior to reaching the suspended specimens. This avoided any thermal segregation of gases. The gas flow rate was 500 cm^3/min . The furnace bottom was filled with high purity porous Al_2O_3 beads up to the constant temperature zone. The gas mixture of argon, H_2 , H_2S , and

H_2O was allowed to permeate through the porous Al_2O_3 bed, thus ensuring complete mixing and heating.

All the specimens, approximately $1\text{ cm} \times 1\text{ cm} \times 0.1\text{ cm}$, were ground to 600 grit with silicon carbide paper and cleaned with alcohol and acetone. Holes were drilled in the specimens and they were suspended from the holder using Kanthal wires. The powders were prepared by mixing and grinding high purity powders. Then a few grams of the powder mixtures were placed in high purity alumina crucibles and were suspended at the bottom of the specimen tree. The specimen tree was put into the furnace and the system flushed with argon for 30 minutes before changing over to the corrosive gas.

A pre-mixed H_2S/H_2 gas containing 2% H_2S was used to insure a constant P_{S_2} in the gas mixture. Water vapor was introduced by bubbling pre-determined amounts of argon through a pair of water bubblers. To insure 100% saturation, the temperature of the first bubbler was maintained at a lower temperature than the second bubbler. The temperature of the second bubbler was accurately controlled to within $\pm 0.1^\circ C$. Heated gas lines (maintained at over $200^\circ C$) were used to prevent the condensation of the moisture. The argon saturated with H_2O and the H_2/H_2S mixture were combined beyond the water saturation bubblers and before entering the furnace. The gas flow was controlled and monitored using individual rotameters. The H_2O content was adjusted to give a P_{O_2} of 10^{-15} atmosphere and P_{S_2} of 10^{-6} atmosphere at $982^\circ C$. The same gas mixture was used at $871^\circ C$. The P_{O_2} was 10^{-17} atmosphere and P_{S_2} was 5×10^{-7} atmosphere at the lower temperature.

At the end of 48 hours, the reactive gas flow was discontinued, the system was flushed with argon for 30 minutes and the specimen holder was removed within one minute. The reacted specimens and powder mixtures were then examined by X-ray diffraction techniques to identify the reaction products.

RESULTS

The reacted powder mixtures showed the presence of spinels at both temperatures. At 982°C, the chromia and alumina spinels were detected in large amounts while at 871°C, only the chromia spinel was detected in large amounts although both were present. No quantitative estimation was performed to determine the percent conversion.

Following exposure, all alloys were examined for the presence of spinels. Only the Fe-10Al alloy showed the presence of any spinel, in this case FeAl_2O_4 . All of the other alloys showed only the presence of Al_2O_3 scales. These scales were all thin, uniform, and adherent whereas the alumina spinel was quite thick. It is interesting to note that the addition of chromium to the Fe-10Al alloy improved the corrosion resistance.

DISCUSSION

Based on the stability diagram, the gas mixtures were selected such that only the oxide spinels would be stable with respect to FeS at both temperatures. The implication was that if FeS could form it would do so beneath a protective oxide layer where the P_{O_2} would

be much lower than on the surface of the oxide. This would prevent channels of FeS from connecting the alloy to the external environment through the protective oxide. This would prevent rapid diffusion of sulfur through FeS channels. Although the oxide spinels may not be as protective as Al_2O_3 or Cr_2O_3 , they should be more protective than FeS. Furthermore, if at a different set of conditions, an initially formed protective oxide fails, there could be a stage of rapid corrosion if FeS is stable on the surface.

The results of the powder experiments clearly demonstrate that both the chromia and alumina spinels can form at 982°C and 871°C as predicted by the stability diagrams. The chromia spinel forms abundantly at both temperatures while the alumina spinel forms abundantly only at the higher temperature. This probably indicates that the formation of the chromia spinel is kinetically more favorable. This may be involved with the observation that additions of Cr to the alumina-forming alloys improves the corrosion resistance.

The alloys developed only thin Al_2O_3 scales and did not form spinels with the exception of the Fe-10Al alloy. These alloys contain sufficient Al and Cr to form protective oxide scales. Once the protective oxide is formed, sulfur has to diffuse through the oxide layer to form FeS. Before this can occur, the diffusing sulfur has to react to form the more stable Al- or Cr-rich sulfides in the alloy matrix (see Figures 1 and 2) which depletes the alloy of both Al and/or Cr, permitting formation of FeS. This involves the kinetics of formation of the sulfides and long exposures may be required to form FeS. If the formation of FeS is a

prerequisite for the formation of the spinels through equations 5 and 6, then it is possible that this explains why spinels were only observed on the Fe-10Al alloy. Perhaps the formation of the spinels from FeO or Fe is much slower than the formation of the spinels from FeS and the chromium containing alloys have too much Al and Cr to permit the formation of FeS. In the Fe-10Al alloy, which formed the spinel at both temperatures, the specimens probably form an Al_2O_3 scale initially. This results in Al depletion just beneath the oxide. As a result, FeS forms readily in the matrix since there is insufficient Al and no Cr in the alloy to getter the sulfur by formation of Al- or Cr-rich sulfides. The formation of FeS ruptures the Al_2O_3 scale, exposing fresh alloy for corrosion. At this juncture, FeS and Al_2O_3 could react to form the spinel. The continuous formation of FeS leads to more spinel formation and depletion of Al from the alloy. As the alloy loses most of the aluminum, the formation of either Al_2O_3 or the spinel ceases and the alloy is subject to catastrophic sulfidation.

CONCLUSION

The stability diagrams presented here predict the formation of iron-alumina and iron-chromia spinels. Experimental observations of spinel formation in $\text{FeS}/\text{Al}_2\text{O}_3$ and $\text{FeS}/\text{Cr}_2\text{O}_3$ powder mixtures confirm the existence and formation of these spinels. The relatively greater stability of the iron-chromia spinel as compared to the iron-alumina spinel is predicted by the diagrams.

The fact that no spinels are observed on any of the Cr-containing alloys could result from FeS being a necessary precursor for the rapid formation of the spinels. The presence of Cr may hinder the formation of FeS by serving as a getter for sulfur. The observed improved corrosion resistance of the ternary alloys over the Fe-10Al binary is the result of chromium additions.

Such thermodynamic techniques will be useful in predicting alloy behavior in aggressive environments.

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Table 1. Ranges of component concentrations in coal gasifiers operating between 871°C and 982°C (1600°F-1800°F) (9).

Component	Range (mole %)
H ₂	15-50
H ₂ O	15-40
CO ₂	4-20
CO	5-15
CH ₄	8-20
H ₂ S	0.03-1.0

Table 2. Free energies of formations of relevant compounds used in calculating the stability diagrams.

Phase	$\Delta G_{871^\circ\text{C}}^f$ (Kcal/mole)	$\Delta G_{982^\circ\text{C}}^f$ (Kcal/mole)	Ref.
CrS	-28.5	-26.9	6
Cr ₂ S ₃	-77.2	-72.4	6
Cr ₂ O ₃	-198.1	-191.5	7
FeO	-45.4	-43.6	3
FeS	-21.4	-20.0	3
Al ₂ O ₃	-314.0	-305.2	3
Al ₂ S ₃	-121.2	-113.1	8
FeCr ₂ O ₄	-253.9	-245.4	4
FeAl ₂ O ₄	-365.2	-354.5	5

Table 3. Alloys selected for corrosion experiments.

(1)	Fe - 10Al
(2)	Fe - 10Al - 5Cr
(3)	Fe - 10Al - 10Cr
(4)	Fe - 10Al - 15Cr
(5)	Fe - 18Cr - 5Al
(6)	Fe - 18Cr - 7Al

Figure 1. Thermodynamic stability diagram for the Fe-Cr-Al 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 $P_{S_2} = 10^{-12}$, the stable phases are $FeCr_2O_4$, Cr_2O_3 , and Al_2O_3 . The rectangular region indicates P_{O_2} and P_{S_2} ranges of typical coal gasifiers corrected for temperature.

Key: — — — — — phase boundaries involving only Fe
 ----- phase boundaries involving Al
 ————— phase boundaries involving Cr

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Figure 2. Thermodynamic stability diagram for the Fe-Cr-Al system represented at 982°C (1800°F). The arrows indicate P_{O_2} and P_{S_2} lines at which the specific oxide or sulfide phase becomes stable. The rectangular region indicates P_{O_2} and P_{S_2} ranges of typical coal gasifiers corrected for temperature.

Key: — — — — phase boundaries involving only Fe
----- phase boundaries involving Al
————— phase boundaries involving Cr

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Figure 3 (a). Triangular diagram showing how the stoichiometry determines which phases are actually present when the stability diagram indicates that five phases are possible. The scales are intended to represent atomic percent of the metals on an oxygen-free and sulfur-free basis. A point within a region on the diagram 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. As drawn, this figure applies to the right side of the stability diagram. It could represent the other two regions where five phases are possible if FeO is replaced by either Fe or FeS .

Figure 3 (b). Triangular diagram showing how the stoichiometry determines which phases are actually present when the stability diagram indicates that four phases are possible. As drawn, this figure applies to the bottom of the stability diagram in a region where FeAl_2O_4 is no longer stable. For a similar region toward the top of the stability diagram, this figure applies with Fe replaced by FeS .

Figure 3 (c). Triangular diagram showing how the stoichiometry determines which phases are actually present when the stability diagram indicates that three phases are possible. As drawn, this figure applies to the bottom of the diagram in a region where FeCr_2O_4 is no longer stable.

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Figure 4. Thermodynamic stability diagram for the Fe-Cr-Al system represented at 982°C (1800°F) for an iron activity $a_{\text{Fe}} = 0.1$. Note that the effect of decreasing activity is to stabilize the pure metal with respect to oxidation and sulfidation.

Key: — — — — phase equilibria involving only Fe
----- phase equilibria involving Al
————— phase equilibria involving Cr

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Figure 5. 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} by one order of magnitude,

the shift of the phase boundaries relative to the enclosed rectangle is much less than that.

a) Fe-Cr-Al system at 871°C.

b) Fe-Cr-Al system at 982°C.

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