

The Kinetics of the Nitrogen Reaction with Liquid Iron-Chromium Alloys

P. C. GLAWS and R. J. FRUEHAN

The isotope exchange technique was employed to study the interfacial reaction kinetics of nitrogen with liquid iron-chromium and iron-chromium-sulfur solutions. Chromium was found to increase the rate of the nitrogen exchange reaction. The increase in the rate occurs, at least in part, through promotion of N_2 dissociation on the chromium surface sites. Although mass transport effects in the liquid are eliminated through the use of the isotope exchange technique, it was found that a correction for gas phase mass transfer was required for the determination of the interfacial reaction rate constant due to the faster exchange rates encountered in liquid iron solutions containing chromium.

I. INTRODUCTION

THE advent of the use of nitrogen gas as an inexpensive alternative for argon in the AOD stainless steelmaking process has led to a renewed interest in the kinetics of the absorption and desorption of nitrogen in liquid iron alloys, especially those containing chromium. Nitrogen gas can be used in place of argon in the early stages of the AOD refining process. Although nitrogen is absorbed into the melt, it is flushed out in the later stages when argon is used. In order to optimize the use of nitrogen in this process, an understanding of the kinetics of the nitrogen reaction with liquid iron-chromium alloy is important.

In the early 1960's, Pehlke and Elliott¹ used a constant pressure Sieverts' apparatus to investigate the rate of nitrogen absorption into liquid Fe-Cr solutions. Later, Inouye and Choh² employed a sampling technique to study the nitrogen reaction kinetics with these alloys. In both of these studies, the rate of nitrogen absorption was controlled by liquid phase mass transport and chromium was found to have no significant effect on the mass transfer coefficient.

Recently, Fruehan and Martonik³ measured the rate of nitrogen dissolution into liquid Fe-Cr alloys containing varying concentrations of sulfur using a constant volume Sieverts' technique. They established that chromium dramatically increased the rate of nitrogen absorption into Fe-Cr-S solutions. However, except in cases of high sulfur activity in the melt when the chemical reaction rate is slow, accurate determinations of the interfacial reaction rates were not possible due to the large influence of liquid phase mass transfer on the measured absorption rate. Accordingly, no definitive mechanism by which Cr affects the chemical reaction rate could be provided.

In those investigations employing traditional experimental techniques the rate of nitrogen absorption into Fe-Cr alloys is often controlled by mass transfer in the melt. When this is the case, the measured rate constant would be dependent on chromium content only if chromium severely reduced the rate of the chemical reaction at the surface or had a significant influence on the diffusion of nitrogen

through the iron alloy melt. Any increase in the interfacial reaction rate due to the presence of chromium would not appear in the measured rate constant for these types of experiments.

To avoid the problem of the interfacial reaction rate being affected by liquid phase mass transfer, Byrne and Belton⁴ employed the isotope exchange technique in their study of the kinetics of nitrogen reaction with liquid Fe and Fe-S solutions. This technique permits experimental determination of the rate of N_2 dissociation on the liquid metal surface *via* measurement of the rate of the exchange reaction:



The experiment is run under the condition of equilibrium between the gas at the interface, the liquid surface, and liquid bulk phases. This eliminates any liquid phase mass transfer restrictions, thus permitting measurement of chemical reaction rates that would normally be considered too fast for conventional kinetic experimental techniques involving inductively-stirred melts. Although the isotope exchange rate measurements are independent of mass transfer processes in the liquid, it can not be assumed that these rates are not influenced by mass transport in the gas phase.

By comparing their isotope exchange results on liquid Fe-S alloys with data from studies using a sampling technique² and the modified Sieverts' technique⁵ in the range where the rates were accurate and controlled by chemical kinetics, Byrne and Belton demonstrated that the rates of N_2 dissociation and nitrogen absorption agree within experimental error. Later, Glaws and Fruehan⁶ used both the modified Sieverts' technique and an improved isotope exchange technique in the same experimental apparatus to verify that N_2 dissociation is the rate limiting elementary step in the intrinsic chemical reaction mechanism. This provides strong evidence that the dissociation of the N_2 molecule is the rate limiting step in the intrinsic chemical kinetics of nitrogen absorption into liquid Fe-S alloys.

The intent of this study was to investigate the kinetics of the nitrogen reaction with liquid iron-chromium solutions. Through the use of the isotope exchange technique, the faster nitrogen reaction rates encountered in these alloys could be measured in the absence of any liquid phase mass transport effects. An equation correcting for gas phase mass transfer effects was developed and employed for determination of the interfacial reaction rate constant. In addition, an investigation of the nitrogen isotope exchange rates

P. C. GLAWS, formerly with the Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, Pittsburgh, PA, is with the Department of Metallurgy, New South Wales, Australia. R. J. FRUEHAN is a Professor with the Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, Pittsburgh, PA 15213.

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with Fe-Cr of negligible sulfur content was carried out to provide some insight into the mechanism by which chromium enhances the interfacial reaction rate.

II. EXPERIMENTAL

In the present study, the isotope exchange technique was employed to investigate the kinetics of the nitrogen reaction with liquid Fe-Cr and Fe-Cr-S solutions. The experimental apparatus and technique has been described in detail previously.⁶ Briefly, metal samples, made from high purity vacuum processed iron, iron-chromium, and iron-chromium-sulfur master alloys, were contained in a double crucible arrangement. The inner crucible was high density, high purity (99.8 pct) alumina with 20 mm I.D. and 33 mm height. The outer safety crucible was slip cast lime-stabilized zirconia with approximately 25 mm I.D. and 50 mm height. The crucible-held sample, weighing approximately 25 grams, was placed in a fused silica reaction chamber and carefully induction heated to 1600 °C. Sample temperature was monitored by a two-color ratio pyrometer, sighted onto the metal surface. The pyrometer was calibrated against the melting temperature of pure iron. Any necessary temperature adjustments were made manually *via* the powder controls on the R. F. generator. The desired metal surface temperatures were maintained within ± 5 °C.

During heat-up, a N₂-H₂-H₂S gas mixture was passed over the sample at a combined flow rate of approximately 200 ml/min STP. Hydrogen was used to suppress the effects of the few ppm of oxygen in the isotopically labeled gas, which could not be purified by normal O₂ gettering techniques without some isotope exchange occurring. The H₂-H₂S gas, comprising about 15 pct of the total gas mixture, was adjusted to maintain the desired sulfur activity in the sample. Once the liquid metal temperature had reached the desired level and was stable, the standard nitrogen gas, present in the flowing gas mixture, was replaced by the labeled nitrogen gas, containing a concentrated level of the isotope ³⁰N₂ (~1 at. pct). The isotopically labeled nitrogen gas was jetted onto the surface of the liquid metal for a sufficient time to allow for equilibrium between the gas at the interface and the liquid metal surface and bulk phases to be achieved. Continuous gas analysis was possible through the use of an in-line UTI 100C Precision Mass Analyzer interfaced with the UTI Peak Programmable Selector, a microprocessor unit that permits nearly simultaneous data collection from as many as nine different channels (amu peaks). As a check on the resolution and alignment of the mass spectrometer, four amu peaks were monitored during each isotope exchange experiment (28, 29, 30, and the 31 amu peaks). The instrumentation was set to provide complete readout of the four channels in use, about once every five seconds. During each experiment, over fifty ³⁰N₂/²⁸N₂ measurements were taken for each of three or more different gas flowrates in order to insure that accurate values for the exchange reaction rate constant were being obtained. The flow rates varied between 200 and 450 ml/min and the ranges used were based on the sample composition. Early trials indicated that the lag time involved with changing the gas flow rate was 5 to 10 minutes, depending on the flow rate. Continuous monitoring of the gas analysis allowed for quick recognition of the stabilization of the ³⁰N₂/²⁸N₂ ratio

for each new flow rate, thus affecting a minimal waste of the expensive concentrated ³⁰N₂ isotope gas.

After each experiment, the metal samples were analyzed for sulfur content. The analyzed sulfur concentrations were in good agreement with expected equilibrium levels set by the H₂/H₂S ratio employed. Chromium analysis was performed on several post-experiment samples using atomic absorption spectrometry. No significant chromium losses were encountered.

III. RATE EQUATION FOR THE ISOTOPE EXCHANGE REACTION

Several authors^{4,7} have derived rate equations for the ¹⁴N-¹⁵N exchange reaction. Byrne and Belton⁴ used the following equation to calculate exchange rate constants from their experimental data:

$$\frac{V'}{ART} \ln \left[\frac{{}^{30}F - {}^{30}F_{eq}}{{}^{30}F_0 - {}^{30}F_{eq}} \right] = -k \quad [1]$$

where V' is the volumetric flowrate of the combined gas (nitrogen + inerts) at temperature T , A is the interfacial area, R is the gas constant, ${}^{30}F$, ${}^{30}F_0$, and ${}^{30}F_{eq}$ are the reacted, initial, and equilibrium fractions of ³⁰N₂ molecules. However, in the derivations of these rate equations the influence of gas phase mass transport on the measured exchange rate was not considered.

Figures 1(a) and 1(b) show that the nitrogen reaction rate constants for several Fe-Cr-S alloys are fairly invariant with changes in gas flowrate. This should not be interpreted that the measured exchange rate is unaffected by gas phase mass transport. Based on experimental evidence for Reynolds numbers below 50, the gas phase mass transfer coefficient is virtually independent of the Reynolds number and thus is nearly invariant with gas flowrate.^{8,9} The calculated Reynolds numbers for this work are of the order of 10 to 20; therefore, the experimentally derived rate constants should not be a strong function of gas flowrate, regardless of whether or not the measured rate is being influenced by gas phase mass transport.

A correction can be made for gas phase mass transfer effects on the observed exchange rate. The correction is small for slow exchange rates, but becomes important for the fast interfacial reaction rates that are commonly encountered in liquid iron alloys containing low concentrations of surface active elements or high concentrations of chromium.

Consider an interfacial exchange reaction in which the overall measured rate is controlled by the rates of a gas phase mass transport step in series with a chemical reaction step occurring at the surface. The rate of the gas phase mass transfer step is given by the flux equation for transport of N₂ molecules through a gas film boundary layer to the reaction surface:

$$\vec{J} = k_g [p_{N_2}^b - p_{N_2}^s] \quad [2]$$

where k_g is the rate constant for mass transport in the gas phase, $p_{N_2}^b$ and $p_{N_2}^s$ are the nitrogen partial pressures in the bulk gas phase and at the surface. The rate of the exchange reaction at the gas/liquid metal interface is given by:

$$R = k_s [p_{N_2}^s] \quad [3]$$

where k_s is the forward rate constant for the surface reaction.

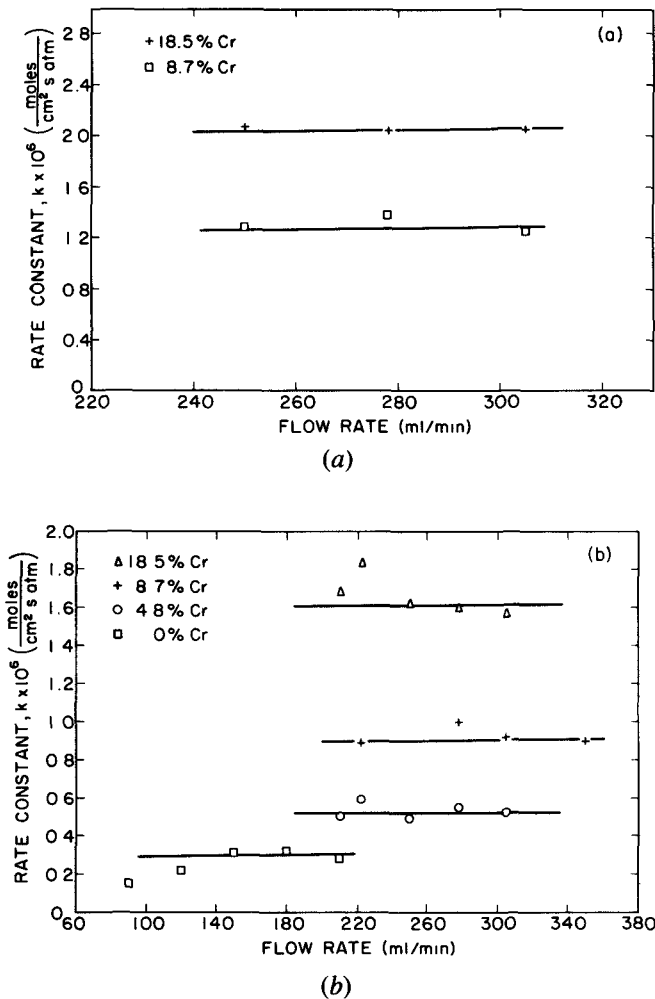


Fig. 1—Isotope exchange rate constants in Fe-Cr-S alloys as a function of total gas flowrate (at STP) for (a) $a_s = 0.35$ and (b) $a_s = 0.45$, at 1600°C .

At steady state, the flux of N_2 molecules to the liquid metal surface is equal to their rate of depletion on the surface. Therefore, setting Eqs. [2] and [3] equal and solving for the experimentally unmeasurable quantity, $p_{\text{N}_2}^s$, the following expression is obtained:

$$p_{\text{N}_2}^s = \left[\frac{k_g}{k_s + k_g} \right] (p_{\text{N}_2}^b) \quad [4]$$

Substituting for $p_{\text{N}_2}^s$ in Eq. [3], the following expression for the exchange rate, R , is obtained:

$$R = [1/k_s + 1/k_g]^{-1} (p_{\text{N}_2}^b) \quad [5]$$

k_g is given by:

$$k_g = \frac{m}{RT} \quad [6]$$

and m is the gas phase mass transfer coefficient for a particular experimental geometry. The experimentally derived value of m/T for the present geometry was determined from the rate of oxidation of graphite in CO-CO_2 gas mixtures under conditions that the rate is controlled by gas phase mass transfer.¹⁰ The values converted to nitrogen gas are approximately $2.2 \times 10^{-3} \text{ cm s}^{-1} \text{ K}^{-1}$,¹⁰ which is in

reasonably good accord with earlier studies using similar experimental configurations.^{8,9}

When Eq. [5] is employed, the integrated form of the exchange reaction rate becomes:

$$\frac{V'}{ART} \ln \left[\frac{{}^{30}\text{F} - {}^{30}\text{F}_{\text{eq}}}{{}^{30}\text{F}_0 - {}^{30}\text{F}_{\text{eq}}} \right] = -[1/k_s + 1/k_g]^{-1} \quad [7]$$

where all the symbols are as previously defined.

Comparison between Eq. [1] and Eq. [7] indicates that:

$$k = [1/k_s + 1/k_g]^{-1} \quad [8]$$

Therefore, the interfacial rate constant (k_s) can be determined from the measured exchange rate constant (k) and the constant for gas phase mass transfer (k_g) which is calculated from Eq. [6] using the experimentally derived value for m/T .

Previous work^{4,6} has demonstrated that for a predominately surface reaction controlled rate, k_s is equivalent to the rate constant for nitrogen absorption, k' , given in the nitrogen absorption equation:

$$\frac{d \text{ pct N}}{dt} = \frac{2800Ak'}{W} (p_{\text{N}_2} - p_{\text{N}_2}^e) \quad [9]$$

where p_{N_2} is the nitrogen pressure over the melt given in atm, $p_{\text{N}_2}^e$ is the nitrogen pressure in equilibrium with the instantaneous nitrogen concentration in the liquid iron solution, k' is the rate constant in $\text{mol cm}^{-2} \text{ s}^{-1} \text{ atm}^{-1}$, A is the exposed surface area of the melt in cm^2 , and W is the sample weight in grams.

IV. RESULTS

The rate data on Fe-Cr-S alloys from this study were obtained by isotope exchange experiments. The results are presented graphically in Figures 1 through 5. All isotope exchange results in Figures 2 through 5 have been corrected for gas phase mass transfer effects according to the method previously outlined.

The N_2 exchange reaction rate constants for several Fe-Cr alloys with sulfur activities of 0.35 and 0.45, based on the 1 wt pct standard state, are plotted against total gas flowrate in Figure 1. The experimental rate constants are, in general, independent of flowrate. This is to be expected, even if these rates were controlled by gas phase mass transfer. Due to the small degree of isotopic exchange occurring in these experiments, the uncertainty of the results is approximately ± 20 pct. The accuracy of this technique improves somewhat at lower sulfur activities and higher chromium concentrations until corrections for gas phase mass transfer become exceedingly large, as with the Fe-Cr alloys with negligible amounts of sulfur.

The variation of rate constant, k_s , in $\text{moles cm}^{-2} \text{ s}^{-1} \text{ atm}^{-1}$ with $1/a_s$ for several chromium concentrations is shown in Figure 2. As previously shown with the Fe-S alloys,^{4,6} the rate constants for the exchange reaction increase dramatically as the sulfur activity decreases. However, unlike Fe-S solutions, there is neither clear evidence of a linear dependence on $1/a_s$, nor does there appear to be any sign of a residual rate at high sulfur activities as was found with Fe-S alloys.^{5,6} Figure 3 is a similar type of plot to Figure 2, except that it includes a graphical display of the extent of the correction for gas phase mass transfer in Fe-4.8 pct Cr-S

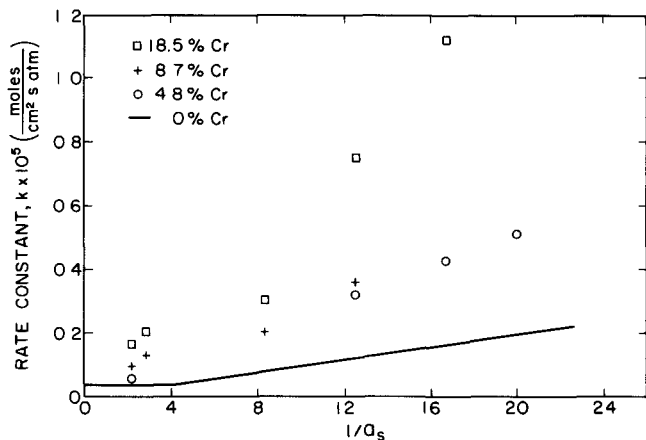


Fig. 2—Nitrogen reaction rate results in iron-chromium-sulfur solutions as a function of $1/a_s$, at 1600 °C.

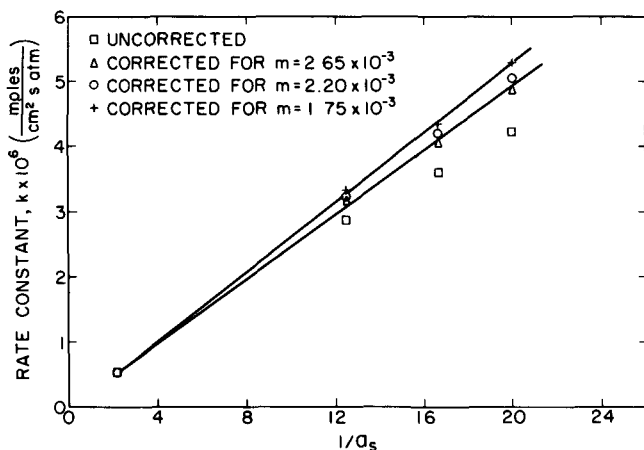


Fig. 3—Corrected and uncorrected isotope exchange rate constants in Fe-4.8 pct Cr-S alloys as a function of $1/a_s$, at 1600 °C.

alloys. The two lines in Figure 3 reveal the variation in the corrected rate constant corresponding to a ± 20 pct, the maximum uncertainty, change in the experimentally derived mass transfer coefficient. It can be noted that as the degree of isotopic exchange increases, the magnitude of the required correction increases.

Figures 4(a) and 4(b) are plots of the interfacial reaction rate constants, k_s , in moles $\text{cm}^{-2} \text{s}^{-1} \text{atm}^{-1}$ as a function of chromium content given in wt pct for several constant sulfur activities. Included in Figure 4(a) are nitrogen absorption data, corrected for liquid phase mass transfer, for several Fe-Cr alloys with a sulfur activity of 0.23 with respect to the 1 wt pct standard state.³ The rate constants increase approximately linearly with chromium content up to about 20 pct chromium for constant sulfur activity. However, not much significance should be accorded to this linear dependence, since for the faster exchange rates, *i.e.*, the high chromium, low sulfur alloys, the mass transfer corrections, and thus the uncertainties, become increasingly large.

In order to furnish some insight into the mechanism through which chromium enhances the rate of the nitrogen reaction, the isotope exchange technique was employed to determine the nitrogen exchange rates on liquid iron and iron-chromium alloys of negligible sulfur content

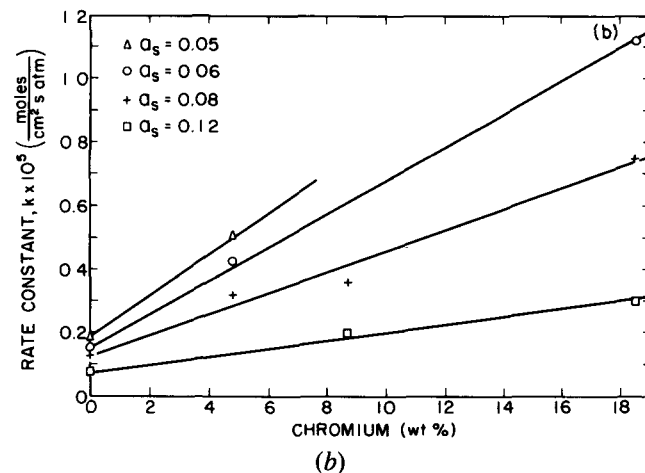
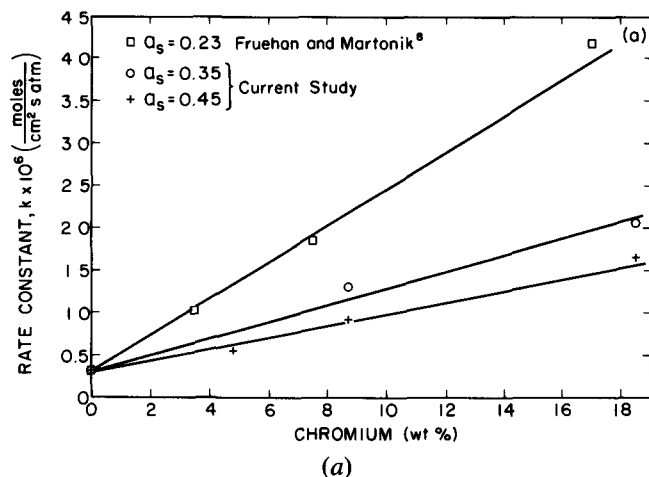


Fig. 4—Isotope exchange rate constants in Fe-Cr-S alloys as a function of chromium content for (a) high sulfur alloys and (b) low sulfur alloys, at 1600 °C.

(≤ 0.005 wt pct sulfur). The results of this study are presented in Figure 5. It is readily apparent that the nitrogen reaction rate increases dramatically with chromium concentration, as was the case with the Fe-Cr-S alloys.

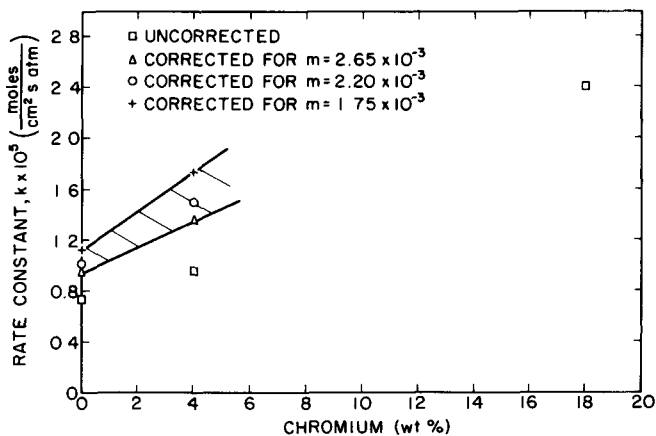


Fig. 5—Corrected and uncorrected isotope exchange rate constants in Fe-Cr alloys as a function of chromium content, at 1600 °C.

Figure 5 shows both the uncorrected and corrected values of the nitrogen exchange rate constant. The shaded area reveals the variation in the corrected rate constant corresponding to a ± 20 pct change in the experimentally derived mass transfer coefficient. The corrections for gas phase mass transfer in these alloys are large and so little emphasis is accorded the absolute values for the corrected rate constants. It is the increasing trend in the rate constants that is of interest.

V. DISCUSSION

The major emphasis of this research was to determine the effect of chromium on the interfacial reaction kinetics between nitrogen and liquid iron solutions. Based on the extent of the current knowledge of the nitrogen reaction with liquid iron-chromium alloys, including the work from the present study, several trends can be noted with plausible but as yet uncertain explanations accompanying them.

It was found that the faster measured isotope exchange rates encountered with these Fe-Cr alloys required a correction for mass transport in the gas phase. This correction was shown to be unnecessary for the nitrogen reaction with liquid Fe-S solutions.⁶

Current isotope exchange results on liquid Fe-Cr-S alloys indicate that for a constant sulfur activity as set by the H_2/H_2S ratio in the gas phase, the rate of the nitrogen reaction increases dramatically with increasing chromium concentration. This is clearly apparent in Figures 4(a) and 4(b). The increase appears to follow a linear relationship. However, as mentioned previously, little significance can be accorded this observation due to the large influence of mass transfer on the measured reaction rates in the high chromium and low sulfur alloys. There is no theoretical basis to support this notion of linearity between the nitrogen reaction rate and the chromium content. However, the fact that chromium is not surface active on liquid iron¹¹ and exhibits nearly ideal behavior in solution with liquid iron^{12,13,14} seems to be consistent with the reaction rate being a linear function of chromium content.

This increase in nitrogen reaction rate with increasing chromium concentration is in full agreement with the nitrogen absorption results of Fruehan and Martonik.³ These authors used the modified Sieverts' technique in their investigation of the kinetics of nitrogen absorption into liquid Fe-Cr-S alloys. In this dynamic absorption technique, the measured rates are affected by liquid phase mass transport, considerably so when the surface reaction is fast as in the case with iron alloys containing chromium. In the determination of the intrinsic chemical reaction rate constant, Fruehan and Martonik had to correct for mass transport in the melt. These corrections and the associated uncertainties become unsuitably large in alloys containing chromium. For example, the experimentally measured rate constant for nitrogen absorption into a Fe-7.5 pct Cr-0.09 pct S alloy was 2.54×10^{-6} moles $cm^{-2} s^{-1} atm^{-1}$. After accounting for liquid phase mass transfer effects, the corrected rate constant was 4.18×10^{-6} moles $cm^{-2} s^{-1} atm^{-1}$. This is a correction of nearly 65 pct.³ The correction for gas phase mass transfer in the present isotope exchange experiments for an alloy of similar composition is 20 pct. The attraction of the isotope exchange technique as an experimental tool in the

study of kinetics becomes obvious. It is worthy to note that there is reasonable agreement between the corrected absorption results of Fruehan and Martonik and the current isotope exchange results in similar Fe-Cr-S alloys. This indicates that the dissociation of the nitrogen molecule is the rate limiting elementary step in the intrinsic chemical reaction mechanism of nitrogen absorption into liquid Fe-Cr-S solutions, as was found with Fe-S alloys.⁶

Since the rate of the nitrogen reaction increases with increasing chromium concentration, it follows that either chromium affects the adsorption characteristics of sulfur in liquid iron or that the N_2 dissociation reaction is faster on chromium surface sites than on iron sites, or that both, or possibly other mechanisms are at work. Chromium has been shown to affect the adsorption behavior of carbon on liquid iron,¹⁵ possibly through associative adsorption of a CrC complex.¹⁶ Fruehan and Martonik³ surmised that if a similar phenomenon occurs in Fe-Cr-S alloys, then possibly fewer sites would be blocked by sulfur and, instead, would be occupied by chromium atoms. Another interpretation is that the proposed surface active complex CrS, itself, could be a favorable reaction site. The other feasible explanation for the effect of chromium on the reaction rate is that the N_2 dissociation rate is faster on chromium surface sites than on iron sites. The strong interaction between chromium and nitrogen, as evidenced by chromium's influence on the solubility of nitrogen in iron, would seem to support this contention.

An examination of the effect of chromium on the chemical reaction rate in liquid Fe-Cr alloys of negligible sulfur activity revealed an increase in the rate of nitrogen exchange on these alloys with increasing chromium content. These results indicate that the N_2 dissociation rate is faster on Cr sites than it is on Fe sites. It may be argued that the presence of even small amounts of sulfur results in significant surface coverage by the sulfur. Thus the effect of chromium in these alloys could be due to a restructuring of the chemisorbed sulfur layer rather than a difference in the N_2 dissociation rate on the two types of surface sites. However, since the oxygen and sulfur content was low and due to the presence of H_2 in the reacting gas, the sulfur and oxygen activity at the gas/liquid interface is negligible. Furthermore, the currently measured exchange rate on a Fe-18 pct Cr alloy was found to be significantly faster than the isotope exchange rate detected by Byrne and Belton⁴ on very high purity iron, *i.e.*, a clean iron surface. This is convincing evidence that the dissociation of molecular nitrogen is faster on chromium sites than on iron sites. This is, at least, one mechanism by which chromium enhances the rate of the nitrogen reaction in liquid Fe-Cr-S solutions. No inference can be made pertaining to other possible rate enhancing mechanisms based solely on these kinetic results on Fe-Cr alloys.

It should be noted that only through the emergence of the isotope exchange technique could this investigation into the effect of chromium on the kinetics of the nitrogen reaction with Fe-Cr binary alloys be performed. Surface reaction rates on liquid iron alloys with negligible sulfur (or oxygen) concentrations are so fast that measurements by conventional kinetic techniques are entirely controlled by mass transfer in the liquid and any effect on the rate of the nitrogen reaction on the surface due to the presence of chromium would be completely masked. Since liquid phase mass transfer effects are eliminated in the isotope exchange technique,

faster surface reactions can be directly monitored and the effect of chromium and other nonsurface active elements in the binary liquid iron solution can be investigated.

Consideration of the relationship between nitrogen reaction rate data and reciprocal sulfur activity may provide insight into whether chromium also affects the reaction kinetics through an influence on the adsorption behavior of sulfur in liquid Fe-Cr-S solutions. Previously, Darken and Turkdogan¹⁷ and Belton,¹⁶ assuming ideal behavior, have derived equations indicating that the interfacial rate constant is inversely proportional to the activity of a strongly adsorbed solute. Previous research on the nitrogen reaction with liquid Fe-S solutions reveals this inverse relationship between the rate constant and sulfur activity.^{4-6,18} From current work on Fe-Cr-S alloys shown in Figure 2, it is not obvious that the reaction rate constants for all chromium levels are a linear function of the reciprocal of the sulfur activity, as was found with Fe-S solutions. The proportionality seems to hold at low chromium concentrations, but changes to a nonlinear relationship with increasing chromium. In addition, there appears to be an absence of the residual reaction rate commonly found in the high sulfur region of Fe-S alloys.

Due to the progressively nonlinear relationship that exists between the reaction rate constant and the reciprocal sulfur activity with increasing chromium content, and the apparent lack of a residual rate at high sulfur activities in Fe-Cr-S solutions, it is possible that the rate promoting effect of chromium occurs, in part, through an alteration in the sulfur adsorption behavior in these alloys. This would be in addition to the differing N₂ dissociation rates on different surface sites mechanism discussed above. However, the nature of the relationship between k_s and $1/a_s$ is not precisely known, due to the large influence of gas phase mass transport on the measured exchange rates in high chromium, low sulfur alloys. Furthermore, a residual nitrogen reaction rate occurring at sulfur activities above those studied in this and other investigations³ could be explained by the following interpretation. It is assumed that there is a small but finite nitrogen reaction rate on the adsorbed sulfur layer which becomes significant when the fraction of unblocked iron sites is small. The presence of chromium surface sites, on which nitrogen dissociation has been shown to be faster than on iron sites, would suppress the significance of the rate on the adsorbed sulfur layer until much higher surface coverages were achieved, and so the residual rate region would appear only at higher sulfur activities than it is commonly found in Fe-S alloys. All this means is that from the current data on the rate of the nitrogen reaction with Fe-Cr-S alloys, conclusive evidence in support of, or quantitative information on the manner in which chromium may affect the adsorption of sulfur can not be supplied. Nor can it be, in a study of this type. It seems likely that surface tension measurements taken on these alloys would provide more definitive insight into the effect of chromium on the adsorption of sulfur in liquid iron.

VI. CONCLUSIONS

Chromium was found to enhance greatly the rate of nitrogen dissociation and absorption into liquid iron solutions. The mechanism by which this occurs is, at least in part, due to N₂ dissociation being faster on chromium surface sites than on iron sites as was shown by the increasing exchange rate with chromium in Fe-Cr solutions of negligible sulfur content.

Due to the faster nitrogen reaction rates encountered in liquid iron alloys containing chromium, the influence of gas phase mass transport must be taken into account in the determination of the interfacial rate constants. The method of correction is presented.

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