

The Rate of Absorption of Hydrogen into Iron and of Nitrogen into Fe-Cr and Fe-Ni-Cr Alloys Containing Sulfur

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The rate of absorption of hydrogen into liquid iron and of nitrogen into liquid Fe-Cr alloys containing various levels of sulfur was measured by using a constant-volume Sieverts apparatus employing a sensitive pressure transducer. The rate for the absorption of hydrogen was measured by using H_2 containing a small amount of H_2S (<0.2 pct) such that the activity of sulfur on the surface of the melt was the same as in the bulk metal. The hydrogen-absorption rate for Fe-S melts containing up to 0.72 pct sulfur was virtually independent of sulfur content and controlled by liquid-phase mass transfer. The liquid-phase mass-transfer coefficient for hydrogen in liquid iron, calculated from the results, was comparable to that for nitrogen transfer in liquid iron. The rate of absorption of nitrogen into Fe-Cr melts with low-sulfur contents was controlled by liquid-phase mass transfer. For melts containing significant amounts of sulfur it was controlled by both mass transfer and the chemical rate of the dissociation of nitrogen on the surface in series. Equations were developed to calculate the chemical rate from the measured rate, correcting for mass transfer. The chemical rate decreased with increasing sulfur content as expected, because sulfur is strongly adsorbed on the surface and increased with chromium content at constant sulfur activity, possibly because available Cr sites promote nitrogen dissociation.

WITH the advent of the AOD and Q-BOP steel-making processes, a knowledge of the rate of absorption and desorption of nitrogen into liquid stainless steel and of hydrogen into liquid steel has become more important. In the AOD process for producing stainless steel, nitrogen can be used in place of argon in the early stages of refining. Although the nitrogen is absorbed into the steel, it is flushed out during the later stages of the refining process when argon is used. It is desirable to replace as much argon as possible with nitrogen, thus reducing the cost, while still achieving the proper level of nitrogen content at tap. To accomplish this, a knowledge of the rate of the nitrogen reaction with stainless steel is useful.

In the Q-BOP, hydrocarbon gases are used as tuyere coolants during refining, and consequently the hydrogen content at first turndown may be slightly higher than in steelmaking practices which do not employ hydrocarbon gases as coolants. However, when the furnace is being rotated from the tapping position and an inert gas (Ar or N_2) is being blown through the tuyeres, the hydrogen content is reduced to acceptable levels. If lower hydrogen content is desired, this can be achieved by inert gas flushing. To estimate the amount of flushing gas required, a knowledge of the rate of the hydrogen reaction would be helpful.

In previous work, the authors have investigated the rate of the nitrogen reaction with liquid iron containing oxygen and sulfur.¹ It was shown that the absorption rate was second order with respect to nitrogen and probably controlled by the dissociation of the N_2

molecule on the surface. Also, the combined effects of oxygen and sulfur on the rate of nitrogen absorption were determined. Pehlke and Elliott² investigated the nitrogen absorption rate for Fe-Cr alloys and found that it was controlled by liquid-phase mass transfer because the activity of oxygen was low. However, sulfur present in stainless steels may retard the rate, and the present work will be primarily concerned with the effect of sulfur.

Boorstien and Pehlke³ investigated the rate of hydrogen solution in iron alloys. They found that most alloying elements did not affect the rate, which was controlled by liquid-phase mass transfer. They did find that large quantities of sulfur decreased the rate slightly; 2 wt pct sulfur decreased the rate to half that for pure iron. However, they used pure hydrogen as the reaction gas, which could lead to uncertainties. As discussed later in detail, because of the formation of H_2S the activity of sulfur on the surface could be poorly defined. In the present work the effect of sulfur on the rate was measured in such a way that the activity of sulfur on the surface was well defined.

EXPERIMENTAL

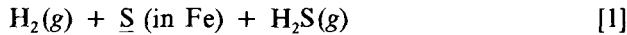
The experimental apparatus and techniques are essentially the same as described previously.¹ Briefly, a constant-volume Sieverts apparatus employing a sensitive pressure transducer was used to measure the gas-metal reaction rate. The melt weighed about 60 g and was contained in an alumina crucible with an internal diameter of 31 mm. The volume of the apparatus was adjusted such that the total pressure change would be small enough (~ 0.03 atm) that the experiments were done at essentially constant pressure, yet the pressure change would be large enough that the ab-

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sorption rate could be measured accurately. All the experiments were made at 1600 ± 2 °C and the melts were chemically analyzed for oxygen, sulfur, and chromium at the end of the experiment.

The technique for determining the rate of the hydrogen reaction was similar to that used for nitrogen. The rate was measured for low-sulfur iron with pure hydrogen. However, for the alloys containing sulfur, pure hydrogen could not be used because the following reaction would occur at the surface:



This reaction would not affect the measurement of the hydrogen reaction rate because one mole of hydrogen is used to form one mole of H_2S . However, it would significantly affect the activity of sulfur at the surface; the activity would be poorly defined and could be significantly less than in the bulk metal. To avoid this problem, the rate was measured in an H_2 - H_2S gas mixture that would be in equilibrium with the Fe-S alloy. The amount of H_2S in the gas was small; for example, for an alloy containing 0.38 pct sulfur the equilibrium gas phase⁴ contains only 0.10 pct H_2S . The sulfur content of the melt was first estimated from the relative amounts of the master alloy and pure iron used and the melt was then reacted with its equilibrium H_2 - H_2S gas mixture for about one hour at 1600 °C. The hydrogen was removed from the melt and then the alloy was reacted with the appropriate equilibrium H_2 - H_2S gas mixture. In this way the activity of sulfur on the surface was constant and known. Analysis of the metal for sulfur verified that the sulfur content was that in equilibrium with the gas mixture. Because of the high thermal conductivity of hydrogen, the temperature control was less precise (± 5 °C) than in the case of nitrogen and the rates were measured at hydrogen pressures of 0.5 atm or less.

RESULTS AND DISCUSSION

Rate of Hydrogen Solution

The rate of solution of hydrogen in liquid iron containing 0.002, 0.21, 0.37, and 0.72 wt pct sulfur was measured in H_2 or the equilibrium H_2 - H_2S gas mixture. The sulfur content of the alloys remained virtually constant with the present experimental technique. For example, an Fe-S alloy containing 0.38 pct sulfur initially reacted in its equilibrium H_2 - H_2S gas mixture (0.10 pct H_2S) had a final sulfur level of 0.37 pct, which is within the experimental thermodynamic uncertainty. Therefore, the sulfur activity at the surface was known and constant.

The reaction rates in all cases were relatively fast and apparently controlled by liquid-phase mass transfer. The rate is first order with respect to hydrogen, and the integrated form of the rate equation is given by

$$\ln \frac{\text{pct } H_t - \text{pct } H_e}{\text{pct } H_o - \text{pct } H_e} = - \frac{A \rho m_H}{W} t \quad [2]$$

where pct H_t , H_e , and H_o are the instantaneous, equilibrium and initial hydrogen contents, ρ is the liquid metal density, W is the weight of the melt, A is the

surface area and m_H is the liquid-phase mass-transfer coefficient for hydrogen in liquid iron.

The results are plotted in Fig. 1 in accordance with Eq. [2]. All the experimental results, with possible exception of those obtained with the 0.72 pct sulfur alloy, are within the experimental scatter and on the same line, indicating the rate is first order with respect to hydrogen and independent of sulfur content. The value of the mass-transfer coefficient calculated from the slope of the line is 9.7×10^{-2} cm/s with an estimated error limit of ± 15 pct. In previous work done with nitrogen in the same equipment, m_N was 2.5×10^{-2} cm²/s. The liquid-phase mass-transfer coefficient for inductively stirred melts is proportional to the square root of the diffusion coefficient of the element as shown by Machlin⁵ and later by Ohno and Ishida⁶ over large ranges for the diffusivity. The accepted values for the diffusivity of nitrogen and hydrogen in liquid iron at 1600 °C are 1.1×10^{-4} cm²/s and 1.3×10^{-3} cm²/s respectively.⁴ The ratio of the square roots of the diffusivities of hydrogen and nitrogen is 3.4 which is in good agreement with the ratio of the mass-transfer coefficients, 3.9. It should be noted that in recent work Ban-ya *et al*⁷ found m_H to be proportional to diffusivity of hydrogen in iron alloys. However, this correlation was only for a limited range and was not theoretically justified as is the square root relationship.⁵

It could be argued that for the highest sulfur alloy (0.72 pct) the rate is somewhat lower. Previously, Boorstien and Pehlke³ reported a decrease in the rate by about 25 pct at this sulfur level. The dashed line in Fig. 1 is for the alloy containing 0.72 pct sulfur and is about 25 pct lower than the line for pure iron (0.002 pct S). It is therefore possible that sulfur has a small effect on the rate of the hydrogen reaction. However, the effect is quite small compared with the effect of sulfur on the nitrogen reaction. That high a sulfur content (0.72 pct) decreases the rate of nitrogen absorption by about a factor of 10.¹ It can therefore be concluded that the rate of hydrogen absorption is essentially inde-

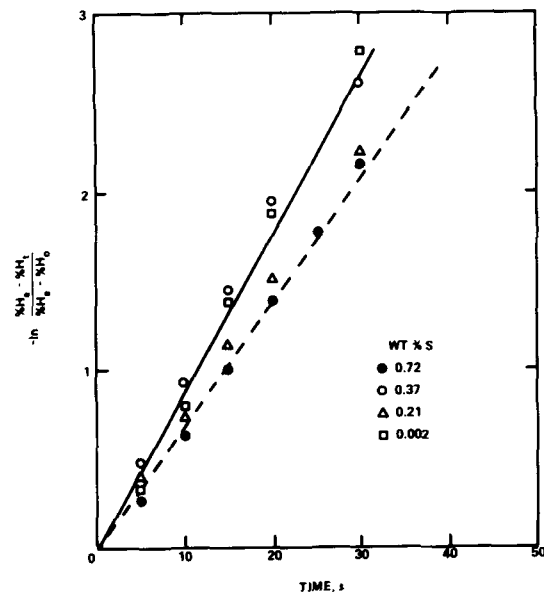


Fig. 1—The rate of absorption of hydrogen in Fe-S melts at 1600 °C.

pendent of sulfur content for the sulfur contents normally encountered in steelmaking (*i.e.* <0.2 pct) and that the rate in the present work is controlled by liquid-phase mass transfer.

Nitrogen Solution in Fe-Cr and Fe-Ni-Cr Melts

The rate of nitrogen solution in Fe-Cr and Fe-Ni-Cr melts depends on the sulfur content as shown in Fig. 2. As demonstrated in Fig. 3, for low-sulfur contents (<0.003 pct) the rate is first order with respect to nitrogen content and independent of the chromium and nickel contents. Also shown in Fig. 3 is the rate previously obtained for pure iron with the same experimental equipment. As shown previously by Pehlke and

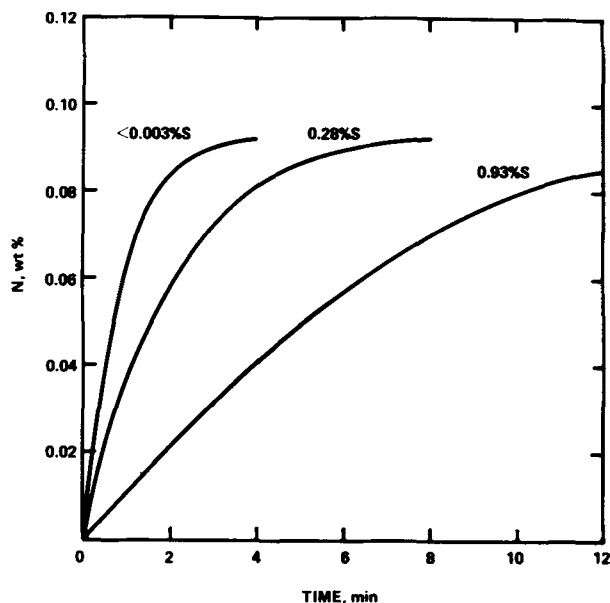


Fig. 2—The rate of absorption of nitrogen in Fe-7.5 pct Cr-S melts at 1600 °C and 0.96 atm N₂.

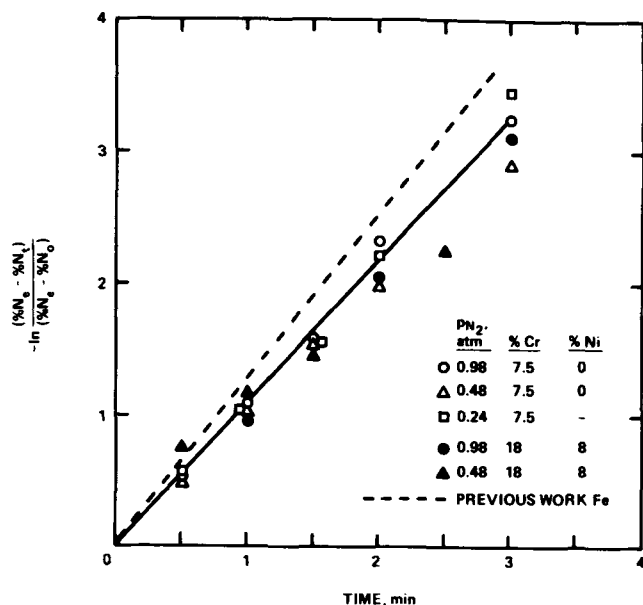


Fig. 3—The rate of absorption of nitrogen in Fe-Cr, and Fe-Ni-Cr at 1600 °C. (S < 0.005 wt pct.)

Elliott,² the rate is obviously controlled by the mass transfer of nitrogen in the liquid phase. The value of the mass-transfer coefficient m_N is 2.3×10^{-2} (± 10 pct) cm/s for the Fe-Cr and Fe-Ni-Cr melts compared with 2.5×10^{-2} cm/s for pure iron. The slight difference could be attributed to the experimental uncertainty or to the slight difference between the diffusivity of nitrogen in iron and in the alloys.

At higher sulfur concentrations the rate depends on sulfur content because, as discussed in detail previously, sulfur is surface-active and blocks surface sites.¹ It was shown previously that when a surface-active element such as oxygen or sulfur is present, the rate of nitrogen absorption is second order with respect to nitrogen content or proportional to the nitrogen pressure P_{N_2} ,

$$\frac{d \text{ pct N}}{dt} = \frac{100A k_2}{W} (P_{N_2} - P_{N_2}^e) \quad [3]$$

where k_2 is the rate constant and $P_{N_2}^e$ is the equilibrium nitrogen pressure calculated from the nitrogen content, and W is the weight of the melt.

In Fig. 4 the rates of nitrogen pickup for Fe-7.5 pct Cr-S alloys are plotted in accordance with Eq. [3]; a reasonable linear relationship exists. However, if the reaction sequence is examined, it becomes apparent that the chemical reaction alone is not controlling the rate and the linear relationship could be misleading. At lower sulfur levels, the chemical rate is relatively fast and the mass transfer of nitrogen from the surface is influencing the measured rate.

The rate of nitrogen transfer from the surface is given by

$$\frac{d \text{ pct } N_B}{dt} = - \frac{A \rho m_N}{W} (\text{pct } N_B - \text{pct } N_s) \quad [4]$$

where pct N_B and pct N_s are the nitrogen contents in the bulk metal and at the surface, respectively. It is possible to calculate the surface concentration by using Eq. [4] and the value of m_N determined from the results for the alloys not containing sulfur. In some cases the concentration of nitrogen on the surface was considerably higher than in the bulk metal.

The rate of the chemical reaction at the surface is given by

$$\frac{d \text{ pct } N_s}{dt} = \frac{A k'_2}{W} (\text{pct } N_e^2 - \text{pct } N_s^2) \quad [5]$$

where k'_2 is the rate constant in terms of nitrogen concentration. The constant k'_2 is related to k_2 by

$$k_2 = k'_2 (\text{pct } N_e)^2 \quad [6]$$

where (pct N_e) is the nitrogen content in equilibrium with one atmosphere of nitrogen.⁴

The rate of change of the calculated surface concentration is plotted in Fig. 5 in accordance with Eq. [5] for the Fe-7.5Cr-0.28S alloy. From the slope of the line the corrected value of the rate constant k_2 is 5.2×10^{-5} as compared with 4.1×10^{-5} g/cm²s·atm which is calculated from the slope of the rate curve in Fig. 4. The corrected value for the rate constant in this case is not significantly greater than that measured directly because mass transfer for this melt did not greatly affect the overall rate. The values of the corrected chemical

rate constant and measured overall rate constants are given in Table I. As seen in Table I, the effect of mass transfer on the rate is greatest at low-sulfur contents and negligible at high-sulfur contents.

It should be noted that whereas this method of determining the chemical rate constant is theoretically correct, it is not very precise at low-sulfur levels. The uncertainty in the corrected chemical rate constant at low-sulfur levels is estimated to be about 25 pct.

The effect of adsorbed sulfur on the rate of the nitrogen reaction with liquid iron has been discussed previously in detail.¹ The measured rate of reaction with iron is affected by mass transfer at low-sulfur levels and by the rate on the adsorbed surface layer at high-sulfur levels. In the present work, the rate on the adsorbed sulfur layer is negligible for Fe-7.5Cr alloys and the measured rates were corrected for mass-transfer effects. In this case the chemical rate constant (k) will simply be inversely proportional to the sulfur activity. In Fig. 6

the corrected rate constants for the Fe-7.5Cr alloys are plotted vs $1/a_s$, where a_s is the activity of sulfur in terms of weight percent sulfur. The small effect of chromium on the activity coefficient of sulfur⁴ has been accounted for. The deviation from the line at low-sulfur contents reflects the uncertainty in the results due to the large correction for mass-transfer effects. Also shown in Fig. 6 is the relationship between $1/a_s$ and the chemical rate constant obtained previously for iron.¹ The rate constant at a given sulfur activity is significantly higher for the Fe-7.5Cr alloys than for iron.

This observation was explored in more detail by measuring the nitrogen absorption rate for iron containing 3.5 and 17.0 pct chromium at sulfur contents of 0.26 and 0.34 pct, respectively. The activity of sulfur in these alloys is nearly the same because chromium decreases the sulfur activity coefficient. The rates are plotted in Fig. 7 in accordance with Eq. [3]. The rates are not necessarily a linear function of $(P_{N_2} - P_{N_2}^0)$ because mass transfer is affecting the measured rates. The chemical rate constants were calculated from the measured rates and described previously and are listed in Table I. In Fig. 8, the chemical rate constants are plotted vs chromium content for a relatively constant sulfur activity of 0.23 ± 0.01 pct. The rate increases significantly with increasing chromium content.

If the chemical rate is controlled by the dissociation of the nitrogen molecule on the surface of the melt, the

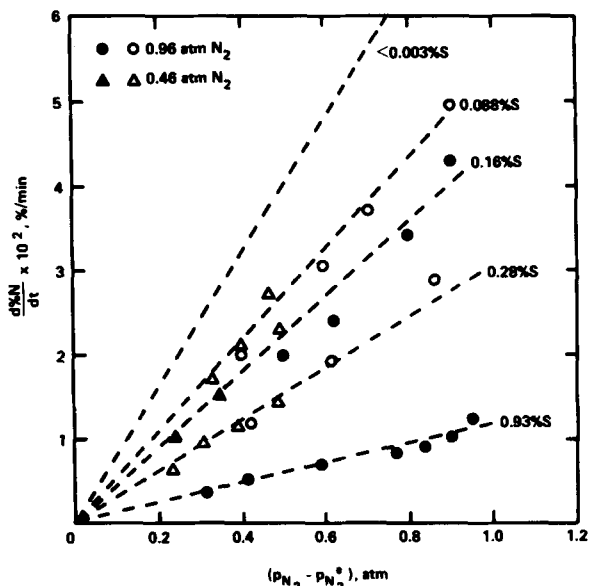


Fig. 4—The rate of absorption of nitrogen in Fe-7.5 pct Cr-S melts at 1600 °C.

Table I. Measured and Corrected Values for the Chemical Rate Constant for the Absorption of Nitrogen into Fe-Cr-S and Fe-Cr-S Alloys at 1600 °C

Cr, Wt Pct	S, Wt Pct	a_s Wt Pct	k_2 (Measured) (g N/cm ² s atm)	k_2 (Corrected) (g N/cm ² s atm)
7.5	0.088	0.073	7.1×10^{-5}	11.7×10^{-5}
7.5	0.16	0.13	6.0×10^{-5}	9.6×10^{-5}
7.5	0.28	0.23	4.1×10^{-5}	5.2×10^{-5}
7.5	0.93	0.77	1.5×10^{-5}	1.6×10^{-5}
3.5	0.26	0.24	2.1×10^{-5}	2.9×10^{-5}
0	0.24	0.24	0.9×10^{-5}	0.9×10^{-5}
17.0	0.34	0.22	7.1×10^{-5}	8.0×10^{-5}

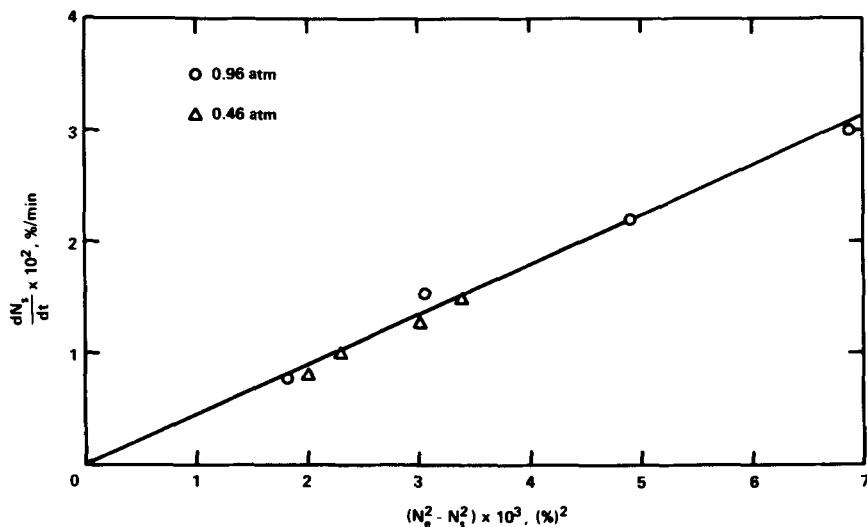


Fig. 5—Rate of absorption of nitrogen into an Fe-7 pct Cr-0.28 pct S corrected for mass transfer.

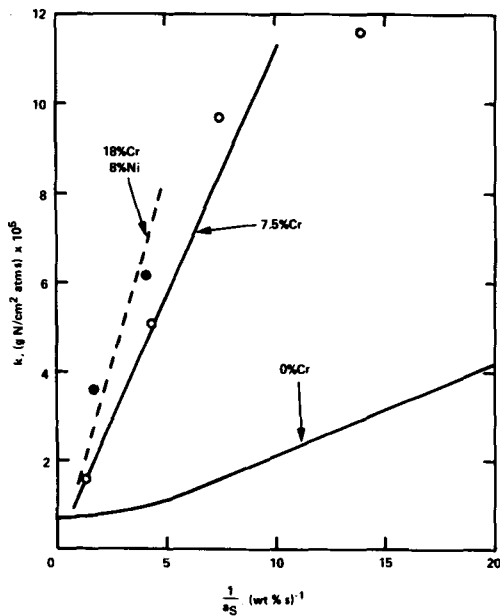


Fig. 6—Rate constant for the absorption of nitrogen, corrected for mass transfer into Fe-7.5 pct Cr-S alloys at 1600 °C vs $1/a_S$.

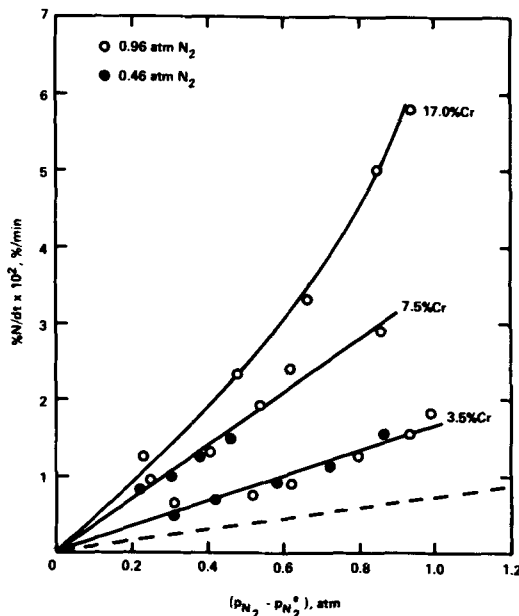


Fig. 7—Rate of absorption of nitrogen into Fe-Cr-S melts at 1600 °C, sulfur activity approximately 0.23 wt pct S.

fact that at constant sulfur activity the rate increases with chromium content implies that either 1) chromium significantly affects the adsorption of sulfur on the surface of iron or 2) the rate of dissociation of nitrogen on chromium sites on the surface is considerably higher than on iron sites.

If the presence of chromium decreases the number of sites occupied by sulfur, there would be more sites available for the dissociation of the nitrogen molecule. It has been found that chromium does affect the adsorption of carbon on the surface of iron. Belton's⁸ analysis of surface-tension data indicates that there may be an associative adsorption of a CrC complex on Fe-Cr-C alloys. If a similar phenomenon occurs in the

Fe-Cr-S, possibly fewer sites would be blocked by sulfur and, instead, would be occupied by chromium atoms.

However, possibly a more plausible explanation is that the rate of dissociation of N_2 is considerably faster on chromium sites than on iron sites. This seems possible because of the strong interaction between nitrogen and chromium reflected in the high solubility of nitrogen in Fe-Cr alloys. Therefore, even though the surface of an Fe-Cr-O, 3 pct S melt may be almost completely covered by adsorbed sulfur, the rate of nitrogen absorption increases with increasing chromium content because the chemical rate on the vacant chromium sites is considerably faster than on vacant iron sites. It should be emphasized that these two possible explanations are only speculative, and the actual reason

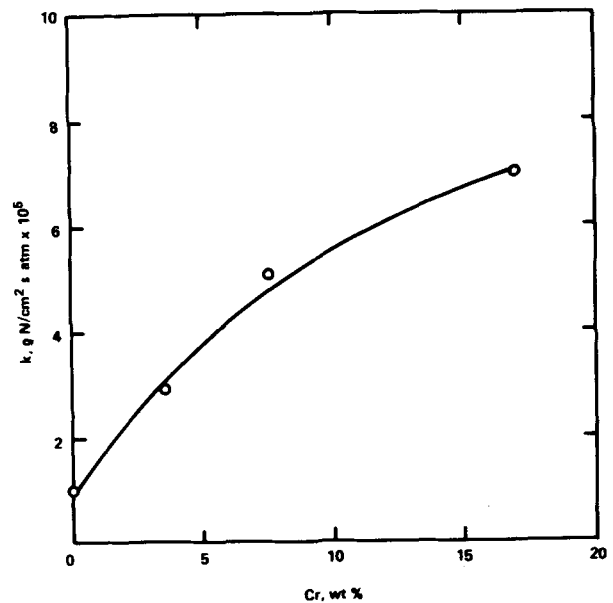


Fig. 8—Effect of Cr on the rate of absorption of nitrogen into Fe-Cr-S melts at 1600 °C, sulfur activity approximately 0.23 pct S.

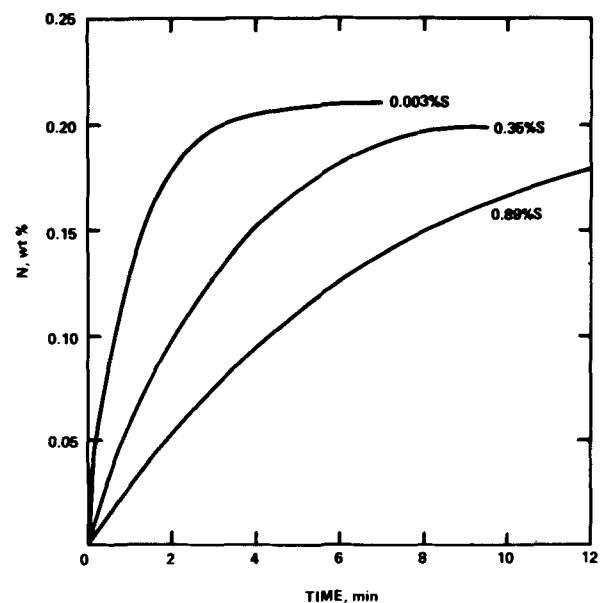


Fig. 9—The absorption of nitrogen into Fe-18 pct Cr-8 pct Ni-S melts at 1600 °C and 0.96 atm.

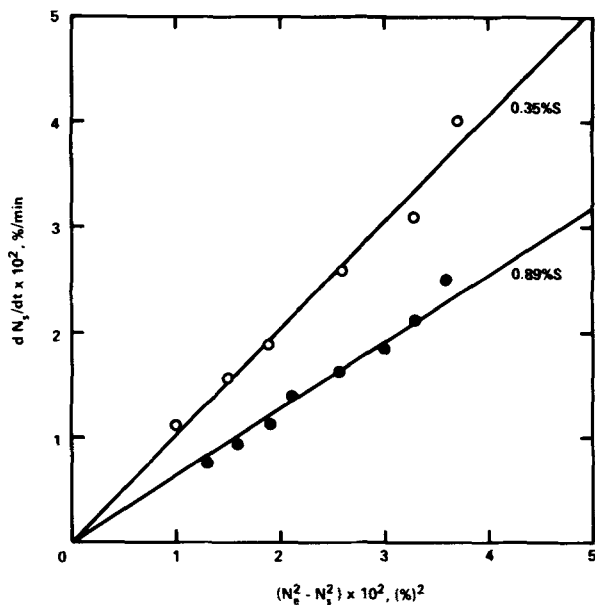


Fig. 10—Rate of absorption of nitrogen into Fe-18 pct Cr-8 pct Ni-S melts corrected for mass transfer.

chromium increases the chemical rate is not known.

The rate of nitrogenation of Fe-Cr-Ni melts similar to 18-8 type stainless steel was also measured. The rate at low-sulfur activity was controlled by liquid-phase mass transfer, as shown in Fig. 2. The rate does decrease at high-sulfur levels, as shown in Fig. 9. The rate constants corrected for mass transfer were calculated from the slopes of the lines in Fig. 10 by using Eq. [4]. The effect of sulfur could not be studied extensively for these alloys because at low-sulfur contents the correction for mass transfer became too great to obtain meaningful results. The results for the two alloys are given in Fig. 6 as a function of $1/a_s$; due allowance is made for the effect of chromium on the activity of sulfur. The results indicate that chromium, as well as sulfur, effects the rate of absorption.

CONCLUSIONS

The rate of absorption of hydrogen in liquid Fe-S alloys was measured by using H_2 - H_2S gas mixtures

(<0.2 pct H_2S) such that the activity of sulfur on the surface of the melt was constant and well defined. The rate of hydrogen absorption was virtually independent of sulfur content and was controlled by liquid-phase mass transfer (that is, diffusion from the surface to the interior). The mass transfer coefficient calculated for hydrogen from the results was consistent with that determined for nitrogen in liquid iron.

The rate of absorption of nitrogen into Fe-Cr and Fe-Cr-Ni alloys containing sulfur was measured and the rate at low sulfur contents was controlled by liquid-phase mass transfer of nitrogen. However, at higher sulfur concentrations the rate of nitrogen absorption was controlled by mass transfer and the chemical rate on the surface, in series. Equations were developed to calculate the chemical rate from the measured rate of nitrogen absorption, correcting for mass-transfer effect. At low sulfur levels the chemical rate was about half the measure rate, whereas for high sulfur levels the correction for mass transfer was negligible. For Fe-Cr alloys the rate depended on both the sulfur and chromium contents. The rate decreased with increasing sulfur content as expected, but increased with increasing chromium content. Two possible explanations are that of dissociation of nitrogen on chromium sites considerably faster than on iron sites or that chromium affects the adsorption of sulfur on iron.

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