The Kinetics of the Nitrogen Reaction with Carbon Saturated Iron Alloys

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Synopsis

The kinetics of the nitrogen reaction with liquid Fe–C alloys was investigated by using the isotope exchange technique. The effect of small amounts of S, P, Pb, Sn, Bi and Te in Fe–Csat. alloys on the rate constant of the interfacial nitrogen reaction was studied at 1450°C. The rate constant for Fe–Csat.–S alloys was in agreement with the previous results for Fe–S alloys. It was also confirmed that the influence of carbon in Fe–C–S alloys on the rate of the nitrogen reaction is negligible. The effect of tin on the rate constant is small even when the tin content is as high as 0.6 at%.. However Pb, Bi and Te have significant effects on the rate constant and the addition of small amounts of these elements decreases the rate significantly. Phosphorus also decreased the rate constant. According to the adsorption model, the interfacial reaction rate should approach zero at high concentration of surface active elements, but in the case of Fe–Csat.–P, Fe–Csat.–Pb and Fe–Csat.–Te alloys, there was evidence of a residual rate at high concentrations of P, Pb and Fe.

Key words: kinetics; nitrogen reaction rate; carbon saturated iron alloy phosphorus; tin; lead; bismuth; tellurium; sulfur.

I. Introduction

In recent years the reaction of nitrogen with iron and steel has taken on added importance. Dissolved nitrogen can be harmful in several ways. For example, it can be responsible for porosity or it may react to form nitrides which decrease the formability of the steel. Nitrogen gas is used in many new ladle metallurgical processes and subsequently can be absorbed into the metal. Once nitrogen is absorbed into the metal it is difficult to remove; vacuum degassing, at best, only removes 10 to 20% of the nitrogen present. Therefore it is important to control the nitrogen absorption during all the steelmaking processes. Nitrogen can also be harmful in the production of cast iron. In particular, porosity in iron castings resulting from gas evolution can be a major problem. It may be possible to control the reaction of nitrogen with Fe–Csat. alloys by the addition of surface active elements which retard the rate.

Several researches have been reported on the rate of the reaction of nitrogen with liquid Fe alloys.1–23) Pehlke and Elliott1,2) studied the thermodynamics and the kinetics of nitrogen reaction in liquid Fe and Fe alloys using a constant pressure Sieverts’ apparatus. They found that the rate is first order with respect to the nitrogen content and at low sulfur and oxygen levels the rate was controlled by mass transfer in the liquid phase. They investigated the effect of Al, Cb, Cr, Ni, O, S and W on the rate of the nitrogen reaction and showed that oxygen and sulfur retarded the rate of the reaction. Later Inouye and Choh4) studied the rate of absorption of nitrogen at low nitrogen content in liquid Fe and Fe alloys using a sampling technique and found that at low sulfur and oxygen concentrations the rate of nitrogen absorption was half order with respect to nitrogen pressure. However, at high sulfur and oxygen levels the rate was proportional to the nitrogen pressure. Mori and Suzuki7) measured the rate of nitrogen removal from liquid iron and found the rate to be second order with respect to dissolved nitrogen content. Mowers and Pehlke8) investigated the rate of solution of nitrogen in liquid Fe–Se and Fe–Te alloys using a modified Sieverts’ apparatus at pressure of 1 atm and a temperature of 1600°C. They demonstrated selenium and tellurium present in low concentrations have a marked retarding effect on the rate of solution of nitrogen in liquid Fe alloys, Narita et al.9) investigated the kinetics of nitrogen desorption reaction of liquid iron and steel and found that the desorption reaction rate is second order. Ban-ya et al.10) also studied the rate of removal of nitrogen from liquid iron investigating the influence of O, S, Si, C, Cr and Ni on the rate and they found that the rate is second order with respect to nitrogen content and the surface active elements such as sulfur and oxygen retard the nitrogen desorption. Amano et al.11) studied the absorption and desorption reaction of nitrogen by levitation technique. They reported that the reaction is first order when there exists no gas boundary layer and the reaction is between first and second order when there are two boundary layers. Kadoguchi et al.12) studied the rate of absorption of injected nitrogen in molten iron and found that the rate controlling steps are the chemical reaction and the mass transfer in liquid phase. Kawakami et al.13) studied absorption and desorption rates of nitrogen in molten iron by bottom injection. They found that nitrogen absorption rate from pure nitrogen is controlled by the mass transfer in metal phase and the desorption of nitrogen by Ar–N2 mixture was controlled by the mass transfer in gas phase.

Fruchan and Martonik14) measured the rate of nitrogen absorption into and desorption from liquid iron containing sulfur and oxygen by employing a modified Sieverts’ technique with a highly sensitive pressure transducer. They conclusively demonstrated
that the rate of nitrogen absorption into iron alloys with surface active solute was second order with respect to nitrogen concentration or first order with respect to nitrogen partial pressure and the rate was controlled by the dissociation of the nitrogen molecule on the surface.

In the later work, Fruehan and Martonik\(^1\) measured the effect of sulfur on the nitrogen reaction with Fe–Cr and Fe–Cr–Ni alloys. They found that chromium increases the rate. At low levels of sulfur content absorption rate was controlled by liquid phase mass transfer of nitrogen, but at high sulfur levels the rate was controlled by mass transfer and the chemical rate on the surface in series. A correction was made for the influence of liquid phase mass transfer on the measured rates. These effects are negligible at high sulfur concentrations, but become significant at intermediate sulfur contents. At low levels of sulfur this method of determining the intrinsic chemical reaction rate constant, becomes very imprecise, since the mass transfer effects become significant.

To measure the interfacial reaction rate and eliminate the influence of liquid phase mass transfer, Byrne and Belton\(^2\) employed the isotope exchange technique in their study of the kinetics of nitrogen reaction with liquid Fe and Fe–S alloys. This technique permits a direct experimental determination of the rate of\(^3\) dissociation on the liquid metal surface via measurement of the rate of exchange reaction

\[ ^{28}\text{N}_2 + ^{30}\text{N}_2 = 2^{29}\text{N}_2 \]

The experiment is run under the condition of equilibrium between the gas at the interface and liquid bulk phase. This permits the measurement of interfacial chemical reaction rates that would normally be considered too fast for the conventional kinetic experimental technique for inductively stirred melts. Byrne and Belton\(^2\) found the exchange rate to be first order with respect to nitrogen partial pressure on high purity iron and the rate for Fe–S indicated that sulfur closely followed an ideal chemisorption model.

Recently Glaws and Fruehan\(^2\) used both the modified Sieverts’ technique and an improved isotope exchange technique in the same experimental apparatus to verify that\(^3\) dissociation is the rate limiting elementary step in the intrinsic chemical reaction mechanism. This provided strong evidence that the dissociation of the \(\text{N}_2\) molecule is the rate limiting step in intrinsic chemical reaction mechanism of nitrogen absorption into liquid Fe–S alloys. More recently Glaws and Fruehan\(^2\) investigated the kinetics of the nitrogen reaction with liquid Fe–Cr alloys using the isotope exchange technique. They found that chromium greatly enhances the rate of nitrogen dissociation and absorption into liquid iron solutions. The mechanism is due to\(^3\) dissociation being faster on chromium surface sites than on iron sites. Due to the faster nitrogen reaction rates encountered in liquid Fe–Cr alloys, the influence of gas phase mass transport was taken into account in the determination of the interfacial rate constant.

It is the purpose of the present work to determine the effect of S, P, Pb, Bi, Sn and Te on the nitrogen reaction with liquid Fe–C\(_{\text{sat.}}\) alloys. The rate was measured by using the isotope exchange technique, since the measured rate is not affected by liquid phase mass transfer or the evolution of other gases from the melt.

### II. Experimental

As described in the papers of Glaws and Fruehan\(^2,\) it is possible to employ both the isotope exchange and the Sieverts’ technique in a single apparatus. As Ishii et al.\(^4\) have pointed out, since CO gas is evolved from Fe–C alloys, the Sieverts’ technique was not suitable for the measurements in the present study. Therefore the isotope exchange technique was employed to investigate the kinetics of the nitrogen reaction with liquid Fe–C–X solutions, where X is a solute element. The experimental apparatus and technique were previously described in detail.\(^2\) Metal samples weighing approximately 30 g were contained in a crucible which is high density and high purity (99.8 %) alumina with 20 mm I.D., 22 mm O.D. and 33 mm height. Alumina crucible was set in the outer safety crucible which was slip cast lime-stabilized zirconia with approximately 25 mm I.D. and 50 mm height. The crucible was placed in a fused silica reaction chamber and carefully inductively heated to the experimental temperature. The experimental temperature was mainly 1 450°C, and some experiments for Fe–C–S alloys were also conducted at 1 600°C. The 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 power controls on the R.F. generator. The desired metal surface temperatures were maintained within ±5°C.

During heat up, a \(\text{N}_2\)–\(\text{H}_2\) 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, and to reduce the sulfur content in metal which affects on the rate. In the case of experiments of Fe–C–S alloys, a \(\text{N}_2\)–\(\text{H}_2\)–\(\text{H}_2\text{S}\) gas mixture was passed over the sample to maintain the desired sulfur activity in the sample. The \(\text{H}_2\) or \(\text{H}_2\)–\(\text{H}_2\text{S}\) gas is approximately 15 % of total gas mixture. Once the liquid metal temperature was reached, the standard nitrogen gas was replaced by the labeled nitrogen gas, containing approximately 1 at % of the isotope \(^{30}\text{N}_2\). The isotopically labeled nitrogen gas was jetted onto the surface of the liquid metal for a sufficient time to allow for equilibrium to be achieved. Continuous gas analysis was possible through the use of an in-line Dycor Precision Mass Analyzer. Peaks of mass numbers of 28, 29 and 30 amu were monitored continuously during each isotope exchange experiment and over fifty \(^{30}\text{N}_2/^{28}\text{N}_2\) ratio measurements were taken for each gas flow rate in order to insure that accurate values for the exchange reaction rate

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constant were obtained. The flow rate was 200, 250, 300, 360 and 450 ml/min. Continuous monitoring of the gas analysis allowed for quick recognition of the stabilization of the 30N2/36N2 ratio for each new flow rate, thus affecting a minimal waste of the expensive concentrated 30N2 isotope gas.

To prepare sample alloys, electrolytic iron was pre-melted in a graphite crucible and added each element and mixed at experimental temperature. Samples of the original alloys were analyzed before and after each element for the relevant elements. Sulfur was analyzed by combustion method and phosphorus was determined by molybdenum blue photometric method. Sn, Pb, Bi and Te analysis was conducted by using atomic absorption spectrometry.

In this study the effect of S, P, Sn, Pb, Bi and Te on the rate constant of nitrogen reaction with Fe-Csat. alloys was investigated. In the case of lead and bismuth experiment, the lead or bismuth content in metal would change because of vaporization of these metals. Therefore Ag–Bi or Ag–Pb alloys were contained in the crucible with the Fe–C alloys to maintain a constant potential of these elements. Although the bismuth and lead contents in silver decreased during experiments, the bismuth and lead contents in Fe-Csat. alloys did not change significantly. In the case of the tellurium experiment, since the vapor pressure of tellurium is much higher than that of lead and bismuth, almost all of tellurium in Fe-Csat. alloys evaporate during a long experiment. Therefore, the measurement was started as soon as possible after metal alloy melted and the measurement was conducted for only one flow rate for each experiment. The change of tellurium content in metal with time was measured and the tellurium content at the beginning of measurement was estimated. No significant phosphorus and tin losses were encountered.

III. Rate Equation for the Isotope Exchange Reaction

Several authors21,25 have derived rate equations for the nitrogen exchange reaction. Byrne and Belton21 derived the following rate equation

\[
\frac{V}{RT} \frac{d(30F)}{dt} = kA(30F_{eq} - 30F) \quad \text{.........(2)}
\]

and integrated Eq. (2) to obtain exchange rate constant, \( k \), (Eq. (3)), from their experimental data,

\[
-k = \frac{Q}{ART} \ln \frac{30F - 30F_{eq}}{30F_{eq} - 30F_{eq}} \quad \text{.........(3)}
\]

where, \( V \): a volume of reacting gas
\( Q \): the volumetric flow rate of the combined gas (nitrogen+inerts) at the temperature \( T \)
\( A \): the interfacial area
\( R \): the gas constant
\( 30F \): the fractions of 30N2 molecules in the gas after reaction

\[
30F_{eq} : \text{the initial fractions of 30N2 molecules}
30F_{eq} : \text{the probability of forming a molecule of 30N2, which is equal to the fraction of 30N2 molecules at isotope exchange equilibrium.}
\]

However, the influence of gas phase mass transfer on the measured exchange rate was not considered in this rate equation. Glaws and Fruehan23 showed that although the nitrogen reaction rate constants for several Fe–Cr–S alloys are fairly invariant with changes in gas flow rate, a correction for gas phase mass transfer effects on the observed exchange rate still may be necessary. 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 solute elements. Glaws and Fruehan23 derived the following relationship

\[
k = \frac{1}{k_0 + \frac{1}{k_s}} \quad \text{.........(4)}
\]

where \( k_0 \) is given by

\[
k_0 = \frac{m}{RT} \quad \text{.........(5)}
\]

and \( m \) is the gas phase mass transfer coefficient for a particular experimental geometry. Therefore, the interfacial rate constant \( (k_s) \) can be determined from the measured exchange rate constant \( (k) \) and the rate constant for gas phase mass transfer \( (k_0) \) which is calculated using the experimentally derived value for \( m/RT \) for the specific experimental conditions. The experimentally derived value of \( m/RT \) for the present geometry was determined from the rate of oxidation of graphite in CO–CO2 gas mixtures under conditions that the rate is controlled by gas phase mass transfer.26

The flow rate of gas mixture was varied between 250 and 600 ml/min. The value of \( m/RT \) converted to nitrogen gas is approximately 2.2 × 10^{-3} cm/s K26 and \( m \) is 3.8 cm/s at 1450°C.

Surface active elements such as sulfur and oxygen retard the reaction on the surface. As shown by Darken and Turkdogan27 the apparent interfacial rate constant, \( k_s \), at high degree of surface coverage by the surface active element is given by

\[
k = k_0 \phi_i \quad \text{.........(6)}
\]

where, \( k_0 \): the rate constant for the pure iron
\( \phi_i \): a constant
\( a_i \): the activity of the surface active element.

Belton23 derived the following equation assuming an ideal Langmuir adsorption

\[
k = k_i/(1 + K_i a_i) \quad \text{.........(7)}
\]

where, \( K_i \): the equilibrium adsorption coefficient. Under conditions of a high concentration of a strongly adsorbed solute, where \( K_i a_i \gg 1 \), the interfacial rate constant is inversely proportional to the activity of the solute, consistent with Darken and Turkdogan’s relation (Eq. (6)).
IV. Results

All isotope exchange results have been corrected for gas phase mass transfer effects according to the method previously outlined. Figure 1 shows the variation of rate constant, $k_5$, in mol/cm²-s-atm with activity of sulfur at 1450 and 1600°C for Fe-C_{sat.}-S alloys. The present results at 1600°C agree with the results with Fe-S alloys obtained by Glaws and Fruehan. The rate constants for the exchange reaction increase linearly as the sulfur activity decreases, as previously shown with the Fe-S alloys. As the metal is saturated with carbon, activity coefficient of sulfur of 6.3 with respect to 1 wt% as standard state was used for the calculation of activity of sulfur.

The rate constants shown in Fig. 1 for the sulfur activities of 0.06 and 0.028 are plotted against the reciprocal of the temperature in Fig. 2. The results measured by Byrne and Belton are also shown in Fig. 2 for high purity iron. From the slope of line in Fig. 2, the activation energy of nitrogen reaction was calculated to be 27 kcal/mol. This activation energy is in good agreement with the activation energy estimated by Byrne and Belton. Furthermore, the sulfur content in Fe alloys does not have significant influence on the activation energy of nitrogen reaction.

In Fig. 3 the effect of carbon on the rate constant was shown for the metal in which the activity of sulfur was 0.11 with respect to 1 wt% as standard state at 1600°C and compared with the results of Glaws and Fruehan. The rate constant is independent of carbon concentration up to 5.4% C which is the solubility limit at 1600°C.

In Fig. 4, the effect of phosphorus on the interfacial rate constant at 1450°C is shown. The rate constant is $1.0 \times 10^{-9}$ mol/cm²-s-atm at 0.03 wt% P, and decreases linearly with increasing phosphorus content and then at 0.16 wt% P the rate constant becomes $0.5 \times 10^{-6}$ mol/cm²-s-atm. At high phosphorus concentration the rate constant becomes independent of phosphorus content indicating the presence of the residual rate. Figure 5 shows the effect of tin con-
tent in Fe-Csat.-Sn alloys on the rate constant at 1450°C. Although the content of tin in metal is very high such as 0.8%, the change of rate constant is not significant.

The effect of lead on the rate constant at 1450°C, shown in Fig. 6, indicates a linear relation with the inverse of the activity of lead, with pure lead as the standard state, at low lead concentrations in Fe-Csat. alloys. The activity of lead was calculated from the lead content in Ag-Pb alloys using the thermodynamic data of Ag-Pb alloys. However at high activities of lead, the rate constant deviates from the linear relationship. Small amounts of lead have a remarkable effect on the rate constant. For example, addition of 0.014 wt% Pb decreases the rate constant by nearly an order of magnitude to $4 \times 10^{-6}$ mol/cm²-s-atm. In the case where the activity of lead is unity, the liquid Fe-C alloy was in equilibrium with pure lead instead of an Ag-Pb alloy. The measured concentration of lead in the Fe alloy, 0.078 wt% Pb, is the solubility limit of lead in the Fe-Csat. alloy. The solubility of lead in iron is 0.24 wt% at 1550°C. Since the interaction coefficient of carbon on lead is 0.066 at 1600°C, if it is assumed that this value is valid to high carbon contents, the estimated lead content in Fe-Csat. alloys becomes 0.07 wt%. The observed value of 0.078 wt% is therefore a reasonable value.

Very small amounts of bismuth have a strong influence on the rate constant with 56 ppm Bi reducing the rate constant to $4.4 \times 10^{-7}$ mol/cm²-s-atm. Figure 7 shows the effect of activity of bismuth, with pure bismuth as standard state, on the rate constant. The rate constant varies linearly with the inverse of the activity of bismuth and there is no evidence of residual rate. At present, it is not clear whether the behavior of the residual rate constant is present at higher bismuth contents or not, because of the difficulty of running the experiment at high bismuth concentrations in Fe-Csat. alloys due to the vaporization of the bismuth.

In the case of the Fe-Csat.-Te experiments, much of the tellurium vaporized during the experiments at 1450°C; therefore the change of tellurium content in the Fe-C alloy, during an experiment, was investigated. Figure 8 shows the change of tellurium content with time; at about 50 min the metal begins melting and the deposition of metal vapor was ob-

![Fig. 5. Effect of the tin in Fe-Csat.-Sn alloys on the rate constant of the nitrogen reaction at 1450°C.](image)

![Fig. 6. Effect of the activity of lead in Fe-Csat.-Pb alloys on the rate constant of the nitrogen reaction at 1450°C.](image)

![Fig. 7. Effect of the activity of bismuth in Fe-Csat.-Bi alloys on the rate constant of the nitrogen reaction at 1450°C.](image)

![Fig. 8. Change of tellurium content with time during an experiment at 1450°C.](image)
The effect of tellurium in Fe-C-Te alloys on the rate constant of the nitrogen reaction at 1,450°C is shown in Figure 9. The rate constant, as a function of tellurium content, is observed to decrease rapidly. For example, with 120 ppm Te, the rate constant reduces to 2.8 x 10^{-7} mol/cm^2s.atm. However, at high tellurium contents, the rate constants deviate from the linear function of the inverse of the tellurium content at low tellurium contents. At high tellurium contents, the rate constants deviate from the linear relationship and the behavior of a residual rate constant is observed.

V. Discussion

Byrne and Belton summarized previous research for the effect of sulfur on the rate of the nitrogen reaction and have corrected the rate constant for the effect of liquid phase mass transfer. Their results show that the corrected rate constant is proportional to the inverse of the sulfur content in the Fe alloy. Assuming a Langmuir adsorption isotherm for sulfur, they derived the relationship between the rate constant of nitrogen reaction and the activity of sulfur at 1,550 and 1,600°C as follows:

\[ k_a = 1.7 \times 10^{-5}(1+130a_S) \text{ mol/cm}^2\text{s.atm} \]

at 1,600°C (8) ...........................................(8)

\[ k_a = 1.4 \times 10^{-5}(1+140a_S) \text{ mol/cm}^2\text{s.atm} \]

at 1,550°C (9) ...........................................(9)

where, \(a_S\): the activity of sulfur with 1 wt% as the standard state.

For example, the present result shows that the rate constant is 2.3 x 10^{-6} mol/cm^2s.atm at the sulfur content of 0.0030 % in Fe-C_{\text{sat}} alloys at 1,450°C. The rate constant which was obtained by extrapolating Eqs. (8) and (9) to 1,450°C and using the activity coefficient of sulfur in Fe-C_{\text{sat}} alloys is 2.2 x 10^{-6} mol/cm^2s.atm. However, the influence of gas phase mass transfer was not considered in this rate constant. Therefore, the same value of gas phase mass transfer coefficient previously outlined is used to correct this extrapolated value for gas phase mass transfer, since the geometry and conditions of Byrne and Belton’s experiments are similar to those of present study. The corrected rate constant is 2.4 x 10^{-6} mol/cm^2s.atm, which is in good agreement with the observed rate constant in the present study.

Glaws and Fruehan found that the influence of sulfur on the rate constant is negligible for a constant sulfur activity. This result is consistent with Byrne and Belton’s measurements for high purity iron (sulfur content is 9 ppm) and Fe-C (carbon is 2.0 and 4.3 %) alloys at 1,650°C. In this study the rate constant was measured at 5.4 %, which is the solubility limit of carbon at 1,600°C, and the results show that at high carbon content the effect of carbon on rate constant is still negligible as indicated in Figure 3. As Glaws and Fruehan have pointed out, this phenomenon is consistent with the surface tension data of Kozakevitch et al., who found that the surface tension of liquid Fe-C-S solutions was a function of sulfur activity only; however, it is necessary to take into account the effect of carbon on the activity of sulfur.

Consideration of the relationship between nitrogen reaction rate data and reciprocal activity of solute elements may provide insight into whether solute element affects the kinetics through an influence on the adsorption behavior of solute element in liquid Fe-C solutions. As discussed previously, at high activities of surface active elements the rate constant should approach zero. However, from the more accurate results of the modified Sieverts’ experiments at high solute concentration, the presence of a residual rate at high sulfur contents was clearly indicated by Glaws and Fruehan. Studies on the decarburization of liquid Fe-C-S alloys by Saïn and Belton, Lee and Rao, and Haycar and Whiteway provide evidence of the presence of a residual rate for the CO2 reaction on a liquid Fe-C surface at high sulfur levels. In the present study, a residual rate is found for Fe-C-Te, Fe-C-Pb and Fe-C-P alloys. On the other hand, the residual rate is not found for Fe-C-Bi alloys. The residual rate constant of tellurium and lead are about 0.3 x 10^{-6} mol/cm^2s.atm. This rate constant is about 3 % of the rate constant for pure iron obtained by Byrne and Belton. The residual rate constant for Fe-C-P alloys was slightly higher at 0.5 x 10^{-6} mol/cm^2s.atm.

Mowers and Pehlke in their experiments with Fe-Te alloys showed no indication of residual rate. The gas volume measurement system that they used was not as sensitive as the technique employed in previous work and may not have been sensitive enough to detect a slow residual rate. Tellurium has a stronger effect on the rate constant of the nitrogen reaction than sulfur which is in the same group VIa as tellurium. This agrees with the results of Mowers and Pehlke. This behavior is consistent with the results of the present study.
and Pb. The present results indicate these elements decrease the rate constant of the nitrogen reaction; possibly indicating they are surface active and reduce the surface tension of carbon saturated iron melts.

For the Fe–C–Pb alloys an Ag–Pb alloy was used to maintain the lead potential in the system; silver has a small solubility in iron. However, since the solubility data in Fe–Csat, alloys is not available an experiment was conducted to estimate the effect of silver using silver with a Fe alloy instead of an Ag–Pb alloy. The rate constant obtained, 1.0×10−3 mol/cm²•s•atm, at high silver activity is nearly equal to the rate constant obtained at very low activity of solute elements such as Te, Pb and Bi. Therefore it can be concluded that the effect of silver on the rate constant is negligible. The activity of lead for the Fe–C–Pb alloys is determined by the lead content in Ag–Pb alloys. The thermodynamic data for Ag–Pb alloys is available at 1000°C, this data was extrapolated to 1450°C. Since the lead content in Fe–Csat, alloys was analyzed, plotting the relation between the activity of lead in Ag–Pb alloys and the lead content in Fe–Csat, alloys, the activity coefficient of lead in Fe–Csat, alloys can be obtained; that value is 2.7×10³. It is not confirmed whether the system is in equilibrium or not and thus it should be emphasized that above calculation is only an estimation.

In the same manner as the lead experiment, Ag–Bi alloys were used to maintain a constant bismuth activity. Therefore, activity of bismuth was calculated from the bismuth content in Ag–Bi alloys using the thermodynamic data for the Ag–Bi system. The calculated activity coefficient of bismuth in Fe–Csat, alloys is 2.4×10⁶; again it should be emphasized this is only an estimation.

VI. Summary and Conclusions

The isotope exchange technique was employed to investigate the kinetics of nitrogen reaction with liquid Fe-C alloys and the following results are obtained.

1. The addition of small amounts of P, Pb, Bi and Te to liquid Fe–Csat, solution decreases the rate constant of the nitrogen reaction. However, the effect of tin content on the rate constant of nitrogen is small.
2. The effect of carbon on the rate constant for a constant bulk sulfur activity is negligible in Fe–C–S alloys.
3. The presence of a residual reaction rate is observed for Fe–C–Pb, Fe–C–P and Fe–C–Te alloys, but not for Fe–C–Bi solutions over the composition range investigated.
4. The rate constant of nitrogen reaction for Fe–C–S alloys are proportional to the inverse of sulfur activity at low sulfur activity and the rate constants agree with previous measurements.

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