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ORIGINAL RESEARCH ARTICLE

A Study of the Effect of Alloying Elements and Temperature on Nitrogen Solubility in Industrial Stainless Steelmaking

JYRKI PITKÄLÄ, LAURI HOLAPPA, and ARI JOKILAAKSO

The role of nitrogen varies in different stainless steels from a harmful impurity to a valuable alloying element. Therefore, the strict control of nitrogen content is a very important issue in the steel making process. Better understanding about the thermodynamics of nitrogen solubility is the basis for this control. The aim of this study was to determine whether the nitrogen solubility at atmospheric pressure at any given composition and temperature in an Argon Oxygen Decarburization (AOD) converter could be reliably predicted. This was done by comparing different equations for nitrogen solubility to industrial measurements of several different steel grades with a wide range of compositions and temperatures. The test set consisted of 100 heats to ensure reproducibility and sufficient variability. The focus was on examining the effect of the main alloying elements (Cr, Ni, Mo, Mn) and temperature on nitrogen solubility. Nitrogen solubility is increased most by the chromium content, followed by manganese and molybdenum, whereas nickel decreases the solubility. The interaction effect of an alloying element on nitrogen declines at increasing temperatures, resulting in a negative temperature dependence, *i.e.*, the maximum nitrogen solubility is obtained near the liquidus temperature. The study showed that most of the examined thermodynamic equations predicted the nitrogen solubility quite well in common stainless steels and even in high alloyed steels. On the other hand, clear discrepancies were observed for steels with a high manganese content as well as with strongly deviating temperatures. Therefore, based on the present measurements and the literature data, a new equation was developed for predicting the solubility of nitrogen in a wide range of stainless steels. This equation can be coupled with the existing process models to control the AOD process.

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I. INTRODUCTION

NITROGEN has a multifunctional role as an alloying element in stainless steels. On the one hand, in some applications, nitrogen is a very harmful element, and it is desirable to keep its content as low as possible. For instance, in ferritic stainless steels a typical maximum is 0.03 pct. On the other hand, nitrogen alloying is used for improving the properties of stainless steels. Nitrogen improves their corrosion resistance and mechanical properties, such as the wear properties, weldability, hardness, and strength of the steel. Nitrogen is also a good replacement for expensive nickel alloy as an austenite stabilizer. Such steel grades can contain up to 0.3 to 0.5 pct N.[1–7] In the Argon Oxygen Decarburization (AOD) process, nitrogen is often used as an inert process gas for lowering the CO pressure instead of the much more expensive argon gas used during decarburization, and as a stirring gas in the final stages. The control of nitrogen and its behavior is, therefore, an important part of the stainless steelmaking process.

The final nitrogen content of the steel depends on the raw materials used, the process gases, process temperatures, slag, refractory linings, and interaction of the steel with the surrounding gas atmosphere. In order to optimize the productivity and cost of a melt shop, it is very important to know and control nitrogen behavior throughout the whole melt shop process chain, which usually consists of an Electric Arc Furnace (EAF), AOD converter (AOD), Ladle Furnace (LF), and Continuous Casting (CC). The final nitrogen content is largely determined by the AOD process. Optimizing practices in the AOD process is easier when the maximum solubility

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of nitrogen at different compositions and temperatures is known. New steel grades are often developed for composition areas with a lack of experimental data, on nitrogen solubility, for example. When designing blowing practices for new steels, it is necessary to know the capability of the available process models to predict the nitrogen content. The aim and focus of this study was to survey the nitrogen solubility models in the literature, test their reliability over a wide range of compositions, and then develop a new prediction model for in-plant use.

In this article the prior literature is reviewed to find the relations that could be used to calculate nitrogen solubility in stainless steels. These equations have been used to predict the nitrogen solubility of different types of steel alloys that are produced at the Outokumpu Avesta plant.[8] The experimental heats were produced by rinsing the steel melts with pure nitrogen gas for at least six minutes; thus the nitrogen content can be assumed to be very close to its equilibrium solubility in the prevailing conditions. The measured nitrogen contents from 100 heats with a wide composition range were compared to nitrogen solubilities calculated with different published models. The objective was to find out how nitrogen solubility was affected by different alloying elements and temperatures.

II. THERMODYNAMICS OF NITROGEN SOLUBILITY IN ALLOYED STEELS

The nitrogen dissolution into iron alloys can be written as

$$\frac{1}{2}\mathrm{N}_2 \leftrightarrow [\mathrm{N}] \qquad [1]$$

and the equilibrium constant, K_N, for reaction (1) can be written as

$$K_\mathrm{N} = \frac{a_\mathrm{N}}{\sqrt{P_{\mathrm{N}_2}}} = \frac{f_\mathrm{N}[\mathrm{Pct\ N}]}{\sqrt{P_{\mathrm{N}_2}}} \qquad [2]$$

where a_N is the activity of dissolved nitrogen, f_N is the activity coefficient for nitrogen, P_{N_2} the is partial pressure of nitrogen, and [pct N] the dissolved nitrogen content in steel.

The Gibbs free energy of the solution and equilibrium constant K_N of the reaction are related according to

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -\mathrm{RTln}\frac{f_\mathrm{N}[\mathrm{pct\ N}]}{\sqrt{P_{\mathrm{N}_2}}} = -\mathrm{RTln}K_\mathrm{N} \qquad [3]$$

where ΔG^0 is the change in the Gibbs free energy of reaction (J), ΔH^0 is the change in enthalpy of reaction (J), T is the reaction temperature (K), ΔS^0 is the change in entropy (JK^{-1}), and R is the gas constant (8.314 JK^{-1} mol^{-1}). After taking the logarithm of both sides of Eq. [2], a new expression for nitrogen content can be obtained:

$$\log[\mathrm{Pct\ N}] = \frac{1}{2}\log P_{(\mathrm{N}_2)} + \log K_\mathrm{N} - \log f_\mathrm{N} \qquad [4]$$

In an ideal solution, f_N is equal to 1 and the activity equals the weight or molar fraction [pct N]. In a nonideal dilute solution [pct N] $\rightarrow$0, and activity coefficient f_N is approximated to a constant.

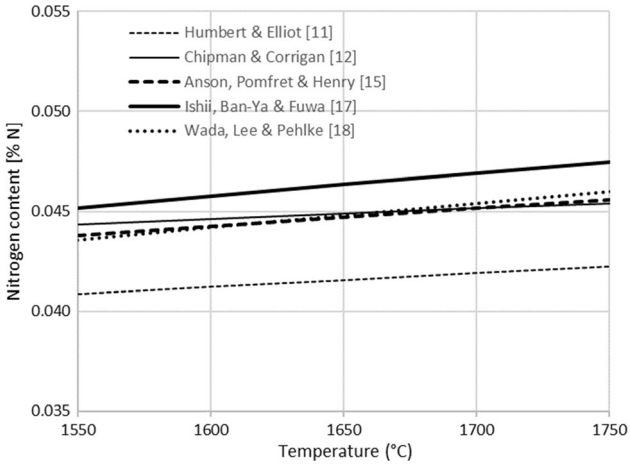

Fig. 1—Nitrogen solubility in pure liquid iron at 1 atm according to different researchers.

According to Eq. [4], the solubility of nitrogen in metal is proportional to the square root of the partial pressure of nitrogen in thermodynamic equilibrium, which is called Sievert's Law[9]:

$$[\mathrm{Pct\ N}] \propto \sqrt{P_{\mathrm{N}_2}} \qquad [5]$$

The solubility of nitrogen in pure iron has been studied for at least a century and a wide variety of equations have been derived. Accordingly, the solubility of nitrogen in pure liquid iron at 1600 °C and 1 atm N_2 pressure is about 440 to 460 ppm and it increases slightly with increasing temperature,[10–18] as can be seen in Figure 1. According to Chipman and Corrigan,[12] nitrogen solubility in pure liquid iron at 1 atm P_{N_2} pressure is

$$\log[\mathrm{Pct\ N}] = -\frac{188}{T} - 1.25 \qquad [6]$$

When alloy elements such as C, Si, Cr, Ni, Mn, Mo *etc.* appear in iron solution, they affect each other's activity and nitrogen solubility. The thermodynamic properties of this kind of solution can be characterized by the activity coefficient of the solutes.[19] Wagner[20] proposed a methodology for dilute solutions where he applied Taylor's series expansion of the activity coefficient, disregarding the second and higher derivatives. Wagner's formalism can be written as follows:

$$\begin{aligned}\ln f_2(x_2, x_3, \ldots) = \ln f_2^0 &+ \left[x_2\frac{\partial \ln f_2}{\partial x_2} + x_3\frac{\partial \ln f_2}{\partial x_3} + \cdots\right] \\ &+ \left[\frac{1}{2}x_2^2\frac{\partial^2 \ln f_2}{\partial x_2^2} + x_2x_3\frac{\partial^2 \ln f_2}{\partial x_2 \partial x_3} + \cdots\right] + \cdots\end{aligned} \qquad [7]$$

$$\ln f_2(x_2, x_3, \ldots) = \ln f_2^0 + x_2\varepsilon_2^{(2)} + x_3\varepsilon_2^{(3)} + \cdots \qquad [8]$$

where x_i is the mole fraction and ε_i is the interaction parameter of element i in a metallic solution. Wagner's concept of interaction coefficients was further developed by Lupis and Elliot.[21] They proposed that the "introduction of higher order interaction coefficients is a necessary and convenient addition to our mathematical apparatus".

The effect of an alloy element j on the activity coefficient of nitrogen f_N at very low concentrations in Fe-j alloy can be expressed in Eq. [9][10]:

$$\log f_N = e_N^N[\text{Pct } N] + \sum e_N^j[\text{Pct } j] + \sum \gamma_N^j[\text{Pct } j]^2 + \sum e_N^{ij}[\text{Pct } i][\text{Pct } j] \quad [9]$$

Wagner's Interaction Parameter Formalism is strictly valid only at infinite dilute concentrations. According to Kang,[19] a correction to Wagner's formalism is needed but Gibbs–Duhem relation and Maxwell relation between all the components, including the solvent–solute, are required for ensuring thermodynamic consistency among the activity coefficient of all components.

The effect of alloying elements on the solubility of nitrogen in different alloys has already been studied for decades. Several researchers and research groups have studied and performed experiments in order to determine the effect of different single alloying elements on nitrogen activity and solubility in steel.[10–18,22–31] Mostly these studies have been done by measuring the absolute quantity of absorbed gas (Sieverts' method), by the sample freezing method or by levitation melting in a magnetic field. These methods have been briefly described for example by Siwka.[29]

It could be assumed that binary mixtures are not sufficient to describe the solubility of nitrogen in various steel alloys. Langenberg[22] has suggested that the activity coefficient of nitrogen in a multi-component alloy could be obtained by summing the $\log f_N$ values of the respective alloying element.

Chipman and Corrigan[12] extended Langenberg's[22] nitrogen solubility study, which was limited to a constant temperature (1600 °C), and developed Eq. [10] for the prediction of nitrogen solubility in iron-based alloys as a function of temperature:

$$\begin{aligned}\log[\text{Pct N}] = -\frac{188}{T} - 1.25 - \Bigg\{\left(\frac{3280}{T} - 0.75\right)&(0.13[\text{Pct C}] + 0.047[\text{Pct Si}] - 0.023[\text{Pct Mn}] - 0.045[\text{Pct Cr}] + 0.01[\text{Pct Ni}] \\ &- 0.011[\text{Pct Mo}] - 0.002[\text{Pct W}] + 0.01[\text{Pct Co}] - 0.1[\text{Pct V}] + 0.003[\text{Pct Cu}] + 0.006[\text{Pct Sn}] \\ &- 0.067[\text{Pct Nb}] - 0.034[\text{Pct Ta}])\Bigg\}\end{aligned} \quad [10]$$

However, this equation contains only the first-order terms and is suitable for only low alloyed steels, although it is still widely used in industrial models for high alloyed steels, too. Another uncertainty of this equation is that it states a common temperature dependence on nitrogen activity for all alloying elements.

When steel is highly alloyed, second-order interactions parameters are needed. Professor Pehlke and his co-workers measured nitrogen solubility in a wide range of different liquid Fe alloys and determined the first and second-order interactions in iron between nitrogen and different alloying elements.[10,13,14,18,25,26] Wada and Pehlke[26] extended the experimental work on Fe–Cr–Ni–Mo–Mn alloys to determine the effects of the main alloying elements and temperature on nitrogen behavior in these alloys. Their results can be summarized by the following equation:

$$\begin{aligned}\log[\text{Pct N}] = &\left(\frac{-247}{T} - 1.22\right) - \Bigg\{\left(\frac{-164}{T} + 0.0415\right)[\text{Pct Cr}] + \left(\frac{8.33}{T} + 0.0019\right)[\text{Pct Ni}] + \left(\frac{-33.2}{T} + 0.0064\right) \\ &[\text{Pct Mo}] + \left(\frac{-134}{T} + 0.035\right)[\text{Pct Mn}] + \left(\frac{1.68}{T} - 0.0006\right)[\text{Pct Cr}]^2 + \left(\frac{-1.83}{T} + 0.001\right)[\text{Pct Ni}]^2 + \left(\frac{-2.78}{T} + 0.0013\right) \\ &[\text{Pct Mo}]^2 + \left(\frac{8.82}{T} - 0.0056\right)[\text{Pct Mn}]^2 + \left(\frac{1.6}{T} - 0.0009\right)[\text{Pct Cr}][\text{Pct Ni}] + \left(\frac{1.2}{T} - 0.0005\right) \\ &[\text{Pct Cr}][\text{Pct Mo}] + \left(\frac{2.16}{T} - 0.0005\right)[\text{Pct Cr}][\text{Pct Mn}] + \left(\frac{-0.26}{T} + 0.0003\right) \\ &[\text{Pct Ni}][\text{Pct Mo}] + \left(\frac{0.09}{T} + 0.0007\right)[\text{Pct Ni}][\text{Pct Mn}]\Bigg\}\end{aligned} \quad [11]$$

This equation can be used in a relatively wide range but is also quite complex due to the large number of coefficients. Wada and Pehlke[26] also derived an equation for predicting the nitrogen solubility in alloy steels at any temperature, when log $f_{N,\ 1873\ K}$ is known. This equation is

$$\log[\text{Pct N}] = -\frac{247}{T} - 1.22 - \left(\frac{4780}{T} - 1.51\right)\left(\log f_{N,1873K}\right) - \left(\frac{1760}{T} - 0.91\right)\left(\log f_{N,1873K}\right)^2 \quad [12]$$

As the authors remarked, there are deviations from the experimental results due to differences in the heat of solutions for different solutes.[26]

Jiang *et al.*[28] modified the Chipman and Corrigan model by adding second-order terms for Cr, Ni, Mo, and Mn. Their expression for nitrogen solubility at 1 atm pressure was written as follows:

$$\log[\text{Pct N}] = -\frac{188}{T} - 1.17 - \left\{\left(\frac{3280}{T} - 0.75\right)(0.13[\text{Pct N}] + 0.118[\text{Pct C}] + 0.043[\text{Pct Si}] - 0.024[\text{Pct Mn}] - 0.048[\text{Pct Cr}] + 0.011[\text{Pct Ni}] - 0.01[\text{Pct Mo}] + 0.000032[\text{Pct Mn}]^2 + 0.00035[\text{Pct Cr}]^2 + 0.000035[\text{Pct Ni}]^2 + 0.000079[\text{Pct Mo}]^2)\right\} \quad [13]$$

According to Jiang *et al.*,[28] an extra term, concerning the effect of pressure on nitrogen activity, is needed when the nitrogen pressure is more than one atmosphere. However, the AOD process is normally not pressurized, so this can be ignored.

Anson[15] presented a model, which uses pure iron as the reference state and considers the interaction parameters of both first and second-order and the temperature dependencies. This equation follows most clearly the Wagner-Lupis-Elliot formalism, without simplifications:

$$\log[\text{Pct N}] = \left[-\frac{322}{T} - 1.182\right] - \left(\frac{361.924}{T} + 0.14\right)[\text{Pct Cr}] + \left(\frac{110.23}{T} - 0.0499\right)[\text{Pct Ni}] + \left(-\frac{279.46}{T} + 0.1244\right)[\text{Pct Mn}] + \left(-\frac{298.28}{T} + 0.1494\right)[\text{Pct Mo}] + \left(\frac{9.71}{T} - 0.0049\right)[\text{Pct Cr}]^2 + \left(-\frac{2.3463}{T} + 0.0011\right)[\text{Pct Mn}]^2 + \left(\frac{21.507}{T} - 0.0115\right)[\text{Pct Mo}]^2 \quad [14]$$

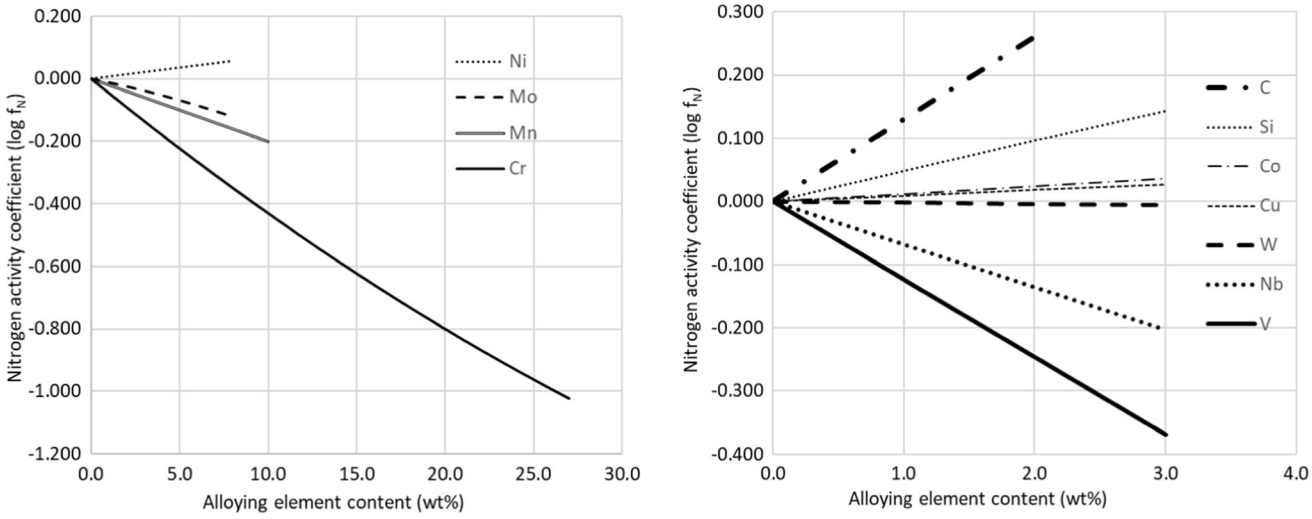

Fig. 2—Effect of major alloying elements (left) and some minor alloying elements (right) on the activity coefficient (log) of nitrogen in Fe–Me melts at 1600 °C according to the Steelmaking Data Sourcebook.[32]

Table I. Log *K* Values and Interaction Parameters With Nitrogen for Different Alloying Elements

	Chipman and Corrigan[12]	Jiang[28]	Anson[15]	Wada and Pehlke[26]	Steelmaking Data Sourcebook[32]
Log K_N	$\frac{-188}{T} - 1.25$	$\frac{-188}{T} - 1.17$	$\frac{-322}{T} - 1.182$	$\frac{-247}{T} - 1.22$	$\frac{-518}{T} - 1.063$
Mn	$\frac{-75}{T} + 0.017$	$\frac{-79}{T} - 0.02$	$\frac{-279.46}{T} + 0.1244$	$\frac{-134}{T} + 0.035$	$- 0.02$
Cr	$\frac{-148}{T} + 0.033$	$\frac{-157}{T} + 0.036$	$\frac{-361.924}{T} + 0.14$	$\frac{-164}{T} + 0.0415$	$\frac{-148}{T} + 0.033$
Ni	$\frac{33}{T} - 0.008$	$\frac{36}{T} - 0.008$	$\frac{110.23}{T} - 0.0499$	$\frac{8.33}{T} + 0.0019$	0.007
Mo	$-\frac{36}{T} + 0.008$	$-\frac{33}{T} + 0.008$	$\frac{-298.28}{T} + 0.1494$	$\frac{-33.2}{T} + 0.0064$	$\frac{-33.2}{T} + 0.0064$
Cr^2		$\frac{1.15}{T} - 0.000263$	$\frac{9.71}{T} - 0.0049$	$\frac{1.68}{T} - 0.0006$	$\frac{1.56}{T} - 0.00053$
Ni^2		$\frac{0.11}{T} - 0.0000263$		$\frac{-1.83}{T} - 0.001$	
Mn^2		$\frac{0.1}{T} - 0.000024$	$\frac{-2.3463}{T} + 0.0011$	$\frac{8.82}{T} - 0.0056$	$- 0.0004$
Mo^2		$\frac{0.26}{T} - 0.0000593$	$\frac{21.507}{T} - 0.0115$	$\frac{-2.78}{T} + 0.0013$	$\frac{-5.57}{T} + 0.0025$
Cr*Ni				$\frac{1.6}{T} - 0.0009$	
Cr*Mo				$\frac{1.2}{T} - 0.0005.$	
Cr*Mn				$\frac{2.16}{T} - 0.0005$	
Ni*Mo				$\frac{-0.26}{T} + 0.0003$	
Ni*Mn				$\frac{0.09}{T} + 0.0007$	

Kijac *et al.*[16] have also presented interaction parameters in the same way for some minor alloying elements in low alloyed steels in oxygen steelmaking. In their equation, however, the temperature dependence differs significantly from the others, and the interaction terms for nickel and molybdenum are absent.

The Steelmaking Data Sourcebook[32] is a comprehensive collection of thermodynamic data. Equation [15] is obtained by extracting the "recommended parameters" as follows:

$$\begin{aligned}\log[\text{Pct N}] = &\left[-\frac{518}{T} - 1.063\right]\\ &\{0.01[\text{Pct Al}] + 0.018[\text{Pct As}] + 0.094[\text{Pct B}]\\ &+0.13[\text{Pct C}] + 0.012[\text{Pct Co}] + \left(\frac{148}{T} + 0.033\right)[\text{Pct Cr}]\\ &+\left(\frac{1.56}{T} - 0.00053\right)[\text{Pct Cr}]^2 + 0.009[\text{Pct Cu}] - 0.02[\text{Pct Mn}]\\ &+\left(-\frac{33.2}{T} + 0.0064\right)[\text{Pct Mo}] + \left(\frac{-5.57}{T} + 0.0025\right)[\text{Pct Mo}]^2\\ &-0.068[\text{Pct Nb}] + 0.007[\text{Pct Ni}] - 0.12[\text{Pct O}]\\ &+0.059[\text{Pct P}] + 0.007[\text{Pct S}] + 0.0088[\text{Pct Sb}]\\ &+0.006[\text{Pct Se}] + 0.048[\text{Pct Si}] + 0.007[\text{Pct Sn}]\\ &+\left(-\frac{524}{T} + 0.231\right)[\text{Pct Ta}] + 0.07[\text{Pct Te}]\\ &+\left(-\frac{5700}{T} + 2.45\right)[\text{Pct Ti}] + \left(-\frac{1420}{T} + 0.635\right)[\text{Pct V}]\\ &-0.002[\text{Pct W}] - 0.63[\text{Pct Zr}]\}\end{aligned} \quad [15]$$

The effect of different elements on nitrogen solubility can be compared based on Figure 2, where the effect of the alloying elements on the activity coefficient of nitrogen according to the Steelmaking Data Sourcebook[32] is shown. Elements with a negative coefficient increase the solubility of nitrogen and vice versa. The total effect is naturally based on the content of the elements in the alloy.

Table I shows a collection of different groups of interaction parameters for the main alloying elements of stainless steels presented in a comparable way. Chipman and Corrigan[12] represent first-order equations, Jiang[28] first and second-order equations, Anson[15] formalism, where each element has its own temperature coefficient, and the Wada and Pehlke[26] model also considers the cross-interaction between elements. For reference the parameters from the Steelmaking Data Sourcebook[32] are also shown.

In the examination above, pure iron was taken as the reference point. In high alloyed steels another reference point can be selected. One example is Anson's[15] development in which he used Fe-20 pct Cr as a reference:

$$\begin{aligned}\log[\text{Pct N}] = &\left[\frac{1467.6}{T} - 1.28\right]\\ &-\left[\left(-\frac{185.45}{T} + 0.0694\right)[\text{Pct Cr} - 20]\right.\\ &+\left(\frac{86.569}{T} - 0.0371\right)[\text{Pct Ni}]\\ &+\left(-\frac{155.68}{T} + 0.0701\right)[\text{Pct Mn}]\\ &+\left(\frac{49.89}{T} - 0.0344\right)[\text{Pct Mo}]\\ &\left.+\left(\frac{358.87}{T} - 0.0724\right)[\text{Pct C}]\right]\end{aligned} \quad [16]$$

This model is mathematically simple and suitable for duplex steel grades (20 to 30 wt pct Cr and 5 wt pct Ni) at temperatures between 1550 °C and 1650 °C. With this method, the solubility of nitrogen can be simply expressed only by first-order interaction coefficients. Kobayashi *et al.* [31] developed Anson's model further by reassessing the N–Ni interaction in Fe-20 pct Cr. They found that the effect of Ni can be assumed to be temperature-independent in the range of 1823 K to 1873 K and thus can be replaced by a Ni-factor 0.0063. The new Eq. [17] predicts nitrogen solubility more accurately

$$\begin{aligned}\log[\text{Pct N}] = &\left[\frac{1467.6}{T} - 1.28\right] \\ &- \left[\left(-\frac{185.45}{T} + 0.0694\right)[\text{Pct Cr} - 20]\right. \\ &+0.0063[\text{Pct Ni}] + \left(-\frac{155.68}{T} + 0.0701\right)[\text{Pct Mn}] \\ &+\left(\frac{49.89}{T} - 0.0344\right)[\text{Pct Mo}] \\ &\left.+\left(\frac{358.87}{T} - 0.0724\right)[\text{Pct C}]\right]\end{aligned} \quad [17]$$

A chromium equivalent method has been proposed by Satir-Kolorz *et al.*[33] In this empirical method, complex alloys can be reduced to a ternary Fe–Cr–N solution by giving each alloying element its own Cr-equivalent factor. Accordingly, Cr has factor 1.0; Ni −0.22; Mo 0.27, and Mn 0.50. The expression for nitrogen content was written as

$$\begin{aligned}\log[\text{Pct N}] = &-\frac{247}{T} - 1.22 - \left(\frac{3280}{T} - 0.75\right) \\ &\left(-0.048[\text{Pct Cr}]_{\text{eq}} + 0.00035[\text{Pct Cr}]^2_{\text{eq}}\right)\end{aligned} \quad [18]$$

This approach seems promising, but it ignores individual temperature dependencies for different alloying elements.

III. NITROGEN SOLUBILITY IN AN INDUSTRIAL AOD PROCESS—EXPERIMENTAL RESULTS AND COMPARISON WITH SOLUBILITY EQUATIONS

In order to compare nitrogen behavior in an industrial process to the correlations discussed above, a set of experiments was carried out. The measurements were performed in an industrial 95 ton AOD converter. The aim of the AOD process is to reduce the carbon content, remove sulfur, adjust other alloying elements close to the target composition of steel and, finally, adjust the temperature to make it suitable for the subsequent process stages. All these are done by blowing gases into the converter, and by adding alloying and cooling materials and slag forming agents. Carbon removal (decarburization) occurs when oxygen and inert gases (Ar, N_2) are blown into the converter. During decarburization, some of the oxygen also reacts with alloy metals and the chromium oxide content of the slag rises to 30 to 40 pct. When nitrogen is used as the inert gas, the nitrogen content in steel can be assumed to be close to its maximum solubility the whole time, and especially at the end of decarburization, when the partial pressure of nitrogen is high, *i.e.*, over 0.8 atm. When the desired carbon content in steel is reached, the slag is reduced with silicon or aluminum. During the reduction step the melt is stirred with inert gases and valuable metal oxides will be reduced, the oxygen and sulfur content of the steel will be lowered and transferred from liquid metal to liquid slag. The final sulfur and nitrogen contents depend on the composition and temperature of the melt, the basicity and viscosity of the slag, the gases used, and the duration and efficiency of the gas stirring. When producing nitrogen-alloyed steels, nitrogen can be used as an "inert gas" through both the decarburization and the reduction steps, after which the nitrogen content in steel can be lowered (if needed) by argon gas stirring.

A representative collection of a total of 100 heats of different steel grades was chosen for this study. They differ in composition (Cr 13 to 28 pct; Ni 0 to 35 pct; Mo 0 to 7 pct; Mn 0 to 16 pct) and temperature (1470 °C to 1780 °C) in order to provide a good understanding of the factors affecting nitrogen solubility. The selected steel grades were high nitrogen-alloyed, so nitrogen was used as an inert gas through both the decarburization and reduction steps.

All the samples were taken from the AOD converter after the reduction stage. Before sampling, the melt had been purged with pure nitrogen for at least six minutes to ensure the equilibrium nitrogen content at this temperature, steel composition, and 1 atm nitrogen pressure. These samples were analyzed using the following methods: Optical Emission Spectroscopy (Thermo Scientific™ ARL™ 4460 OES) or infrared combustion (LECO TC-600) for N, S, and C; and X-ray fluorescence (Thermo Scientific™ ARL™ 9900 Simultaneous-Sequential XRF) for other elements. The measurements (temperatures and steel chemistry for the main alloying elements) are listed in Table II and are categorized into 13 groups (in each group, there are only minor variations in Cr, Ni, Mo, and Mn contents). Each group is arranged according to ascending nitrogen content. The contents of the other elements analyzed (P, S, Ti, Nb, Sn, As, W, Ce, V, Al, B) are not shown in Table II; they were very low (typically < 0.1 pct) in all the samples and, therefore, their impact on the outcome can be considered negligible. From Table II, thirteen (highlighted in italics) samples (numbers 5, 20, 32, 35, 44, 53, 57, 72, 76, 83, 90, 95, and 99) with nitrogen content close to the average of each group were selected for further examination. This choice covers the entire composition range well.

Table II. Measured Temperatures and Compositions of Experimental Heats Rinsed With N_2 (1 atm)

		Measured Chemical Composition, (Wt pct)								
Sample Number	Temperature °C	C	Si	Mn	Cr	Ni	Mo	Cu	Co	N
1	1632	0.27	0.2	15.5	13.8	0.2	0.0	0.4	0.0	0.30
2	1633	0.29	0.3	15.7	14.0	0.2	0.0	0.5	0.0	0.31
3	1659	0.27	0.3	15.8	14.0	0.2	0.0	0.4	0.0	0.31
4	1541	0.28	0.2	15.6	13.8	0.2	0.0	0.4	0.0	0.33
5	*1518*	*0.28*	*0.4*	*16.0*	*14.0*	*0.3*	*0.0*	*0.4*	*0.0*	*0.34*
6	1479	0.28	0.2	15.8	13.7	0.2	0.0	0.4	0.0	0.34
7	1507	0.29	0.3	15.8	13.9	0.2	0.0	0.4	0.0	0.35
8	1565	0.27	0.4	16.0	14.0	0.3	0.0	0.4	0.0	0.35
9	1512	0.31	0.2	15.9	13.8	0.1	0.0	0.4	0.0	0.35
10	1486	0.31	0.3	15.3	13.9	0.2	0.0	0.5	0.0	0.36
11	1472	0.29	0.2	16.3	13.3	0.2	0.1	0.4	0.0	0.37
12	1700	0.31	0.2	9.2	14.4	0.2	0.0	0.4	0.0	0.19
13	1678	0.31	0.2	9.2	14.4	0.3	0.0	0.4	0.2	0.20
14	1699	0.26	0.1	9.1	14.7	0.2	0.0	0.4	0.0	0.20
15	1706	0.25	0.3	9.1	14.4	0.2	0.0	0.4	0.0	0.20
16	1666	0.28	0.3	8.8	14.7	0.2	0.0	0.5	0.0	0.20
17	1689	0.15	0.3	9.4	14.8	0.3	0.1	0.4	0.0	0.21
18	1686	0.26	0.3	10.0	14.4	0.2	0.0	0.4	0.1	0.22
19	1710	0.21	0.2	9.9	14.6	0.3	0.0	0.4	0.0	0.22
20	*1646*	*0.23*	*0.2*	*9.5*	*14.8*	*0.3*	*0.0*	*0.4*	*0.0*	*0.22*
21	1644	0.30	0.2	8.8	14.9	0.2	0.0	0.5	0.0	0.22
22	1631	0.15	0.2	8.9	14.9	0.2	0.0	0.4	0.0	0.22
23	1637	0.17	0.2	10.0	14.6	0.2	0.0	0.5	0.0	0.23
24	1643	0.14	0.3	9.1	14.9	0.2	0.0	0.0	0.0	0.23
25	1640	0.19	0.2	9.2	14.9	0.3	0.0	0.3	0.0	0.23
26	1636	0.22	0.2	9.1	14.9	0.2	0.0	0.5	0.0	0.23
27	1595	0.27	0.5	9.9	14.4	0.2	0.0	0.5	0.0	0.23
28	1610	0.16	0.4	9.2	14.8	0.2	0.0	0.5	0.0	0.23
29	1635	0.27	0.3	11.1	14.4	0.2	0.0	0.4	0.0	0.25
30	1740	0.02	0.4	0.9	16.8	6.3	0.4	0.3	0.1	0.20
31	1711	0.01	0.6	0.9	17.0	6.4	0.4	0.5	0.2	0.20
32	*1720*	*0.01*	*0.4*	*0.8*	*17.2*	*6.5*	*0.4*	*0.3*	*0.2*	*0.21*
33	1685	0.01	0.4	0.8	17.0	6.4	0.4	0.4	0.1	0.21
34	1691	0.01	0.3	0.8	17.0	6.4	0.4	0.3	0.1	0.22
35	*1779*	*0.00*	*0.3*	*1.2*	*17.1*	*12.2*	*2.6*	*0.3*	*0.1*	*0.18*
36	1706	0.01	0.3	1.3	18.2	8.7	0.3	0.4	0.2	0.21
37	1710	0.01	0.3	1.2	18.2	8.6	0.4	0.4	0.2	0.21
38	1755	0.01	0.2	1.3	18.2	8.7	0.4	0.4	0.2	0.21
39	1727	0.01	0.3	1.4	18.2	8.7	0.4	0.3	0.2	0.22
40	1712	0.01	0.3	1.3	18.3	8.7	0.5	0.4	0.2	0.22
41	1682	0.01	0.4	1.2	18.2	8.6	0.4	0.4	0.2	0.22
42	1713	0.01	0.3	1.2	18.2	8.7	0.3	0.3	0.2	0.22
43	1708	0.01	0.3	1.2	18.2	8.7	0.3	0.3	0.2	0.22
44	*1697*	*0.01*	*0.4*	*1.4*	*18.4*	*8.5*	*0.4*	*0.4*	*0.2*	*0.23*
45	1670	0.01	0.4	1.3	18.1	8.7	0.4	0.4	0.2	0.23
46	1673	0.01	0.3	1.3	18.2	8.7	0.4	0.3	0.2	0.23
47	1762	0.02	0.3	1.0	19.4	9.2	0.1	0.1	0.2	0.23
48	1692	0.02	0.3	1.0	19.5	10.0	0.1	0.1	0.2	0.23
49	1658	0.01	0.3	1.1	18.8	9.7	0.1	0.1	0.2	0.24
50	1666	0.01	0.5	1.1	18.6	9.5	0.1	0.1	0.2	0.24

		Measured Chemical Composition, (Wt pct)								
Sample Number	Temperature °C	C	Si	Mn	Cr	Ni	Mo	Cu	Co	N
51	1776	0.03	0.2	3.7	18.4	3.5	0.2	0.4	0.1	0.24
52	1735	0.03	0.3	3.9	18.0	4.3	0.2	0.4	0.1	0.24
53	*1678*	*0.02*	*0.3*	*3.3*	*18.3*	*4.1*	*0.5*	*0.4*	*0.1*	*0.26*
54	1688	0.02	0.3	4.6	17.9	4.1	0.5	0.4	0.1	0.26
55	1733	0.01	0.2	0.6	20.6	18.6	6.3	0.8	0.6	0.23
56	1705	0.01	0.1	0.4	20.5	17.8	6.2	0.7	0.4	0.25
57	*1697*	*0.01*	*0.4*	*0.5*	*20.8*	*16.5*	*6.2*	*0.7*	*0.3*	*0.25*

Table II. continued

Sample Number	Temperature °C	Measured Chemical Composition, (Wt pct)								
		C	Si	Mn	Cr	Ni	Mo	Cu	Co	N
58	1680	0.01	0.2	0.5	20.6	16.5	6.2	0.6	0.3	0.26
59	1659	0.01	0.5	0.5	20.8	17.5	6.1	0.7	0.4	0.27
60	1745	0.01	0.6	0.5	20.8	18.5	6.2	0.8	0.6	0.23
61	1718	0.01	0.4	0.5	20.6	17.3	6.0	0.7	0.4	0.24
62	1715	0.01	0.2	0.6	20.6	18.3	6.3	0.8	0.6	0.26
63	1696	0.01	0.2	0.7	20.9	18.1	6.4	0.8	0.7	0.26
64	1660	0.01	0.4	0.6	20.9	18.4	6.4	0.8	0.5	0.27
65	1659	0.02	0.2	0.6	20.7	18.1	6.0	0.8	0.6	0.27
66	1751	0.07	1.4	0.7	21.4	10.1	0.2	0.2	0.2	0.23
67	1678	0.04	1.3	0.8	20.6	10.7	0.2	0.2	0.2	0.23
68	1728	0.04	1.3	0.5	21.1	10.8	0.2	0.1	0.2	0.23
69	1676	0.06	1.8	0.6	21.2	11.0	0.3	0.2	0.2	0.24
70	1661	0.05	1.6	0.6	20.7	10.8	0.2	0.2	0.2	0.24
71	1685	0.06	1.3	0.7	21.1	10.3	0.3	0.2	0.2	0.25
72	*1695*	*0.04*	*1.3*	*0.7*	*20.9*	*10.4*	*0.2*	*0.2*	*0.2*	*0.25*
73	1657	0.06	1.4	0.5	21.2	11.7	0.2	0.2	0.2	0.25
74	1670	0.06	1.3	0.8	20.8	10.9	0.2	0.2	0.2	0.26
75	1647	0.06	1.6	0.9	21.5	10.0	0.4	0.3	0.2	0.27
76	*1698*	*0.01*	*0.3*	*0.7*	*21.3*	*23.6*	*6.6*	*0.6*	*0.2*	*0.24*
77	1644	0.01	0.2	0.7	21.3	22.1	6.8	0.5	0.2	0.29
78	1720	0.02	0.6	4.3	21.3	1.5	0.2	0.3	0.0	0.30
79	1727	0.02	0.5	3.8	21.4	1.5	0.2	0.3	0.1	0.31
80	1717	0.02	0.6	4.2	21.5	1.5	0.2	0.3	0.0	0.31
81	1709	0.03	0.6	3.9	21.3	1.5	0.2	0.3	0.1	0.31
82	1690	0.02	0.7	3.8	21.3	1.5	0.3	0.3	0.0	0.31
83	*1702*	*0.02*	*0.6*	*4.3*	*21.4*	*1.4*	*0.3*	*0.3*	*0.0*	*0.32*
84	1701	0.03	0.6	4.3	21.5	1.6	0.2	0.3	0.1	0.32
85	1720	0.02	0.5	4.8	21.5	1.5	0.3	0.3	0.0	0.33
86	1672	0.03	0.4	4.1	21.5	1.5	0.2	0.3	0.0	0.34
87	1734	0.01	0.4	1.3	23.8	4.3	0.5	0.3	0.1	0.33
88	1678	0.01	0.8	1.3	23.2	4.3	0.5	0.3	0.1	0.33
89	1687	0.01	0.5	1.4	23.9	4.3	0.5	0.3	0.1	0.35
90	*1692*	*0.01*	*0.4*	*1.4*	*23.9*	*4.3*	*0.5*	*0.3*	*0.2*	*0.35*
91	1694	0.02	0.5	1.3	23.9	4.1	0.4	0.3	0.1	0.35
92	1682	0.01	0.3	1.4	24.1	4.2	0.5	0.4	0.1	0.37
93	1678	0.01	0.5	1.3	24.2	4.1	0.5	0.3	0.1	0.37
94	1710	0.01	0.3	1.3	22.4	5.6	3.2	0.3	0.2	0.34
95	*1738*	*0.01*	*0.1*	*0.7*	*25.2*	*6.6*	*3.7*	*0.3*	*0.2*	*0.38*
96	1702	0.02	0.4	0.7	25.7	7.0	3.7	0.3	0.2	0.38
97	1699	0.01	0.1	0.7	24.9	6.4	3.6	0.3	0.2	0.40
98	1697	0.01	0.0	0.7	26.9	35.4	6.5	0.2	0.0	0.30
99	*1620*	*0.01*	*0.0*	*0.8*	*27.4*	*34.6*	*6.4*	*0.1*	*0.0*	*0.36*
100	1576	0.01	0.0	0.8	27.4	34.5	6.4	0.1	0.0	0.41

Due to unavoidable variations in scrap-based steel production, it is impossible to keep any factor unchanged, and consequently it is challenging to draw quantitative conclusions about the effects of different factors on nitrogen solubility based on these measurements. This means that the analysis of multi-component alloys has to be based on a mathematical model. Such models were introduced above. These models were developed using pure raw materials and within a certain range of composition and temperature. Notwithstanding, they were utilized as the basis of our own modified model. The decision included building the model in a simplified way; only the first-order terms for the main alloying elements were to be temperature-dependent and the interaction term for nickel had to remain constant. In this way, the model may lose a little of its sensitivity but is expected to be more stable even outside the typical operation limits. Based on these boundary conditions and measurements, a regression analysis was performed with Minitab®[34] and Excel®,[35] which resulted in a new revised Eq. [19]. In addition to our own measurements, the results of Kobayashi[31] and the nitrogen content in pure iron according to Chipman and Corrigan[12] (listed in Table III) were used in the regression analysis.

Table III. Additional Nitrogen Solubility Data Used in Regression Analysis

Temperature °C	Mn	Cr	Ni	Mo	N	Refs.	Temperature °C	Mn	Cr	Ni	Mo	N	Refs.
1550					0.044	12	1550	1.0	29.0	29.7	8.2	0.500	31
1600					0.045	12	1450		29.0	29.7	8.2	0.620	31
1650					0.045	12	1550		29.0	29.7	8.2	0.500	31
1700					0.045	12	1600			29.7	8.2	0.450	31
1550		24.9	30.0	8.0	0.370	31	1550		25.2	30.1	3.1	0.340	31
1550		25.0	28.7	7.9	0.380	31	1550		24.7	29.9	11.7	0.410	31
1450		25.0	28.7	7.9	0.470	31	1550		23.9	22.1	7.3	0.390	31
1600		25.0	28.7	7.9	0.350	31	1470		23.9	22.1	7.3	0.420	31
1550	1.0	25.0	28.7	7.9	0.390	31	1600		23.9	22.1	7.3	0.350	31
1550	2.9	25.0	28.7	7.9	0.420	31	1470	3.0	23.9	22.1	7.3	0.450	31
1450	2.9	25.0	28.7	7.9	0.470	31	1550		20.4	18.0		0.260	31
1600	2.9	25.0	28.7	7.9	0.400	31	1600		20.4	18.0		0.240	31
1550	2.0	25.0	28.7	7.9	0.370	31	1550	3.7	24.6	7.2		0.460	31
1550		27.0	29.8	8.2	0.430	31	1600	3.7	24.6	7.2		0.430	31
1550		29.0	29.7	8.2	0.500	31	1600		20.0			0.310	31
1550		25.0	29.9	6.2	0.360	31	1650		20.0			0.290	31
1550	2.9	29.0	29.7	8.2	0.520	31							

$$\log[\text{Pct N}] = \left(\frac{-175}{T} - 1.257\right) - \left\{\left(\frac{-81}{T} - 0.00709\right)[\text{Pct Cr}] + 0.00617[\text{Pct Ni}] + \left(\frac{-65.1}{T} + 0.0264\right)[\text{Pct Mo}] + \left(\frac{-43.5}{T} + 0.01898\right)[\text{Pct Mn}] + 0.000403[\text{Pct Cr}]^2 - 0.000048[\text{Pct Mo}]^2 - 0.000958[\text{Pct Mn}]^2 + 0.25[\text{Pct C}] + 0.025[\text{Pct Si}] + 0.009[\text{Pct Cu}] + 0.012[\text{Pct Co}] - 0.002[\text{Pct W}] - 0.123[\text{Pct V}] - 0.068[\text{Pct Nb}]\} \quad [19]$$

The interaction terms for the main elements (Cr, Ni, Mn, Mo, Si and C) have been revised in Eq. [19]. For other important alloying elements (Cu, Co, W, V and Nb), the values from the Steelmaking data Sourcebook[32] (Eq. [15]) were used because the measurement data were insufficient for a reliable revision. When necessary, known table values (including Eq. [15]) can be used for other minor alloying elements (P, S, O, Ti, Al, B, Sn, As, Ce). Their contents in the AOD process are generally so low that they do not affect the solubility of nitrogen and can thus be disregarded. In Eq. [19], the high interaction term of carbon is noteworthy: 0.25 is much higher than the 0.13 which is used in the Steelmaking Data Sourcebook.[32] This may be due, on the one hand, to the fact that in these measurements high carbon and higher manganese content and low temperature occurred in the same heats. On the other hand, the coefficient used in the Steelmaking Data Sourcebook is based on Nelson's[36] measurements, which were based on one, very high carbon content (about 4 pct) steel. It is understandable that no special attention has been paid to the carbon factor because most steels have a low carbon content. On the other hand, steels with a higher carbon content are generally not nitrogen-alloyed. This may require further investigation and measurements in the future to determine whether a second-order coefficient or temperature dependence would be necessary for carbon.

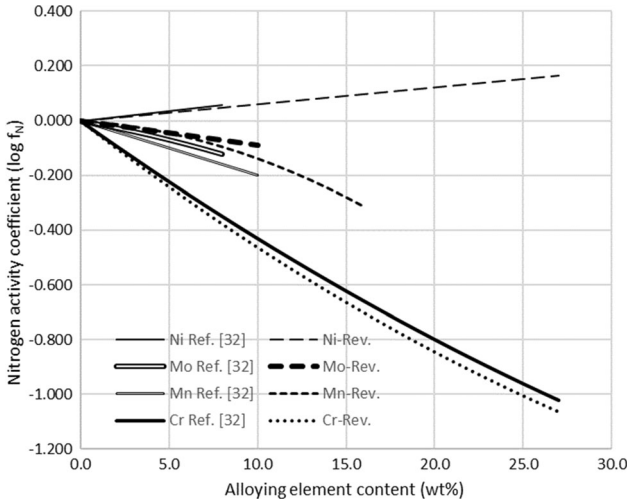

Fig. 3—The effect of major alloying elements on the nitrogen activity coefficients (logarithm) at 1600 °C. Comparison between the present model and the values presented in the Steelmaking Data Sourcebook[32]

Figure 3 shows a comparison of the revised activity coefficients for the main alloying elements. For nickel, these results support the previous findings, and its validity range can be extended. The effects of manganese and moybdenum on nitrogen solubility are somewhat smaller than previously presented, and the values for manganese and molybdenum also seem to be closer to each other. For chromium, the second-order factor brings about an obvious curvature as the Cr content increases.

In Figure 4(a), the measured nitrogen content (from Table II) and the calculations from Eq. [19] are shown. Good agreement is found with the biggest deviation being 0.022 wt pct. In Figure 4(b), a comparison

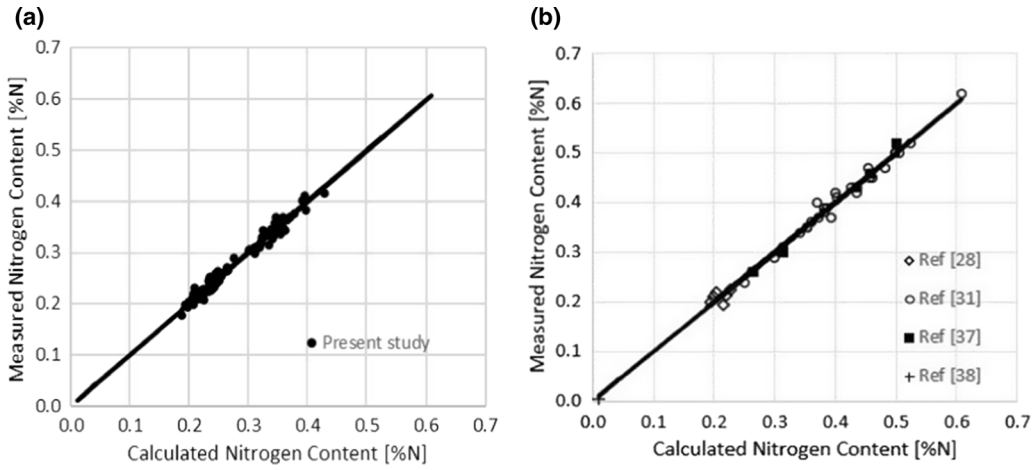

Fig. 4—(*a*) Comparison between measured (present study (Table II) and calculated (by Eq. [19] nitrogen contents. (*b*) Comparison between measurements by other researchers and calculated (by Eq. [19]) nitrogen contents.

Table IV. Comparison Between Calculated and Measured Nitrogen Contents

		Measured Chemical Composition, (Wt pct)								
Sample Number	Temperature °C	C	Si	Mn	Cr	Ni	Mo	Cu	Co	N
5	1518	0.28	0.4	16.0	14.0	0.3	0.0	0.4	0.0	0.337
20	1646	0.23	0.2	9.5	14.8	0.3	0.0	0.4	0.0	0.219
32	1720	0.01	0.4	0.8	17.2	6.5	0.4	0.3	0.2	0.209
35	1779	0.00	0.3	1.2	17.1	12.2	2.6	0.3	0.1	0.177
44	1697	0.01	0.4	1.4	18.4	8.5	0.4	0.4	0.2	0.225
53	1678	0.02	0.3	3.3	18.3	4.1	0.5	0.4	0.1	0.261
57	1697	0.01	0.4	0.5	20.8	16.5	6.2	0.7	0.3	0.254
72	1695	0.04	1.3	0.7	20.9	10.4	0.2	0.2	0.2	0.249
76	1698	0.01	0.3	0.7	21.3	23.6	6.6	0.6	0.2	0.242
83	1702	0.02	0.6	4.3	21.4	1.4	0.3	0.3	0.0	0.317
90	1692	0.01	0.4	1.4	23.9	4.3	0.5	0.3	0.2	0.350
95	1738	0.01	0.1	0.7	25.2	6.6	3.7	0.3	0.2	0.375
99	1620	0.01	0.0	0.8	27.4	34.6	6.4	0.1	0.0	0.364

Ref. [12] Eq. [10]	Ref. [26] Eq. [11]	Ref. [28] Eq. [13]	Ref. [15] Eq. [14]	Ref. [32] Eq. [15]	Ref. [15] Eq. [16]	Ref. [31] Eq. [17]	Ref. [33] Eq. [18]	Ref. [39] Factsage	Pres. Study Eq. [19]
0.456	**0.838**	**0.518**	**0.746**	*0.342*	***0.366***	***0.367***	*0.335*	*0.327*	*0.352*
0.286	**0.371**	**0.327**	**0.273**	***0.251***	***0.262***	***0.262***	***0.236***	***0.254***	*0.223*
0.195	***0.186***	*0.199*	***0.164***	***0.182***	***0.228***	***0.228***	***0.173***	*0.204*	*0.204*
0.174	*0.166*	*0.179*	***0.135***	***0.171***	***0.221***	***0.214***	***0.159***	*0.182*	*0.186*
0.221	***0.209***	*0.218*	***0.191***	***0.202***	***0.241***	***0.243***	***0.192***	*0.224*	*0.223*
0.273	0.252	*0.270*	***0.230***	*0.241*	*0.270*	*0.272*	***0.225***	*0.259*	*0.246*
0.256	***0.231***	***0.234***	***0.210***	*0.239*	***0.269***	***0.275***	***0.217***	*0.245*	*0.258*
0.235	*0.237*	***0.218***	***0.221***	***0.204***	*0.263*	***0.266***	***0.203***	*0.234*	*0.241*
0.239	***0.210***	***0.208***	***0.200***	*0.230*	*0.251*	***0.259***	***0.206***	*0.232*	*0.246*
0.382	***0.336***	***0.351***	***0.295***	*0.314*	***0.334***	***0.335***	***0.286***	***0.334***	*0.318*
0.413	***0.331***	*0.346*	***0.321***	***0.324***	*0.355*	*0.358*	***0.302***	*0.360*	*0.353*
0.435	***0.334***	***0.354***	**0.292**	***0.349***	*0.370*	*0.368*	**0.310**	*0.377*	*0.373*
0.405	**0.300**	**0.251**	***0.339***	***0.347***	**0.293**	*0.353*	**0.305**	***0.345***	*0.359*

between the present model and the measurements from Jiang *et al.*,[28] Kobayashi *et al.*,[31,37] and Shahapurkar and Small[38] is also shown. The biggest difference between the measurements of other researchers and the revised model is 0.03 wt pct.

A comparison between the highlighted samples in Table II and predictions calculated using the above-mentioned models and our new revised model is presented in Table IV. The sample number, temperature, chemical composition, and the measured nitrogen

content are shown on the left, followed by the predicted nitrogen contents on the right, *i.e.*, the values calculated using the equations in the corresponding references. The two rightmost columns show the results calculated with thermochemical software (FactSage® 8.1 and FSstel database[39]) and the results calculated with the new revised model. In cases where the absolute difference compared to the measurement is less than 0.015 wt pct, the result is highlighted in italic, for a deviation of more than 0.050 wt pct highlighted in Bold, and for a deviation between 0.015 and 0.050 wt pct, the highlighted in Bolditalic.

Some observations arise from a close inspection of Table IV. In most cases the predicted nitrogen content agree well with the measurements. This is true when the temperature is not too low and the contents of the main alloying elements are moderate. Low temperature (< 1600 °C), high Cr (> 20 pct), high Mn (> 5 pct), high Ni (> 25 pct), and especially combinations of these tend to cause anomalies between the models and industrial measurements. Even the Cr equivalence model[33] gave fairly good results, confirming that the nitrogen content is largely dictated by chromium. However, this model encounters problems at extreme temperatures and compositions, meaning that the thermal behavior of the alloy differs from that of chromium. Anson's approach with Fe-20 pct Cr as the reference state[15] (Eq. [16]) follows the variations quite well, not only for duplex steel, but also for other steels. The only exception is the highest Ni content, sample 99. Kobayashi's[31] finding of a constant Ni-factor corresponds well, which is why our new model also uses a constant term for Ni. The Anson-Kobayashi models (Eqs. [16] and [17]) also run into problems as the Mn content increases. It can also be seen how the FactSage thermochemical software gave results which were in surprisingly good agreement with the present work. The highest deviations (0.035 pct N) occurred again due to a high manganese content. The present model works well in all cases presented in Table IV, which was of course to be expected when the measurement results were the basis for optimization. Further corroboration was received from Figure 4(b), which proved that the new revised model also agreed fairly well with the measurements of other researchers.

The effect of the main alloying elements on nitrogen solubility in binary Fe-Me alloys at 1600 °C was calculated with the new model with valid contents (Cr up to 27 pct, Ni 30 pct, Mn 15 pct, and Mo 7 pct), as shown in Figure 5. The effect of molybdenum on the solubility of nitrogen is very close to that of manganese, up to an alloying content of about 6 pct. The shape of the Cr curve agrees well with the observations and measurements of Kim *et al.*[40]

In industrial steelmaking, the temperature varies strongly and is of great importance, not least for the behavior of nitrogen. Figures 6 and 7 illustrate the effect of temperature on nitrogen solubility. The figures include a few selected measurements from Table II as well as temperature-solubility curves with identical compositions calculated by both the new model and by FactSage.

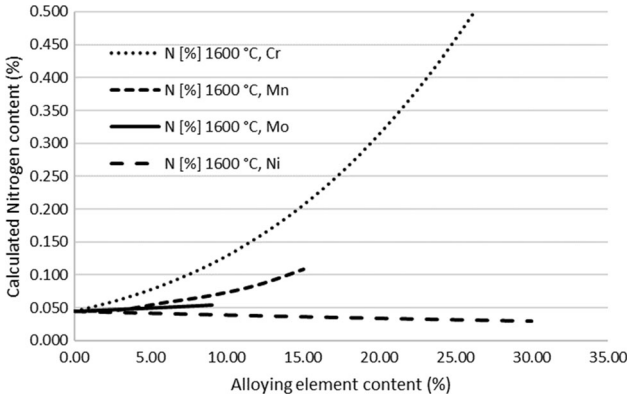

Fig. 5—Effect of main alloying elements in Fe–Me–N (where Me is Cr, Ni, Mo, or Mn) on nitrogen solubility calculated by the new revised model.

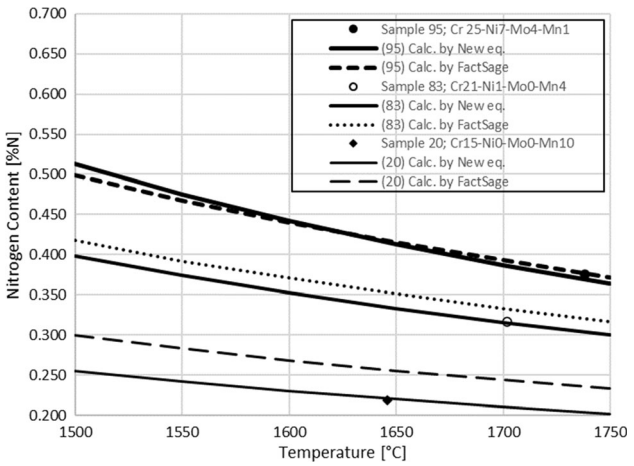

Fig. 6—Temperature dependence of nitrogen solubility in stainless steels. The calculations with the new equation and FactSage are based on the steel compositions according to the sample numbers (main alloying element contents are shown in the legend).

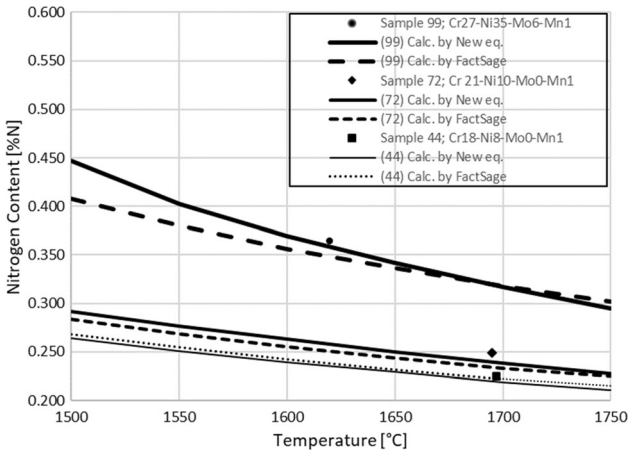

Fig. 7—Temperature dependence of nitrogen solubility in stainless steels. The calculations with the new equation and FactSage are based on the steel compositions according to the sample numbers.

On the basis of Figures 5 through 7 (and Table II), it can be observed that the Cr content plays the main role in the solubility of nitrogen. Figures 6 and 7 also confirm the aforementioned thermodynamic fact that nitrogen solubility in stainless steels is temperature-dependent and decreases with increasing temperature.

When looking at Figures 6 and 7, attention should be paid not only to the effect of alloying elements on nitrogen solubility, but also to the differences in the temperature dependencies between different steel alloys. The slope coefficients of the lines differ from each other, which means that the temperature dependence of nitrogen solubility is due to the interaction of all alloying elements. Therefore, an individual temperature dependence term should be used for at least each main alloying element. The models of Wada and Pehlke[26] and Anson[15] are in line with this principle. Since chromium is the main alloying element in stainless steels and it largely determines the solubility of nitrogen at different temperatures, the temperature dependence is also strongly related to the chromium content.

IV. CONCLUDING REMARKS

Nitrogen is essential in many stainless steels as an alloying element and a substitute for expensive nickel. Nitrogen alloying can be performed in a cost-saving way by nitrogen gas rinsing. For the precise control of the nitrogen content in the final product, it is important to know the nitrogen solubility in steels in order to choose the right blowing procedure in the AOD converter. In stainless steels, the solubility of nitrogen is strongly related to the chromium content. Mn and Mo also increase nitrogen solubility, while Ni decreases it. Nitrogen solubility decreases with increasing temperature due to the effect of alloying.

The solubility of nitrogen in binary and ternary Fe-Me-N alloys has been intensively studied and is thus fairly well-known. First-order interaction descriptions work satisfactorily, at least up to approximately 0.2 pct N. At higher concentrations, second-order interactions should be included as well. Large variations in the steel composition and/or the process temperature can lead to significant deviations between the calculated nitrogen solubilities and the analyzed contents in experimental heats.

In this work, a new equation for predicting nitrogen solubility in stainless steels has been developed based on industrial AOD converter samples. This was considered necessary because the results of industrial measurements tended to differ significantly from the results calculated with the equations published in the literature. The largest deviations were observed in the following situations: low temperature (< 1600 °C), high Cr (> 20 pct), high Mn (> 5 pct), or high Ni (> 25 pct) and especially in combinations of these. The new revised equation was developed by regression analysis based on the measurements made in this study and the measurement results found in the literature.

By using interaction parameters from the Steelmaking Data Sourcebook, nitrogen solubility can be predicted relatively well, but even so the difference can be of the order of 500 ppm. FactSage thermochemical software is also capable of predicting nitrogen solubility, reducing the maximum difference to about 350 ppm. The results of the new equation agree well with the measurements in this study and other measurements in the literature. The maximum difference observed was 220 ppm, which is significantly less than in earlier models. Thus, the new equation can be used to control the AOD process.

It would be desirable to improve nitrogen control further. In the development of the model, more measurements at low temperatures throughout the whole composition range are needed. By combining these measurements with the measurements done in this study, the interaction parameters could be updated by regression analysis.

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CONFLICT OF INTEREST

On behalf of all the authors, the corresponding author states that there is no conflict of interest.

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