

# Controlling Nitrogen Pickup during Induction Melting of Ultra-High Strength Cr-Ni-Mo-V Steels

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## ABSTRACT

Nitrogen pickup during air induction melting can result in porosity and a loss of fracture toughness in ultra-high strength quenched and tempered steel castings. Nitrogen atoms are easily adsorbed into liquid steel upon exposure to the air and argon shrouding alone has limited effectiveness. Previous studies have shown that proper charge sequencing and maintaining a high amount of dissolved oxygen in the melt prior to tapping and deoxidation can limit nitrogen pickup in the melt. In the current study, the effect of melt practice and charging procedure on nitrogen pickup was studied as a function of hold time in a series of lab scale and commercially produced heats of a Cr-Ni-Mo-containing steel intended for ground engaging equipment. By controlling the melting time, purity of charge materials, and development of a dome shrouding method, the nitrogen content was reduced from 170 PPM to less than 80 PPM.

**Keywords:** nitrogen pickup control, induction melting, high strength steels, steelmaking

## INTRODUCTION

The high content of nitrogen, oxygen, and hydrogen during the steelmaking and casting process is known to cause blow holes and pinhole porosity during solidification or formation of filling-related nonmetallic inclusions. High nitrogen concentrations in levels as great as 120ppm can produce gas-related defects. These gas-related defects, such as pinhole porosity, cause a reduction in steel ductility.<sup>1-3</sup> Also, when aluminum is used for deoxidation, high nitrogen contents can cause “rock candy” fracture that results from solid state precipitation of aluminum nitride, AlN, on grain boundaries, especially in heavy section castings.<sup>4</sup>

Titanium, Ti, and zirconium, Zr, are often used during deoxidation to get nitrogen from the melt by producing nitride and carbonitride inclusions that are stable at steelmaking temperatures. However, these inclusions/precipitates are faceted and can often grow to considerable size in the steel, reducing toughness and hot ductility.<sup>5,6</sup> For these reasons, nitrogen in steel is required to be low to yield a desirable steel quality. Different studies have reported that a high content of dissolved oxygen and sulfur in the liquid steel reduces nitrogen absorption.<sup>5,7-11</sup> Steel toughness, however, is dependent on both the nitrogen level and the type, shape, size, and distributions of nonmetallic inclusions formed as a consequence of deoxidation and the pouring and filling process.<sup>8</sup>

Singh et al. studied the effect of steelmaking parameters in nitrogen absorption in steels. The reported ratio of high scrap to hot metal charge, long tapping time, less surface-active elements, and deoxidation as some of the key factors promoting nitrogen pickup during steelmaking in electric arc furnaces (EAF) and in basic oxygen furnaces (BOF). Nitrogen pickup was found to increase in deoxidized steel melting practice than in non-deoxidized melting practice. This is because of the reduction in oxygen, a surface-active element, during deoxidation. Hence, deoxidation and desulfurization results in an increased nitrogen pickup during steel melting and refining. The authors concluded that increasing the hot metal to scrap ratio decreases nitrogen pickup in the BOF and this was the result of the low carbon content of scrap and the associated reduction in the generation of CO gas that produces a nitrogen flushing action.<sup>8</sup>

Zhang et al. studied the kinetics and thermodynamics of nitrogen reaction in an electric arc furnace and showed that nitrogen saturated solubility in steel decreases with an

increase in carbon content and increases with an increase in temperature and nitrogen partial pressure. As nitrogen saturated solubility increased, the nitrogen absorption rate also increased. The authors also confirmed that high oxygen content reduces the rate of mass transfer of nitrogen into liquid steel.<sup>12</sup> In the EAF, different methods to improve nitrogen removal during steel melting have been attempted and are somewhat easier than with induction melting. These methods include adding iron ore powder, which removed dissolved nitrogen utilizing the CO bubbles formed in the molten steel. Even though these methods proved to be successful in reducing nitrogen pickup during steelmaking, they were characterized with technical challenges which make them to be seldom used.<sup>12</sup>

In the air induction melting process, it is more difficult to reduce nitrogen pickup or remove dissolved nitrogen because of limited refining capacity and the relatively smaller volume to area ratios of the furnaces. The limited refining capacity of the induction melting process also means that the molten steel absorbs the initial nitrogen content of the ferroalloys, and this contributes significantly to the final nitrogen level of the casting. Hence, the purity of the charge materials is very critical in controlling the overall nitrogen level of the induction melted steel.<sup>3</sup> In a recent investigation, Xu et al.<sup>5</sup> studied the control of nitrogen pickup during induction melting of low alloy steel using four different steel induction melting trials. The authors delivered active oxygen into the furnace to control nitrogen pickup during the induction melting of steel. The use of surface-active elements such as high oxygen and sulfur prevents nitrogen from adsorbing onto the surface of the liquid steel during steel melting. However, excess sulfur on the other hand can cause high volume of sulfide inclusion which diminishes impact toughness. The author reported that sequence of alloy addition and the use of inert argon gas flow were more effective in controlling nitrogen pickup. Inert argon gas flow, at 50 SCFH (standard cubic feet per hour), was delivered into the furnace to shield the liquid metal from reaction with atmospheric nitrogen. Xu et al. also observed that less nitrogen will be picked up if the induction iron, which was charged first, is all liquid before alloying additions. This is because alloying additions would lower the oxygen activity of the melt. Using this approach, nitrogen levels in the final casting were brought down from 200ppm to less than 80ppm.<sup>5</sup> Their steel composition is different from the chemistry of the steel used in this present study. For instance, the steel

studied currently is higher in chrome content, which according to Chatterjee and Rout, Cr and Mo being on the left hand side of Fe on periodic table, would result in strong attraction between N and Cr/Mo, leading to a higher solubility of nitrogen in the liquid steel.<sup>13</sup> According to Li et al.<sup>11</sup> elements with high potential to form nitride in steel, such as Nb, V, Cr etc., increase nitrogen solubility in steel. Gaseous nitrogen exists primarily as diatomic molecules which dissociates in liquid steel at steelmaking temperatures:<sup>14,15</sup>



The equilibrium constant of the reaction is represented in Equation (2) and the solubility of nitrogen in steel obeys Equation (3) which is an expression of Sievert's law:<sup>11,14,15</sup>

$$K = [N]^2/p_{N_2} \quad \text{Eqn. 2}$$

$$[\text{wt. \%N}] = K_N \cdot (p_{N_2})^{0.5} \quad \text{Eqn. 3}$$

Where  $p_{N_2}$  is the partial pressure of diatomic nitrogen gas and  $K_N$  is Sievert's constant. The Sievert's constant is equal to the solubility of nitrogen at 1atm.

The use of inert gas cover is also another method used to control nitrogen pickup in induction melted steels.<sup>16</sup> For this purpose, argon gas is blown into the furnace or dripping liquid argon is used. The Expanding Gas Air Liquide (EGAL) process employs the use of flowing liquid argon to reduce interactions between molten metal and atmospheric gases. The EGAL is a process derived from the Surface Protective Air Liquid (SPAL) argon drip process. In a study aimed at understanding the inert atmosphere protection of molten metals, Anderson et al.<sup>17</sup> compared the effect of induction melting of steel in three different atmospheres namely: air, SPAL argon and SPAL nitrogen. They reported the lowest oxygen and nitrogen at any given pour temperature in the SPAL argon atmosphere compared to the other two atmospheres. The authors also reported oxygen content below that of the ingot charge. The effect of these results was also evident in the mechanical properties of the 4130 steel and Stellite 21 steel used in the study, as the steel melted in SPAL argon atmosphere gave better tensile strength and elongation values compared to the steel melted in air and SPAL nitrogen atmospheres.<sup>17</sup>

The Cr-Ni-Mo-V steel used in this study is a Stage-I tempered ultrahigh strength steel. Its ultimate tensile strength is greater than 1585 MPa (230 ksi). According to Van Aken et al.'s study, to obtain an elongation to failure greater than 10% in cast steel with ultimate tensile strength of 1585 MPa (230 ksi), porosity must be kept below 0.05% by volume,<sup>18</sup> and in Athavale et al.'s study, to achieve 10% elongation to failure in steel with ultimate tensile strength greater than 1774 MPa (257 ksi), area coverage of porosity should be less than 0.024%.<sup>19</sup> This implies that the higher the strength of the steel, the more detrimental the effect of porosity to its elongation to failure. Hence, the study of nitrogen pickup in this air induction melted steel becomes more imperative considering how difficult it is for foundries to induction melt this steel because of the limited refining capacity of the air induction furnace, the high propensity of absorbing atmospheric gases, and the ability of the absorbed atmospheric nitrogen to form pinholes and detrimental nitride inclusions in the steel during solidification. Moreover, to achieve good toughness properties in high strength steel, nitrogen pickup control is as important as steel cleanliness, especially sulfide and oxide inclusions control.<sup>20-22</sup>

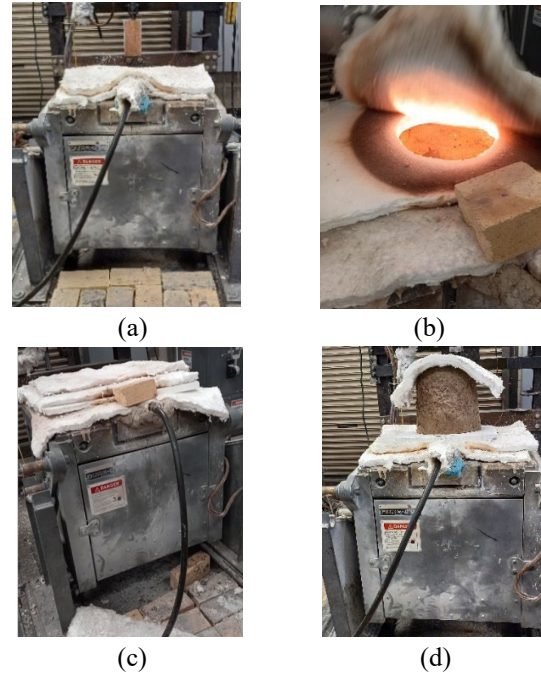
In this current study, the effect of alloy purity, sequence of alloy addition, shrouding, and melt practice as a function of time on nitrogen pickup during induction melting of ultra-high strength Cr-Ni-Mo steels were evaluated.

## MATERIALS AND METHODS

### HEAT PROCEDURES

The following heat procedures were followed for the seven different heats conducted in this study. All ferroalloys were baked in a furnace at 600.8F(316C) for 6 hours to remove hydrogen before melting. A coreless 200lb (90.7 kg) induction furnace (Figure 1(a)) was used to melt the steel in all the heats except for Heat-B where a coreless 1000 lb (453.6 kg) induction furnace was used. Different shrouding practices were used such as the single refractory blanket, double refractory blankets, refractory board, and the incorporation of a dome in addition to the refractory blankets and board as shown in Figure 1(views b-d). Oxygen and nitrogen pin samples were taken at different points during the heat, such as after induction iron was completely melted into liquid, after alloy addition, before tapping, and inside the ladle. Ferroalloys

were added in two stages to eliminate excessive stirring and exposure to atmospheric air. Vermiculite was used to de-slag the melts after alloy addition. The tapping temperature was approximately 3002F (1650C). The heats were equally used for deoxidation studies of this steel. Calcium-treatment was done by dipping calcium cored wire into the melt at high speed.



**Figure 1. Shrouding practices used during the heats with an argon gas pipe delivered into the furnace. (a) Furnace covered with double Kaowool. (b-c) Furnace shrouded with Kaowool and a compressed refractory board with opening for charge addition and sampling. (d) Furnace shrouded like in (b) and (c) incorporating a dome.**

### CHEMICAL ANALYSIS

The pin samples taken during heats and samples taken from the final casting were prepared for chemical analysis. Pin samples surfaces were ground with silicon carbide paper to remove oxide layers. All samples were then sectioned into sizes between 0.5g and 1.0g and cleaned with ethanol in an ultrasonic bath. Total nitrogen, oxygen, carbon, and sulfur contents were ascertained following ASTM E1019 standards, using combustion and inert gas fusion analysis on Laboratory Equipment Corporation (LECO) CS6000 and LECO TC500 analyzers. Chemistry analysis of the alloys was performed with an Oxford Instruments optical emission arc spectroscopy system on the samples taken from the castings. The expected chemistry for the heats is shown in

Table 1, while the charge materials, measured nitrogen composition and corresponding nitrogen contents expected to be introduced by each ferroalloy used in the heats are shown in Table 2. Using the measured nitrogen

contents of the ferroalloys, the amount of nitrogen expected to be introduced into the melt by the individual ferroalloys were determined using the charge calculator and a 100% recovery for nitrogen.

**Table 1. Target Chemistry for Heats**

(wt.%)	C	Mn	Si	Cr	Ni	Mo	V	N(ppm)	Al	S(ppm)	P(ppm)	Zr
<i>Min.</i>	<i>0.26</i>	<i>0.50</i>	<i>0.9</i>	<i>2.50</i>	<i>0.90</i>	<i>0.85</i>	<i>0.05</i>	<i>30</i>	-	-	-	
<i>Max.</i>	<i>0.28</i>	<i>0.80</i>	<i>1.10</i>	<i>2.80</i>	<i>1.20</i>	<i>1.05</i>	<i>0.15</i>	<i>90</i>	<i>0.02</i>	<i>50</i>	<i>150</i>	<i>0.02</i>

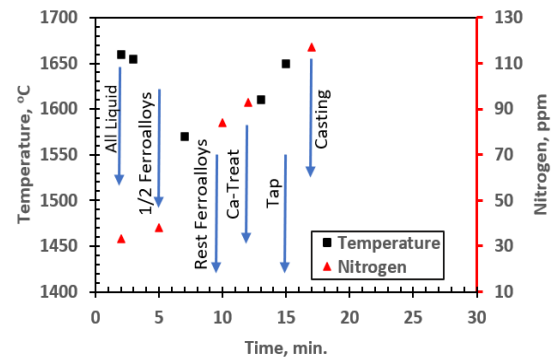
**Table 2. N (ppm) Content of Charge and How Much it Contributed to 170-180lb (77.1-81.7 kg) Heats**

Charge Materials	N (ppm)	N (ppm) Contribution from the Alloys to Heats A-C	N (ppm) Contribution from the Alloys to Heats D-F
Induction Iron	17	14.60	15.64
Ferro-Si	109	1.53	1.57
Ferro-V	1120	2.06	2.22
Nickel Shots	63	0.65	0.66
Ferro-Mo	204	3.00	3.10
Electrolytic Manganese	426	3.29	3.54
Ferro-Cr	2008	94.40	-
Metallic-Cr	196	-	5.23
<b>Total N (ppm) via ferroalloys addition</b>		<b>104.93</b>	<b>16.32</b>

## RESULTS

### HEAT-A

Heat-A was an Al-killed and Ca-treated heat conducted in a 200lb (90.7 kg) induction furnace, to determine the effect of sequence of ferroalloy addition on nitrogen pickup. Alloy addition was made in sequence: electrolytic Mn, half of FeSi, graphite, rest of the alloys and stirred. Later the remaining half of the FeSi addition was made. Ca treatment was done in the furnace, while Al deoxidation (0.02wt%) was done in the ladle. Argon gas (50 SCFH) was delivered into the furnace during melting and the furnace was shrouded with Kaowool as shown in Figure 1(a). Upon complete melting of the induction iron, nitrogen and oxygen measurements of the liquid were 33ppm and 1403ppm. After alloy addition, nitrogen and oxygen contents were 84ppm and 186ppm respectively, while nitrogen and oxygen contents of 117ppm and 109ppm respectively were measured in the final casting (Figure 2).

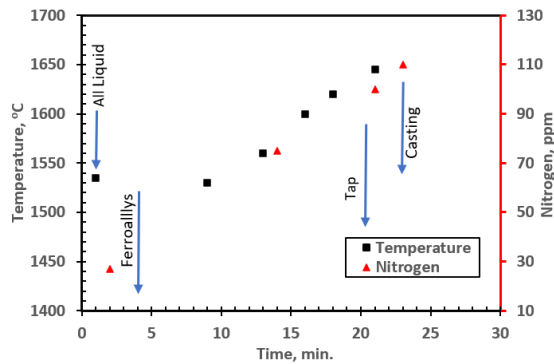


**Figure 2. Nitrogen pickup as a function of time and temperature for heat-A. Ferroalloy addition and Ca-treatment contributed to the high nitrogen content of the melt before tapping.**

### HEAT-B

Heat-B was a second Al-killed heat. This 1000lb (453.6 kg) heat of Ni-Cr-Mo steel was induction melted in a participating industrial foundry. The aim was to determine the effect of surface protective liquid argon drip (SPAL) in minimizing nitrogen absorption into the melt. Expanding Gas Air Liquide (EGAL), a SPAL process, which utilizes liquid argon to reduce interactions between molten metal and atmospheric gases was used.

Throughout the melting, a constant flow of argon liquid was maintained above the molten metal, while the furnace was covered with refractory blanket. Alloy addition was made in the sequence: FeSi, graphite and the rest of the alloys. A 0.02wt% aluminum deoxidation addition was made in stream during tapping into the ladle. Upon meltdown of the induction iron, nitrogen and oxygen measurements of the liquid were 27ppm and 1219ppm. Nitrogen and oxygen contents of 75ppm and 157ppm respectively were measured after alloy addition, while nitrogen and oxygen contents of 110ppm and 115ppm respectively were measured in the final casting (Figure 3).

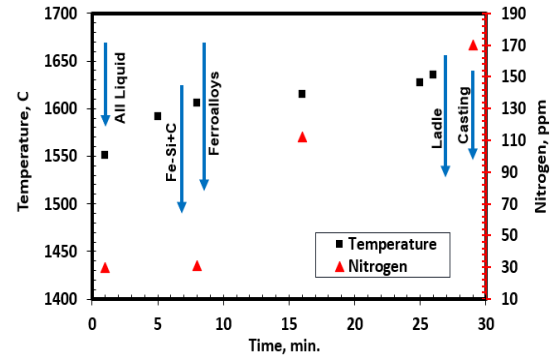


**Figure 3. Nitrogen pickup as a function of time and temperature for (a) heat-B. About 25ppm nitrogen or more was absorbed from the atmosphere during tapping and pouring.**

### HEAT-C

The control of nitrogen during induction melting using nitride formers such as Zr or Ti was considered. Ti is always added to Al deoxidation to reduce nitrogen related gas porosity especially in thick sections; however, this can promote the formation of Type II sulfides and TiN inclusions that are deleterious to dynamic impact toughness.<sup>23</sup> Athavale<sup>23</sup> used Zr addition to control nitrogen in induction melted Ni-Cr-Mo steel and observed that good mechanical properties were achieved when the size of the ZrN inclusion formed is limited to 2µm. Harmful effects of Type II MnS were also not observed. Hence, Zr-deoxidation using FeSiZr was carried out in this present study. The heat was performed in a 200lb (90.7 kg) induction furnace. The alloy addition sequence from Heat-B was replicated here. Argon gas (50 SCFH) was delivered into the furnace during melting and the furnace was shrouded with Kaowool. Calcium treatment was done in ladle. However, the melt time was the longest in this study and this together with other factors reflected in the very high nitrogen content measured in the heat.

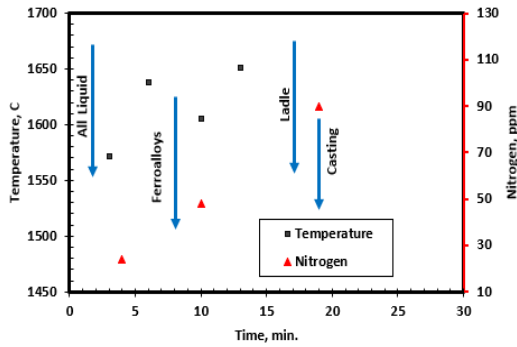
The liquid induction iron measured 30ppm and 554ppm for nitrogen and oxygen, respectively. Nitrogen and oxygen contents of 112ppm and 101ppm respectively were measured after alloy addition, while in the final casting, nitrogen and oxygen contents of 170ppm and 83ppm respectively were measured (Figure 4).



**Figure 4. Nitrogen pickup as a function of time and temperature for heat-C. The figures show high nitrogen absorption from ferroalloys addition, specifically ferrochrome.**

### HEAT-D

This was also a Zr-killed heat conducted in a 200lb (90.7 kg) induction furnace. The previous heats have shown significant contribution of nitrogen from the ferroalloys to the melt, especially from the ferrochrome used. Hence, a metallic chrome of high purity and less nitrogen content was used for this heat and subsequent heats. The alloy addition sequence used in Heat-B was replicated. Argon gas (50 SCFH) was delivered into the furnace during melting and the furnace was shrouded with Kaowool and a refractory board with a 7.0 inch diameter port for charging (Figure 1 views (b) and (c)) to control molten steel exposure to the atmosphere during alloy addition, and sampling. The Zr-deoxidation using FeSiZr and calcium treatment was done in ladle. The liquid induction iron measured 24ppm and 1290ppm for nitrogen and oxygen, respectively. Nitrogen and oxygen contents of 48ppm and 222ppm respectively were measured after alloy addition, while in the final casting, nitrogen and oxygen contents of 90ppm and 96ppm respectively were measured (Figure 5).



**Figure 5. Nitrogen pickup as a function of time and temperature for heat-D. There was minimal nitrogen absorption from metallic chrome addition.**

#### HEAT-E

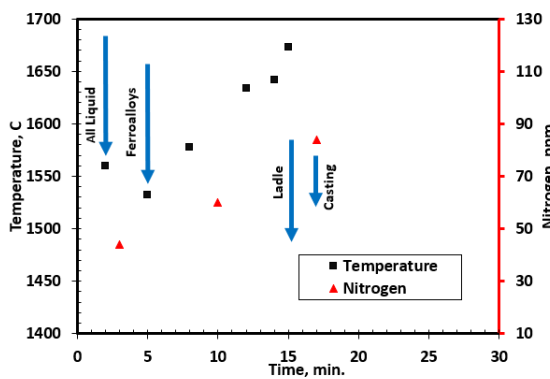
This heat was a Mn-Si killed heat conducted in a 200lb (90.7 kg) induction furnace. In place of ferrochrome, low carbon metallic chrome (low nitrogen content) was used. Alloy addition sequence used in Heat B was replicated. Argon gas (50 SCFH) was delivered into the furnace during melting. The furnace was shrouded with Kaowool and a refractory board with a 6.0 inches diameter port (Figures 1(b) and 1(c)) to control molten steel exposure to the atmosphere during alloy addition, and samples taking. A dome (Figure 1(d)) was also incorporated in this heat to control nitrogen pickup. The dome was used until the alloy addition stage was then removed for easy alloy addition, and sampling. The amount of Mn and Si used for deoxidation was added in stream during tapping. The liquid induction iron measured 44ppm and 517ppm for nitrogen and oxygen, respectively. Nitrogen and oxygen

contents of 60 ppm and 190 ppm respectively were measured after alloy addition, while in the final casting, nitrogen and oxygen contents of 84 ppm and 62ppm respectively were measured (Figure 6(a)).

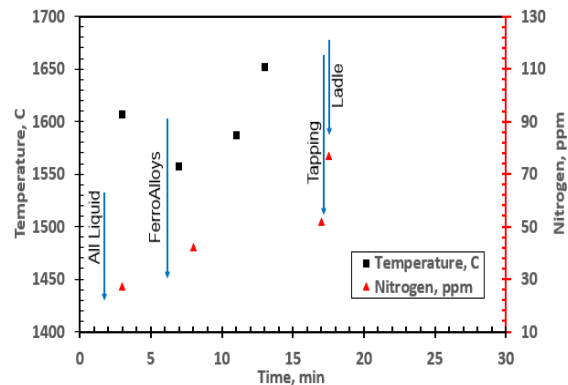
#### HEAT-F

This heat was an Al-killed Ca-treated heat conducted in a 200lb (90.7 kg) induction furnace. Low carbon metallic chrome (low nitrogen content) was used. Alloy addition sequence used in Heat B was also replicated here. Argon gas (50 SCFH) was delivered into the furnace during melting. The furnace was shrouded with refractory blanket and a refractory board with a 6.0 inches diameter port (Figure 1, views (b) and (c)) to control molten steel exposure to the atmosphere during alloy addition, and samples taking. A dome (Figure 1(d)) was also incorporated in this heat to control nitrogen pickup. The dome was used from the beginning of the melting until deslagging and tapping stage. It was, however, removed during alloy addition and placed back afterwards.

The amount of Al used for deoxidation was added in stream during tapping and Ca wire was injected immediately into the melt for Ca-treatment. Upon meltdown, the liquid induction iron measured 27ppm and 1050ppm for nitrogen and oxygen, respectively. Nitrogen and oxygen contents of 42ppm and 179ppm respectively were measured after alloy addition, while in the final casting, nitrogen and oxygen contents of 77ppm and 58ppm respectively were measured (Figure 6(b)).



(a)



(b)

**Figure 6. Nitrogen pickup as a function of time and temperature for (a) heat-E and (b) heat-F. Nitrogen content before tapping was 52ppm in Heat-F.**

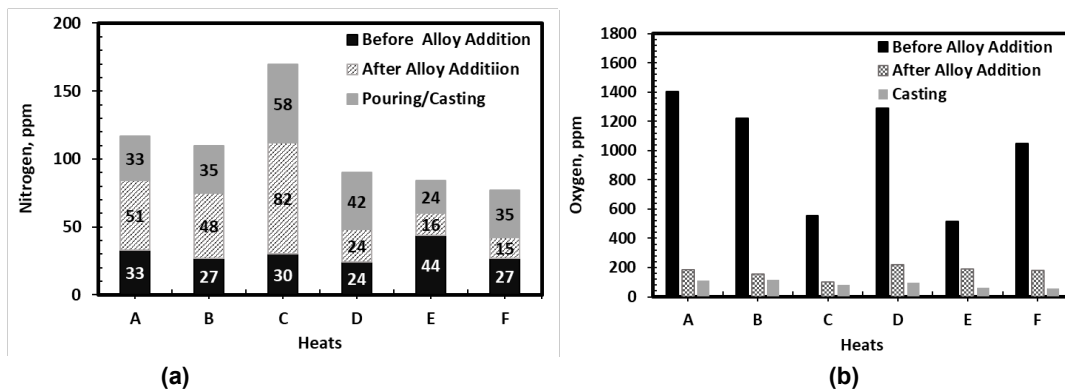


## DISCUSSION

The chemistry analysis of the charge shows that the induction iron used contributed about 16ppm nitrogen to the melt. Note that Ca-treatment was done in furnace for Heat A, but in ladle for Heat F. When a charge is added to the furnace, the protective refractory blanket must be removed, exposing the melt to the atmosphere. The addition and stirring of large amounts of ferroalloy entrains nitrogen from the atmosphere. Because of this, the ferroalloy additions were made in two stages to eliminate excessive stirring and exposure to the air in Heat-B shown in Figure 3. In Heat-A, about 51ppm nitrogen was picked up after meltdown to after alloy addition. A larger fraction of which is believed to have been from the ferroalloys, especially the ferrochrome. An additional 9ppm was recorded after Ca-treatment was done bringing the nitrogen content to 93ppm. To reduce the nitrogen pickup recorded in the laboratory induction melting, the EGAL process was utilized in an industrial induction melting trial. However, this process did not show a significant effect on the nitrogen level before

tapping previously obtained in the laboratory trials with inert argon gas covering.

Heat-B, where EGAL process was used, produced 100 ppm nitrogen in the ladle that is comparable to the results from prior laboratory heats. The hold time between ferroalloy addition and tapping was 15minutes. About 48ppm nitrogen was picked up after alloy addition. Figure 3 shows that from after alloy addition to when in ladle, 25ppm were picked in 7 minutes, and a larger percentage of it is believed to be picked up during tapping. Nitrogen content after alloy addition in Heat-B was 75ppm, showing significant contribution of the charge materials to the final nitrogen content of the casting (Figure 3). However, nitrogen pickup during tapping and pouring resulted in greater than 30 ppm pickup of nitrogen from the atmosphere and the nitrogen content in the final casting was 110 ppm, similar to the previous heat. The oxygen and nitrogen pickup at various stages for all the heats were determined and shown in Figure 7, views (a) and (b).



**Figure 7. Shows the (a) oxygen contents, and the (b) Nitrogen contents of the heats before, after alloy additions were made and after pouring/in the casting. Ferroalloy addition contributed significantly to the total nitrogen when ferrochrome was used (Heats A-C), but less than a quarter of the total nitrogen when metallic chrome was used (Heats D-F).**

Heat-C produced the highest overall nitrogen pickup at all stages of this study. This is chiefly attributed to a longer hold time, ferrochrome addition, frequent removal of the shrouding for chemistry sampling, nitrogen and oxygen sampling, and temperature measurements. A comparatively lower level of oxygen in the melt, which was 554ppm before alloy addition, also gave room for an increased nitrogen pickup. Figure 4 shows that Heat-C had the longest hold time of all the heats. 170ppm of nitrogen was measured in the final casting of Heat-C

showing that an approximate 58ppm of nitrogen was picked up between the time after the alloy addition sample was taken and time of pouring. Nitrogen (82 ppm) was picked up chiefly from the ferroalloys and marginally from the atmosphere after alloy addition. Considering the results obtained from the heats conducted so far, it was clear that the nitrogen content of the charge materials, especially ferrochrome, contributes to the high nitrogen content measured in the heat samples and ferrochrome comprises almost 48% wt. of the alloy additions in Heats

A-C. However, the shrouding practice used and the shrouding removal practice during alloy addition, sampling and temperature measurement also determine how much the melt is exposed to atmospheric nitrogen entrainment. Hence, a low carbon, high purity metallic chrome, with less nitrogen content and comprising about

33%wt. of the alloy additions, was used in the rest of the heats (Heats D-F), employing a shorter hold time. Table 3 contains the different variables used for each melting process and the nitrogen measurement at different stages of the heat.

**Table 3. Melting Process Variables and Nitrogen Pickup in Respective Heat Trials.**  
**Hold Time was the Period between Melt-Down and Tapping**

Heats	Induction Melting Process	Chrome Source	Hold Time (min.)	N (ppm) Before Alloy Addition	N (ppm) After Alloy Addition	N (ppm) Casting
Heat A	Al-killed, Ca-treated in furnace, argon gas and single refractory blanket cover	Ferro-Cr	13.0	33	84	117
Heat B	Al-killed in ladle, EGAL process, and refractory blanket cover	Ferro-Cr	19.0	27	75	110
Heat C	Zr-killed, Ca-treated in ladle, longer hold time, argon gas and double refractory blanket cover	Ferro-Cr	26.0	30	112	170
Heat D	Zr-killed, Ca-treated in ladle, Argon gas, refractory blanket and refractory board cover	Metallic Cr	15.0	24	48	90
Heat E	Mn+Si killed, Argon gas, refractory blanket, refractory board and dome cover	Metallic Cr	13.0	44	60	84
Heat F	Al-killed, Ca-treated in ladle, Argon gas, refractory blanket, refractory board and dome cover.	Metallic Cr	15.0	27	42	77

Heat-E recorded 44ppm nitrogen before alloy addition due to the frequent opening of the furnace during charging and melting of the induction iron (Figure 5). This allowed substantial nitrogen gas to enter the furnace. During this period, argon gas flow was set at 25 SCFH. Argon gas flow was increased to 50 SCFH after all induction iron charge was completely molten. The improved shrouding practice used in Heats-E, and F, shown in Figure 1, views (b), (c), and (d), did not allow for a wide area of the furnace opening to be exposed during charging or sampling, hence limiting nitrogen pickup from the atmosphere. Shrouding was also covered immediately after opening to limit exposure time. The use of a dome allows for a deep layer of argon gas above the melt for significant volume of argon gas circulation to act as a barrier between the melt and atmospheric nitrogen. The effectiveness of this practice was evident in the nitrogen measurements taken after alloy addition and before tapping. The results showed that 24 ppm, 16 ppm, and 15 ppm nitrogen were absorbed in the melt after alloy addition in Heats- D, E and F, respectively. In the final castings from Heats- D, E, and F, 90 ppm, 84 ppm and 77

ppm nitrogen content were measured, respectively. This is comparable to the result reported in Xu et al.'s study,<sup>5</sup> where the best nitrogen pickup result in the final casting was 79 ppm. Xu et al. achieved 55 ppm nitrogen in the melt before tapping but further absorbed an extra 24 ppm during tapping and pouring. In addition to other factors mentioned in literature review, their very short hold time between induction iron meltdown and tapping, which was 5 minutes, helped to reduce atmospheric absorption in their heat. Their hold time was three times lower than the hold time used in Heats-D, E and F. Hence, the best nitrogen concentration achieved in this present study can still go down with a shorter hold time and lesser opening of the shrouding and sampling time. Nitrogen pickup measured between after alloy addition and pouring in Heats E and F were 24 ppm and 35 ppm, respectively. The Ca-treatment performed in Heat F is believed to cause slightly more nitrogen pickup in Heat F after tapping, since similar procedures were used in both heats. Ca-treatment was not done in Heat-E. Between alloy addition and tapping, only 10 ppm N was absorbed in Heat-F over 9 minutes of hold time suggesting a 1.1



ppm/min rate of nitrogen pickup with an improved shrouding technique.

The nitrogen content of the melt right before tapping was 52ppm. An additional 25 ppm of nitrogen was entrained in the melt between tapping and pouring, resulting mainly from tapping and Ca-treatment operations. In their study, Marique et al. in Ratnaraj<sup>15</sup> also observed a higher nitrogen pickup after calcium treatment in ladle or when intense stirring is involved. According to literature, alloying elements such as V, Nb, Mo and Cr increase the solubility of N in liquid binary iron alloy/steel.<sup>11,13,15</sup> Comparing the nitrogen level control achieved in this study with what was achieved by other research, also taking into consideration their melt process and Cr content of their steel (Table 4), it can be observed that nitrogen contents recorded in Heats E, and F castings are comparably better than the best nitrogen pickup result

reported in Ali et al.'s study on induction melted ultrahigh strength steel with similar Cr contents, which was 130ppm after induction melting and 110ppm after electros slag refining.<sup>23</sup> The steel composition used in in heats 3 and 4 of Athavale et al.'s study<sup>24</sup> (Table 4) had lower Cr content (<1.22wt%Cr) compared to this present study (2.4-2.8wt%Cr); and a comparably lower average sum of Cr, V and Mo too. Using the laminar barrier inerting (LBI) method to control nitrogen pickup, Sharma and Nowotarski<sup>25</sup> also reported nitrogen levels of 130ppm and 170ppm in 8620 and 4140 steel grades respectively, while in the open-air induction melted 8620 and 4140 steel, they reported 130ppm and 200ppm, respectively. In the laminar barrier inerting, the authors used argon purge and nitrogen barrier gas for nitrogen sensitive alloys, and nitrogen purge alone for other alloys where nitrogen pickup from the process can be tolerated.<sup>25</sup>

**Table 4. Comparison of Nitrogen Pickup, Melting Process, Atmosphere and Cr Content in Different Studies**

Alloy	Melting Process (Atmosphere)	Wt.% Cr	N (ppm)	Ref.
<b>Cr-Ni-Mo (Heat E)</b>	Induction melting (Argon gas cover)	2.62	84	Current study
<b>Cr-Ni-Mo (Heat F)</b>	Induction melting (Argon gas cover)	2.41	77	Current study
<b>Cr-Ni-Mo (Heat 3)</b>	Induction melting, high oxygen (Argon gas cover)	0.63	55	Ref. 24
<b>Cr-Ni-Mo (Heat 4)</b>	Induction melting, high oxygen (Argon gas cover)	1.19	86	Ref. 24
<b>8620</b>	Induction melting (Lamina barrier inerting - Argon purge)	0.4-0.7	130	Ref. 25
<b>4140</b>	Induction melting (Lamina barrier inerting - Argon purge)	0.75-1.1	170	Ref. 25
<b>CrNiMoWMnV (Heat A - IF)</b>	Induction melting	2.32	130	Ref. 23

Furthermore, a consideration of the effect of oxygen concentration on nitrogen pickup shows that except for Heats C and E, whose oxygen content before alloy addition was about 551ppm and 514ppm respectively, the rest of the heats had oxygen contents over 1000ppm before alloy additions (Figure 7(a)). This could explain the low rate of nitrogen absorption in the heats before alloy additions. Heat-E, which has the lowest oxygen content (514ppm) before alloy addition, also produced the highest nitrogen content before alloy addition (44ppm). Also, the increase in the rate of nitrogen absorption after tapping was largely boosted by the deoxidation carried out in the ladle, which removed oxygen from the active sites and promoted nitrogen pickup. These agree with the

reports from previous studies that surface active elements such as oxygen and sulfur hinder nitrogen absorption in the melt.<sup>5,9,10</sup> Hence, it is possible to further reduce the final nitrogen content obtained in Heat-E by increasing the oxygen content of the melt and improving tapping/pouring techniques, in addition to other methods used in the heat. Protection of the stream during tapping and pouring will significantly reduce the nitrogen content in the final casting. Similar observation has also been made in continuous casting. It was reported that insufficient protection of the stream between the ladle, the tundish and the mold is considered as the main cause of nitrogen pickup during continuous casting.<sup>15</sup> Since approximately one-third of the total nitrogen in the final

casting of the last three heats of this present study was observed to have been picked up during tapping and pouring, the authors suggest the following designs to help control nitrogen pickup during tapping: a refractory pipe to tap directly into the ladle while not removing the furnace shrouding completely and also leaving the ladle shrouded; or tapping directly but safely into the mold with

a refractory pipe to shield the stream and with the furnace half-shrouded; deoxidation to be done in stream or inside the furnace right before direct tapping. The results of the chemical analysis of casting samples taken from all the heats used in this study are shown in Table 5. This includes the alloys (wt.%) composition, oxygen, sulfur, and nitrogen contents (ppm) of the castings.

**Table 5. Chemistry of the Castings from Different Heats Obtained from LECO And OES Analyses**

Alloy (wt.%)	C	Mn	Si	Cr	Ni	Mo	V	N(ppm)	Al	S(ppm)	P(ppm)	O(ppm)	Zr
<b>Min.</b>	<b>0.26</b>	<b>0.50</b>	<b>0.9</b>	<b>2.50</b>	<b>0.90</b>	<b>0.85</b>	<b>0.050</b>	-	-	-	-	-	
<b>Max.</b>	<b>0.28</b>	<b>0.80</b>	<b>1.10</b>	<b>2.80</b>	<b>1.20</b>	<b>1.05</b>	<b>0.150</b>	-	<b>0.0200</b>	<b>50</b>	<b>150</b>	-	<b>0.020</b>
<b>Heat A</b>	0.26	0.53	0.84	2.75	0.99	1.03	0.100	117	0.0190	41	60	109	-
<b>Heat B</b>	0.28	0.60	0.95	2.62	1.10	0.96	0.095	110	0.0140	46	80	115	-
<b>Heat C</b>	0.26	0.54	1.06	2.80	1.05	0.99	0.101	170	0.0062	122	46	83	0.025
<b>Heat D</b>	0.27	0.64	1.03	2.64	1.06	1.04	0.106	90	0.0047	94	35	96	0.030
<b>Heat E</b>	0.28	0.61	0.98	2.62	1.02	0.93	0.089	84	0.0044	72	85	61	-
<b>Heat F</b>	0.28	0.67	0.92	2.41	1.01	1.02	0.101	77	0.0110	43	61	58	-

## CONCLUSIONS

This work has investigated the contributions of alloy purity, melt time, shrouding practice and inert argon covering to nitrogen pickup control during induction melting of NiCrMoV steel. The following observations were made, and recommendations also provided for foundries on how to control nitrogen pickup during induction melting of this steel grade:

- The purity of the charge materials is very critical to the overall nitrogen content of the melt. High nitrogen content in the charge materials would increase the nitrogen concentration of the melt.
- With longer melt time, more nitrogen gas is entrained into the melt. The rate of nitrogen absorption is dependent on the efficiency of the shrouding practice used. Nitrogen solubility in steel also increases with increasing Cr content.
- The oxygen content of 1000 ppm or above seemed to reduce nitrogen entrainment in the melt before alloy additions.
- Excess sampling and temperature measurements expose the melt surface to nitrogen entrainment. With advanced shrouding practice which reduces the melt surface area exposed and time of exposure during sampling, temperature measurement, de-slagging, and stirring, lower nitrogen content as low as 77ppm was achieved in the final casting.
- A good percentage of the nitrogen pickup during induction melting of this steel was during tapping, Al-deoxidation, Ca-treatment, and pouring. About 25ppm were picked up during these processes in Heat F. For foundries to effectively control nitrogen level in the casting of this steel produced using induction melting, an improved shrouding technique to ensure effective shrouding of the melt during tapping, deoxidation, and pouring is equally recommended.
- Inert argon gas flow covering cannot independently control nitrogen absorption during induction melting. The other methods and

precautions listed above must be applied too to achieve effective nitrogen pickup control.

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