INCREASE THE NITROGEN CONTENT IN CHROMIUM MELT BY OXYGEN-NITROGEN NOZZLES UNDER THE CONDITIONS OF METALLURGICAL PILOT PLANT

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Abstract

In MATERIAL AND METALURGICAL RESEARCH LtD. we made a proposal, manufacturing and verification of oxygen-nitrogen nozzle. This nozzle is a part of a vacuum and pressurized induction melting furnace (VPIM) and it works at pressure 10-20 kPa(a). Experimental melt with increasing the nitrogen content in molten steel by nitrogen gas will be carried out at low pressure. First, we will use the oxygen-nitrogen nozzle and then we will use a porous block located at the bottom of the casting ladle.

Keywords: Melt, chromium, nitrogen, nozzle, oxygen

1. INTRODUCTION

The production of stainless steels is technologically and energetically demanding. Stainless steels contain chrome as well as relatively expensive nickel, which is replaced by cheaper nitrogen. From the current development of stainless steel constructions, it is clear that nitrogen alloying is mainly used for low-carbon. The production of the steel melt is carried out on primary and secondary metallurgical aggregates, where a refining melt is performed on a VOD (Vacuum Oxygen Decarburization). The aim of this work is research and development and design of technology, which leads to an acceleration of the increase the content of nitrogen in the melt during the processes in the Vacuum Oxygen Decarburization (VOD). This will reduce the time of the melt. Reducing the time of the melt entails a reduction in the energy intensity of the production, namely a reduction in energy consumption, less lining wear and so on.

Experimental melts will be first realized in MATERIAL AND METALLURGICAL RESEARCH s.r.o. (MMR) to use knowledge for industrial manufacturing facilities. The technology is designed for quality X4CrNiMo16-5-1 with a slightly modified chemical composition, see **Table 1**.

Table 1 Chemical composition of quality X4CrNiMo16-5-1, standardized and for experiments (wt. %)

		C	Mn	Si	P	S	Ni	Cr	Mo	V	N
Standard	min	-	-	-	-	-	4.00	15.00	0.80	-	0.0200
	max	0.06	1.50	0.70	0.040	0.030	6.00	17.00	1.50	-	-
Experiments in MMR	min	0.15	0.25	0.25	-	-	4.50	15.00	0.90	-	-
	max	0.20	0.35	0.35	0.025	0.020	5.50	16.50	1.20	0.10	-

The transition of nitrogen into molten steel is governed by the Sieverts relationship, which assumes its atomic dissolution. The dependence of the nitrogen content in the iron melt on the partial nitrogen pressure describes the relationship (1) by [1].

$$[\%N]_{Fe} = \frac{K_N}{f_N} \cdot \sqrt{\{p_{N_2}\}_{rel.}} \quad (1)$$

where:

K_N ... The equilibrium constant of the dissolution process [weight %],

f_N ..Coefficient of nitrogen activity in the iron melt, [1],

$\{p_{N_2}\}_{rel.}$ ... The relative partial pressure of nitrogen over the iron melt, [1].

Equilibrium constants of the CN express the solubility of nitrogen in iron under standard conditions. This means its maximum content at a pressure of 0.1 MPa, $\{p_{N_2}\}_{rel.}$ = 1, f_N = 1 and by [1] is [%N] = 1/2N_2 (g). The dependence of nitrogen solubility on temperature describes the relationship (2).

$$\log K_N = -\frac{188}{T} - 1.246 = \log[\%N]_{Fe} \quad (2)$$

and the corresponding dependence of the reaction free enthalpy on temperature is given by the equation (3).

$$\Delta G^0 = 3{,}600 + 23.86T \quad [J] \quad (3)$$

The equation (2) shows that the solubility of nitrogen in iron at 1,600 °C is 450 ppm, but decreases significantly when the melt solidifies. In iron, due to the formation of nitrides, it again increases slightly, then decreases in iron α to about 15 ppm at 600 °C.

Alloying elements have a significant influence on the solubility of nitrogen in steels, especially in high alloy stainless steels. The effect of aliasing elements presents the value of the activity coefficient f_N, see (4).

$$\log f_N = \sum e_N^X [\%X] \quad (4)$$

This influence can be expressed using interaction coefficients $e^X_{N(1,873K)}$. The temperature dependence of the interaction coefficients expressing the influence of the elements on the nitrogen activity was described by Chipman relationship (5).

$$e^X_{N(T,K)} = \left(\frac{3{,}280}{T} - 0.75\right) \cdot e^X_{N(1,873K)} \quad (5)$$

Thus, the dependence of the solubility of the nitrogen in the liquid steel on the temperature can be expressed by the equation (6) and (7).

$$\log[\%N]_{steel} = \log K_N - \log f_N + \frac{1}{2} \cdot \log\{p_{N_2}\}_{rel.} \quad (6)$$

$$\log[\%N]_{steel} = \left(-\frac{188}{T} - 1.246\right) - \sum\left(\frac{3{,}280}{T} - 0.75\right) \cdot e^X_{N(1,873K)} + \frac{1}{2} \cdot \log\{p_{N_2}\}_{rel.} \quad (7)$$

For high-alloy steels (e.g. CrNi steels), the calculation is refined by the knowledge of the interaction coefficients not only of the first order but also of the second order and of the cross values coefficients, see equations (8).

$$\log[\%N]_{steel} = \log[\%N]_{Fe} - \sum e_N^X [\%X] - \sum r_N^X \cdot [\%X^2] - \sum r_N^{X,Y} \cdot [\%X] \cdot [\%Y] \quad (8)$$

The values of the interaction coefficients, for important alloying additives for stainless steels, are quoted, for example, by Bůžek at work [2], **Table 2**.

Table 2 Interaction coefficient values 1, 2 and cross values [2]

X, [wt. %]	$e_{N(1,873K)}^{X}$	$r_{N(1,873K)}^{X}$	$r_{N(1,873K)}^{X,Y}$
Cr	-0.0468	+0.00034	-
Nb	-0.0667	+0.00019	+0.00136 (Cr-Nb)
Mo	-0.0106	-	+0.00002 (Cr-Mo)
Ni	+0.0107	-	-0.00041 (Cr-Ni)
Si	+0.047	-	-0.00149 (Cr-Si)

The above elements are further subdivided according to their influence on the solubility of the nitrogen in the steel, where:

- It has a positive influence on the solubility of nitrogen: Cr, Mn, V, Nb a Mo,
- It has a negative influence on the solubility of nitrogen: Ni, C, P and Si.

The contents of the alloying elements affect on the solubility of the nitrogen in the steel melt as well as on the resulting structure. So we divide them into austenitic and ferrite forming:

- The austenitic forming elements extend area γ in the equilibrium diagram: C, Ni, Cu, Mn, N
- The ferrite-forming elements decrease area γ in the equilibrium diagram: Cr, Mo, Si, Al, W, Ti, Nb, V

The deoxidizing additive Si increases the fluidity of the steel and thus improves the weldability of the material. A very high silicon content results in the elimination of intermetallic phases and the reduction of nitrogen solubility in steel, we are talking about high nitrogen contents of approx. 0.3% and more.

The author [3] recommends steel alloying to a maximum content of 0.8 % Si, preferably up to 0.5% Si.

1.1. Alloying of nitrogen gas through the bottom of the ladle

Increasing the nitrogen content in the liquid nitrogen by the nitrogen gas at the beginning of the VOD utilized a lining block placed in the bottom of the ladle. The use of the blow mold was during or after the reduction phase. In this way, the steels listed in **Table 3** were produced. [4]

Table 3 Steels alloyed by nitrogen gas by the lining block [4]

Quality	**Nitrogen (wt. %)**	**Quality**	**Nitrogen (wt. %)**
X5CrNiN 19.7	0.15-0.25	X3CrNiMoN 13.5	0.12-0.17
X15CrNiSiN 25.13	0.15-0.25	X2CrNiMoN 22.5	0.08-0.15
X2CrNiMoN 18.12	0.12-0.22	X2NiCrMoCu 25.20.5	0.04-0.075
X2CrNiN 18.I0	0.12-0.22	X4CrNiMnMoN 19.10.5	0.28-0.35
X10CrN 28	0.10-0.14	X5MnCr 18.13	0.22-0.20
X70CrMnNiN 21.0	0.18-0.28	-	-

1.2. Alloying of nitrogen gas by using a nozzle

According to the author [5], it is possible to overcome the steel melt quality AC11EXDP-304DP (cca 20 % Cr, 8 % Ni, 0.03 % C, 1 % Mn) in a VOD with a nitrogen-only nozzle that blows only nitrogen. The efficiency of this process is about 45 %, with an increase the nitrogen content in the steel about 0.084 % N (from 0.021 % to 0.105 %), in 90 t casting ladle with total nitrogen gas consumption 126 m^3 per ladle. The maximum speed of nitrogen blowing is 600 $m^3.hour^{-1}$.

Basic effects on nitrogen solubility in steel

- melt temperature,
- partial nitrogen pressure above the melt,
- chemical composition of the melt.

The reaction of dissolution of nitrogen in the melt is governed by the relationship (9). This reaction is endothermic, which means that the nitrogen consumes heat during dissolution in the melt of steel. The time required to achieve thermodynamic equilibrium in the melt determines the kinetics of the reaction (9).

$$\frac{1}{2}N_2(g) = [N] \qquad (9)$$

Sulfur and oxygen also have an effect on nitrogen alloying into steel. The author introduces a slightly modified form of the relation of oxygen and sulfur to the suppression (10).

$$\beta_C = \frac{3.05.f_N^2}{1+220a_O+130a_S} \qquad (10)$$

The efficiency of nitrogen alloying in dependence on nitrogen flow in practical conditions for ladle of 30 t and 85 t presents **Figure 1**.

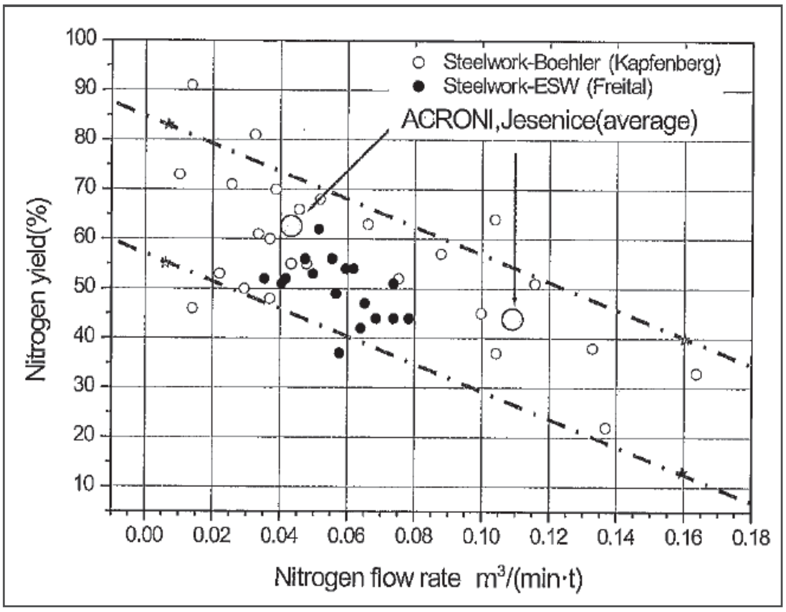

Figure 1 Efficiency of alloying of nitrogen gas in relation to nitrogen flow in 30 t and 85 t ladle of VOD

1.3. Laboratory alloying of nitrogen gas from the top using a nozzle

Laboratory alloying [6] of nitrogen was carried out in a resistive induction melting furnace with a melt weight of 0.8 kg, in a corundum crucible with a melt of 316L with a liquidus temperature of 1,458 °C, the chemical composition see **Table 4**.

At reduced and at atmospheric pressure, the nitrogen was bubbled through the upper nozzle and the argon was blown by bottom. Scheme of laboratory experiment see **Figure 2**.

Table 4 Chemical composition of quality AISI 316L (wt. %)

Element	C	Si	Mn	P	S	Cr	Ni	Mo	N
Content	0.031	0.57	1.00	0.021	0.004	16.13	10.12	2.12	0.028

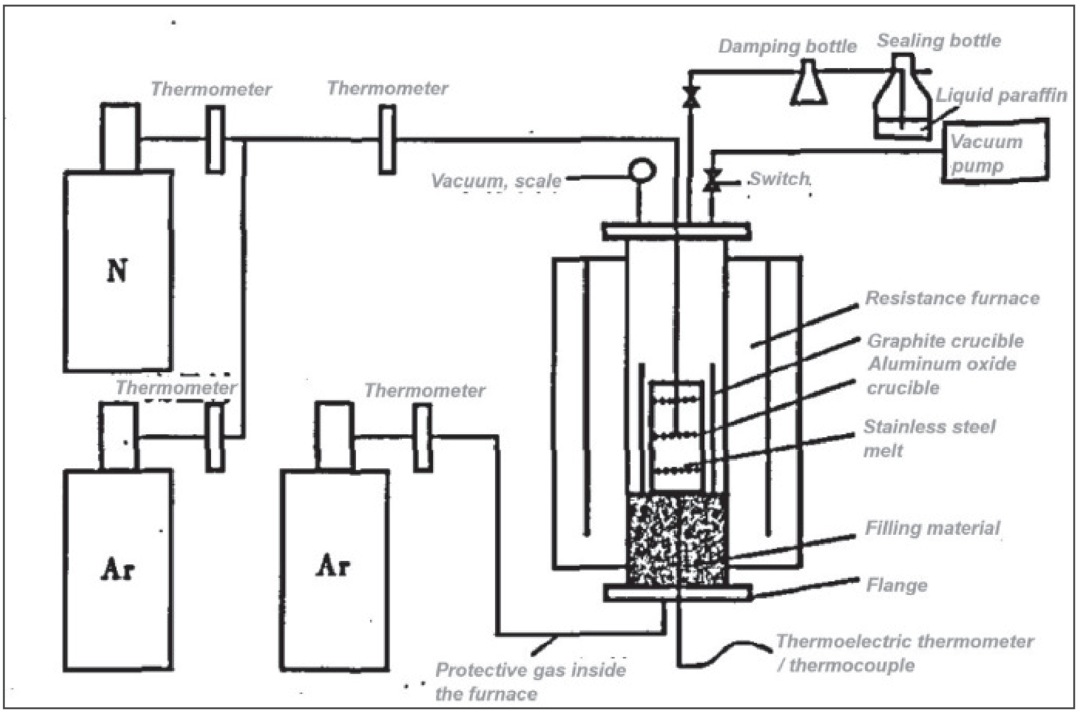

Figure 2 Experimental device for vacuum nitrogen blowing process

The **Figure 3** shows the effect of the nitrogen content in the 316L stainless steel melt depending on the initial temperature 1,853 K (1,580 °C) and 1,833 K (1,560 °C) and on the blowing time.

Nitrogen blowing was 0.1 l.min^{-1} in the first half of the flow, and the second half was 0.3 l.min^{-1}. Within 40 minutes at a pressure of 2 kPa and then at a pressure of 100 kPa. The final temperatures were 1,793 K (1,520 °C) and 1,773 K (1,500 °C). It can be seen from the figure that at a pressure of 2 kPa a higher nitrogen content than 0.05 % N can not be achieved. Subsequent increasing the flow and increasing the pressure increase the nitrogen content of the melt. The figure shows the effect of the temperature on the N content in the melt.

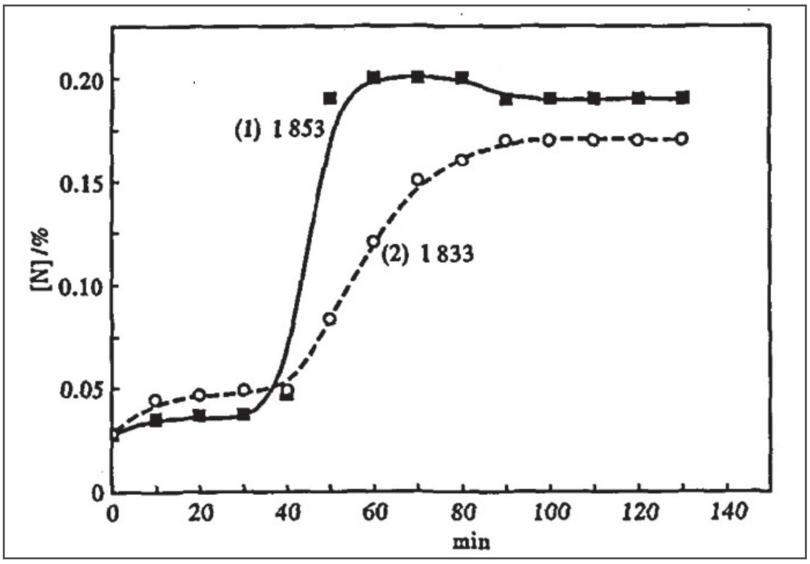

Figure 3 Nitrogen content in 316L stainless steel melt depending on initial temperature 1,853 K (1,580 °C) and 1,833 K (1,560 °C) and blow time

2. TECHNOLOGICAL PROCEDURE OF NITROGEN ALLOYING

On the basis of the literary analysis of the problem of alloying melt by nitrogen under reduced pressure, a technological process of alloying of nitrogen under reduced pressure was proposed.

For maximum approximation of the operating state, industrial metallic charge, alloying elements, slag-forming and reducing additives will be used in experimental tiles. Experimental melts will be carried out in the MMR in the VPIM device with a nominal mass of 1,750 kg, see **Figure 4**. For experiments, unit VPIM will be loaded with a 1000 kg melt. Unit VPIM can operate under low pressure 40 Pa(a) and overpressure at 500 kPa(a) when overpressure is made by Ar or N_2. At the bottom of the induction furnace is implemented a blowing block capable of breathing Ar or N_2. The VPIM is also equipped with an upper blowing nozzle on Ar and O_2 in any ratio 0-100%. This oxygen-argon nozzle was adjusted to an oxygen-nitrogen nozzle to allow breathing of any ratio of the gas mixture N_2 and O_2, see **Figure 5**.

Figure 4 Vacuum and overpressure induction melting furnace of nominal weight of 1,750 kg

Figure 5 Vacuum and pressure induction melting furnace with oxygen-nitrogen nozzle, detail

Stainless steel weighing 1,000 kg will be melting in a VPIM crucible by open chamber. After melting the steel, the following procedure will be followed for alloying the steel melt by nitrogen, first simultaneously with the VOD process and the second immediately after it:

- under a low pressure of 20 kPa(a) and maintaining melting power, the mixture of O2 and N2 is blown and a sample of metal is taken between each blast sequence and the temperature is measured. The O: N ratios will be in the range 20-80: 80-20 at 21 Nl.min-1, for 20 minutes.

- Under a nitrogen pressure of 100 kPa, nitrogen will be blown on the surface and a sample of the metal is taken between each blast sequence and the temperature is measured. The nitrogen will be blown at a rate of 21 Nl.min-1 for 20 minutes when approximately 0.5 kg of nitrogen is alloyed and at 210 Nl.min-1 for 20 minutes when 5 kg of nitrogen is alloyed.

3. CONCLUSION

The paper show the analysis of the alloying of stainless steel melt using nitrogen gas, focusing on the use of the knowledge at low pressure during the VOD process. On the basis of the literary analysis, the initial design of the pilot plant experiments was carried out, the first alloying of nitrogen will take place during the VOD process and the second after the VOD process is completed.

The literary analysis shown that after the VOD process, the alloying by nitrogen gas is also carried out via the porous block. This variant will be further examined in terms of its practical technical and technological implementation into operating VOD.

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REFERENCES

[1] Koroušic, B., Triplat, J., Tehovnik, F., Arh, B. The development of a high-performance production of nitrogen-alloyed stainless steels. *Materiali in technologie* 36, vol. 2002, no 6, p. 329-335. ISSN 1580-2949

[2] Bůžek, Z. Basic thermodynamic calculations in the steel industry. *Hutnické aktuality*, 1988, vol. 29, no. 7. ISSN 0332-8525

[3] Ferritic-austenitic stainless steel and steel utilization, patent no. WO9500674 (A1), Swedish Patent no. SE501321-C2. Swedish Patent Office: 1993.

[4] Pietschmann, G., Epler, M., Kucharz, A., Huber, R. Anwendung von Stickstoff beim VOD-Verfahren. Neue Hűtte, no. 33, june 1988.

[5] Kikuchi, N., Kishimoto, Y., Takeuchi, S., Nabeshima, Y., Nishikawa, H., Take, H. Enhancement of decarburization rate in strongly-stirred, combined-blowing converter and VOD process for producing ultra low carbon and nitrogen ferritic stainless steel. In *Electric Furnace Conference proceedings*. 1999, p. 643-651.

[6] Yanlin, S., Yanping, B., Zhongqi, D. A Study on Blowing Nitrogen Alloying of Stainless Steel 316L with VOD Refining. Special steel, vol. 32. No. 1. February 2011, p. 16-18.

[7] Kurka, V., Adolf, Z., Pindor, J. Production of high nitrogen steels in induction melting furnaces. In *7th European oxygen steelmaking conference*, September 9-11, 2014. Czech Republic, Trinec: 2014.

[8] Kurka, V., Pindor, J., Kosňovská, J., Adolf, Z. Increasing micropurity and determining the effect of different production technologies on the qualitative parameters of forged steel pieces with high aluminium content. In *22nd International conference on materials and technology* 20-22 October 2014, Portorož, Slovenia

[9] Li J., Xu Y., Xiao X, Zhao J., Jiang L., Hu J. A new resource-saving, high manganese and nitrogen super duplex stainless steel 25Cr-2Ni-3Mo-xMn-N, *Materials Science and Engineering*: A, Volume 527, Issues 1-2, 15 December 2009, p. 245-251.10: 3-922599-24-9

[10] Verlag Stahlschluessel Wegst GmbH. Stahlschluessel 2007. Marbach: 2007.

[11] Weidong, L. Production practice and analysis on two-step and three-step process for stainless steels steelmaking. Specia steel. Vol. 34, no. 5. October 2013. p. 34-37.