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Recenzované výzkumné články

Nitrogen in Chromium Melt during Use of Oxygen-nitrogen Nozzle at Low Pressure, Preparation of the Experiment

Dusík v chromové tavenině během používání kyslíko-dusíkové trysky za sníženého tlaku, příprava experimentu

Ing. Vladislav Kurka, Ph.D.[1]; **doc. Ing. Petr Jonšta, Ph.D.**[2]; **Ing. Zdeněk Carbol, Ph.D.**[2]; **prof. Ing. Jiří Bažan, CSc.**[3]; **doc. Ing. Ladislav Socha, Ph.D.**[3]

[1] MATERIAL & METALLURGICAL RESEARCH Ltd., Pohraniční 693/31, 703 00 Ostrava-Vítkovice, Czech Republic
[2] VÍTKOVICE HEAVY MACHINERY a.s., Ruská 2887/101, 703 00 Ostrava-Vítkovice, Czech Republic
[3] VŠB – Technical University of Ostrava, 17. listopadu 15/2172, 708 33 Ostrava-Poruba, Czech Republic

For removal of chromium from slag we have designed, manufactured and verified an oxygen-nitrogen nozzle. The nozzle is implemented in a vacuum and pressurized induction melting furnace (VPIM) and it works at a pressure of 10 - 20 kPa(a). In the company MATERIAL & METALLURGICAL RESEARCH LtD. we will perform an experimental melt with increasing the nitrogen content in molten steel by nitrogen gas at low pressure. Alloying by nitrogen was focused on the alloying 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. In the first experiments, we will use the oxygen-nitrogen nozzle and then we will use a porous block located at the bottom of the casting ladle.

***Key words**: chromium; nitrogen; nozzle; oxygen; melt*

Antikorozní ocel obsahuje chrom, stejně jako poměrně drahý nikl, který je nahrazen levnějším dusíkem. Obecně lze říci, že výroba nerezových ocelí je technologicky a energeticky náročná. Ze současného vývoje konstrukcí z nerezavějící oceli je zřejmé, že legování dusíkem se používá hlavně u ocelí s nízkým obsahem uhlíku. Výroba ocelových tavenin se provádí na primárních a sekundárních hutních agregátech, kde probíhá tavná rafinace na VOD (degradaci vakuového kyslíku). Cílem této práce je výzkum, vývoj a návrh technologie, která povede ke zrychlení zvyšování obsahu dusíku v tavenině během zpracování procesem VOD. Tím se sníží doba tavení. Snížením doby tavení se dociluje snížení energetické i materiálové náročnosti výroby, tj. snížení spotřeby energie a snížení opotřebení obložení. Byl proveden návrh, kompletace a ověření funkčnosti kyslíko-dusíkové trysky. Tato tryska je součástí zařízení Vakuová a přetlaková indukční tavicí pec (VPIM) a pracuje za sníženého tlaku 10 – 20 kPa. Po plném odzkoušení a osvojení chodu zařízení budou provedeny experimentální tavby nadusičení vysoce chromové taveniny pomocí plynného dusíku za sníženého tlaku, a to jednak pomocí kyslíko-dusíkové trysky a také pomocí porézní tvárnice umístěné ve dně licí pánve.

***Klíčová slova**: chrom; dusík; tryska; kyslík; tavenina*

In general, it can be said that 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 structures, it is clear that nitrogen alloying is mainly used for low-carbon steel. Production of the steel melt is carried out in primary and secondary metallurgical units, where a refining melt is treated by 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 of the nitrogen content in the melt during its processing by Vacuum Oxygen Decarburization (VOD). This will reduce the time of the smelting. Reduction of the smelting time entails a reduction in the energy intensity of the production, namely a reduction in energy consumption, as well as smaller lining wear.

Experimental melts will be first realized in the company MATERIAL & METALLURGICAL RESEARCH Ltd. (MMR) in order to use the gained knowledge for industrial manufacturing facilities. The technology is designed for the steel grade X4CrNiMo16-5-1 with a slightly modified chemical composition (Tab. 1).

Tab. 1 Chemical composition of steel grade X4CrNiMo16-5-1 according to standard and during experiments (wt.%)
Tab. 1 Chemické složení oceli X4CrNiMo16-5-1, normované a během experimentů (hm. %)

		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 dependence of the nitrogen content in the iron melt on the partial nitrogen pressure is described by the equations (1) to [6]. Transition of nitrogen into molten steel is governed by the Sieverts relationship, which assumes its atomic dissolution.

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

where:

K_N ... the equilibrium constant of the dissolution process (wt. %),

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 according to [6] is [%N] = 1/2N_2 (g). The dependence of nitrogen solubility on temperature is described by the relationship (2).

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

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

$$\Delta G^0 = 3{,}600 + 23.86T \ \ \text{(J)} \qquad (3)$$

The eq. (2) shows that the solubility of nitrogen in iron at 1,600°C is 450 ppm, but it decreases significantly when the melt solidifies. In iron, due to the formation of nitrides, it again increases slightly, then it decreases in iron α to approx. 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 alloying elements is presented by the value of the activity coefficient fN, see eq. (4).

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

This influence can be expressed using interaction coefficients $e^X_{N(1873K)}$. The temperature dependence of the interaction coefficients expressing the influence of the elements on the nitrogen activity was described by Chipman eq. (5).

$$e^X_{N(T,K)} = \left(\frac{3{,}280}{T} - 0.75\right) \cdot e^X_{N(1873K)} \qquad (5)$$

For high-alloy steels (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 eq. (6).

$$\begin{aligned} log[\%N]_{ocel} &= log[\%N]_{Fe} - \sum e_N^X [\%X] \\ &- \sum r_N^X \cdot [\%X^2] - \sum r_N^{X,Y} \cdot [\%X] \cdot [\%Y] \end{aligned} \qquad (6)$$

The values of the interaction coefficients, for important alloying additives for stainless steels, are quoted, for example, by the author Bůžek in the work [2] (Tab. 2).

Tab. 2 Interaction coefficients of the 1st and 2nd order, and cross coefficients [2]
Tab. 2 Iterační koeficienty 1., 2. řádu a křížové [2]

X, (wt. %)	$e^X_{N(1873K)}$	$r^X_{N(1873K)}$	$r^{X,Y}_{N(1873K)}$
Cr	-0.0468	+0.00034	-
Mo	-0.0106	+0.000079	+0.00002 (Cr-Mo)
Nb	-0.0667	+0.00019	+0.00136 (Cr-Nb)
Mn	-0.024	+0.000032	
Ni	+0.0107	-	-0.00041 (Cr-Ni)
Si	+0.047	-	-0.00149 (Cr-Si)

Very high silicon content results in the elimination of intermetallic phases and in the reduction of nitrogen solubility in steel, we are talking about high nitrogen contents of approx. 0.3% and more. The author [4] recommends alloying of steel to a maximum content of 0.8 % Si, preferably up to 0.5% Si.

According to the author [5], it is possible to overcome the steel melt grade AC11EXDP-304DP (approx. 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 approx. 45 %, with an increase of the nitrogen content in the steel by approx. 0.084 % N (from 0.021 to 0.105 %), in 90 t casting ladle

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with total nitrogen gas consumption of 126 m^3 per ladle. The maximum speed of nitrogen blowing is 600 $m^3 \cdot h^{-1}$.

Sulfur and oxygen also have an effect on nitrogen alloying of steel. The author introduces a slightly modified form of the relation of oxygen and sulfur on the content of nitrogen (7).

$$\beta_C = \frac{3.05 \cdot f_N^2}{1 + 22\,0a_O + 13\,0a_S} \qquad (7)$$

Laboratory alloying 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 AISI316L with a liquidus temperature of 1458°C. At reduced and at atmospheric pressure, the nitrogen was bubbled through the upper nozzle and the argon was blown by bottom. Fig. 1 shows the effect of the nitrogen content in the 316L stainless steel melt depending on the initial temperature 1853 K (1580°C) and 1833 K (1560°C) and on the blowing time. Nitrogen blowing lasted for. 0.1 $Nl \cdot min^{-1}$ in the first half of the blow, and the second half lasted for 0.3 $Nl \cdot min^{-1}$. It continued for 40 minutes at a pressure of 2 kPa and then at a pressure of 100 kPa. The final temperatures were 1793 K (1520°C) and 1773 K (1500°C). It can be seen from the figure that at a pressure of 2 kPa a higher nitrogen content than 0.05% N cannot be achieved. Subsequent increase of the flow and increase of the pressure lead to an increase of the nitrogen content in the melt. Fig. 1 shows the effect of the temperature on the N content in the melt. [7]

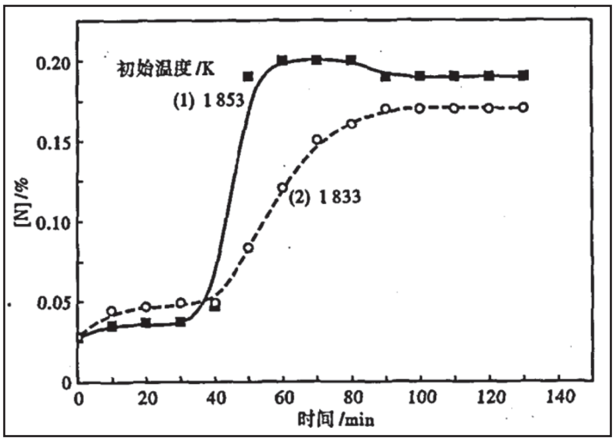

Fig. 1 Nitrogen content in 316L stainless steel melt depending on the blow time at initial temperature 1853 K (1580°C) and 1833 K (1560°C)

Obr. 1 Obsah dusíku v tavenině oceli 316L v závislosti na době dmýchání při teplotě 1853 K (1580 °C) a 1833 K (1560 °C)

Technological procedure of nitrogen alloying

We proposed the experimental technology after bibliographic analysis of the problem of alloying melt by nitrogen under reduced pressure, a technological process of nitrogen alloying under reduced pressure. Experimental melts will be carried out in the MMR in the Vacuum and pressurized induction melting furnace (hereinafter VPIM) unit for a nominal weight of melt of 1,750 kg (Fig. 2). The VPIM can operate under low pressure of 40 Pa (a) and also under overpressure of 500 kPa (a) when overpressure is made by Ar or N_2. The VPIM will be loaded for our experiments with a 1,000 kg melt. At the bottom of the induction furnace is implemented a blowing block capable of blowing Ar or N_2. The VPIM is also equipped with an upper nozzle for blowing of Ar and O_2 in any ratio from 0 to 100%. This oxygen-argon nozzle was adjusted to an oxygen-nitrogen nozzle to allow blowing of any ratio of the gas mixture consisting of N_2 and O_2 (Fig. 3). Fig. 4 shows the nozzle during the VOD process. The VOD process is controlled by the control computer, which shows and record the current gas contents of CO, CO_2, O_2 and H_2 (Fig. 5).

Fig. 2 Vacuum and pressure induction melting furnace for nominal weight of melt of 1,750 kg

Obr. 2 Vakuová a přetlaková indukční tavící pec o nominální hmotnosti 1750 kg

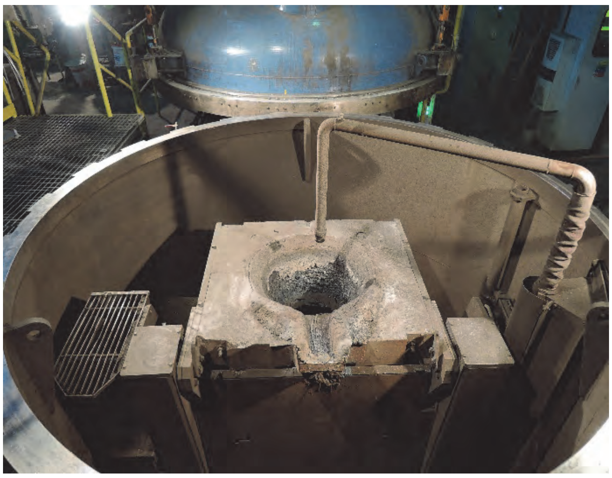

Fig. 3 Vacuum and pressure induction melting furnace with detail view of the oxygen-nitrogen nozzle

Obr. 3 Vakuová a přetlaková indukční tavící pec s detailním pohledem na kyslíko-dusíkovou trysku

Fig. 4 Nozzle during the VOD process
Obr. 4 Tryska během procesu VOD

Fig. 5 Control and record computer
Obr. 5 Ovládací a řídicí počítač

During the experiment, metallurgical conditions will be simulated in a big metallurgical company. A melt of approx. 1,650 kg will be produced in the induction melting furnace, with the required chemical composition. It will be then poured into the pouring ladle and the pouring pan will be placed in the keson of the VPIM.

The melt will be then cast into the casting ladle (CL) and the CL will be placed in the VPIM chamber. The pressure in the VPIM chamber will be reduced down to 20 kPa (a) and at this pressure:

- The nitrogen will be bottom blown at 120 $Nl \cdot min^{-1}$ to the CL with melt for 10 minutes. A total of 1.5 kg of nitrogen will be blown into the melt. At a melt mass of 1,500 kg, the theoretical alloying is 0.10 % (Tab. 3). The aim of this experiment is to find out the real possibilities of nitrogen alloying at low pressure.
- A nitrogen/oxygen mixture, at a rate of 20-80:80-20, will be blown at 210 $Nl \cdot min^{-1}$on the surface of the melt in CL for 10 minutes. For each variant, the nozzle will blow on the surface of the melt between 0.53 and 2.1 kg of nitrogen. For a melt weight of 1,500 kg the theoretical alloying by nitrogen will be from 0.04 to 0.14% (Tab. 4).

Before and after each experiment, samples of metal for chemical analysis will be taken from the melt.

Tab. 3 Design of the N_2 alloying by bottom of the casting ladle to the melt at a low pressure of 20 kPa (a)
Tab. 3 Návrh legování dusíku spodem do taveniny v licí pánvi za nízkého tlaku 20 kPa (a)

	Values	**Units**
Melt weight	1,500	(kg)
Blowing speed N_2	0.120	$(m^3 \cdot min^{-1})$
Blowing time N_2	10	(min)
Density N_2	1.2506	$(kg \cdot m^{-3})$
Alloying N_2	1.50	(kg)
Theoretical final N_2 content in the melt	0.10	(%)

Tab. 4 Design of the N_2 alloying by oxygen/nitrogen nozzle on the surface of the melt in the casting ladle at a low pressure of 20 kPa (a)
Tab. 4 Návrh legování dusíku pomocí kyslíko-dusíkové trysky na povrch taveniny v licí pánvi za nízkého tlaku 20 kPa (a)

	Values				**Units**
Melt weight	1,500				(kg)
Blowing speed N_2	0.210				$(m^3 \cdot min^{-1})$
Blowing time N_2	10				(min)
Density N_2	1.2506				$(kg \cdot m^{-3})$
Proportion of N_2 in the mixture	0.2	0.4	0.6	0.8	-
Alloying N_2	0.53	1.05	1.58	2.10	(kg)
Theoretical final N_2 content in the melt	0.04	0.07	0.11	0.14	(%)

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Conclusions

Paper gives an analysis of alloying of the stainless steel melt by nitrogen gas. Alloying by nitrogen was focused on the alloying at low pressure during the VOD process. On the basis of the bibliographic analysis, the initial design of the pilot plant experiments was out prepared, the first alloying experiment will be performed in a ladle at low pressure. In order to determine the possibilities of alloying nitrogen at a low pressure, in the first experiment the nitrogen will be bottom blown to the casting ladle with melt. In the second experiment a nitrogen/oxygen mixture, at a rate of 20-80:80-20, will be blown on the surface of the melt in the casting ladle as in the big metallurgical company, during the VOD process. Due to ongoing work, the practical results from the experiments will be presented in a subsequent publication.

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Výroba oceli se zvýšila

Westdeutsche Allgemeine *12.04.2017*

Výroba surové oceli v Německu v březnu 2017 vzrostla oproti březnu 2016 o 1,9 % na 3,9 mil. tun. Výroba oceli v prvním čtvrtletí 2017 je o téměř 2 % vyšší než před rokem. Konjunktura v množství vyrobené oceli tak pokračuje ve svém mírném zotavovacím kurzu, který byl předznamenán vývojem v množství zakázek v minulém roce. Konstatuje to Hospodářské sdružení Ocel (WV Stahl) z Düsseldorfu, které zastupuje 99 % výrobců surové oceli v Německu a k tomu řadu dalších evropských producentů. K ocelářskému průmyslu v Německu patří zhruba 70 podniků s 90 000 zaměstnanci.

Podniková rada Tata je proti fúzi s ocelářskou divizí Thyssenkrupp

Rheinische Post *19.04.2017*

Zaměstnanci Tata Steel mobilizují proti možné fúzi s ocelářskou divizí Thyssenkrupp. Ve včera zveřejněném sdělení celopodnikové rady Tata Steel Nederland stojí, že rada je toho mínění, že „tato fúze ignoruje zájmy zaměstnanců“. Rada mluví o podstatných následcích pro zaměstnance a obtížné spolupráci vzhledem k obrovským kulturním rozdílům v obou podnicích.