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Numerical modelling of the vacuum degassing process of molten steel with advanced characteristics

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A mathematical model of mass-transfer processes in off-furnace degassing of metal in blasting by inert gas bubbles has been developed. Vacuum degassing procedure, described in this paper, can be used in production of low carbon, high strength, micro alloyed, stainless and other classes of steel with advanced characteristics. On the basis of numerical model results, it is possible to calculate time required for hydrogen removal from molten steel under different operational conditions.

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1. Introduction

The first and most obvious application of vacuum to extraction metallurgy is to the removal of dissolved gases like hydrogen from refined steel [1]. This is carried out by subjecting a ladle of the metal to low pressure within a vacuum chamber which is hermetically sealed and connected to vacuum pumping system. Vacuum is forcing dissolved gases out of the melt. This procedure can be used in production of low carbon, high strength, micro alloyed, stainless and other classes of steel with advanced characteristics. The removal of gasses can be improved by introducing an inert gas such as argon into the metal melt. This causes more vigorous sputtering, the argon carries away dissolved gases and the area exposed is greatly increased. Argon is being injected through a porous plug in the ladle bottom. The melt starts to boil when certain underpressure is achieved in the chamber, this indicate the beginning of the degassing. During degassing, phase border (slag/melt) is also included in the vacuum refining. If there is no stirring, vacuum acts only in upper active layer. The active layer depth is about 1.2 m when processing rimming steel and 0.6 m for killed steel. Deeper layers of the melt are being vacuumed only with argon stirring of the melt [2].

The production of vacuum-degassed steel, as an importam advanced material, worldwide is increasing considerably more rapidly than steel production as a whole [3]. For example, roughly 65 million tons of steel was subjected to vacuum degassing in 1998, and this figure is expected to increase to 200 million tons by 2010 [4]. The rapid rise in the vacuum degassing of steel is due to the development of new grades of structural steel that need this treatment to achiev advanced characteristics, as well as to a tightening of customers' requirements on the quality of traditional metal products. The quality of steel concerning its further machinabiliti is largerly dependant on its interstitials content. Gavriljuk [5] compared interstitials N, C and H in steels in terms of their effect on the electronic structure and stacking fault energy, atomic distribution, phase transformations and precipitation, mobility of dislocations, mechanisms of deformation, strengthening and fracture.

Vacuum degassing of steel is subject of interest of many researchers, especially from the aspect of novel degassing processes development. Kitamura et al. [6] investigated a novel vacuum degassing process consisting of a large immersion snorkel and a bottom bubbling ladle for the efficient production of ultra-low carbon steel. More recently, degassing models have been formulated that relay on coupled numerical solutions of mass, dimensions of refining unit, starting temperature of steel and extent of gaseous inclusions [7]. Also, modelling of kinetic parameters of vacuum degassing process was described by Nicolae et al. [8].

The object of degassing process investigations, described in this paper, was hydrogen removal. Hydrogen is known as a harmful element causing the hydrogen embrittlement of steel [9]. Hydrogen in steel is in atomary form as an interstitial solid solution with high speed of diffusion [10]. Higher level of dissolved hydrogen can be deleterious for heavy-section products such as pipeline steels and ship plate products (ASM Handbook [11]). For steels with these applications using of modern steelmaking technologies is usually necessary, a very important one being degassing, namely the removal of hydrogen.

2. Theoretical assumptions and constraints of the model

Significant decrease in hydrogen content in steel is only possible with vacuum degassing process. Low content of hydrogen could be obtained only if using vacuum processing including intensive stirring with inert gasses. If the atmosphere pressure above the melt is decreased by vacuuming or argon blowing then the partial pressure decrease which leads to decrease of hydrogen content in the melt. Besides equilibrium content, degassing of melt is influenced by nucleation and mass transfer inside the argon bubble. Spontaneous homogenous nucleation (or heterogeneous nucleation) at the metal/refractory lining inner surface is taking place in the melt. Hydrogen removal is mostly occurring inside existing gas bubble (blowing with pure inert gas) and followed with diffusion from the melt toward upper surface of the melt.

Before defining the model, relatively constant indicators of the system, should be defined:

Carbon content in steel C 0.47 mass%
Sulfur content in steel S 0.020 mass%
Phosphorus content in steel P 0.012 mass%
Starting hydrogen concentration in steel 7 ppm
Final concentration of hydrogen in steel 1 ppm
Ladle capacity 110 t
Temperature at the beginning of the treatment 1670 ^{O}C
Temperature at the end of the treatment 1630 ^{O}C
Pre-advanced vacuum 250 mbar
Advanced vacuum 1 mbar

Mathematical model, suggested in this paper, is referring to the case of continued blasting of the melt by argon through porous elements at the ladle bottom, which gives the best results in a nucleate flow of inert gas to the melt. The commonly adopted main assumptions used in construction of the mathematical model of mass-transfer processes in off-furnace degassing of liquid metal by floating bubbles of the inert gas are [7]:

(a) due to the mixing effect of gas bubbles the concentration of removed gas is homogeneous over the volume of the metal (except for nonmixed diffusion boundary layers on the gas-metal interfaces);

(b) the metal temperature is constant in space and time;

(c) the thermodynamic equilibrium is reached on gas-metal interfaces;

(d) gas mixing in bubbles is ideal;

(e) there is no gas transfer from the environment to the metal.

The nucleation of a gaseous product is a high order reaction of very high activation energy. The pressure of a small bubble is given by P=2σ/r where σ is the surface tension of the wall material, and r the bubble radius. In molten metal this pressure is high because the surface tension is high. In steel $\sigma = 1.6$ N m^{-1} at 1600 ^{O}C. Gas in a bubble of radius 10^{-9} m in liquid steel at 1600^{O}C would be under a pressure of 32 atm. Employing the relationship $P \cdot V = nR \cdot T$, where R=8.205 x 10^{-5} m^{3}atm, it can readily be calculated that for a bubble of this size at 1600^{O}C, n = 8.72 x 10^{-22} moles which corresponds to about 525 gas molecules. Such an accumulation of molecules might be supposed to be more then enough to form a stable nucleus capable of rapid growth in a supersaturated solution of gas in metal. The internal pressure in so small a bubble is too high, however, to permit gas molecules to enter the bubble from surrounding metal with gas in solution at normal industrial concentrations. In the case of hydrogen in steelmaking the normal range of concentration is 2-10 ppm. The appropriate reaction is [1]:

$$\tfrac{1}{2} H_2 = H_{\text{ppm in Fe melt}}\,;\ \Delta G^O_T = 31973\text{-}44.36 \cdot T \quad \text{J} \qquad (1)$$

at 1670^{O}C (1943 K) $\Delta G^O_{1943} = -54218$ J

so that

$$ln\, k_{1873} = \frac{-\Delta G^O_T}{RT} = 3.356 \ \text{ and } \ k = \frac{ppm\, H}{\sqrt{p_{H2}}} = 28.68 \qquad (2)$$

$$\text{or} \qquad \text{ppm H} = 28.68 \cdot \sqrt{p_{H2}} \quad \text{(Sieverts' law)} \qquad (3)$$

The total pressure in a bubble of gas in molten steel is the sum of the external atmospheric pressure p_a, the pressure due to the head of liquid metal above the bubble, p_{Fe}, and the pressure due to the surface tension, $2\sigma/r$, i.e.

$$p_{total} = p_a + p_{Fe} + 2\sigma/r \qquad (4)$$

$$\text{where: } p_{Fe} = \rho \cdot g \cdot h \qquad (5)$$

Maximal depth of molten steel in the ladle (inner height of the ladle) is $h = 4$ m, specific gravity of steel ρ at 1670^{O}C is 6823 kg/m^3. Specific gravity of steel with above defined composition is depending on temperature, according to the equation [12]:

$$\rho = 6.9625\text{-}8.3422 \text{x} 10^{-4} (T\text{-} 1776) \qquad (6)$$

To become possible for the bubble of gas in metal to rise through, it is necessary that inside pressure of the bubble is larger then p_{total}. Dimension of such a bubble is: $r = 2\sigma / p_{total}$.

Velocity of the bubble under those conditions can be calculated using Stokes' law [13]:

$$w = \frac{(2 \cdot r)^2 \cdot (\varphi - \varphi_g) \cdot g}{18 \cdot \mu} \qquad (7)$$

where: ρ is specific gravity of argon, g = 9,81 m/s^2 and μ is dynamic viscosity of the molten steel.

Using above equations (1-7), it is possible to calculate the time required for hydrogen removal from the steel melt under different conditions.

Argon purging in the melt is used for intense agitation of the melt and for collecting of the hydrogen bubbles with much larger argon bubbles. Argon is introduced to the melt with pressure high enough to annulate the pressure of the metal column (p_{Fe}), however, the pressure shouldn't be too high because it leads to extensive fizzing of the melt and possible overflow.

3. Results and discussion

Exact calculation of the time required for hydrogen removal could be performed using segmental approach for segments of 0.1m of the ladle height. For starting hydrogen concentration of 7ppm and the temperature of 1670^{O}C, results of calculations of time required for degassing are presented in the Table 1.

Table 1. Time required for hydrogen removal from the molten steel.

Argon pressure, atm	Melt depth, m	p_{Fe}, atm	P_{total}, atm	r, m	t, min
1.5	4	2.772844	1.273831	2.48E-05	1,039092
1.5	3.9	2.703523	1.20451	2.62E-05	0,929076
1.5	3.8	2.634202	1.135189	2.78E-05	0,825214
1.5	3.7	2.564881	1.065868	2.96E-05	0,727507
1.5	3.6	2.495559	0.996546	3.17E-05	0,635954
1.5	3.5	2.426238	0.927225	3.41E-05	0,550556
1.5	3.4	2.356917	0.857904	3.68E-05	0,471312
1.5	3.3	2.287596	0.788583	4E-05	0,398222
1.5	3.2	2.218275	0.719262	4.39E-05	0,331287
1.5	3.1	2.148954	0.649941	4.86E-05	0,270507
1.5	3	2.079633	0.58062	5.44E-05	0,215881
1.5	2.9	2.010312	0.511299	6.18E-05	0,16741
1.5	2.8	1.940991	0.441978	7.15E-05	0,125093
1.5	2.7	1.87167	0.372657	8.47E-05	0,08893
1.5	2.6	1.802348	0.303335	0.000104	0,058922
1.5	2.5	1.733027	0.234014	0.000135	0,035068
1.5	2.4	1.663706	0.164693	0.000192	0,017369
1.5	2.3	1.594385	0.095372	0.000331	0,005825
1.5	2.2	1.525064	0.026051	0.001212	0,000435
1	2.1	1.455743	0.45673	6.91E-05	0,133583
1	2	1.386422	0.387409	8.15E-05	0,09611
1	1.9	1.317101	0.318088	9.93E-05	0,064792
1	1.8	1.24778	0.248767	0.000127	0,039629
1	1.7	1.178459	0.179446	0.000176	0,02062
1	1.6	1.109138	0.110125	0.000287	0,007766
1	1.5	1.039816	0.040803	0.000774	0,001066
0.5	1.4	0.970495	0.471482	6.7E-05	0,142351
0.5	1.3	0.901174	0.402161	7.85E-05	0,103569
0.5	1.2	0.831853	0.33284	9.49E-05	0,070942
0.5	1.1	0.762532	0.263519	0.00012	0,044469
(0) Argon blowing stops	1	0.693211	0.694198	4.55E-05	0,308601
0	0.9	0.62389	0.624877	5.05E-05	0,250046
0	0.8	0.554569	0.555556	5.68E-05	0,197645
0	0.7	0.485248	0.486235	6.5E-05	0,151399
0	0.6	0.415927	0.416914	7.58E-05	0,111307
0	0.5	0.346605	0.347592	9.09E-05	0,07737
0	0.4	0.277284	0.278271	0.000113	0,049587
0	0.3	0.207963	0.20895	0.000151	0,027959
0	0.2	0.138642	0.139629	0.000226	0,012485
0	0.1	0.069321	0.070308	0.000449	0,003165
				Total time, min	8,808122

Change and regulation of the argon pressure should be performed during the entire process to avoid extensive fizzing of the melt and damaging of the vacuum chamber covering. The argon pump should be turned of after 7.25 minutes and subsequent degassing is carried out under inertia of gas bubbles already present in the melt.

Since the temperature of the molten steel decrease, during process of degassing, specific gravity of steel will change according to the equation (6). This will lead to change in time required for degassing process. Above calculations were repeated for different temperatures in the range 1670-1630^{O}C. Applying the mathematical statistic processing, on obtained results, following mathematical model can be proposed as most adequate:

$$fct\ t(T,h)= a\cdot T^3+b\cdot h^3+c\cdot T\cdot h^2+d\cdot T^2\cdot h+e \qquad (8)$$

where: t – time, T – temperature and h- the depth of the metal bath

Three iterations were required for fitting above model on results obtained during calculations. Final values of characteristic parameters in equation (8) are presented in the Table 2.

Table 2. Values of the final model parameters.

parameter	value	error	dependency
a	-2.839971576e-10	1.609011538e-10	0.9993498711
b	0.5084748698	0.01540664542	0.9976913391
c	-0.001534889192	5.800523059e-05	0.9993053146
d	1.591500046e-06	6.226648891e-08	0.9978420429
e	0.1882817483	0.7203237641e-05	0.9993449367

Results presenting the time requirement for degassing process, calculated using the equation (8), for different starting temperatures of molten steel and different ladle depth are presented in Fig. 1.

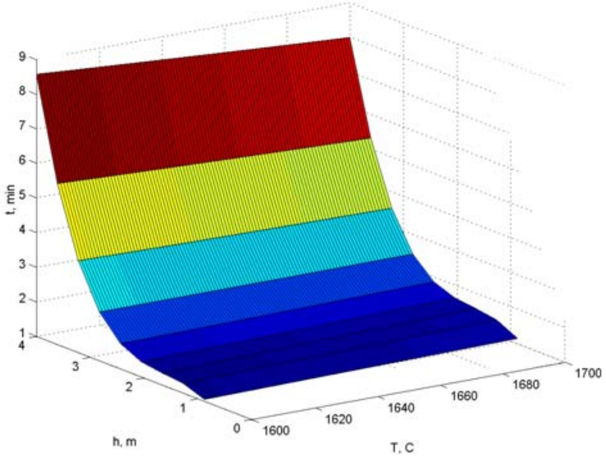

Fig. 1. Time required for hydrogen removal from the molten steel as the function of temperature and the metal bath depth.

4. Conclusions

Gaseous impurities from the steel melt can be removed by vacuum methods coupled with bubbling an inert non-reactive gas through the melt. As each bubble of inert gas comes into equilibrium with the metal it will dissolve out the gaseous impurity to the point that its partial pressure in the bubble will be in accord with Sievert's law. As each bubble passes, concentration of impurities will be reduced slightly but since it is proportion which is removed each time, only an infinitely large number of bubbles can cleanse the metal of the gaseous impurities.

Argon which is used for industrial application usually contains small amount of nitrogen as an impurity, fortunately it doesn't contain hydrogen. Capture of the hydrogen with much larger argon bubble could be defined with same law as removal of the hydrogen bubble at the surface of the melt, which was already described with Sieverts' law. From this, it can be seen that if the concentration of hydrogen in the metal is 7ppm, the equilibrium partial pressure of hydrogen in the gaseous phase is 0.059571 atm. It would therefore be possible to reduce the hydrogen content in the metal below 7 ppm only by reducing the partial pressure of hydrogen below 0.059571 atm. At, lets say, 2m depth in liquid steel of specific gravity 6823 mg/m^3, under vacuum and with introducing argon under pressure of 1 atm, the equilibrium pressure is 0.387 atm. A bubble of argon containing no hydrogen as an impurity would absorb hydrogen to concentration appropriate to hydrogen partial pressure of 0.059571 atm. Since the bubble travels upwards, at a lesser depth argon would be tending to absorb new portions of hydrogen while p_{total} decrease.

From above consideration, it is clear that purity is a relative term and that absolute elimination of any element is, even in theory, not possible. Fortunately the achievement of extreme purity is seldom necessary, even in production of steel with advanced characteristics. In this paper we considered the decrease of hydrogen content in molten steel from 7 to 1 ppm during degassing process. Using model described in the paper it is possible to calculate time required for this process, considered different starting temperature and different depth of molten steel in the ladle.

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