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Carbonization of Steel in the Ladle
(dedicated to the 120th anniversary of Darby process)

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The process of carbonization of steel in the ladle is analyzed.

Keywords: STEEL, CARBONIZATION, LADLE

Introduction

With the appearance of steel-making processes that produce steel in the liquid state, there arose the problem of its carbonization, first smelted in the Thomas converter, where it was reblown to $\leq$ 0,01% C for obtaining a sufficiently low content of phosphorus. Initially, it was carbonized by mirror iron, but in 1888 Sir J.H. Darby, director of the Brymbo Steel Works (UK) (in the late 1950's this plant was one of the first to develop Brymbo process of blowing liquid iron oxygen in the EAF), suggested instead to add coal into the ladle during tapping, what significantly reduced the price of the operation. This technology was implemented at the plant Phöenix (Germany) 120 years ago; it was named Darby process and was used for carbonization of not only Thomas, but Martin and Bessemer steel at plants of Western Europe and the USA. At the Düdelingen steelmaking plant (Luxembourg) briquettes from anthracite or charcoal cemented with lime milk were used for carbonization. In Germany boxes made of thin sheet metal with small coke were charged into the converter, in Austria coal was poured into the bottom of the ladle and deoxidized metal was tapped in it, in the United States coal in paper bags was injected into open-hearth furnace.

Despite the economic efficiency Darby process was not widely used in the 1890-1930's, because manganese alloys used in most cases for steel carbonization were relatively cheap, and simplified the process, provided less fluctuation of carbon absorption, ensured greater steel uniformity in its content. Also the use of clean cast iron of grades Lonsdel, Solvey and smelting in EAF purified from sulfur and phosphorus synthetic cast iron containing 3.0-3.5% C were preferred.

However, eventually everything fell into place. In the 1940s the simplest technology of coal adding under the flow during metal tapping into the ladle gained currency. In 1975, the company Pfizer Inc. (USA) used so-called flux-cored wire for entering powders into metal and a new technology was implemented for carbonizer injection [1-3]. Powders are blown into steel in the ladle with argon [4]. They are produced of high purity for special steels [5] and, thus, Darby process received a new birth.

Despite the fact that the injection of carbonizers by flux-cored wire provides its stable absorption at a level close to 100%, in most cases a more cost-effective technology of bulk additive is preferred, the regularities of which are not well studied.

Methodology

Steel carbonization in the ladle is carried out in certain hydrodynamic conditions, which were studied in works [6] during modeling tapping from the converter. According to [7] during the steel egress from the converter tap-hole with diameter d_{ex} at speed W_{ex} and falling from a height h speed reaches

$$W = \left(W_{ex}^2 + 2gh\right)^{1/2}, \qquad (1)$$

where g – gravitational acceleration, and the diameter according to the equation of continuity is

$$d = d_{ex}\left(W_{ex}/W\right)^{1/2} \qquad (2)$$

Flowing in a metal bath of the ladle, the flow creates a toroidal circulation circuit, the average speed in which is W_c. If we neglect the energy

losses in the circuit, it follows from the flow energy equation at the entrance to the bath E_{en} and in the circulation circuit E_c

$$W_c = W_{en}\, d_{en} / d_c, \tag{3}$$

where W_{en}, d_{en} – the flow speed and diameter during entering the bath; d_c – the circulation circuit diameter (bath), which is equal to the ladle diameter $D_к$. During the production of steel distance between the tap-hole and the surface of the bath in the ladle h decreases, what according to (1) and (2) causes W_{en} decrease and den increase.

Solving (1) - (3) together it is obtained that in the process tapping W_c equals

$$W_c = W_{ex}^{1/2}\left(W_{ex}^2 + 2gh\right)^{1/4}\left(d_{ex}/d_c\right) \tag{4}$$

and decreases due to W_{ex} and h decrease and a slight increase in d_c because of the small conicity of the ladle.

Usually steel carbonization is started in 10-20 s after the beginning of tapping and finished within 1-1.5 min. In this case, according to (4) for Ukrainian converters with loads 60-350 t it is performed at the metal speed in the ladle bath 45-55 cm/sec. The speed of floating carbonizer pieces of size d_p from the equation of a solid body motion in fluid equals

$$U = \left(4\Delta\rho g d_p / 3C_f \rho_1\right)^{1/2}, \tag{5}$$

where ρ_1 – metal density; $\Delta\rho = \rho_1 - \rho_к$, $\rho_к$ – carbonizer density плотность; $C_f \approx 1$ – resistance coefficient.

Hydrodynamic processes during entering a carbonizer by flux-cored wire are not studied in any natural or model physical experiments. The creator of the process Pfizer Inc in 1970 felt it necessary to inject a flux-cored wire with silicocalcium through the lance submerged in the bath for about half of its depth, what stabilized the path of the floating a part of powder. In the 1980's the company placed a guide tube over the bath that simplified the technology, but made the behavior of the flux-cored wire in the bath less predictable.

Local coefficient of metal heat exchange with a steel shell δ thick flux-cored wire diameter d according to Pohlhausen equation [8] will be

$$\alpha = 2^{1/2} C_1^{1/3} \rho_1^{1/2} \lambda_1^{2/3} W^{1/2} / 3\eta_1^{1/6} d^{1/2}, \tag{6}$$

where C_1, λ_1, η_1 – specific heat capacity, heat-conduction coefficient and dynamic viscosity of metal; W – flux-cored wire entering speed.

Specific intensity of heat exchange will be $q = \alpha\left(t_1 - t_m\right)$, where t_1, tm –temperature of the metal and the shell melting, and on the surface area F for the time d_t heat $dH = gFd\tau$ will be transferred, causing the melting of $dm = dH/\left(C_1 tm + \Delta H_m\right)$ shell , where ΔH_m – melting heat and reduction of its thickness to $d\delta = dm/F\rho_s$, where ρ_s – shell density. After performing the substitution, transformation and integrating the resulting expression within $\delta = \delta$ at $\tau = 0$ and $\delta = 0$ at $\tau = \tau_m$, we get a shell melting time

$$t_m = 3\rho_s \eta_1^{1/6} d^{1/2}\left(C_1 t_m + \Delta H_m\right)\delta\Big/ \\ /2^{1/2} C_1^{1/3} \rho_1^{1/2} \lambda_1^{2/3}\left(t_1 - t_m\right)W^{1/2} \tag{7}$$

Applied to the conditions of [9] calculations [7] show that tm is about 0.5 s and according to expert evaluation 1-1.5 s [9].

During blowing the carbonizer it is necessary to inject particles into the metal, what is achieved with their speed determined by the expressions (6.83) - (6.84) [7].

In all three technologies of steel carbonization in the ladle: adding it under the flow during metal tapping (1) flux-cored wire entering (2) or blowing (3) dissolution of carbon particles of size d_p in steel is carried out due to external mass transfer.

When using the first technology particles are involved in the circulation and remain in the circulation loop, if the time of metal motion along the ladle radius $\tau_m = D_к / 2W_c$, where $D_к$ - the ladle diameter, is less than the time of floating the particle in the flow $H_к/2$, where $H_к$ - ladle height, $\tau_m = D_к / 2W_c$

The analysis of the tapping parameters in converters with loads 60t (A), 160t (B), 250t (C) and 350t (D) showed that W_c (3) changes in a narrow range of 42-54 cm/s and for all the converters it is advisable to limit the size of the carbonization particles, based on the condition $\tau_p < \tau_c$ that keeps them in their circulation loop during tapping. According to calculations (4) - (5), their size should be less than 30-40 mm, increasing with the increase in the load of the converter what corresponds the data of the researches.

During the particle floating, mass transfer coefficient of carbon will be $\beta_c = \left(D_c U/d_p\right)^{1/2}$, where D_c – molecular diffusion coefficient of

carbon, and specific intensity of mass transfer will be $i_c = \beta_c c^* \rho_1 / 100$, where c* - solubility of carbon in the steel. During the time dτ carbon mass $dm_c = i_c Fdt$ will dissolve, where F – surface area of the particle, which causes a change in its size by quantity $dd_p = 2dm_c / \rho_c \pi d_p^2$, where ρ_c – particle density. After performing the substitution and transformation, and integrating the resulting expression within $d_p = d_p$ at τ = 0 and $d_p = 0$ at τ = τ_c, we find that the particle residence time in the circulation circuit, required for its dissolution, is

$$\tau_c = 100 \rho_c d^{3/2} / 3\rho_1 D_c^{1/2} C^* W_c^{1/2} \qquad (8)$$

In **Figure 1a** there are shown the results of calculation of τ_c for $d_p = 10^{-1}$ (line 1), 10^0 (2) and 10^1 (3) and the actual duration of the tapping for converters with loads 60-350 m (line I), which roughly corresponds to line 3. Thus, if the coal additive is carried out from the beginning of tapping, its duration will be sufficient for the dissolution of the steel pieces with d_p <10 cm.

When entering a carbonizer into a ladle bath with flux-cored wire or blowing after the tapping its pieces should be dissolved in the process of flotation. Using the same line of reasoning, that during finding the equation (8), we obtain that necessary for the flotation depth equals

$$h_c = 4 \cdot 100 \Delta \rho^{1/4} \rho_c g^{1/4} d_p^{7/4} / \\ / 2^{1/2} 3^{1/4} 7 C_f^{1/4} \rho_1^{5/4} D_c^{1/2} C^* \qquad (9)$$

Figure 1b presents the results of calculations according to (9), for coke (line 1a) and anthracite (1b), which are compared with the depth of a ladle

bath for converters with loads from 60 (line 2a) to 350 t (line 2b). The approximate sizes of pieces should be $d_p \leq 10$ mm, so that their dissolution was over. Thus, for carbonization technologies B and C the allowable size of pieces should be a single order smaller than according to the technology A, but actually less than two orders of magnitude.

Results and Discussion

Figure 2 shows the change in the characteristics of carbonization $\Phi_c = M_{MIII} \Delta C / 100 M_c$, where ММШ, M_c – metal stock and carbonizer mass, depending on the value $\Delta C = C_к - C_н$; in various steelmaking shops with different technologies: 1 - Thomas converter in Dudelingen (Luxembourg, 1890) using coal briquettes, 2, 3 - domestic converters of top oxygen blast, working with a stop at a given concentration of carbon (K_1) and with afterblowing (K_2) (in all three cases carbonizer was poured out of the bunker under a flow of metal during tapping); domestic converters of the top oxygen injection during the flux-cored wire carbonizer injection into the ladle [3], 5-ЭСПЦ (RF) with carbonizer blowing [4].

In cases 1-3, despite very different conditions, dependences are almost identical, with an increase of ΔC the value is $\Phi_c \rightarrow 0,7$. During blowing and flux-cored wire injection value of Φ_c is almost equal to 1. Character of the dependences 1-3 allows to suggest the existence of more or less constant losses of carbonizer because of deoxidation of the metal and slag, and the interaction with the air in a wide range of ΔC, the share of which increases with the decrease of the deposited mass.

| a | b |
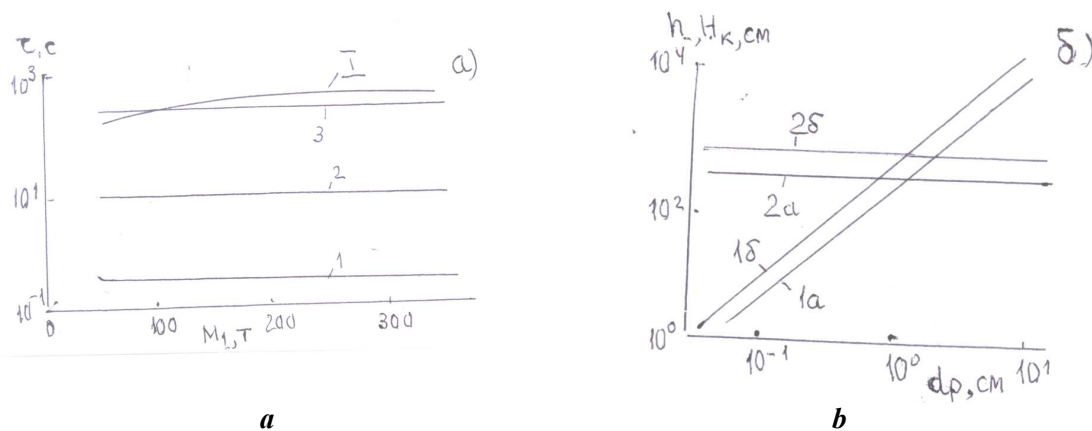
Figure 1. Necessary for the carbonizer assimilation tapping time (a) and floating depth (b) of its particles
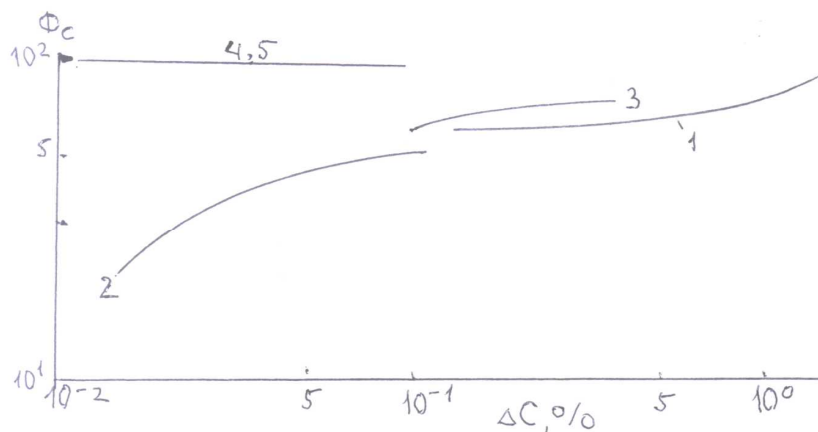
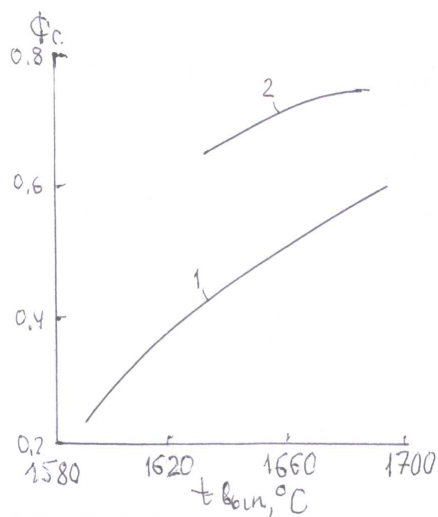**Figure 2.** Carbonizer assimilation by metal by means of different injection technologies

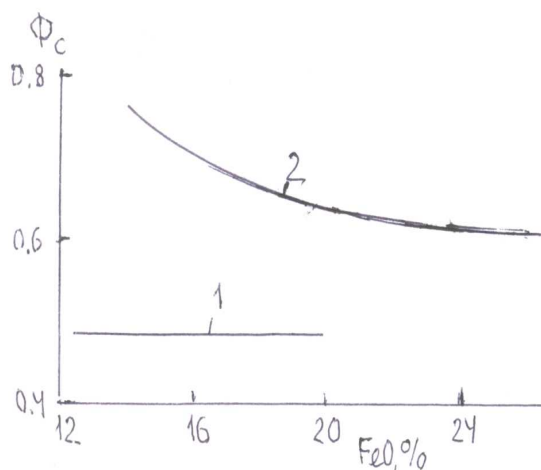**Figure 3.** The influence of tapping temperature on carbonizer assimilation

Figure 4. The influence of the slag oxidation on carbonizer assimilation
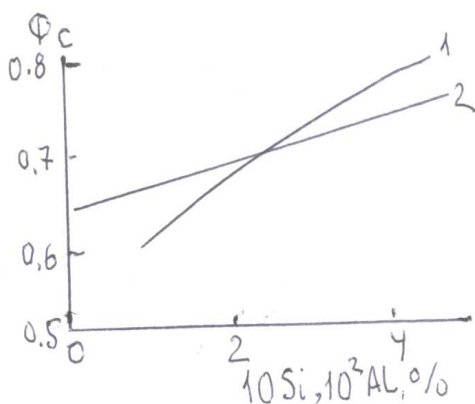

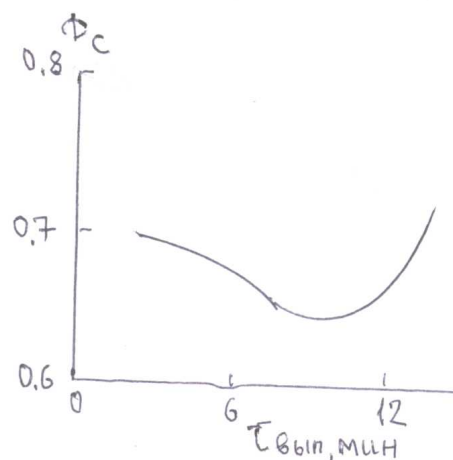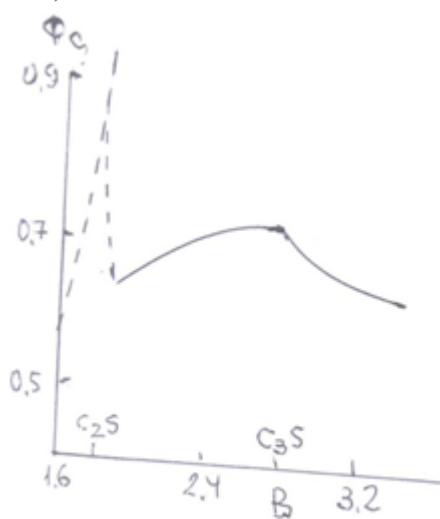**Figure 5.** The carbonizer assimilation with different steel deoxidation

Figure 6. Optimization of the tapping time

The most noticeable is effect on Φ_c of temperature of spout metal (**Figure 3**) for the converter K_1 (line 1) and K_2 (line 2). If we assume that this dependence has the form $\Phi_c = A\exp(-B/T)$, in the first case, B = 20 737, while in the second – 9216, which is close to the value of B = 10 787 in the coefficient of molecular diffusion of carbon [7] and confirms the validity of the model of dissolution carbon particles in steel with the external mass transfer (equations (8) and (9)).

The value of Φ_c remains almost constant for K_1 and decreases for K_2 with increasing oxidation of the slag (**Figure 4**, lines 1 and 2). This is obviously related to the amount of slag formed, which is more in the second case, what increases its weight in the ladle. Besides, the afterblowing causes also growth of the metal oxidation, a fixed feature of which is an increase of oxidation of the slag. This is confirmed by the influence on the value Φ_c, the silicon (line 1) and aluminum (2) content in steel (**Figure 5**).

Apparently, there is an optimal tapping time release $\tau_{\text{вып}}$ for each converter, as for K_2 (**Figure 6**), depending on the diameter of the tap-hole $d_{\text{от}}$: with small $d_{\text{от}}$ and large $\tau_{\text{вып}}$ the intensity of the metal circulation during tapping decreases, what increases the proportion of carbonizer entering the slag and with large $d_{\text{от}}$ and small $\tau_{\text{вып}}$ the amount of slag in the ladle and the probability of the carbonizer entry increase. Slag viscosity has also an important value, what is indicated by maximum values of Φ_c, corresponding to dicalcium (C2S) (shown in dotted lines because of the limited number of points) and tricalcium (C3S) silicate (**Figure 7**).

When carbonizing K2 meltings by cast iron the value of Φ_c was 0,94-1,08, in average 0.98.

Based on the given data the use of flux-cored wire is useful during limited carbonization, especially when obtaining a narrow range of carbon content, as in case [9].

Conclusions

Regularities of steel carbonization using different technologies are observed.

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Название Науглероживание стали в ковше (к 120-летию Darby process)

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Проанализирован процесс науглероживания стали в ковше.

Figure 7. Φ_c for different slag basicity B