

Experimental Researches on the Graphite Particles Dissolution during Injection Process in Ferrous Metallic Melts

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The paper aims to present the experimental researches regarding dissolution phenomena of graphite powder particles during the injection process into ferrous metallic melts. The mass transfer was analyzed and specific calculation was performed for practical determination of dissolution time for graphite particles with different dimensions in melts with different chemical compositions varied from the carbon content point of view, based on injected material characteristics. In the paper are also presented the alloying process efficiency by injection for different metallic melts function of chemical composition, injected powder quantity and its characteristics.

Keywords: dissolution time, injection, alloying, chemical composition, mass transfer, efficiency

One of the stages of steelmaking is represented by alloying, used for obtaining the chemical composition interval desired and necessary for each steel grade. The alloying process should be well controlled to avoid the downgrading the metallic material due to exceeding the standard limits as well as the obtaining low specific consumptions for ferroalloys and others alloying elements. The obtaining technology suppose introduction into the metallic bath of alloying materials with dimensions between 40 – 80 mm, but also powder materials. Introduction of this materials is due to the fact that some ferroalloys could be obtained only as powders and on the other hand, after their manipulation an important quantity of powders fraction (<5mm) results which should be used for an appropriate recovery. A way of proper valorizing of powders during the alloying process is injecting them with the aid of a carrier inert gas.

In the case of alloying (micro-alloying) of metal bath with carbonic materials, for obtaining the desired chemical composition, materials containing this element have been used (coke, petroleum coke, graphite). For a precise chemical composition the re-carburization of the bath with coke is often necessary, realized by introducing coke in the metal bath, but the assimilation ratio is low. A method of increasing the alloying efficiency (micro-alloying), with high assimilation rates and maximum reproducibility is the powders injection inside of the metal bath. Increasing the efficiency of the alloying process is very important from technological and commercial point of view.

A particularity of the powders materials injection is represented by the dissolution time of the graphite powders particles used for this purpose [1, 2]. For complete dissolution in the metal bath, a graphite particle should be in contact with this one on a well determined period of time. Thus, if the particle size is higher and the contact time too short there is a situation that this particle to reach the surface of the bath without totally react, resulting in material losses. If the particles are very fine and the injection speed is too low, these particles can pass the metal bath inside of the gas bubbles, without a contact with the metal bath meaning, also metallic losses.

During the alloying process should be controlled from

the hydrodynamic point of view several working parameters as: injection pressure, materials flow rate, size of injected particles etc. Also, the optimum dissolution time of the powder particles in the metal bath is very important.

Establishing an equation for dissolution time of graphite particles in ferrous metallic baths

Inside the metal bath, the injected particles move to the bath surface due to the recirculation currents produced in the melt by inert gas injection. A part of the particles can remain inside the gas bubbles and reach the melt surface without reacting with this one; the part passing through the interphase barrier has the possibility to be dissolved in the metal bath.

The mass of a graphite particle dissolved in the melt is [3]:

$$m_p = V_p \cdot \rho_p, \quad (1)$$

with

$$V_p = \frac{1}{6} \pi D_p^3, \quad (2)$$

it results:

$$m_p = \frac{1}{6} \pi D_p^3 \rho_p, \quad (3)$$

In the above equations V is the graphite particle volume, cm^3 ; ρ – graphite particle^p density, g/cm^3 ; D_p – graphite particle^p diameter, cm ; λ – shape correction coefficient, for graphite particle set to be 1.5 [4].

If the graphite particle penetrating into the melt exhibits its entire surface, the area through which is produced the mass transfer of the carbon from the particle inside the melt is:

$$A_p = \pi D_p^2 \lambda. \quad (4)$$

Considering that the dissolution reaction will develop at the powder surface, the kinetics of the metallurgical reactions could be expressed as a first order reaction and thus, the substance flux (mass flow) is given by the equation [5]:

$$\frac{dm}{dt} = -k_M A_p \rho_{mb} (C_0 - C_\infty), \quad (5)$$

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where: ρ_{mb} is the metal bath density, g/cm^3 , C_0 - concentration of the bath at the particle - metal bath interface, %;

C - bulk chemical concentration, %.

Because the particle mass which is dissolved depends on the particle diameter and time, thus:

$$m = f(D_p, t) \quad (6)$$

and:

$$\frac{dm}{dt} = \frac{dm}{dD_p} \cdot \frac{dD_p}{dt}, \quad (7)$$

it results the mass transfer equation (8) in the form:

$$\frac{dm}{dt} = -\frac{1}{6} \cdot 3\pi D_p^2 \rho_p \frac{dD_p}{dt} = -\frac{1}{2} \pi D_p^2 \rho_p \frac{dD_p}{dt}. \quad (8)$$

Using the relationship for the mass transfer surface previously presented, from identifying the equations (5) and (8) it results:

$$\frac{1}{2} \pi D_p^2 \rho_p \cdot \frac{dD_p}{dt} = k_M A_p \rho_{mb} (C_0 - C_\infty). \quad (9)$$

By term separation and putting conditions for limit integration for particles diameter and time, the dissolution time of the graphite particles can be determined:

$$\int_{D_p}^0 dD_p = 2k_M \lambda \frac{\rho_{mb}}{\rho_p} (C_0 - C_\infty) \cdot \int_0^t dt. \quad (10)$$

Thus, the particle dissolution time will be as:

$$t = \frac{\rho_p D_p}{2\rho_{mb} \lambda k_M (C_0 - C_\infty)}, \text{ s.} \quad (11)$$

Evaluation of the mass transfer coefficient, taken from the speciality literature after investigating the dissolution of

carbon disks by rotation inside metallurgical Fe - C melts, is shown in figure 1 [6], when it is assumed that the movement speed of the particles in the melt is given by the bubbles speed, estimated to be 25cm/s [4, 6]. Thus, for a peripheral speed of the graphite disk of 25 cm/s, the value of mass transfer coefficient is $k_M = 0.02$ cm/s.

Thus, the process of particles dissolution in the melt, no matter its provenience, can be assessed based on the dissolution time (t) which is directly proportional with particle dimension (D_p) and inverse proportional with the value of mass transfer coefficient (k_M).

Due to the fact that in the equation (11) regarding the dissolution time of a graphite particle the values for diameter particles, mass transfer coefficient and concentration gradient are variable, the practical determination of the dissolution time of graphite particles should be performed for particularly conditions for each metallurgical experiment.

Experimental part

For practical determination of the dissolution time for graphite particles in metallic melts and supposing the mass transfer controlled phenomena, a number of experiments were performed regarding the alloying (micro-alloying) of the metallic melts with graphite powders. An induction furnace was used, working at atmospheric pressure and having the following technical characteristics: 75kg productivity; refractory lining - acid; working frequency - 2500 Hz; working voltage - 380V; installed power - 125 kW. The experimental concept scheme is shown in figure 2.

The experimental process consisted in melting in the induction furnace of six charges of 40kg each, from clean steel scraps. The chemical composition after melting is shown in table 1.

The hydrodynamic parameters considered for the injection process were the working pressure and injection depth, both being in an interdependence relationship, values of $h_{inj} = 0.35$ m and $p_{inj} = 1.6$ atm were selected.

The size of the graphite powders injected into the melt was varied for each experiment, values being presented in

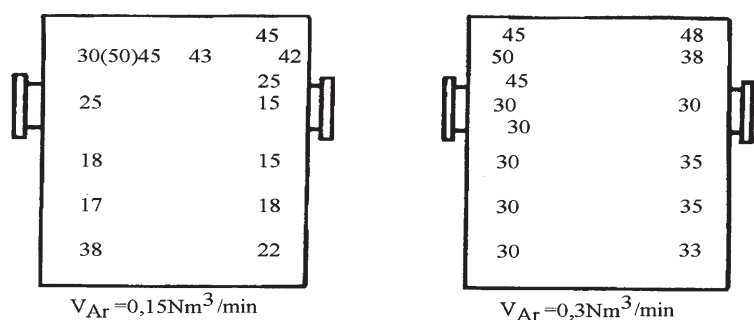


Fig. 1. Values of mass transfer coefficient for carbon in Fe - C melts in different locations of bath [6]

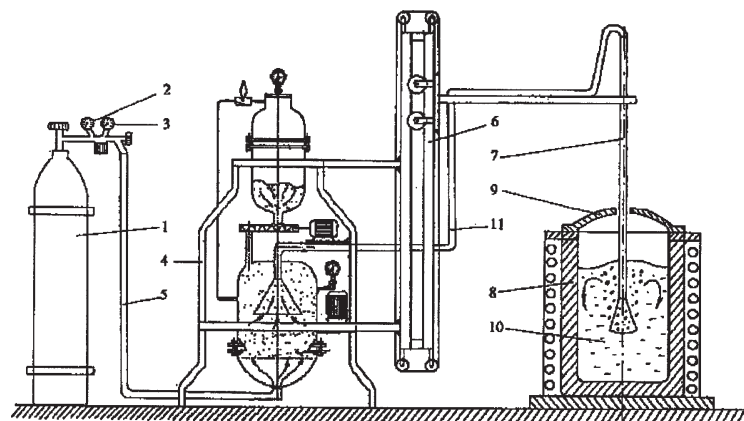


Fig. 2. General scheme of the experimental concept: 1 - inert gas tank; 2 - pressure reducer; 3 - gas flow-meter; 4 - injection installation; 5 - flexible pipeline for inert gas; 6 - device for moving injection lance; 7 - lance; 8 - induction furnace; 9 - cover; 10 - metallic melt; 11 - pipeline for transporting powder materials

Charge code	Chemical composition, %				
	C	Si	Mn	P	S
S1	0.14	0.40	0.25	0.013	0.030
S2	0.12	0.37	0.40	0.022	0.027
S3	0.12	0.40	0.55	0.020	0.030
S4	0.16	0.28	0.25	0.032	0.032
S5	0.10	0.32	0.52	0.017	0.030
S6	0.13	0.27	0.45	0.030	0.038

Table 1
CHEMICAL COMPOSITION
OF METAL BATHS

Charge code	Graphite granulometric class, mm	Particle average diameter, mm	Carbon content, %					
			[C]	[C] ₀	[C] ₁	[C] ₂	[C] ₃	[C] ₄
S1	0.0 – 0.1	0.05	real	0.14	0.20	0.26	0.31	0.48
			max.	-	0.26	0.39	0.51	0.76
S2	0.1 – 0.2	0.15	real	0.12	0.20	0.25	0.36	0.49
			max.	-	0.24	0.37	0.49	0.74
S3	0.2 – 0.3	0.25	real	0.12	0.18	0.32	0.42	0.54
			max.	-	0.24	0.37	0.49	0.74
S4	0.3 – 0.43	0.37	real	0.16	0.27	0.35	0.49	0.61
			max.	-	0.28	0.41	0.53	0.78
S5	0.43 – 0.75	0.59	real	0.10	0.17	0.19	0.25	0.38
			max.	-	0.21	0.31	0.42	0.63
S6	0.75 – 1.0	0.87	real	0.13	0.22	0.25	0.31	0.43
			max.	-	0.25	0.34	0.45	0.67

Table 2
EVOLUTION OF CARBON
CONTENT AFTER GRAPHITE
INJECTION

Charge code	Carbon assimilation rate, %			
	[C] ₁	[C] ₂	[C] ₃	[C] ₄
S1	50.00	48.00	45.95	54.84
S2	66.66	52.00	64.86	59.68
S3	50.00	80.00	68.86	67.74
S4	91.66	80.00	89.18	72.58
S5	63.63	42.85	46.87	52.83
S6	75.00	57.14	46.87	55.55

Table 3
ALLOYING EFFICIENCY

Charge code	Dissolution time, s			
	t ₁	t ₂	t ₃	t ₄
S1	0.64	0.65	0.65	0.68
S2	1.93	1.95	2	2.07
S3	3.2	3.31	3.4	3.51
S4	4.84	4.94	5.12	5.29
S5	7.55	7.58	7.69	7.95
S6	11.27	11.35	11.12	11.88

Table 4
DISSOLUTION TIME VALUES
OBTAINED FOR GRAPHITE
PARTICLES

Table 2. The graphite powder was injected in the metal bath with the aid of an inert carrying gas (Ar), the total powder quantity introduced being 250g/charge. After injection with 50g powders samples were taken for determining the carbon content ([C]₁, [C]₂ and [C]₃). Between the samples [C]₃ and [C]₄ another amount of 100g of powder was injected supplementary.

Results and discussions

The evolution of the carbon content after graphite powders injection in metallic melt is shown in table 2.

Carbon assimilation rate (η_C) was calculated with the relationship [7]:

$$\eta_C = \frac{[C]_{real}}{[C]_{max}} \cdot 100, \% \quad (12)$$

where: $[C]_{real}$ represents the carbon concentration assimilated by the metal bath (determined by chemical analysis), %;

$-[C]_{max}$ – maximum carbon content that could be assimilated (for an assimilation rate of 100%), %.

The values computed for graphite powders alloying process efficiency for the experimental charges are shown in table 3.

For calculation of the graphite particles dissolution time in the metal melts the following values were used: ρ_s – graphite powder density – 2.2 g/cm³; ρ_l – metal bath density – 7.0 g/cm³; k_M – mass transfer coefficient – 0.02 cm/s; C_0 – chemical concentration of the bath at the particle – metal bath interface – 4.3 %; C_∞ – bulk chemical concentration according to table 2, \bar{D}_p – average particle dimension (cm) – which varies according to table 2. For calculation of the characteristic dimensions of the graphite particles, an average diameter was set, resulted from the mean between limit values of the granulometric class for each particle type. The shapes was supposed to be spherical with shape coefficient $\lambda = 1.5$. The dissolution time values of graphite particles computed using relationship (11) are shown in table 4.

Conclusions

The process of metal melts alloying by graphite powder injection is very efficient, easy to be performed from technical point of view, with high assimilation rates.

Between the hydrodynamic and mass transfer processes at metal melt alloying by injection there is a high interdependence.

Graphite particles dissolution time, reflecting the dimensions of transfer processes, is dependent on particles dimensions. Dissolution time is increasing proportionally with the increase of the size of injected particles.

The dissolution time increases with the decrease of concentration gradient of the metallic melt, due to the tendency of saturation of the metal melt. Also it can be observed that the particles dimensions have a higher influence in comparison with the concentration gradient on the dissolution time.

For the presented experimental conditions, the metallurgical efficiency for carbon assimilation in the metal bath, reached values over 59%; in favorable conditions from thermodynamically point of view it could reach values of carbon content close to the maximum. The relatively small quantity of metal bath (approx. 40kg) makes that the values of the metallurgical efficiency to be lower than the one found in the specialty literature.

The carbon assimilation rates are higher for low values of the carbon content, decreasing with the increase of these ones.

The quantity of the injected material determines a proportional increasing of the metal bath carbon content value.

The carbon assimilation rate depends on the dimensions of the material injected in the melt. The small values of floatable particles (e.g. S1, S2) results in lower assimilation rates due to the fact that a part of these ones are transported at the surface of the metal bath, while for the larger particles (e.g. S5, S6) the contact time with the bath is shorter and the dissolution does not occur entirely. For the experimental condition used, the best results were obtained for S3 and S4 samples due to a better correlation of the injection parameters with the metal bath temperature, particles dimension and dissolution speed.

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Manuscript received: 12.04.2013