Self-Propagating High-Temperature Synthesis under the Conditions of Rotation and Characteristic Heat and Concentration Limits on the Example of Oxide Systems

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Abstract

Potential economic possibility of using centrifugal force for production of noble ferroalloys is shown. Connected with this process, the limits of stable combustion are conditioned by formation of adiabatic regime of combustion due to the effect of acceleration of the combustion front by centrifuged particles of melted metal product. There appears the possibility to create a continuous technology of production of ferroalloys on the basis of aluminothermy and of significantly decreased low limit concentration of the sought for metal in the initial row material.

Introduction

Self propagating high-temperature synthesis (SHS) is a technological production process of a number of valuable products in the course of solid phase combustion [1]. SHS method has long been used in industry for production of doping ferroalloys and alloying compositions [2-6]. A problem of considerable losses when depositing a metal melt under the conditions of the slag viscosity increase and a comparatively high lower level of the metal content in the raw material concentrate there arises in production of noble ferroalloys (molybdenum, tungsten, vanadium, niobium, tantalum and others). Therefore, the search for directions eliminating, at least partially, the mentioned disadvantages is actual.

Results

The ratio of deposition rates and the increase of slag viscosity

The completeness of gravitational deposition of ferroalloys is determined by the following functional processes:

1. The reaction rate determining the rate of combustion wave propagation W_c, hence its heat release;
2. The rate of agglomeration and production of larger particles W_a due to the reaction and consequently, the rate of the reaction product deposition;
3. The rate of heat losses owing to the rate of the medium viscosity increase W_η.

The summary rate of the process of the deposited metal mass m, increase – microkinetics of the process – can be expressed as the function of the mentioned components:

$$\frac{dm}{dt} = f\,(W_c, W_a, W_\eta) \qquad (1)$$

The condition for optimum procedure of the process is in prevalence of gravity P over viscosity force (F_η): $P > F_\eta$.

Under the conditions of gravitation, the end of deposition process of small particles with the size r is limited by the equality of forces:

$$P = mg = F_\eta \qquad (2)$$

where $m = {}^4\!/_3\,\pi r^3 \cdot \rho$ and the value of F_η is the force of internal friction (viscosity) of the melt

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$$F_\eta = \eta s \frac{\Delta W}{\Delta x} \qquad (3)$$

η – viscosity coefficient (κg · $m^{-1} \cdot s^{-1}$);
s – he area (m^2) of the deposited particles surface;
$\frac{\Delta W}{\Delta x}$ – velocity gradient with the vector perpendicular to the direction of gravity.

It is of practical importance to determine the ratio of the combustion wave propagation velocity and the deposition rate of particles of different diameters.

Using Stokes formula, let us find the deposition rate (W_d) of a ball-shaped particle with the diameter d supposing that the viscosity of the metal melt is greater than the viscosity of the medium (slag) η:

$$W_d = \frac{d^2(\rho_0 - \rho_m)g}{18\eta} \quad m \cdot s^{-1}, \qquad (4)$$

where d, ρ_0 are the diameter (m) and density of the particle ($kg \cdot m^{-3}$);); ρ_m and η are density and viscosity of the slag.

Fig. 1 presents the curve of distribution of W_d calculated by (3) at $\eta = 1.39\ kg \cdot m^{-1} \cdot s^{-1}$ within values of d from $0.01 \cdot 10^{-3} \div 2 \cdot 10^{-3}$ m for values of $\rho_0 = 19.0 \cdot 10^3\ kg \cdot m^{-3}$ and $\rho_0 = 10.0 \cdot 10^3\ kg \cdot m^{-3}$.

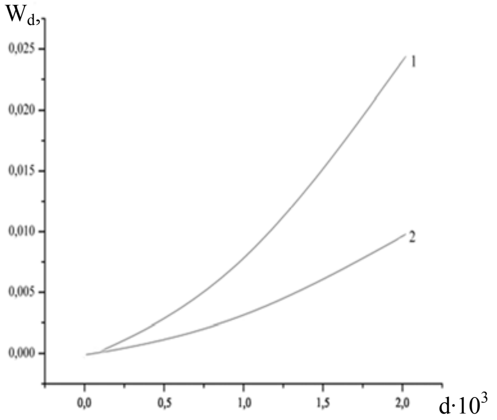

Fig. 1. Distribution of the deposition rate of particles depending on their diameter:
1 – $\eta = 1{,}39\ kg \cdot m^{-1} \cdot s^{-1}$; $\rho_0 = 19{,}0 \cdot 10^3\ kg \cdot m^{-3}$;
$\rho_m = 4 \cdot 10^3\ kg \cdot m^{-3}$; $g = 10\ m \cdot s^{-2}$;
2 – $\eta = 1{,}39\ kg \cdot m^{-1} \cdot s^{-1}$; $\rho_0 = 10{,}0 \cdot 10^3\ kg \cdot m^{-3}$;
$\rho_m = 4 \cdot 10^3\ kg \cdot m^{-3}$; $g = 10\ m \cdot s^{-2}$.

It is seen that in a viscous slag the experimental velocity of the combustion front propagation $Wc \approx 0.01 \div 0.02\ m \cdot s^{-1}$ is considerably greater than the deposition rate of particles in the selected range of their size. In a less viscous slag, only particles with greater density and greater size are dislocated within the propagating combustion front (Fig. 2). However, the corresponding increase in the deposition rate of small particles is still lower that the velocity of front propagation and it takes a long period of time to deposit them at the same viscosity.

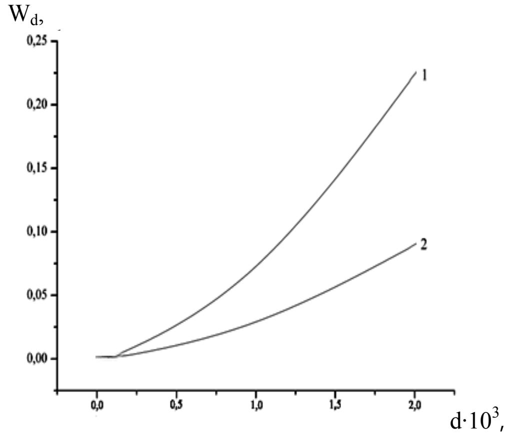

Fig 2. Distribution of the deposition rate of particles depending on their diameter:
1 – $\eta = 0{,}149\ kg \cdot m^{-1} \cdot s^{-1}$; $\rho_0 = 19{,}0 \cdot 10^3\ kg \cdot m^{-3}$;
$\rho_m = 4 \cdot 10^3\ kg \cdot m^{-3}$; $g = 10\ m \cdot s^{-2}$;
2 – $\eta = 0{,}149\ kg \cdot m^{-1} \cdot s^{-1}$; $\rho_0 = 10{,}0 \cdot 10^3\ kg \cdot m^{-3}$;
$\rho_m = 4 \cdot 10^3\ kg \cdot m^{-3}$; $g = 10\ m \cdot s^{-2}$.

The dependency of viscosity on temperature and the process of sticking of small particles onto large ones along the trajectory of their movement can be neglected in the beginning of the combustion process when there is no increase in the deposition rate due to the increase in temperature or if the task is similar to the work [7].

Deposition of smaller particles is possible by a controlled centrifugal force (F_n). The degree of predominance of a centrifugal force over gravitational one is determined by the separation factor:

$$f = \frac{Fn}{P} \approx 4\ Rn^2 \text{ at } F_n = \frac{m \cdot U^2}{R} \text{ and } P = mg \qquad (5)$$

where R is the rotation radius equal to the length (ℓ) of the reaction cylinder and n is the number of rotations per second; U = 2πRn is the velocity of rotation.

For example, at $n = 8.3\ s^{-1}$(500 rot/min) prevalence over the force of gravitational deposition at R = 0.3 m makes up ≈ 80 times. However, SHS process with such and greater separation factor causes characteristic macrokinetic process in the combustion wave front.

Propagation of SHS wave under the action of a centrifugal force

A characteristic peculiarity of SHS according to the reaction

$$3MeO + 2Al = Al_2O_3 + 3Me + Q \qquad (6)$$

under the conditions of the effect of a centrifugal force is recovery of part of enthalpy of combustible mixture to the propagating combustion wave in the form of thermal and kinematic energy of the particles of melted. Having an increased density in regard to the melt, the metal further under pressure developed by a centrifugal force penetrates into the porous space of a fresh reaction mixture and widens the reaction zone of combustion wave with every rotation, thus accelerating its heat production. In the course of centrifugal propagation of combustion wave there arises a situation similar to that described by O.M. Todes [8] on transition of a gaseous reaction to the adiabatic regime which is formed in the reaction provided that the heat release becomes negligibly small compared to the rate of heat generation.

In the considered case this is an accelerated regime of combustion, and complete enthalpy of the sample taking into account its sizes, compactness and, what is most important, concentration of metal becomes important. Without carrying out experiments one can predict:

1. Existence of characteristic concentration limits different from standards ones in the state of rest;
2. Characteristic limiting values of rotation velocity (n) for the lower concentration limit of combustion in SHS regime.

It is difficult to make a quantitative theoretical evaluation of the boundaries of stationary combustion due to uncertainty of instantaneous viscosity of the melt and kinematics of filling of porous space. There is also uncertainty due to negligence of the inhibiting or diluting action on kinematic parameters of the reaction of the product mass (m) penetrating into the limits of combustion wave and the porous space. Nevertheless, the study of characteristic regularities of a centrifugal combustion process is undoubtedly of both theoretical and practical interest.

Let us now consider combustion of a compacted cylindric sample with concentration of the metal being reduced (c_0) with the length ℓ and cross section s having placed it horizontally along the axis x and rotating it around axis y.

Under the conditions of rest, distribution of the reaction product (metal) along the sample will be uniform ($\Delta m/\Delta \ell$ = const).

At rotation with the frequency n, any point of the combustion front with radius R is effected by a centrifugal force F_n and part of the total amount of metal with mass m comes back to the front limits according to the position of the front in the sample.

Assuming that in the equilibrium state $F_n = P$, we find $g = 39.4\ Rn^2$ and centrifugal force is determined by formula:

$$F_n = 39.4\ mRn^2 \qquad (7)$$

Using equation (3) let us find the changed by rotation deposition rate W_n of particles with the radius (r) at $g = 39.4\ Rn^2$.

$$W_n = \frac{2r^2}{9}\frac{(\rho_0 - \rho_m)}{\eta}39.4Rn^2 \qquad (8)$$

Fig. 3 presents values of W_n at $n=8.3\ s^{-1}$ (500 rot/min) at R = 0.3 m and value $\eta=1.39\ kg \cdot m^{-1} \cdot s^{-1}$ and values $\rho_0 = 19 \cdot 10^3\ kg \cdot m^{-3}$, $\rho_0 = 10 \cdot 10^3\ kg \cdot m^{-3}$ and $\rho_m = 4.0 \cdot 10^3\ kg \cdot m^{-3}$.

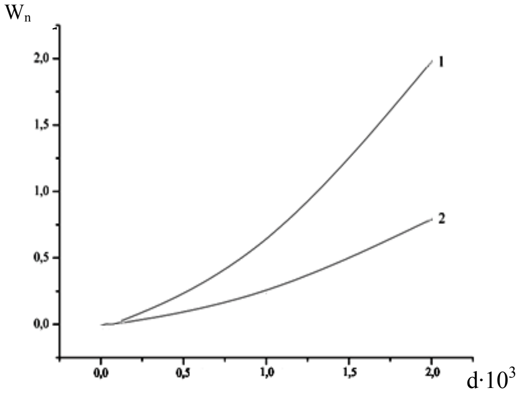

Fig. 3. Distribution of the deposition rate of particles with different diameters at n = 500 rot/min:
1 – $\eta = 1{,}39\ kg \cdot m^{-1} \cdot s^{-1}$; $\rho_0 = 19{,}0 \cdot 10^3\ kg \cdot m^{-3}$; $\rho_m = 4 \cdot 10^3\ kg \cdot m^{-3}$; $g = 10\ m \cdot s^{-2}$; n = 500 rot/min; R = 0,3 m.
2 – $\eta = 1{,}39\ kg \cdot m^{-1} \cdot s^{-1}$; $\rho_0 = 10{,}0 \cdot 10^3\ kg \cdot m^{-3}$; $\rho_m = 4 \cdot 10^3\ kg \cdot m^{-3}$; $g = 10\ m \cdot s^{-2}$; n = 500 rot/min; R = 0,3 m.

It is seen that at any $r > 10^{-4}$ m the rate of centrifugal deposition of the same particles exceeds the rate of combustion front propagation. Thus, the main fraction of the total mass of metal m_0 in the samples takes part in burdening the combustion wave. Therefore, the true value of combustion rate W_c under the conditions of rotation in any point of the sample is the sum of its two components:

1. Combustion rate (W_0) in the condition of rest and without participation of gravitation force, i.e. in a horizontally placed sample;
2. Combustion rate W_n as a centrifugal component of total combustion rate and resulting function of parameters R, n and η:

$$W_c = W_0 + W_n \quad (9)$$

The value W_0 is determined by the reserve of starting enthalpy of combustible mixture and ambient temperature of combustion. Contribution of a centrifugal force to the value of W_c is accelerated with the increase in R and n as well as due to the fact that as a result of the reaction nanosized particles of the combustion product become larger and effectively undergo the action of the force F_n returning to the front limits and thereby increasing its temperature by conductive heat transfer.

Therefore, W_n in (9) increases with time on account of the increase in the deposition rate of particles shown in Fig. 3.

Unlike the increase of W_0, their return to the front zone create pressure ΔP on the surface of pores s of a fresh reaction mixture widening the combustion wave front.

$$\Delta P = \frac{F}{s} = \frac{39.4\ mRn^2}{s} \quad (10)$$

and provides the filtration rate of the metal melt with mass m and density ρ_{Me}

$$W_f = \frac{\Delta P}{f} = \frac{dm}{\rho_{Me} \cdot dt} \text{ or } \frac{dm}{dt} = \frac{\rho_{Me} \cdot \Delta P}{f} \quad (11)$$

where f is resistance of filtration.

Thus, at f and s ≈ const, the growth of W_c according to (9) occurs due to the increase of ΔP.

The described mechanism of the growth of the heat content of combustion wave provides the increase in the reaction zone temperature. For a unit of its volume, the equation of heat balance describes the ratio of heat production and heat lasses:

$$c\frac{dT}{dt} = q\frac{dm}{dt} - \lambda \nabla T \quad (12)$$

where c, λ are heat capacity and heat conductivity, q is the amount of heat.

It follows from the above considered dynamics of heat accumulation within the range of quickly propagating combustion wave that the second term of equality (11) describing heat release from the reaction zone, in our case, decreases by the fraction of the heat being returned and consumed for heating the mixture. On the other hand, the first term of this equality increases on account of centrifugal concentration of already produced mass of the metal melt within the combustion wave. Due to this, a considerable part of the reaction mixture enthalpy is concentrated within the combustion wave. We see a number of bases to assume that since a certain moment of the reaction development

$$\lambda \nabla < q\frac{dm}{dt} \quad (13)$$

as a result of which there takes place the transfer of the combustion wave propagation process to the adiabatic regime W_{ad}:

$$W_{ad} = K_0 c_A \cdot c_B \exp\left({}^{-E}\Big/_{R\left(T_c + \frac{q}{mC}\right)} \right) \quad (14)$$

where c_A, c_B – concentrations of initial substances, K_o – factor of collisions.

The values c_A and c_B of the reaction become determining as only at some limiting c_A a critical, non-stationary procedure of the process (the upper limit) is reached (see Fig. 4).

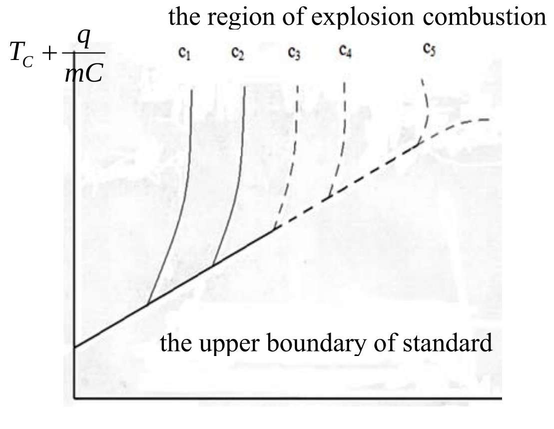

Fig. 4. Characteristics of combustion with filtration of liquid metal under the effect of a centrifugal force at its different initial concentrations in the sample ($c_1 > c_2 > c_3 > c_4 > c_5$).

The lower limit of c_A depends on the value of the force F_n being developed which in (13) is expressed by m and q. In equation (13) a limiting value of n is seen after which the rate of the deposited product weight slowly increases reaching the limit owing to deposition possessing a small impulse of force of a submicron – and nanoparticles. On the other hand, at high revolutions of the reactor, the lower concentration limit of combustion is significantly lower than during combustion in the system in the state of rest. Its value is determined by the number of rotations due to compensation of specific amount of heat in the front in the balance according to (12).

Fig. 5 presents experimental curves of combustion rate growth along the sample at n = (3 and 4) · 10^3 min^{-1} according to [9].

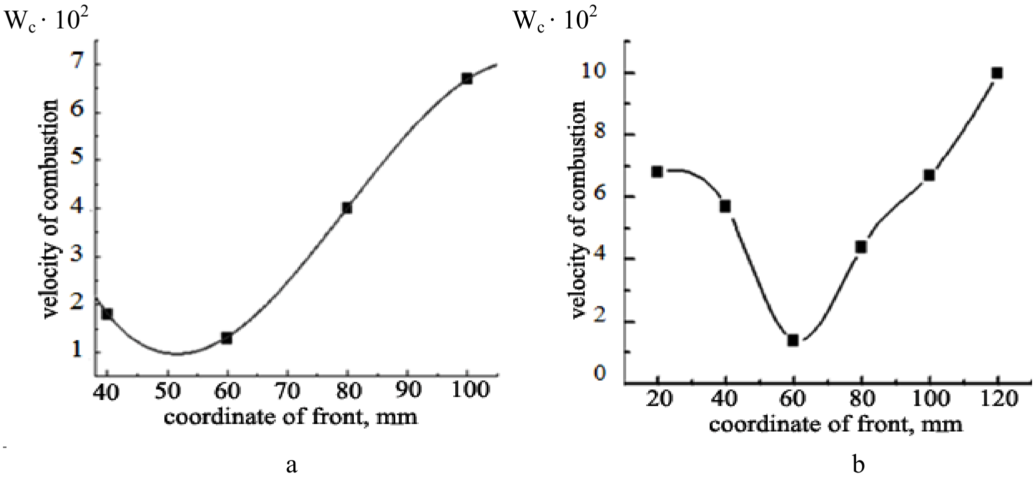

Fig. 5. The change of combustion rate along the sample at the frequency of rotation: a) 3000 rot/min; b) 4000 rot/min.

Omitting the first part of the curves indicating ignition we can see that their slope remains practically the same with the increase of rotation frequency. The charge of the value n by one thousand appeared to be insufficient for submicron – and nanoparticles.

Conclusion

In a whole, discussion and analysis of the peculiarity of the centrifugal combustion process given in this paper indicate the possibility of a significant improvement of the economics in production of ferroalloys in a rotating reactor. There appears the possibility to create a continuous technology of production of ferroalloys on the basis of aluminothermy and at significantly decreased low limit concentration of the sought for metal in the initial raw material. Alongside with this, melting of limited batches of special steels and different alloys will be possible on the basis of centrifugal SHS. In a whole, it significantly rises the importance of SHS technology in organization of new metallurgical technologies.

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