Macrokinetics and Practical Application of SHS Process under the Conditions of a Centrifugal Force

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Abstract

Extension of the possibilities of using SHS based on combustion with the aim to obtain impurity-free alloys, special ceramic materials with enhanced strength and thermal characteristics due to the effect of centrifugal acceleration is a practical task of this investigation. The use of a centripetal force in the method of SHS in layer oxide systems opens the prospect of using high temperature effects for creation of a wide spectrum of target products differing in composition and properties.

Introduction

The development of this theme starts from investigations of layer combustion, i.e. combustion of systems composed of several layers [1, 2]. Practical direction of the work is conditioned by the fact that self propagating high temperature synthesis in layer compositions can be considered as an independent and prospective method for production of technical materials different in composition and functional purpose – both complex metallic alloys and multicomponent ceramics. The specific character of the process conditions determines the peculiarities of the structure and properties of synthesis products.

The main peculiarity of synthesis of substances in layer systems is the possibility of delicate regulation of heat removal from the front of procedure of exothermal reactions, thereby effecting the macrokinetic characteristics of the combustion process.

Creation of a layer system includes an exothermal layer in the combustion process of which an alloy basis is formed, and a thermal effect is used for high temperature reactions in a parallel less active layer where small volumes of the reduced metal dissolve in the alloy basis and sink down in the form of large drops onto the reactor bottom forming an ingot. The main parameters here are the composition of layers, their arrangement in the reactor, dispersity of the components, the conditions of initiation of the combustion wave as well as the direction of its propagation in regard to gravitational field.

With the aim to determine the effect of gravitation on the combustion process of oxide systems we have studied the horizontal and vertical arrangement of the layer composition in space (Figure 1).

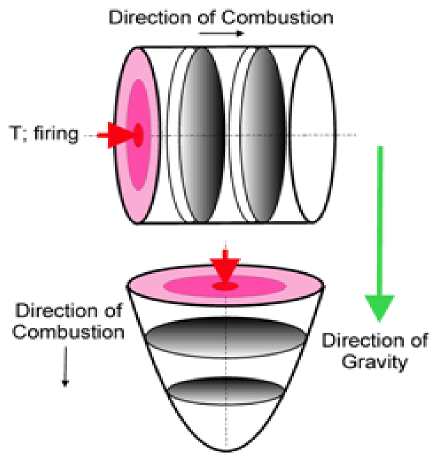

Fig. 1. Variants of layer systems positions in regard to the direction of gravitation

Gravitational effect on the metallothermal process results not only in separation of high temperature synthesis products according to their

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density and in formation of a metallic ingot. It also renders a significant effect on the combustion process parameters [3].

One of the applied directions of investigations on a layer combustion was a step-by-step reduction of metals from their oxides with gradual formation of a multicomponent alloy. For example, ferroboronchromium can be produced by different methods. It was experimentally stated [4] that the most effective of them are characterized by the arrangement of comparatively active layers over less active ones. Besides, the best result is conditioned by the maximum temperature effect at the final stage of the experiment. Such arrangement of the layers facilitates the yield of metal in an ingot due to the decrease in the viscosity of the alloy in the course of dense particles movement to the reactor bottom.

At constant combustion rate U_c, the result of combustion of oxide systems and the composition of the final product vary depending on the rate of metal drops fall in a viscous medium under the effect of natural gravitation. This fact prompted an idea to intensify the action of natural gravitation applying centrifugal acceleration to metal drops.

Experimental

An experimental plant is a centrifuge designed for investigation of combustion processes with the aim to realize a power saving method of producing metals and alloys from mineral raw materials with maximum recovery of metal on account of smelting in the mode of SHS with application of centrifugal forces [5]. The main units of the plant are: an engine placed on the shaft, a spider with balanced crucibles fixed on it, current collectors contacting with a brush unit and a firing spiral.

In operation, the centrifuge shaft is in a vertical position fixed in the upper and lower bearing units. The shaft is electrically operated. Revolutions are controlled by changing voltage applied to electric motor. Control over shaft revolutions is realized with the help of a tachometer specially designed for these purposes.

Three metallic sleeves with crucibles placed inside them, and both ends covered are fitted in at an angle of 120˚ from each other on the shaft (Figure 2). Alundum or quartz glasses with the diameter of 35 mm and length of 130 mm are used as crucibles. The covers are provided with holes for the escape of gases formed in the process of combustion and for firing the initiating composition. The sleeves with crucibles rotate in a horizontal plane.

Fig. 2. The main unit of the centrifuge for investigation of furnace-out combustion processes under the effect of centrifugal forces

Current collectors which serve for application of electric pulse to the firing spiral are fixed on the same shaft. The spiral which was drawn to the crucible through the cover and connected with the current collector initiates SHS process in the crucible. Measuring elements of combustion velocity and temperature energized from current collector allow controlling the smelting process.

After switching on the engine and reaching the pre-set frequency of shaft rotation, an electric pulse is applied simultaneously to all three spirals thereby firing exothermal mixtures loaded into the crucibles. The combustion wave propagates in the mode of SHS along the axis of cylindrical crucibles. The charge components interact with each other with procedure of exothermal reactions reducing metals. The combustion wave propagates in the whole volume of the charge. In the crucible, temperature reaches the level sufficient for formation of an alloy which under the effect of a centrifugal force separates in density to metals and slag.

After completion of the combustion process, temperature in the crucible falls, the engine stops, and the final products – pure metals or alloys as well as slag are unloaded and studied.

Synthesis products were studied by the method of X-ray phase analysis to determine the composition and percentage content of the phases formed. Quantitative distribution of separate elements along the cylinder axis was carried out using X-ray spectral analysis. The microstructure of metals and slag was studied on the metallographic microscope Neophot-2 and registered by a digital camera Leica DFE 320.

Results and discussion

Comparative experiments on furnace-out combustion of oxide systems based on molybdenum and nickel were carried out with the aim to determine the effect of centrifugal acceleration on concentration limits of combustion of exothermal mixtures, to reveal the peculiarities and advantages of recovering metals under the action of centrifugal forces.

The change of kinetic and technological parameters of the process, when adding aluminium oxide into the stoichiometric compositions (MoO3 + Al) and (NiO + Al), was studied under the conditions of furnace-out experiments which allowed to reveal the character of dependence of metal yields on the velocity of combustion wave propagation.

The dependency of metal yields on the percentage content of the ballast is shown in Figure 3. It also presents the dependency curve of combustion wave propagation velocity in a vertical direction, i.e. under the action of natural gravitation without rotation.

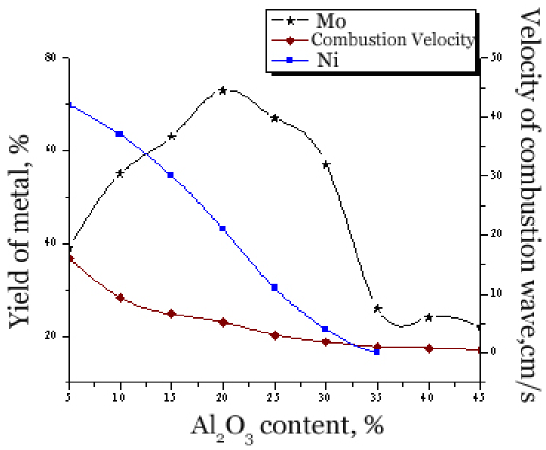


Fig. 3. The effect of the percentage content of the ballast in the initial mixture of reagents MoO_3 + Al on the combustion wave velocity and recovery of molybdenum and nickel under the conditions of natural gravitation

Comparison of the obtained dependencies allows to state the character of interrelation of the parameters under study. It is obvious that the combustion wave velocity is high with a low content of the ballast. It reaches 16.0 cm/s at concentration of aluminium oxide being equal to 5%. A great mass fraction of the reduced metal which hasn't yielded into an ingot is now in the after-combustion zone where viscosity of slag rapidly increases up to its complete solidification.

If the amount of ballast is too great, its heating and smelting consume a considerable part of thermal energy generated in the place of combustion. The increase in the content of the ballast in the charge up to 35% and higher decreases the combustion velocity more than 15 times. Temperature of the melt decreases, viscosity increases and the velocity of a metal drop travel down under the action of gravitational forces falls. Visual analysis of combustion products verifies the true picture of the process: when changing the composition of the initial mixture to the amount greater or lesser than the optimum ratio of components, a great amount of small metal shots are detected in slag. Further increase of the ballast content in slag results in disturbance of stationarity of the combustion mode and its transition to a spin or self-sustained vibrational mode. And in the structure, a characteristic laminated structure, sometimes with small inclusions of a metallic phase, is formed (Figure 4).

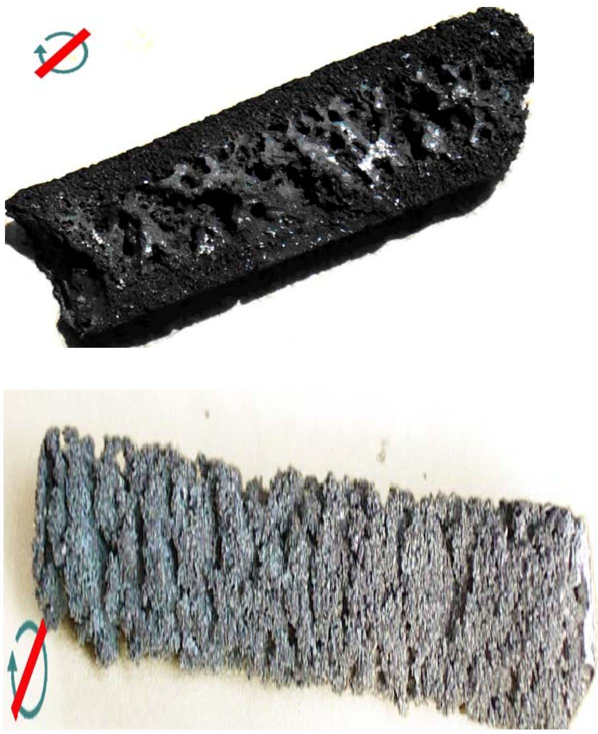


Fig. 4. A characteristic structure of samples based on metal oxides

Thus, it is stated that under the chosen conditions of the experiment the combustion limit of the stoichiometric mixture (MoO_3 – Al) takes place in the field of 45% content of aluminium oxide in it which is introduced into the initial charge as ballast, and for the system based on NiO – in the field of 35%.

The combustion process taking place under the conditions of centrifugal acceleration results in a more intensive lamination of a liquid heterogeneous product of synthesis or (and) more intensive infiltration of liquid drops of metal through a solid substance.

When initiating self propagating high temperature synthesis (SHS) by a thermal pulse in the upper layer of the charge consisting of a stoichiometric mixture of metal oxide and aluminium, the combustion wave propagates downward with the linear velocity U_c. The quantitative and qualitative ratio of the reaction mixture components provides the necessary temperature for a complete procedure of the reaction and transition of the system in the combustion zone to a liquid state.

Metal drops sink down by gravity moving in the same direction as the combustion wave front with the velocity close to the theoretical value of the velocity of a liquid drop fall in a viscous medium according to the equation of Adamar-Rybchinski [6]:

$$U_d = \frac{2}{3} g r_d^2 \frac{\rho_d - \rho_{sl}}{\eta_{sl}} \frac{\eta_{sl} + \eta_d}{2\eta_{sl} + 3\eta_d}, \quad (1)$$

where ρ_d and ρ_{sl} are densities of a reduced metal drop and slag, kg/m^3; η_d and η_{sl} are dynamic viscosities of a drop and slag, kg/(m·s).

The largest drops of reduced metal pass ahead of the front ($U_d > U_c$) and having density exceeding bulk density of the initial charge penetrate into the heating up zone creating in it new sites of ignition. Additional heat release increases the combustion wave velocity U_c, temperature in the after-burning zone simultaneously increases, the viscosity of slag decreases facilitating the travel of liquid metal through it. Coagulating, such drops form a layer of melt under the slag skin getting solidified and at further cooling form a compact ingot.

The velocity of small drops travel is less than that of the combustion wave front propagation ($U_c > U_d$). In the after-burning zone their movement slows down greater due to the increase in the viscosity of slag getting cooled. As a result, part of reduced metal is lost in slag in the form of entrapped cold shots.

Thus, the ratio of the value U_d and the linear velocity of combustion U_c determine the parameters and mode of SHS procedure as well as the yield of reduced metal into ingot. Of greatest significant here is the composition of initial charge determining the value of density and viscosity of combustion products smelting. An important role is played, too, by dispersity of the reacting components, the conditions of their contact, the thermal effect of exothermal reactions and other factors influencing the size of particles of liquid synthesis products.

From the analysis of Stokes and Adamar-Rybchinski's equations (1) it follows that under the action of centrifugal acceleration on the combustion process of oxide systems the melt viscosity loses its determining role. Centrifugal acceleration becomes the main factor. The increase in the value of centrifugal acceleration *n* times results in the *n* times decrease in the volume and mass of particles of reduced metal which can reach the reactor bottom, respectively. This means that only smallest particles remain in slag.

When organizing a technological process, it is necessary to choose optimum frequency of reactor rotation. The choice is based on the value of centrifugal acceleration which depends on the geometric parameters of the plant. The value of centrifugal acceleration determines the sizes of particles which can travel according to the velocity of the combustion wave front propagation and reach the reactor bottom forming a metallic ingot. For particles of known density, their minimum size is related to centrifugal acceleration by the dependency presented in Figure 5.

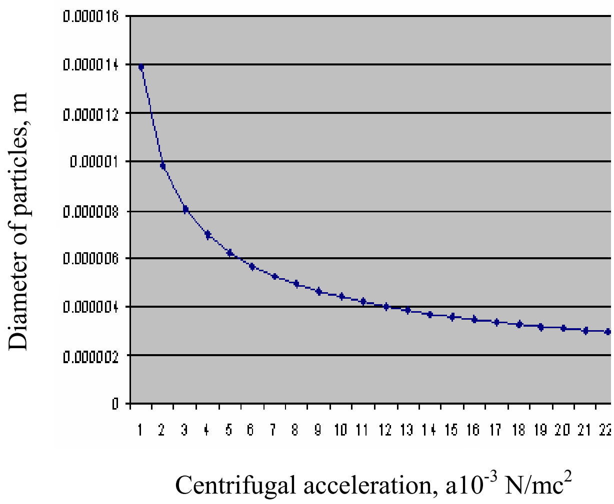
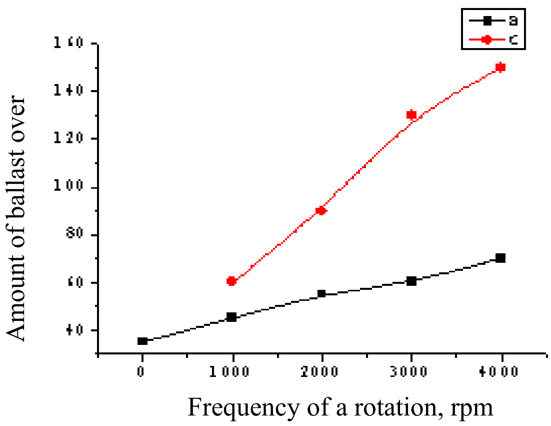


Fig. 5. The change of maximum size of particles remaining in slag with the growth of centrifugal acceleration

The amount of ignition sites in the heating zone before the combustion wave front increases according to this dependency. The increase in the amount of ignition sites in weakly diluted mixture results in the fact that transition to the mode of self-sustained oscillations takes place later, at lower concentrations of active oxide. Concentration limits of combustion widen due to the reduction of the lower boundary of the interval.

The combustion velocity which is determined by the thermal effect of components mixture and the conditions of heat release remains in its characteristic limits (Figure 6).

The main role in the process of formation of synthesis products macrostructure under centrifuge of definite sizes at the constant composition of initial charge is played by frequency of reaction relation. The velocity of the combustion wave front propagation, composition and purity of the phases being formed depend on this parameter. As is shown earlier, concentration limits of combustion of diluted exothermal mixtures are determined by the value of centrifugal acceleration which is in a square-law dependency on the rotation of frequency.



a – is the yield of alloy,
c – is linear velocity of the combustion wave front
Fig. 6. Expansion of concentration limits of combustion of exothermal mixture based on (NiO + Al) with ballast in the form of Al_2O_3

In strongly diluted mixtures, the self-sustained oscillation mode and the layer structure of slag which is characteristic of it do not hinder formation of a metallic ingot on the reactor bottom (Figure 7).

Correspondingly, the importance of heating additives and diluting fluxes in the initial charge decreases, thereby widening the possibilities of obtaining pure, impurity-free substances and materials.

Fig. 7. The macrostructure of the combustion product in the system (NiO + Al + Al_2O_3) proceeding in the mode of self-sustained oscillations under the effect of centrifugal acceleration

In order to increase the economic efficiency of the technology being developed, the initial composition of charge is calculated taking into consideration the production of a second valuable product in slag. At aluminothermal reduction of metals, it can be artificial materials on the basis of aluminium oxide – corundum with different contents of impurity elements (chromium, titanium, iron, etc.) imparting the pre-determined abrasive and refractory properties to it. Introduction of magnesium as a reducer to the charge allows to obtain aluminomagnesium spinel. In case of silicas, synthesis of different aluminosilicates is possible.

Conclusions

Thus, the decrease in the lower limit of combustion with the growth of rotation frequency and, correspondingly, centrifugal acceleration is shown. In strongly diluted mixtures, the self-sustained oscillation mode and layer structure of slag which is characteristic of it do not hinder the formation of a metallic ingot on the reactor bottom. The use of centrifugal acceleration in the course of furnace-out high temperature synthesis of materials provides a high degree of reagents contact, completeness of chemical reactions procedure and separation of synthesis products according to their density. Owing to this fact, it is possible to recover valuable metals from low concentrated ore raw materials with production of multicomponent oxide materials possessing high refractory and abrasive properties in the composition of slag.

It is possible to increase the economic efficiency of the technological process by obtaining in the composition of slag of a second valuable product of high temperature synthesis – refractory and abrasive materials.

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Received 14 September 2010