

WASTE-FREE TECHNOLOGY FOR PREPARING METAL POWDERS

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Abstract. The reduction of metal oxides and oxide catalysis is a very complicated process investigated by many authors. It has been proved with no doubts that under industrial conditions the process is controlled by the internal mass transfer. The reason for this fact is the great size of the particles and the high temperatures. The aim of the present research is to present our investigations of the reduction kinetics of paramagnetic oxides with pure hydrogen in a magnetically structured bed. The kinetics data are obtained in the temperature range 673-973 K. These results are the basis for the development of a technology for obtaining metals and metal powders related to ecology.

Keywords: reduction, preparing, powders, magnet filed.

AIMS AND BACKGROUND

The metal powder preparation methods are characterized by a great variety. The most frequently used method among them is based on direct reduction of metal oxides. According to the literature data more than half of the iron powders are obtained by this method. The various modifications of this method differ from each other in regard to the type and size of reduced particles, physical state of reducing agent, temperature conditions and construction of the applied apparatus¹⁻⁷. Sprong iron is obtained when using pelletized mixtures of iron oxides and a reducing agent is solid state. After an additional mechanical treatment the sprong iron is transformed into iron powder. The reduction is proceeding at a low rate in the course of a long time interval. The fluidized catalyst bed (FB) offers a possibility to intensify the reduction process, whereupon it becomes possible to utilize more completely the large contact surface of the small particles⁵. The results of Lurgi company⁵ with respect to direct reduction are very promising. The process is realized in two steps – circulating fluidized bed and barbotating fluidized bed. The comparatively high linear velocities of the reducing agent (H₂) in a FB ensure intensive mass transfer and fast removal of water vapour. The bubble formation in a FB is connected, without doubt, with the unfavourable effect of adsorption-desorption mixing. This is also a reason for the increased duration of the process.

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The development of reduction process for powdery oxide systems gives an impetus to the contemporary ecological thinking of many authors. The conditions for a waste-free realization of the process are being searched for in addition to its effective kinetics – absence of powder liberation and closing of the gaseous cycle. In our opinion such a decision may be found by using magnetically structured bed (MSB)^{6,7}.

EXPERIMENTAL

The circulation of solid particles in a free FB is the reason for adsorption-desorption mixing of the gaseous phases. This mechanism determines equalization of the concentrations, which is reflected unfavourably in a reduction process both on the kinetics and on the thermodynamics. MSB offers possibilities for removal of some disadvantages of the process application in the form of fluidized bed. Its specific features characterize it as a hybrid between a fixed bed on the one side and a fluidized bed on the other. Under conditions of the presence of an external magnetic field it is possible to regulate the expansion of the bed under the effect of a fluidized stream. Thereupon it is possible to regulate the porosity. In case of linear velocities, exceeding substantially the critical values, then in MSB the formation of a discrete phase is missing. The hydrodynamic resistance is changing following a linear dependence, not an exponential one. A basic requirement for the application of MSB (and its shortcoming at the same time) is that the solid state phase should possess ferromagnetic properties. We suppose that the paramagnetic oxides, during the reduction of which a ferromagnetic component might appear, could also be utilized in MSB. On the basis of this supposition a laboratory set-up was constructed, which is represented in Fig. 1.

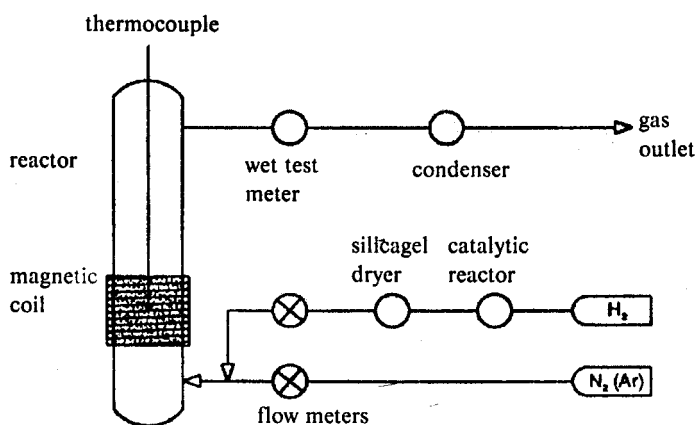


Fig. 1. Laboratory set-up for reduction of metal oxides in a MSB

The flow reactor is made of nonmagnetic stainless steel. Its construction enables the use of reaction tubes of various size (0.01-0.03 m). The reduction of iron oxides was accomplished with a reducing agent (pure hydrogen – 99.995% purity) and an inert medium – pure nitrogen (99.99%). The gaseous reagents were purified in advance from oxygen-containing gases, mixed accidentally with them. This process was carried out by means of sections, filled up with elemental copper and with silica gel, situated sequentially along the route of gaseous flow to the reactor. The amount of gases was regulated with flow rotometers. The liberated reaction water was determined gravimetrically. An electromagnet with $h_m = 0.14$ m and $D_{\text{intern}} = 0.16$ m is located in the vicinity of the reaction space. A direct current electromagnetic field was created by means of a system, consisting of a laboratory autotransformer and a direct current stabilizer. The force field lines are situated coaxially with respect to the gaseous flow. The temperature in the reaction zone was measured by a thermocouple (Cr – Al), located in the volume of the bed. In the reactor the temperature is maintained by an external heater. The reduction of paramagnetic oxides and their mixtures was accomplished by realizing the “step of non stabilized bed”. At the initial stage, due to absence of ferromagnetic behaviour of the sample, the reduction was carried out at the low linear velocities of the reducing agent. The duration of “non stabilized bed step” could be calculated for any oxide system. The total conversion in the case of $\alpha\text{-Fe}_2\text{O}_3$ reduction to Fe_3O_4 corresponds to $\chi \sim 8\%$, which determines a duration of about 5 min. Thereafter, the linear velocity of the gaseous flow was increased up to values, corresponding to realization of the reduction under typical MSB conditions.

The reduction kinetics of pure $\alpha\text{-Fe}_2\text{O}_3$ (Bayer) was studied as well as of its mechanical mixtures with pure Co_3O_4 and NiO , which possess ferromagnetic properties in reduced form. The used particles have diameters within the range 0.06-0.28 mm. The linear velocities of reducing agent exceed considerably the first critical velocities of the particles. The temperature interval was 673-973 K.

Analysis. The degree of metallization of the oxide particles was determined by the amount of water, liberated in the reaction, while in the case of iron powders it was controlled also by Mossbauer analysis. The phase characteristics of the obtained metal powders and the size of their crystallites were determined by X-ray diffraction and electron microscope analysis.

RESULTS AND DISCUSSION

The results on reduction kinetics of $\alpha\text{-Fe}_2\text{O}_3$ in MSB with $dp = 0.18$ mm are well illustrated with the graphical dependencies in Fig. 2. The changes in the velocity at the different temperatures show the considerable effect of this factor especially above 873 K. At the tenth minute of the reduction process the velocity at 973 K is more than twice higher than that at 873 K. This difference is considerably smaller

at temperatures 773 and 873 K. The greatest increase in the velocity at the higher temperature does not exceed 10-12 rel.%. The fact could be attributed to a change in the mechanism of the process at 873 K. Investigations in a free fluidized bed were carried out to evaluate comparatively the method under identical hydrodynamic conditions. The rate of the process under these conditions is considerably lower – it is at least with 30% smaller than that under MSB conditions. The bubble formation in a free FB and the adsorption-desorption mechanism of mixing, originating from it, are the basic reasons for these results. The free FB creates conditions for equalizing the concentrations in radial and axial direction, which leads to deterioration of the thermodynamic and kinetic conditions of the process. The logarithmic dependencies (Fig. 3) are evidence for the absence of obstacles of macrokinetic nature at temperatures 673 and 773 K. The course of the dependencies at the higher temperatures is an indication for the appearance of diffusion problems in the mass transfer. It is possible that even the small particles could experience the effect of an external diffusion layer formation around them at the studied linear velocities V_{lin} .

Summarizing the kinetic investigations we could say that under MSB conditions the reduction of Fe(III)-oxide is proceeding very intensively and the most important point is that there is no removal of solid particles from the space above the layer. The calculated values of the experimentally established apparent activation energy lie within the range of 25.2-38.6 kJ/mol.

An important specific feature of metal oxide reduction is the negative effect of the water vapour, especially strongly manifested when the process is accomplished in the low temperature region. The quantitative estimation, made on the basis of the reduction degree, is important in this respect – to evaluate the influence of the residence time (contact time) of the gaseous phase τ_d . The experimental dependence χ/τ_d is represented in Fig. 4 – results are obtained under identical hydrodynamic conditions. The different values of contact time were achieved by

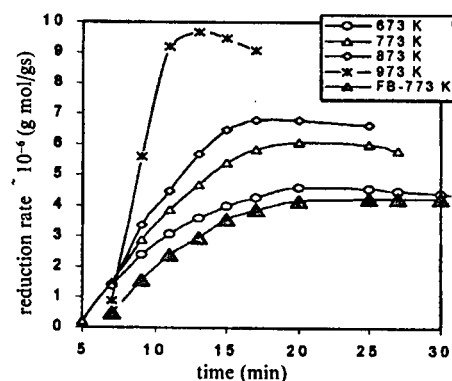


Fig. 2. Relationship between reduction rate of pure Fe_2O_3 and reduction time

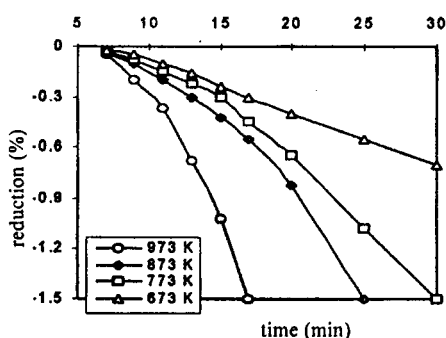


Fig. 3. Logarithmic dependence of the fraction reduction of pure Fe_2O_3 on the time

altering the height of the bed. The experimental data show unambiguously that upon increasing τ_d from 0.1 s up to 0.2 s the conversion degree at 673 K decreases almost three-fold. This tendency is presented at the higher temperatures but the decrease of χ is smaller. These facts are in conformity with the concept, summarized in the current literature, that the water vapour exerts a significant poisoning effect at low temperatures. The data confirm once again our concept that the solution of this problem could be MSB, enabling the use of greater V_{in} of the reducing agent (smaller τ_d , respectively).

The considerable influence of the intact time of the gas, i. e. of the reaction product (water vapour) in the reaction zone at the low temperatures, is mainly the result of deterioration of the conditions from the point of view of the equilibrium. The higher temperatures compensate partially the increased water vapour partial pressure. This is how the idea to study the effect of the other gaseous component – hydrogen, came to us. The experimental data in Fig. 5 point at the fact that p_{H_2} in the gaseous mixture is reflected substantially on χ_{red} provided the other conditions are identical. The increase of p_{H_2} from 0.5 to 1 atm in the autocatalytic part of the kinetic dependencies (between the 10th-20th min) leads to an increase of χ with 8-20 abs.%. These data are an indication that the reduction process will proceed effectively using pure H_2 or gaseous mixtures with high partial pressure of hydrogen.

An important feature of the metal powders is their granulometric composition and for this reason their direct preparation is connected with the possibilities of MSB to reduce particles of various size. The influence of the particle size on χ is illustrated in Fig. 6. The analysis of the results shows that no substantial changes in χ are observed within the interval $dp = 0.09-0.28$ mm independently of temperature. The little bit lower values of χ in the case of large grains is to be associated with the smaller geometrical surface of these particles. It is out of the ques-

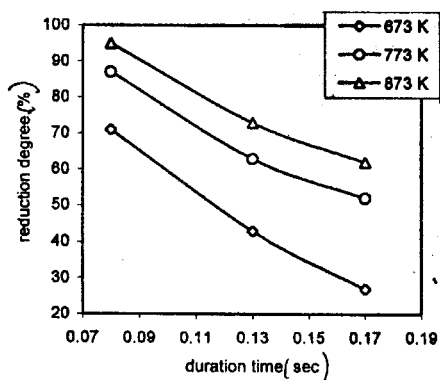


Fig. 4. Dependence of the reduction degree on duration time of the reduction agent by MSB

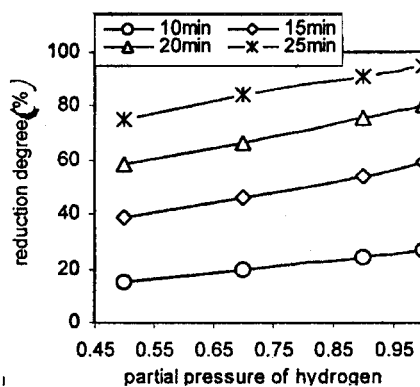


Fig. 5. Dependence of reduction degree on partial pressure of hydrogen

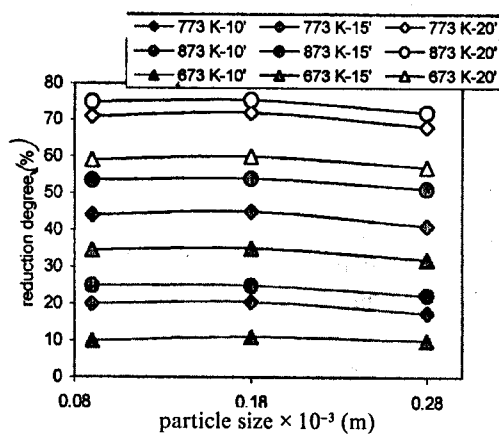


Fig. 6. Dependence of the reduction degree on size of the particles

tion to suppose interference by the mass transfer as our previous investigations proved that the reduction in MSB is proceeding in the kinetic regime at temperature below 873 K even in the case of $d_p = 0.36$ mm. The obtained results reveal an option to prepare Fe-powders by direct reduction of oxides with H_2 without any limitation in regard to the particle size and accordance with the form, in which they find application.

The studies were extended to include metal powders of pure Co and Ni, as well as their mechanical mixtures with iron. The summarized literature data show that the treatment of metal powders as high temperatures is associated with sintering, diminishing their porosity as well as with aggregation of particles. The apparent density and the specific surface area of metal powders, obtained in MSB, were determined for samples, passivated by partial oxidation. The data show that after complete metallization the apparent density decreases with ~ 13 -22% with respect to that of the initial Fe oxide. The small increase of ρ_{app} with the increase of temperature is a consequence of the weak densification of the particles. The sieve fraction analysis indicates that the agglomeration of particles even at 973 K is not be observed, which is important both for the hydrodynamics of the process and for the quality of the obtained metal powders. The reasons for this effect are the parameters of MSB, in which the particles are characterized by coordination numbers smaller than those in a fixed bed. The reduced degree of contacting between the separate grains ensures a favourable aerodynamics and reduces the possibility of interaction between the powdery particles. In addition to this fact we should point out the isothermicity of the bed, determined by the more intensive macrokinetic processes. Not without any importance is the fact that the particles in MSB do not move, they are not subjected to erosion, i. e. their size is not being diminished. The apparent densities of pure β -Co and Ni change in a different way with respect to those of the initial oxides. The density ρ_{app} of powdery Co is larger, whatever the reduction temperature is, while that of Ni – smaller than the initial. The influence of Co_3O_4 and NiO additives on Fe_2O_3 is analogous in regard to ρ_{app} of the obtained mixtures of metal powders, in which Fe is prevailing. The modified values of S_{spec} of the passivated metal powders illustrated also the tendency of some sintering of the particles at higher temperatures. The specific surface area S_{spec} is changing from 10.4 to 2.3 m²/g within the interval 673-973 K. The iron powder, obtained after 20 min of reduc-

tion, possesses 4.4 m²/g. This shows that the temperature is not the only factor, determining the internal structure and surface of the particles. An essential role, without doubt, is played by the macrokinetic processes, the composition of the reducing agent and the rate of the chemical step of the process.

The results obtained by us, on the direct reduction of metal oxides in MSB indicate an option to obtain metal powders with an initial oxide particle dimension set in advance. There exist no hydrodynamic and macrokinetic limitations to the realization of the reduction for particles of size up to 0.9 mm. No loss of solid phase was observed in the course of the experiments. The use of pure H₂ excludes the liberation of harmful exhaust gases.

The high process rate at low temperatures is a prerequisite for its economic expedience. On the basis of the obtained results we consider it possible to create a waste-free technology for the preparation of metal powders, composite materials, in which the main content is one of the ferromagnetic metals by means of MSB. In this respect a technological scheme would contain the following technological processes, which could close the gaseous cycle of the system. The principal technological scheme, represented in Fig. 7, outlines this forseen possibility. The only waste product in the cycle is the water vapour, which could easily be removed from the gaseous flow. The heat of the outlet gases might be used applying the recuperative principle, which will reduce the energy costs for maintaining a definite temperature regime. The ecological advisability of such a technology is enforced also by the temperature conditions of the endothermal process of reduction. The optimum operation temperature of the process, in MSB, is ~773 K and it is lower with about 300-500 degrees than that in a fixed bed.

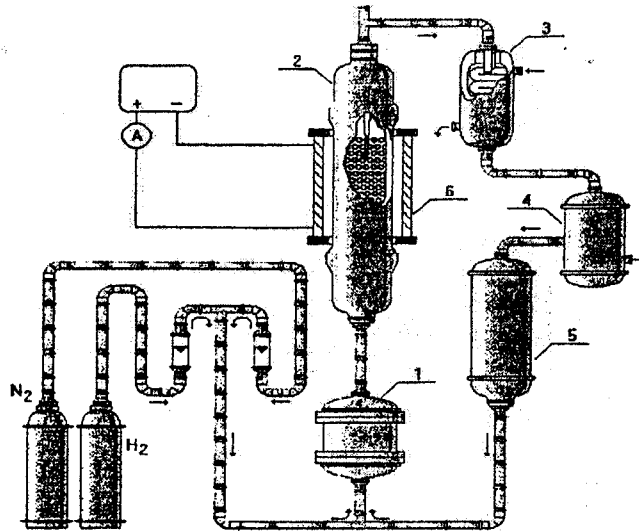


Fig. 7. Principal technological scheme
 1 – heater; 2 – reactor; 3 – cooler; 4 – water-cooler; 5 – condenser; 6 – electromagnet
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CONCLUSIONS

We should note in conclusion that the preparation of metal powders in MSB with reducing agent – pure H_2 or mixtures of H_2 with inert gases, is the basis of a future ecologically advisable technology, founded upon reduced energy costs, absence of dust liberation and a completely closed gaseous cycle.

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