

High chemical activity and passivation of ultradispersed particles synthesized under the conditions of electric-arc low-temperature plasma

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Under conditions of electric-arc low-temperature plasma (LTP), various ultradispersed particles (UDP) have been synthesized. UDP are characterized by their specific surface (from several tens to several hundred $\text{m}^2 \text{g}^{-1}$), particle size (10–100 nm), phase composition, etc. The most efficient passivation agents preventing the high chemical activity of pyrophore, plasmachemically synthesized UDP have been experimentally established. These are: pure nitrogen for manganese, CO for molybdenum, $\text{N}_2(0.5\% \text{O}_2)$ for iron, $\text{N}_2(0.5\%–2\% \text{O}_2)$ or $\text{CO}_2(\leq 2\% \text{O}_2)$ for the reduced catalyst for ammonia synthesis, $\text{N}_2(1\% \text{O}_2)$ for the reduced catalyst for natural gas reforming, and $\text{N}_2(1\% \text{O}_2)$ for the reduced catalyst for low-temperature conversion of CO with H_2O . The high chemical activity of AlN and Mg_3N_2 was decreased by slow annealing at about 900–1000 K in a nitrogen atmosphere or by thermal treatment in an inert gas flow. Passivation was enhanced by the ability of some metals to form surface complexes (due to chemisorption of some gases) of composition similar to that of chemical compounds, e.g. metal carbonyls (Fe, Mo, W, etc.). The sorption (chemisorption) of gases on the surface of UDP can only decrease the oxidation rate rather than prevent oxidation.

1. Introduction

High chemical activity, expressed by either intensive oxidation or spontaneous ignition in contact with the atmosphere, represents a technological problem related to the preparation of ultradispersed particles (UDP). Plasmachemically obtained powders of tungsten [1–6], molybdenum [7–9], rhenium, manganese [9–12], iron [9] and some catalysts [9, 13–16] are pyrophores; they are synthesized by reduction of the respective oxygen compounds in low-temperature plasma (LTP).

The present work aimed to explain the high chemical activity and, in some cases, the pyrophoric properties of plasmachemically synthesized UDP on the basis of experimental results and literature data, as well as to establish effective methods for their passivation (stabilization).

2. Experimental procedure

Our extensive studies were directed to obtaining of ultradispersed manganese by subjecting a manganese oxide concentrate to reduction by hydrogen, ammonia or a propane–butane gaseous mixture under conditions of electric arc LTP [9–12]. The content of manganese oxides (MnO_2 , Mn_2O_3 and Mn_3O_4 ; Mn^{2+} 43.1%, Mn^{4+} 23%) in the starting concentrate was up to 99.9%, with particle-size distribution (mass

%) as follows: < 1 μm , 72.7; 1–2 μm , 21.1; 2–3 μm , 3.0; 3–5 μm , 1.9; 5–7 μm , 0.6; 7–10 μm , 0.2. The specific surface of the starting concentrate was $5.7 \text{m}^2 \text{g}^{-1}$. Investigations were carried out by a plasmachemical installation described in detail elsewhere [9, 11]. A plasma jet with the necessary power of up to 5 kW was generated by a direct current plasmatron. Argon, hydrogen or nitrogen or their mixtures, were used as plasma-forming gases. The plasma jet and the reactants were mixed in a mixing chamber. The plasmachemical reactor was 150 mm long, with a channel diameter of 12 mm. The residence time of the reactants in the channel was about 10^{-3} s. The products of the plasmachemical process were fixed by an abrupt decrease of the temperature in a quenching device where an inert gas or a reactant were fed radially through three nozzles; the quenching rate was 10^6K s^{-1} . The products of the plasmachemical reaction were cooled to room temperature in a dust-chamber where about 70% of the ultradispersed solid phase was deposited. The remaining amount of the powder was deposited in the bag filter at the outlet of the heat exchanger–dust collector. Two modifications of the plasmachemical reactor were used. In the first case the reactor was made of copper and its walls were water-cooled (wall temperature 300 K), while in the second case a refractory material was used without cooling of the walls; their temperature was in the range 1000–1500 K

depending on the process regime. The average temperature of the plasmachemical reactor was determined calorimetrically.

Investigations for the establishment of reduction conditions of a molybdenite concentrate (Mo 34%, S 30%, Cu 3%, Fe 5%, Re 0.05%, SiO₂ and Al₂O₃ balance to 100% by mass, specific surface 4 m² g⁻¹) were also carried out in view of the application of the product in powder metallurgy [7–9]. The installation used comprised an electric arc plasmatron, plasmachemical reactor, quenching device and dust-chamber. Argon (technical grade) was used as plasma-forming gas while butane, ammonia or hydrogen served as reducing agents and dust carriers. Quenching was effected by the cold walls of the dust-chamber as well as by argon blowing.

A similar installation was used for the study of the reduction of iron oxides, and more particularly Fe₂O₃, by hydrogen under the conditions of an electric arc LTP as well as for the synthesis and/or regeneration of numerous catalysts finding application in ammonia production. These are catalysts for steam conversion (reforming) of natural gas [9, 16, 18], for low-temperature steam conversion of carbon oxide [9, 16, 17, 19, 20] as well as for ammonia synthesis [9, 13, 15–17, 20–22].

The plasmachemical reactor with “cold” or “hot” walls served for the synthesis of UDP of AlN [9, 13, 23, 24] and Mg₃N₂ [9, 13, 25] using elemental aluminium or manganese and nitrogen (99.99%) as raw materials.

The synthesized UDP were characterized by their specific surface using the method of Klyachko–Gurvich [26]; their particle size was determined by electron microscopy, their phase and structural composition was studied by X-ray diffraction (Mössbauer

spectroscopy [21, 22]) as well as by derivatographic and elemental analyses. Reduction and activation of catalysts were studied by the flow method.

3. Results and discussion

The experimental results on the reduction of the manganese oxide as raw material by H₂, NH₃ or CH₄ in a cold-walled reactor were unsatisfactory, because the reduction rate was low. This is basically due to high radial temperature gradients in the plasmachemical reactor. Furthermore, intensive oxidation of UDP was observed upon its removal from the dust-chamber. Attempts to passivate the final product by means of nitrogen containing 0.5% O₂ or by CO or CO₂ gave no better results. The presence of nitrogen in the gaseous phase (an argon/nitrogen mixture is used as plasma-forming gas) prevents the spontaneous ignition of the particles due to surface formation of manganese nitrides (Mn₃N₂, Mn₄N, Mn₂N) on the ultradispersed manganese (Table I).

Best results were obtained with the hot-walled reactor using nitrogen as a passivation agent. The reducing agent (hydrogen) was also used as a powder carrier. The results obtained [9–12] show that the process efficiency, expressed as reduction rate of the manganese oxide, was higher than 50% and a highly dispersed product was obtained; its particle size was below 100 nm while its specific surface was about 80 m² g⁻¹ (Table I).

The basic reasons for the decrease of the process efficiency (the reduction rate) are the spontaneous ignition and the low passivation rate of UDP. In our opinion, owing to effective quenching ($dT/d\tau \sim 10^6 \text{ K s}^{-1}$), a complete reduction of the oxides to elemental manganese takes place in the plasma-

TABLE I Some technological parameters and physicochemical properties of chemically active ultradispersed powders synthesized under conditions of electric arc low-temperature plasma

Ultradispersed substance	Basic reaction of plasma chemical synthesis	Temperature range in the plasmachemical reactor (K)	Particle size (nm)	Specific surface (m ² g ⁻¹)	Passivation agent	Composition of the protective layer	Reference
Mn	$\text{Mn}_x\text{O}_y + y\text{H}_2 \rightleftharpoons x\text{Mn} + y\text{H}_2\text{O}$	2000–4000	< 100	≤ 80	N ₂	Mn ₃ N ₂ , Mn ₄ N, Mn ₂ N	[9–12]
Mo	$\text{MoS}_2 + 2\text{H}_2 \rightleftharpoons \text{Mo} + 2\text{H}_2\text{S}$	2000–4000	< 100	20–380	CO	Mo(CO) ₆	[7–9]
α-Fe, γ-Fe	$\text{Fe}_x\text{O}_y + y\text{H}_2 \rightleftharpoons x\text{Fe} + y\text{H}_2\text{O}$	2000–3000	10–100	≤ 160	N ₂	Fe _x O _y , Fe(CO) ₅	[9]
CA-1 type catalyst for ammonia synthesis	$3\text{Fe} + 2\text{O}_2 \rightleftharpoons \text{Fe}_3\text{O}_4$	1100–3400	20–60	10–40	N ₂ (0.5% O ₂) CO (0.5%–2% O ₂) CO ₂ (≤ 2% O ₂)	Fe ₂ (CO) ₉ , Fe ₃ (CO) ₁₂ Fe _x O _y Fe _x O _y	[9, 13, 15, 16, 17, 20–22]
Catalyst for low-temperature conversion of CO with H ₂ O	$(\text{Cu,Zn,Al}) + \text{O}_2 \rightleftharpoons \text{CuO}(\text{Cu}_2\text{O}) + \text{ZnO} + \text{Al}_2\text{O}_3$	up to 5100	10–40	45–51	N ₂ (1% O ₂)	CuO, Cu ₂ O	[9, 16, 17, 19, 20]
Catalyst for natural gas reforming	$(\text{Ni,Al}) + \text{O}_2 \rightleftharpoons \text{NiO} + \text{Al}_2\text{O}_3$	2000–3000	10–30	≤ 110	N ₂ (1%–2% O ₂)	NiO	[9, 16, 17, 18]
AlN	$2\text{Al} + \text{N}_2 \rightleftharpoons 2\text{AlN}$	3300–3800	50–70	60–100	Annealing to 1000 K	–	[9, 13, 23, 24]
Mg ₃ N ₂	$3\text{Mg} + \text{N}_2 \rightleftharpoons \text{Mg}_3\text{N}_2$	2000–2500	10–60	≤ 180	Annealing to 900 K	–	[9, 13, 25]

chemical reactor which, in turn, fixes the non-equilibrium crystal structure of UDP. The elimination of the pyrophoric properties of plasmachemically ultradispersed manganese could be achieved by (i) annealing of UDP in an inert atmosphere (Ar, N₂) leading to the occurrence of recrystallization processes which reduce, to a great extent, the non-equilibrium states in the crystal lattice and the structural defects of manganese, (ii) storage of the reaction product in an inert atmosphere or in an organic liquid, and (iii) complete surface nitration or oxidation of the ultradispersed manganese particles.

Treatment of a molybdenite concentrate with butane in a cold-walled reactor resulted in a reduction rate of 83.5% while the specific surface of the product varied from 20–73 m² g⁻¹. The use of hydrogen as a reducing agent led to a rate of 90% and the specific surface amounts to 380 m² g⁻¹ (Table I, [7–9]).

In our opinion, complete reduction of the concentrate under conditions of electric arc LTP could be achieved by (i) effective quenching, i.e. abrupt decrease of the temperature of the reaction products below 500 K, so that the reaction $\text{Mo} + 2\text{H}_2\text{S} \rightleftharpoons \text{MoS}_2 + 2\text{H}_2$ could not take place. Experimental results [7–9] under the same conditions show that the reduction rate is not influenced by use of gas quenching. Owing to the high chemical activity of ultradispersed molybdenum, the above reaction takes place in the dust-chamber; (ii) Maintenance of a temperature higher than 1200 K in the dust-chamber when the reaction equilibrium is shifted to molybdenum and H₂S. A maximal reduction rate of 93% is achieved in this case. It should be noted that the amount of reducing agent should always be much higher than the stoichiometric one.

The high chemical activity (pyrophoric properties) of the product obtained by reduction of molybdenite concentrate with hydrogen is quite undesirable, because ultradispersed molybdenum is oxidized to MoO₃ by atmospheric oxygen and the specific surface decreases abruptly. These unfavourable conditions are created mainly in the dust-chamber. In order to overcome the spontaneous ignition of ultradispersed molybdenum, passivation with CO is carried out, resulting in the formation of a thin surface layer of Mo(CO)₆. The latter prevents further diffusion of oxygen molecules in the volume of the particles. The molybdenum carbonyl thus obtained sublimates at 310–320 K and decomposes within the temperature range 420–670 K. It should be noted that bulk molybdenum reacts with carbon monoxide at 470 K and a pressure of 20–25 MPa.

Our studies [9] of the reduction of a mixture of iron oxides, and more particularly of Fe₂O₃ with hydrogen under conditions of electric arc LTP show that a reduction rate of almost 100% is achieved; the specific surface of the extremely pyrophoric iron amounts to 160 m² g⁻¹. X-ray structural analysis and Mössbauer spectra show the presence of α -Fe and of the ultra-paramagnetic γ -Fe in UDP. With a rise of quenching rate from 10⁵ to 10⁸ K s⁻¹, the γ -Fe content increases from about 50% to almost 100%. Thus the plasmachemical method could be applied to the preparation

of ultradispersed iron in the high-temperature γ -modification. The extremely high chemical activity of the latter is prevented by treating it in a flow of nitrogen containing 0.5% O₂, resulting in the formation of a thin surface layer of a complex mixture of iron oxides (Fe_xO_y, Table I). A passivation effect is observed by treating the ultradispersed iron particles with carbon monoxide, at which surface layers of several molecules of Fe(CO)₅, Fe₂(CO)₉ and even Fe₃(CO)₁₂ are formed. In order to obtain Fe(CO)₅ by heating of an iron powder with particle size in the micrometre range, a temperature of about 420–470 K and pressure of about 10 MPa are required. It is clear that the high chemical activity of the plasmachemically obtained ultradispersed iron with particle size of 10–100 nm (Table I) is the reason for the formation of iron carbonyls at room temperature and atmospheric pressure.

The plasmachemically synthesized and/or regenerated catalysts of the CA-1 type for ammonia synthesis show a catalytic activity that is higher by 15%–25% than that of their conventional analogues; furthermore, their reduction is three to five times faster [9, 13, 15–17, 20–22]. Regardless of the reduction method (isothermal or stepwise), they show an extremely high chemical activity (pyrophoric properties) on contact with air. The most common method of passivation of reduced catalysts for ammonia synthesis is their treatment with nitrogen containing 0.5%–2% (by volume) of oxygen; elemental iron is thus oxidized to Fe_xO_y (Table I). According to Krilova [27], three forms of oxygen can participate in the passivation of reduced conventional catalysts for ammonia synthesis, i.e. slightly chemisorbed oxygen (a layer of 0.5–1 molecule) which is separated by heating of the catalyst to 423 K regardless of the nature of the carrier gas; strongly chemisorbed oxygen (a layer of 2–4 molecules) which leaves the sorption centres at 500–800 K in helium by diffusion in the bulk; oxygen in the form of oxides (4–6 molecular layers) which separates at 500–800 K only by hydrogenation in a hydrogen atmosphere. The particular form of sorbed oxygen could be determined by the activation energy of hydrogenation; this value is $E = 77.8 \pm 6 \text{ kJ mol}^{-1}$ in the case of plasmachemically synthesized and/or regenerated catalyst for ammonia synthesis and it corresponds to the heat of iron oxidation, i.e. chemisorption occurs during passivation. Carbon dioxide (technical grade) containing up to 2% (by volume) of oxygen is used as a passivation agent. Similar to the case of passivation with nitrogen containing up to 0.5 vol% oxygen, complex oxide mixtures are formed on the surface of the catalyst particles (Fe_xO_y, Table I).

The derivatographic study of passivated plasmachemically synthesized and/or regenerated catalysts after exploitation shows separation of water upon heating (endothermal effect below 373 K) and initiation of oxidation of the CA-1 type catalyst in air at 380 K (appearance of an exothermal effect). A maximum oxidation rate is observed at about 450 K.

It should be noted that cooling in air down to the evaporation temperature of liquid nitrogen (77 K) results in the removal of the pyrophoric properties of

the plasmachemically synthesized and/or regenerated reduced catalysts for ammonia synthesis, low-temperature steam conversion of carbon monoxide or for methane reforming, while the initial temperature of oxidation is increased by about 20 K.

Plasmachemically synthesized ultradispersed aluminium nitride (Table I, [9]) is more chemically active than the bulky one, but it does not show pyrophoric properties. In a humid atmosphere it undergoes slow hydrolysis according to the reaction $\text{AlN} + 3\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3 + \text{NH}_3$ and diffraction maxima of $\text{Al}(\text{OH})_3$ are observed in the X-ray diffractograms in this case. After annealing to about 1000 K in pure nitrogen the chemical activity of the nitride is somewhat decreased. However, plasmachemically synthesized ultradispersed aluminium nitride should be stored in tightly closed containers.

Plasmachemically synthesized magnesium nitride [25] shows a high reactivity and it is rapidly hydrolysed in a humid atmosphere: $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \rightleftharpoons 3\text{Mg}(\text{OH})_2 + 2\text{NH}_3$. Its gradual heating to 900 K followed by cooling to room temperature decreases to a great extent the chemical affinity to water vapour. Nevertheless, plasmachemically synthesized magnesium nitride should be stored in an inert atmosphere (argon, helium or neon, free of oxygen and water vapour).

The high activity of plasmachemically synthesized UDP with respect to atmospheric oxygen and water vapour can be explained by the peculiarities of their crystal structure formed under the conditions of LTP [28]. The abrupt cooling upon quenching of the plasma jet leads to the formation of a less-perfect crystal lattice with a large number of vacancies. Migration of the metal atoms in the defect nodes is hampered by the low temperature. As a rule, defective crystal structures are characterized by an enhanced surface activity [28] and for this reason oxygen is actively chemisorbed on the ultradispersed metal powders. There are no conditions of rapid chemisorption heat transfer and for this reason the metal particles are heated to the temperature of rapid oxidation; increased dispersity enhances the occurrence of these processes.

An equation is derived from the heat balance of powder oxidation [29]

$$T \geq E / 2R \ln \left[\frac{A^{1/2} \Delta H m^{2/3} \gamma^{1/3}}{K \lambda \rho d \tau^{1/2}} \right] \quad (1)$$

relating the temperature of spontaneous ignition with the physicochemical parameters of the specimen. This equation satisfactorily agrees with our experimental results; it shows that the temperature of self-ignition, T , increases with the rise of the activation energy of oxidation, E , the heat conductivity of the powder, λ , the density, ρ , and diameter, d , of the particles, as well as with the heating duration, τ , and decreases with the rise of the preexponential multiplier, A , the thermal effect of oxidation, ΔH , the mass of the specimen, m , and the bulk mass of the powder, γ .

Experimental data show that the impacts of the particle diameter, the mass of the specimen and the

duration of heating qualitatively reply to the above equation. The exact quantitative check of the equation is, however, hampered by the absence of precise values of E , A and K .

4. Conclusion

A high chemical activity and even pyrophoric properties (in some cases) are observed with plasmachemically synthesized UDP of metals (manganese, molybdenum, iron), oxide catalysts after reduction to an active form and some nitrides. Nitrogen, carbon monoxide or dioxide, inert gases containing small amounts of oxygen, metal halides, hydrocarbons, etc., can be used in each particular case as sorbates protecting plasmachemically synthesized UDP from an active interaction with oxygen. Unfortunately, the sorption of gases on the UDP surface can only slow the oxidation rate rather than completely prevent this process. The high reactivity of the powders is decreased in numerous cases by thermal treatment in an inert gas flow or in vacuum. Chemisorption of gases on the surfaces of some metals offers some advantages with respect to passivation because surface metal complexes can be formed, with compositions similar to those of chemical compounds. As an additional requirement, these complexes should rapidly decompose during further treatment of the powders, e.g. sintering. The carbonyls of numerous metals (iron, molybdenum, etc.) prove appropriate in this respect. General theoretical concepts defining a priori the most efficient passivation agents for the various highly active plasmachemically synthesized UDP, are still not formulated.

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