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Plasmachemical technology for high-dispersion products

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Experimental results of the synthesis of ultrafine powders (UFP) under conditions which characterize quasi-equilibrium, as well as non-equilibrium low temperature plasma (LTP), are summarized. The basic steps involved in the plasmachemical processes for producing UFP are considered. The process of powder vaporization is limiting, determining the characteristics of the plasma generator. To obtain UFP with high purity, the reactions must take place in the gaseous phase. Quenching can be accompanied by a chemical reaction, and as a result, powders are obtained with either defects in the crystal structure or in the amorphous state. The mean particle size of UFP is 5 to 100 nm (specific surface $\leqslant 400\,m^2\,g^{-1}$). Quenching determines the phase content of the specific UFP.

1. Introduction

Ultrafine powders (UFP) consist of 5 to 100 nm particles. They have specific mechanical, electrical, magnetic, thermal, optical and chemical (including catalytic) properties. Ultrafine materials are used in the production of pressed articles (powder metallurgy and metal ceramics), alloyed metals, special ceramics, and electronic equipment elements. They are good fillers, abrasives, pigments, catalysts and can be used for corrosion-, wear- an heat-resistant coatings.

The production of UFP in low-temperature plasmas (LTP) is highly convenient because of the high enthalpy content and high rates of evaporation and condensation (crystallization). Additional advantages are the miniaturization of the equipment, introduction of automatic control and optimizing and modelling of the processes. A specific combination of plasma jet, plasmachemical reactor and quenching device determines the size and shape of the particles, their purity and the physical and chemical properties of their surface. The plasma jets, and especially HF and UHF plasma jets, have a low impurity level and therefore are convenient for the production of high-purity powders of metals, alloys, ceramics and composites.

This paper summarizes our experimental results on plasma production of UFP.

2. Experimental procedure

UFP were produced in equilibrium electrical arc LTP [1–43] and nonequilibrium HF LTP [44, 45]. The experimental devices are described in [1, 3].

3. Results and discussion

Table I shows the main plasmachemical processes used in our work [1–45]. They are characterized by the gross reaction, end products, temperature range in the reactor, particle sizes, specific surfaces of the powders and fields of applications. The plasmachemical processes used in the experimental devices can be classified by the plasma media.

1. Noble gases (plasma destruction) – producing UFP manganese by thermal destruction of manganese oxide concentrate [3–5]; molybdenum by destruction of MoO_2 [3, 6–8]; iron by decomposition of iron oxides [3]; destruction of zircon to pigments SiO_2 and ZrO_2 [3].

2. Reducing media – producing UFP manganese [3–5], molybdenum [3, 6–8], zinc [3], iron [3] by reduction with H_2 or NH_3, CH_4, C_3H_8, C_4H_{10}.

3. Nitrogen – synthesis of UFP nitrides AlN [1, 3, 9, 44], Si_3N_4 [3, 10], Mg_3N_2 [1, 3, 45] in equilibrium electrical arc LTP [1, 3, 10, 11] or HF cold plasma [44, 45].

4. Oxidizing media – producing UFP SiO_2 by oxidation [1, 3, 4, 12–15] or hydrolysis [1, 3, 4, 12–15] of $SiCl_4$; iron oxide pigments by oxidation of $FeCl_2 \cdot nH_2O$, $FeSO_4 \cdot H_2O$, iron pyrite wastes [1, 3, 20–22]; γ-Al_2O_3 by oxidation of aluminium [1, 3, 23, 24]; CoO by oxidation of CoS [3]; catalysts for steam conversion of CH_4 – by oxidation of nickel and aluminium with promotors CaO and magnesium; catalysts for low temperature steam convertion of CO – by oxidation of copper, zinc, aluminium or copper, zinc, chromium [1, 3, 33, 34]; catalysts for NH_3 synthesis – by oxidation of iron with promoters K_2O, Al_2O_3, CaO and MgO [1, 3, 26–29, 31, 32, 35–43].

5. Reducing-oxidizing media – producing UFP SiO_2 by reduction of SiO_2 with carbon to SiO and consequently oxidizing to SiO_2 [18, 19]; reduction of deactivated nickel catalysts used for reforming natural gas and oxidizing nickel to NiO in the process of quenching; regeneration of deactivated catalysts used for low-temperature conversion of CO with H_2O and catalysts used for the synthesis of NH_3 in H_2 and oxidizing by quenching in O_2; synthesis of the catalysts mentioned in a reducing–oxidizing medium.

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TABLE I Plasmachemical processes developed for ultrafine powder (UFP) production

N	Basic Reaction	UFP	Temperature range, K	Particle size, nm	Specific surface, $m^2 g^{-1}$	Field of application	Reference
	I. Neutral medium–destruction						
1	$MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO \rightarrow Mn$	Mn	3500–4000	100	40–70	powder metallurgy,	3–5
2	$MoO_3 \rightarrow MoO_2 \rightarrow Mo$	Mo	4000–5000	100	up to 300	metallocramics,	3, 6–8
3	$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$	α-Fe, γ-Fe	2000–3000	100	up to 100	dyeing trade	3
4	$ZrSiO_4 = ZrO_2 + SiO_2$	$ZrO_2 + SiO_2$	4000–5000	500	up to 50		3
	II. Reduction medium–reduction						
5	$(MnO_2, Mn_2O_3, Mn_3O_4) + H_2 \rightarrow Mn + H_2O$	Mn (53%)	2500–4000	100	up to 80	powder metallurgy,	3–5
6	$MoS_2 + 2H = Mo + 2H_2S$	Mo (90–93%)	2500–4000	100	20–380	metalloceramics,	3, 6–8
7	$MoO_2 + 2H_2 = Mo + 2H_2O$	Mo (90–93%)	3000–4000	100	up to 300	chemical industry,	3
8	$CoO + H_2 = Co + H_2O$	Co (100%)	3000–4000	100	up to 160	microelectronics	3
9	$ZnO + H_2 = Zn + H_2O$	Zn (100%)	3000–4000	100	up to 160		3
10	$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O$	Fe (100%)	2000–3000	10–100	up to 160		–
	III. Nitrogen medium–nitrides production						
11	$2Al + N_2 = 2AlN$	AlN (100%)	3300–3800	50–70	60–100	chemical industry,	1, 3, 9, 10
12	$3Si + 2N_2 = Si_3N_4$	Si_3N_4 (97%)	3000–3500	10–60	up to 250	coating	3, 12
13	$3Mg + N_2 = Mg_3N_2$	Mg_3N_2 (73%)	2000–2500	10–60	up to 180		1, 3, 11
	IV. Oxidizing medium–oxidation						
14	$SiCl_4 + O_2 = SiO_2 + 2Cl_2$	SiO_2 (100%)	up to 10 000	100	60–200	chemical industry,	1, 3, 4, 14–17
15	$SiCl_4 + 2H_2O = SiO_2 + 4HCl$	SiO_2 (100%)	up to 11 000	100	90–400	pharmaceutics, powder	1, 3, 4, 14–17
16	$Fe \rightarrow FeO \rightarrow Fe_3O_4 \rightarrow Fe_2O_3$	Fe_2O_3, Fe_3O_4	1200–2200	10–50	90–150	metallurgy pigments,	1, 3, 22–24
17	$4Al + 3O_2 = 2Al_2O_3$	γ-Al_2O_3 (100%)	1200–7000	6–45	120–420	catalysts for conversion	1, 3, 25, 26
18	$CoS + 1,5O_2 = CoO + SO_2$	CoO (100%)	1000–3000	–	up to 60	of CH_4, CO, for ammonia	3
19	$(Ni, Al) + O_2 \rightarrow NiO + Al_2O_3 + NiAl_2O_4$	catalysts for steam conversion	2000–3000	10–30	up to 110	synthesis,	1, 3, 28–34
20	$(Cu, Zn, Al) + O_2 \rightarrow CuO(Cu_2O) + ZnO + Al_2O_3$	of CH_4; catalysists for steam	up to 5100	10–40	45–51	industrial cat.	1, 3, 35, 36
21	$3Fe + 2O_2 = Fe_3O_4$	conversion of CO; catalysts for	1100–3400	20–60	10–40		1, 3, 28–31
22	$4Fe + 3O_2 = 2Fe_2O_3$	ammonia synthesis	1100–3400	20–60	20–40		33, 34, 37–45
23	$2Fe + O_2 = 2FeO$		1500–3500	100	up to 40		
	V. Reduction–oxidizing medium						
24	$SiO_2 + C = SiO + CO_2$ (I)		5000–10 000	50–500	up to 150	microelectronics, food	20–21
25	$2SiO + O_2 = 2SiO_2$ (II)	SiO_2 (100%)	10000–300			processing industry,	
26	$NiO + H_2 = Ni + H_2O$ (I)	catalysts for steam conversion	100–4000	100	up to 40	synthesis and regeneration	–
27	$2Ni + O_2 = 2NiO$ (II)	of CH_4	1000–4000			catalysts for steam	
28	$(CuO, ZnO, Al_2O_3) + H_2 \rightarrow (Cu, Zn, Al) + H_2O$ (I)	catalysts for lower temperature	4000–300	100	up to 50	conversion of CH_4, CO,	–
29	$(Cu, Zn, Al) + O_2 \rightarrow CuO(Cu_2O) + ZnO + Al_2O_3$ (II)	steam conversion of CO	1000–4000			for ammonia synthesis etc.	
30	$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O$ (I)	catalysis for ammonia	4000–300	10–30			–
31	$3Fe + 2O_2 = Fe_3O_4$	synthesis					

In all these cases either the energy input is lower because intermediate compounds with lower heat of evaporation appear, or oxides with specific properties are obtained after the reduction of the compounds to elements – catalysts of high activity (Table I, Reactions 26 to 31).

The production of UFP in plasmachemical installations passes through the following stages.

1. Introduction and mixing of reagents with plasma flow.
2. Heating, melting and evaporation of the solid phase. Stages 1 and 2 fix the time the reagents remain in the plasmachemical reactor. In order to reduce this time, the plasma flow is subjected to turbulence and heated to a high enthalpy content. The powdered reagents consist of very small ($< 50\,\mu$m) particles. The evaporation of the solid phase has a limiting effect [9].
3. Chemical reactions. Their realization in a gas phase ensures the high purity of the final product. The interaction between the gas and the reagents and the presence of not fully evaporated particles leads a change in the composition of the superficial surface layer only due to the low internal diffusion velocity. In some cases the evaporation of particles is incomplete (Table I, Reactions 11, 17).
4. Interaction between the chemically reacting plasma flow and cooling reagents (quenching) results in fixing the chemical composition of the desired product, production of a condensed phase with high dispersity, and, in some cases (Table I, Reactions 25, 27, 29, 31), additional incomplete chemical interactions. After a suitable rapid cooling of the reacting mixture, i.e. at a definite quench velocity $\mathrm{d}T/\mathrm{d}\tau = 10^4$ to $10^6\,\mathrm{K\,sec^{-1}}$, the product is obtained in the desired highly dispersed form. These considerations show the necessity of modelling the processes of condensation of the particles [40].
5. Filtering of UFP. Generally cyclons, mechanical filters, electrofilters are used.

Plasmachemically obtained highly dispersed metal powders are characterized by their high chemical activity, which is manifested as pyrofority [3–8]. As a result of investigations, in some particular cases a passivator may be recommended for ultradispersed manganese (N_2) [5], molybdenum (CO) [6, 7], iron (N_2 with 0.5% O_2).

According to the conditions of the process (temperature and concentration of reagents, conditions of condensation, etc.) the desired product can be obtained as epitaxial films, fibre crystals, polycrystals, amorphous or ultradispersed powder. In order to obtain ultradispersed particles certain conditions must be met with a high velocity of crystallization centre formation and a low velocity of crystal growth.

The UFP production mechanism under conditions of LTP is as follows. As a result of a chemical reaction and in accordance with the system's thermodynamics, condensation takes place. These nuclei initially formed may grow to small droplets, independently or through coagulation until, at a certain moment, quenching begins.

By changing the conditions of temperature and the reagents' residence time in the flow, the process of crystallization is controlled to different degrees, and different crystal modifications of the same plasmachemically synthesized powder are obtained (Table I, Reactions 3, 17).

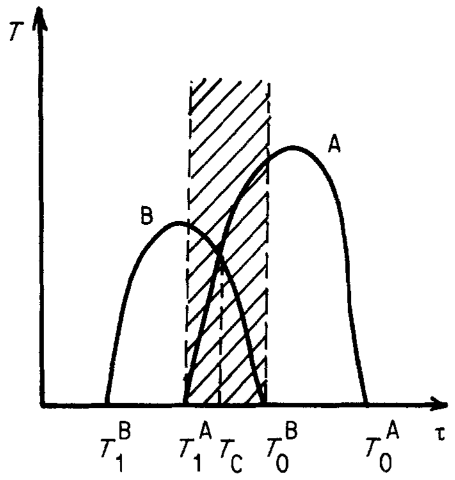

Figure 1 Relative contents of phases A and B produced with temperature. T_1^A, threshold of formation of A; T_1^B, threshold of formation of B; T_0^A, A is not formed; T_0^B, B is not formed; T_c, both phases A and B are formed.

Let us consider a system (Fig. 1) where crystallization yields a high-temperature modification A and a low-temperature modification B. The crystallization process begins at a temperature T_0 characterized by the bond energy of the crystal lattice and ends at a temperature T_1, when liquid particles can no longer migrate to the vacant places of the crystal lattice. This mechanism has been considered in some detail in cases of plasmachemical synthesis of α-Si_3N_4 and of β-Si_3N_4 from silicon and nitrogen gas under the conditions of arc LTP (Table I, Reaction 12 [10]). At the first stage of crystallization when $T > T_c$, the high-temperature modification A is formed. When $T < T_c$, the phase B predominantly condenses. In the temperature range T_1^A–T_0^B, both phases crystallize. When temperature falls, the rate of crystallization becomes less than the rate of condensation, as the process of condensation accelerates monotonically with the fall of temperature, while the process of crystallization first accelerates and then slows down. Quenching fixes the product mainly in A phase. This is in accordance with our experimental data [3].

4. Conclusion

Future investigations should aim at solving the following problems: (1) designing plasmachemical installations which should ensure complete evaporation of ingredients; (2) study of the specific processes of condensation and crystallization of ultradispersed phase in simultaneous chemical reactions under highly unbalanced conditions (quenching).

References

1. G. VISSOKOV, "Prilozhna plasmohimia. Prilozhenie na niskotemperaturnata plasma v neorganitchnata himitchna tehnologija", Pt 1 (Technika, Sofia, 1984).
2. G. VISSOKOV and N. VIDENOV, *Himija i industrija* **54** (1982) 181.
3. G. VISSOKOV, "Prilozhna plasmohimia. Prilozhenie na nisko-temperaturnata plasma v organitchnata himitchna

tehnologya i metalurgijata", Pt 2 (Technika, Sofia, 1987).

4. G. VISSOKOV, N. VIDENOV and N. GERASIMOV, *Godichnik na VHTI-Sofia* **25** (1978) 52.
5. G. VISSOKOV, N. GERASIMOV and D. OLIVER, *Himija i industrija* **52** (1980) 408.
6. G. VISSOKOV and N. VIDENOV, *ibid.* **50** (1978) 389.
7. *Idem*, "Sb. Dokladi ot simposiuma – Fizikata v himitcheskata promichlenost" (MNP, Sofia, 1978) p. 159.
8. *Idem*, *Godichnik na VHTI - Sofia* **25** (1978) 49.
9. G. VISSOKOV and L. BRAKALOV, *J. Mater. Sci.* **18** (1983) 2011.
10. G. VISSOKOV, *Himija i industrija* **58** (1986) 110.
11. *Idem*, "Sb. Parva Natzionalna Konferenzija po himija", Vol. 1 (MNP, Sofia, 1985) p. 208.
12. N. VIDENOV, G. VISSOKOV, N. GERASIMOV, B. STEFANOV and H. KRASTEV, *Himija i industrija* **47** (1975) 243.
13. Bulgarian Patent no. 20888 (1974).
14. N. VIDENOV, G. VISSOKOV, N. GERASIMOV and B. STEFANOV, "Arbeitstagung Physik und Technik des Plasmas" (Physikalische gesellschaft der DDR, Karl-Marx-Stadt, 1974) p. 461.
15. *Idem*, "Sb. Dokladi ot simposiuma – Fisikata v himitcheskata promichlenost" (MNP, Sofia, 1978) p. 150.
16. M. NEDEV and G. VISSOKOV, *Kozharska i obuvna promichlenost* **27** (1976) 26.
17. *Idem*, "Sb. III Nautchno tehnitcheska konferenzija. Novi nasoki v proisvodstvoto na pnevmatitchni gumi" (NTS Vidin, 1975) p. 76.
18. E. BALABANOVA, G. VISSOKOV, A. VRANCHEV, R. ENIKOV and D. OLIVER, *Himija i industrija* **58** (1986) 72.
19. D. OLIVER, G. VISSOKOV, E. BALABANOVA, A. VRANCHEV, R. ENIKOV, K. PETKOV, G. HRISTOV and D. GABROVSKI, "Sb. Parva Natzionalna Konferenzija po himija", Vol. 1 (MNP, Sofia, 1985) p. 234.
20. N. VIDENOV, G. VISSOKOV and L. EREMIEV, *Himija i industrija* **48** (1976) 441.
21. *Idem*, *Express informazija, Himija i tehnologija neorganitcheskih vechtestv* **21** (1977) 6.
22. N. VIDENOV and G. VISSOKOV, "Sb. Dokladi ot simposiuma – Fisikata v himicheskata promishlenost" (MNP, Sofia, 1978) p. 155.
23. G. VISSOKOV, L. BRAKALOV and K. MANOLOVA, *J. Mater. Sci.* **16** (1981) 1716.
24. Bulgarian Patent no. 30383 (1980).
25. G. VISSOKOV, "Sb. Nauchna Konferenzija posvetena na 1300 godini ot sazdavaneto na Balgarskata darzhava", Vol. 1. (MNP, Sofia, 1981) p. 133.
26. *Idem*, *Isvestija po himii BAN* **16** (1983) 114.
27. *Idem*, *ibid.* **16** (1983) 275.
28. *Idem*, Deposit in the Central Technical Library Sofia no. 2792 (1983).
29. *Idem*, *Himija i industrija* **55** (1983) 164.
30. *Idem*, *Godichnik na VHTI – Sofia* **29** (1984) 181.
31. Bulgarian Patent no. 35353 (1982).
32. Bulgarian Patent no. 35481 (1983).
33. G. VISSOKOV and O. JANKOV, "Sb. TNTM 82, Himija, himichna tehnologija i metalurgija. Dokladi ot nauchni sesii i simposiumi" (MNP, Sofia, 1982) p. 329.
34. *Idem*, "Sb. Geterogennii kataliz. Trudi V Mezhdunarodnogo simpoziuma", Vol. 2 (BAN, Sofia, 1983) p. 219.
35. G. VISSOKOV and M. DIMITROV, "Sb. Nauchna Konferenzija posvetena na 1300 godini ot sazdavaneto na Balgarskata darzhava", Vol. 1 (MNP, Sofia, 1981) p. 171.
36. G. VISSOKOV and G. GEORGIEV, *Godichnik na VHTI-Sofia* **29** (1984) 186.
37. G. VISSOKOV and P. PIRGOV, "Sb. TNTM 83, Himija, himichna tehnologija i metalurgija. Dokladi ot nauchni sesii i simposiumi" (MNP, Sofia, 1983) p. 373.
38. G. VISSOKOV, L. JONCHEV and P. PIRGOV, "Sb. Republikanski mladezhki nauchno tehnicheski simposium – Novi metodi i tehnologii v himicheskata promichlenost", Vol. 3 (KNTP, Sofia, 1983) 22.
39. G. VISSOKOV, L. BRAKALOV and P. PIRGOV, "Sb. 15 Nauchna sesija na TNTM, Sb. Dokaldi", Vol. 2 (MNP, Sofia, 1984) 417.
40. G. VISSOKOV and P. PIRGOV, "Sb. TNTM 85, Himija, himichna tehnologija i metalurgija, Dokladi ot nauchni sesii", Vol. 2 (MNP, Sofia, 1985) 433.
41. T. PEEV and G. VISSOKOV, "Sb. Parva Natzionalna Konferenzija po himija", Vol. 1 (MNP, Sofia, 1985) 208.
42. T. PEEV, G. VISSOKOV, I. CZAKÓ-NAGY and A. VÉRTES, *J. Appl. Catal.* **19** (1985) 301.
43. G. VISSOKÓV, T. PEEV, I. CZAKÓ-NAGY and A. VÉRTES, *ibid.* **27** (1986) 257.
44. G. VISSOKOV, K. MANOLOVA and L. BRAKALOV, "Sb. Nauchna Konferenzija posvetena na 1300 godini ot sazdavaneto na Balgarskata darzhava", Vol. 1 (MNP, Sofia, 1981) p. 219.
45. G. VISSOKOV, L. BRAKALOV and K. MANOLOVA, *Godichnik na VHTI-Sofia* **29** (1984) 190.

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