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Preparation of ultradispersed magnesium nitride by the electric-arc low-temperature plasma technique

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The conditions are investigated for the preparation of ultradispersed magnesium nitride (UDMN) from elemental magnesium and nitrogen by the electric-arc low-temperature plasma (LTP) technique. Thermodynamic calculations are carried out with the objective of finding the values of the equilibrium constant for the synthesis reaction of magnesium nitride from its elements in the temperature range 298–1800 K as a function of the aggregation state of the components. By means of a "cold" wall (CW) plasma-chemical reactor (PCR), ultradispersed product (UDP) is synthesized with a specific surface of 33 $m^2 g^{-1}$ containing up to 56% of Mg_3N_2; the use of a "warm" wall (WW) PCR allows the preparation of UDP with a Mg_3N_2 content of up to 73% and a specific surface reaching 184 $m^2 g^{-1}$. The dominant role of the radial temperature gradient in the PCR in the synthesis of UDMN with maximal degree of nitride formation and maximal specific surface values is experimentally demonstrated. The UDMN exhibits a high chemical activity; heat-treatment at 900 K in an inert atmosphere decreases substantially its chemical affinity to water vapour and oxygen in the air.

1. Introduction

In the plasma-chemical synthesis of nitrides, the raw materials are metals and metallic compounds (oxides, chlorides, sulphates, nitrates, etc.) which react with the nitrogen when nitrogen or ammonia are used as a plasma-forming gas. Since under the temperature conditions of a low-temperature plasma (LTP), the nitrogen is thermally dissociated and partly ionized, it can interact with different elements. Nitride preparation from metals can be implemented either by feeding the dispersed metal in a nitrogen plasma jet [1], or via the interaction of a nitrogen plasma with molten metal [2–5]. When oxygen containing compounds are used as raw materials, it is necessary to preform the oxides as briquets or expendable electrodes and to work with the respective amount of carbon [6–10]. All techniques listed above allow the preparation of stoichiometric ultradispersed nitrides. The purity of the nitrides obtained depends primarily on the content of impurities in the initial materials; only in the synthesis in electric-arc equipment can additional impurities from the electrode erosion make their way into the final product.

Magnesium valence electrons have an s^2-configuration; which tends to be transformed into an *sp*-configuration via *s*–*p* transitions; due to the higher quantum number of the *sp*-electrons this possibility is implemented to a lesser degree than in beryllium. Comparing the beryllium to the magnesium nitride, one has to assume that the *s*–*p* transitions in magnesium are suppressed so that the probability increases for the magnesium to release *s*-electrons and form s^2p^6 states with nitrogen. Because of the lower stability of the neon s^2p^6-configuration compared with the helium s^2-configuration, magnesium nitride is chemically less stable and decomposes more easily when heated.

Magnesium nitride is a friable yellow–orange powder strongly fluorescing under ultraviolet irradiation. It has cubic face-centered lattice with the *a* parameter in the interval 0.9930–0.9974 nm, depending on the reference source [11]. Magnesium nitride exists in three allotropic modifications with temperatures of transformations $\alpha \rightarrow \beta$ 823 K, and $\beta \rightarrow \gamma$ 1061 K. It is stable in a dry atmosphere; in a humid atmosphere it decomposes with the release of ammonia:

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3. \quad (1)$$

This is why it can only be preserved in vacuum-tight vessels. It is usually produced by the nitriding of magnesium powder at temperatures in the 1050–1100 K range.

In the literature, data on plasma-chemical magnesium nitride synthesis is scarce [12–15], with no data available at all about the preparation of UDMN under the conditions of an electric-arc low-temperature plasma. Bearing in mind the fact that in the literature there are no data on the thermodynamics of the reaction

$$3Mg + N_2 = Mg_3N_2 + 460\,kJ\,mol^{-1}, \quad (2)$$

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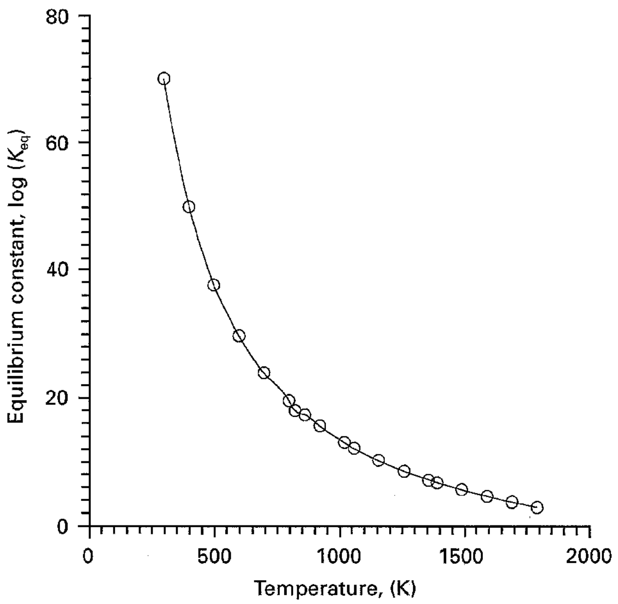

Figure 1 Temperature dependence of the equilibrium constant (log K_{eq}) for reaction (2).

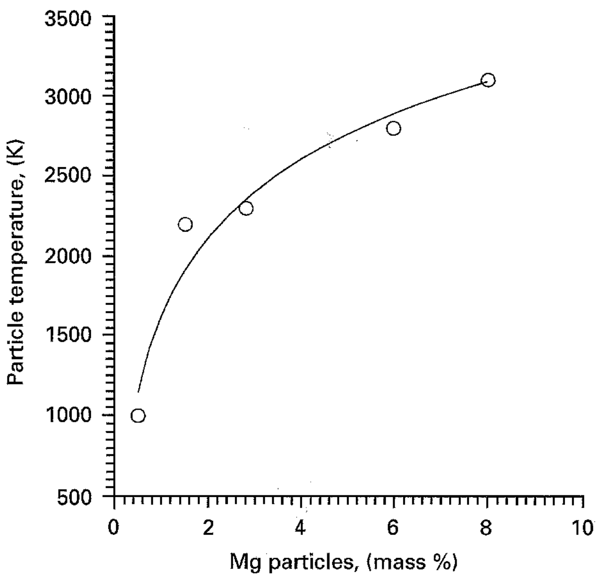

Figure 2 Variation of the magnesium particles temperature (T_p) as a function of their mass-concentration (C) at a plasma temperature of 2900 K.

we carried out detailed thermodynamic calculations in the temperature range 298–1800 K accounting for the aggregation states of the components of reaction (2):

$$3Mg_{(s)} + N_{2(g)} = \alpha Mg_3N_{2(s)} \quad \text{from 298–823 K} \tag{3}$$

$$3Mg_{(s)} + N_{2(g)} = \beta Mg_3N_{2(s)} \quad \text{from 823–923 K} \tag{4}$$

$$3Mg_{(l)} + N_{2(g)} = \beta Mg_3N_{2(s)} \quad \text{from 923–1061 K} \tag{5}$$

$$3Mg_{(l)} + N_{2(g)} = \gamma Mg_3N_{2(s)} \quad \text{from 1061–1393 K} \tag{6}$$

$$3Mg_{(g)} + N_{2(g)} = \gamma Mg_3N_{2(s)} \quad \text{from 1393–1800 K} \tag{7}$$

Above 1800 K magnesium nitride decomposes. Fig. 1 presents the temperature dependence of log K_{eq} for the reaction of magnesium nitriding. One of the basic parameters influencing the electrical conductivity and the emissivity of the high-temperature gas jet is the temperature of the particles. This is determined by the conditions of heat-transfer among the particles in the jet, as well as by the reaction mechanism with the gas-phase components. This is why the dependencies obtained for the particle-temperature (T_p) variation as a function of the dispersed magnesium mass-concentration in the jet are of particular interest. As Fig. 2 demonstrates, the value of T_p increases with the increase of the magnesium-particle concentration to the extent that at concentrations above 6.2%, the temperature of the particles exceeds that of the plasma jet. The significant rise in the temperature of the magnesium particles following the increase of their concentration in the jet is explained by the improved thermal conditions in the presence of chemical interaction between magnesium and nitrogen. Since reaction (2) is exothermic, it is obvious that the heat released causes overheating of the particles and raises their temperature. In addition, the temperature of the plasma jet, and especially its enthalpy, are fully sufficient for magnesium to evaporate and magnesium nitride to be formed in a condensed phase [16]. These studies are of more methodological, rather than technological interest.

A research team at the Research Institute of Temple University in the United States has prepared magnesium nitride by means of a plasma-chemical technique, namely, blowing of magnesium powder in a nitrogen plasma jet using equipment with power from 12–15 kW [14]. Due to magnesium nitride's instability, its purification is a complicated task. The degree of conversion has reached 40%.

As we mentioned earlier, little data is available on the plasma-chemical preparation of magnesium nitride, while there are no reports at all on plasma-chemical formation of UDMN. We, therefore, decided to carry out investigations on the plasma-chemical preparation of UDMN in electric-arc LTP and to study in detail its properties.

2. Experimental procedure

Our experiments on direct synthesis of magnesium nitride following reaction (2) are performed in the conditions of electric-arc LTP using the apparatus whose schematic diagram is shown in Fig. 3. The plasma-chemical equipment comprises a d.c. electric-arc plasmatron, operating at plasma-forming gas (argon) flow-rates of up to 3000 l h^{-1}, a plasma-chemical reactor (PCR) with "cold" or "warm" walls, a quenching device, a powder-trapping chamber, a vibration powder-feeding device, and cooling-water and reagents-feeding systems. The power consumed by the plasmatron is regulated by varying the supply current from 100–400 A. The average temperatures of the plasma and of the PCR are measured calorimetrically with an accuracy of 5%. Quenching is achieved by the cold walls of the powder-trapping chamber and/or by blowing jets of cold nitrogen of technical purity.

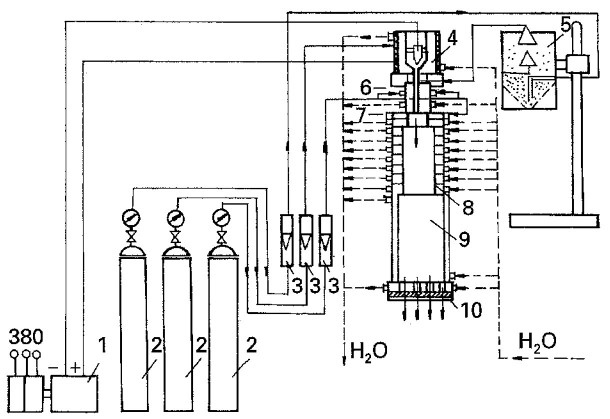

Figure 3 Schematic diagram of the plasma-chemical apparatus for UDMN preparation: 1 – D.C. power-supply; 2 – bottles with plasma-forming, powder-carrying and quenching gases; 3 – flow-meters; 4 – electric-arc plasmatron ($D_C = 5$ mm); 5 – vibration powder-feeding device; 6 – CW PCR; 7 – gas quenching of the reaction products; 8 – quenching device; 9 – powder-trapping chamber; 10 – filter.

Micron-sized elemental magnesium (grain-size of 80–100 μm, specific surface of 2.2 $m^2 g^{-1}$) is fed into the PCR by the powder-feeding device with nitrogen (purity of 99.999%) as a powder-carrying gas. The product obtained is characterized by its specific surface (determined using the Kljachko–Gurvich technique [17]), the chemical content (degree of nitride-formation B_N), and the content of bound nitrogen (using Keldal's technique [18]). In addition X-ray diffraction and electron-microscope analyses are also employed. The degree of nitride-formation is determined according to the formula

$$B_N = \frac{b}{22.72} \times 100\%, \tag{8}$$

where b is the nitrogen content in the product in mass %, and 27.72 is the nitrogen content in Mg_3N_2 in mass %.

3. Results and discussion

Some of the experimental results are summarized in Tables I–III. Table I presents some technological parameters of the process of synthesizing Mg_3N_2 in a PCR with "cold" walls (CW). The CW PCR is a water-cooled metal cylinder with a diameter of 10 mm and length of 100 mm. A general relationship that can be derived by following the $S = f(T)$ dependence is that as the plasma-jet temperature is raised, the specific surface of the reaction product increases. This is due to the fact that an increase of the temperature in the PCR results in an increase of the fraction of evaporated magnesium; thus, the process takes place in the gaseous phase, while after quenching by the cold walls of the powder-trapping chamber, magnesium nitride is formed as an ultradispersed condensed phase.

The dependence $B_N = f(T)$ has a maximum; the highest degree of nitride formation ($B_{N\max} = 56.25\%$) is observed in the cases when nitrogen is used as a powder-carrying gas in the plasma-chemical synthesis (PCS) (Table I). Since in these experiments quenching is achieved at the cold walls of the quenching device – a technique that does not guarantee a sufficient quenching rate – conditions are created for magnesium nitride decomposition at temperatures above 1800 K, i.e. the degree of nitride formation is reduced. With all other conditions kept the same, the degree of nitride formation is lower if nitrogen is used as a component of the plasma-forming gas. Most probably, the presence of ionized nitrogen in the plasma-forming gas does not result in an intensification of the process, while the inefficient quenching still plays a role. Based on the experimental results (Table I), one should recommend that Ar be used as a plasma-forming gas in the plasma-chemical synthesis of UDMN in electric-arc LTP, with the nitrogen being introduced as a powder-carrying gas (Tables II and III). Under such conditions, the watt-ampere characteristics of the plasmatron (Fig. 4), as well as the dependence of the average plasma enthalpy on the power consumed by the plasmatron (Fig. 5), exhibit good stability.

The data in Tables II and III differ in that in the first case the experiments are performed in a "warm" wall (WW) PCR made of heat-resistant ceramics and calorimetric measurements of the temperature are implemented, i.e. it is placed in a metal water-cooled

TABLE I Some technological parameters of the Mg_3N_2 synthesis process in a PCR with a CW and some properties of the product[a]

No.	Current (A)	Potential difference (V)	Power (kW)	Plasma-forming gas		Plasma temperature (K)	Plasma enthalpy (kJ kg^{-1})	N_2 in product (mass %)	Degree of nitride formation (%)	Specific surface ($m^2 g^{-1}$)
				Ar (l h^{-1})	N_2					
1	150	36	5.4	2500	–	5200	2700	4.66	16.78	–
2	200	35.5	7.1	2500	–	6650	3400	6.35	22.87	–
3	300	36	10.8	2500	–	9400	4850	15.61	56.25	–
4	350	34	11.9	2500	–	10700	5550	1.85	6.67	–
5	150	42	6.3	2500	100	5400	3050	0.44	1.58	3
6	200	43	8.6	2500	100	6750	3900	3.72	13.41	10
7	300	43.5	13.05	2500	100	9900	5850	2.58	9.30	22
8	350	43	15.05	2500	100	11700	7000	1.34	4.83	33
9	150	47	7.05	2500	200	4300	2650	0.22	0.8	6
10	200	49	9.8	2500	200	7400	4700	0.54	1.94	24

[a] Flow rate of the plasma-carrying gas (N_2) is 400 l h^{-1}.

TABLE II Some technological parameters of the Mg_3N_2 synthesis process in a PCR with a WW and some properties of the product[a]

No.	Current (A)	Potential difference (V)	Power (kW)	Reactor temperature (K)	Reactor enthalpy (kJ kg^{-1})	N_2 in product (mass%)	Degree of nitride formation (%)	Specific surface (m^2 g^{-1})
1	100	26	0.88	1800	1000	8.3	29.97	77
2	150	25.5	1.38	2800	1600	10.5	37.88	123
3	200	25.5	1.75	3500	2050	12.2	44.01	138
4	250	25	2.26	4500	2600	16.3	58.8	149
5	300	25	2.67	5300	3100	18.8	67.82	165
6	350	25	2.97	5900	3450	15.8	56.99	166
7	400	25	3.33	6600	3850	15.2	54.83	159

[a] Flow rate of the plasma-forming gas (Ar) is 1700 l h^{-1}.

TABLE III Some technological parameters of the Mg_3N_2 synthesis process without forced cooling in the PCR with a WW and some properties of the product[a]

No.	Current (A)	Potential difference (V)	Power (kW)	Plasma temperature (K)	Plasma enthalpy (kJ kg^{-1})	N_2 in product (mass%)	Degree of nitride formation (%)	Specific surface (m^2 g^{-1})
1	100	26	1.20	2900	1500	5.5	19.87	118
2	200	29.5	1.59	3900	2000	7.2	25.97	136
3	250	29	2.17	5300	2750	12.2	44.01	173
4	300	29	3.15	7600	4000	20.2	72.87	184
5	350	28.5	4.40	10700	5550	17.2	62.05	170
6	400	28	5.27	12800	6650	16.6	59.88	155

[a] Flow rate of the plasma-forming gas (Ar) is 1700 l h^{-1} and the plasma-carrying gas (N_2) is 210 l h^{-1}.

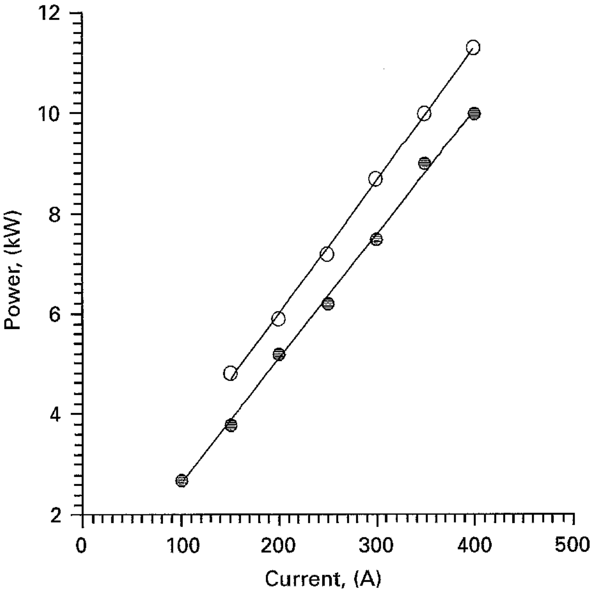

Figure 4 W-A (watt-ampere) characteristics of the electric-arc plasmatron for UDMN synthesis at plasma-forming gas (Ar) flow-rate of 1700 l h^{-1}, powder-carrying gas (N_2) flow-rate: ●–210 l h^{-1}, ○–300 l h^{-1}.

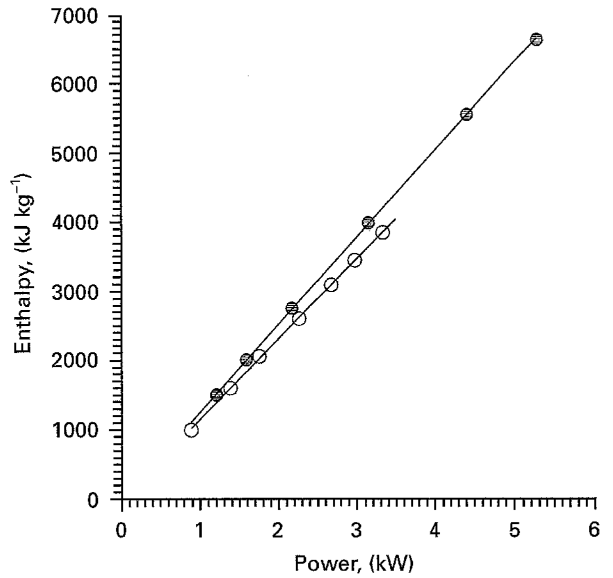

Figure 5 Dependence of the average plasma-jet enthalpy (*H*) on the electrical power supplied (*P*) at plasma-forming gas (Ar) flow-rate of 1700 l h^{-1}, powder-carrying gas (N_2) flow-rate: ●–210 l h^{-1}, ○–300 l h^{-1}.

housing (the experimental data are shown in Table II), whilst in the second case the same heat-resistant ceramic PCR is not cooled (the results are shown in Table III). In the latter case, the radial temperature gradients in the PCR are reduced even further which leads to the complete evaporation of the magnesium particles in the PCR. Under these conditions, the degree of nitride formation is several times higher compared with the case of a CW reactor (Table I).

On the other hand, if one compares the degree of nitride formation in a WW PCR (Fig. 6) with that in samples prepared at the same technological parameters in a WW PCR without calorimetric measurement (i.e. without forced cooling) (Fig. 7), one can see that in the former case $B_{\mathrm{Nmax}} = 67.82\%$, whilst in the latter $B_{\mathrm{Nmax}} = 72.87\%$. This experimental fact gives us reason to emphasize once again that one of the technological factors contributing to achieving a maximal

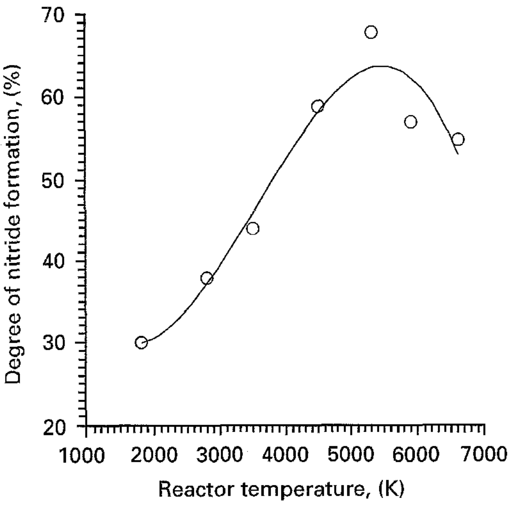

Figure 6 Dependence of the degree of magnesium nitride formation (B_N) on the average temperature of a WW PCR (T) at plasma-forming gas (Ar) flow-rate of $1700 \, l \, h^{-1}$ and powder-carrying gas (N_2) flow-rate of $210 \, l \, h^{-1}$.

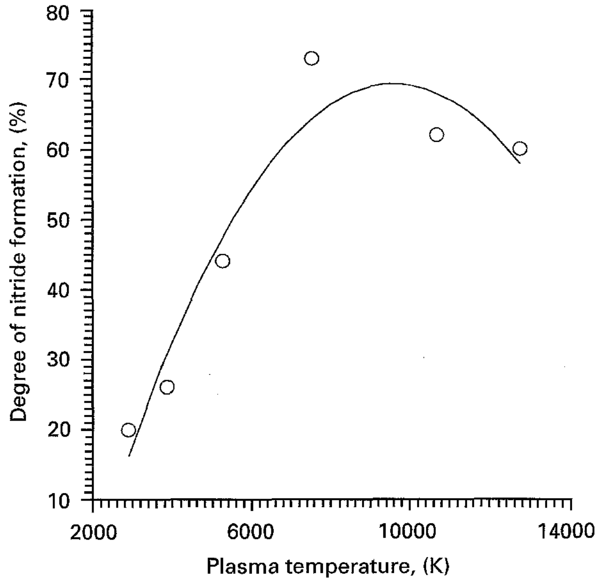

Figure 7 Dependence of the degree of magnesium nitride formation (B_N) on the average temperature of the plasma jet (T) in a WW PCR without calorimetric measurements (no forced water-cooling) at plasma-forming gas (Ar) flow-rate of $1700 \, l \, h^{-1}$ and powder-carrying gas (N_2) flow-rate of $210 \, l \, h^{-1}$.

degree of nitride formation is ensuring conditions for a maximum reduction of the radial temperature gradients in the PCR. This statement also holds true to the same extent in what concerns preparation of UDMN with maximum dispersity or, respectively, with maximum specific surface (Fig. 8).

The UDMN possesses high chemical activity thus it must be kept in an inert dry atmosphere to prevent its hydrolysation by water vapour following reaction (1), or its oxidation by oxygen. In addition to diffraction peaks of magnesium nitride and of unreacted magnesium, the X-ray patterns of the samples (Fig. 9) also exhibit reflections that correspond to magnesium hydroxide and magnesium oxide. It should be noted that these compounds are impossible to obtain during the plasma-chemical process (PCP). Obviously, magnesium nitride is hydrolyzed according to reaction (1) after coming in contact with air; as a consequence, ammonia is released and the degree of nitride formation is diminished. Gradual heating of the magnesium nitride up to 900 K followed by slow cooling down to room temperature reduces to a large extent its chemical affinity to water vapour. Irrespective of this, PCS UDMN must be stored in an inert gas atmosphere well purified of oxygen and water. (Such an inert gas could be argon, helium, or even nitrogen.)

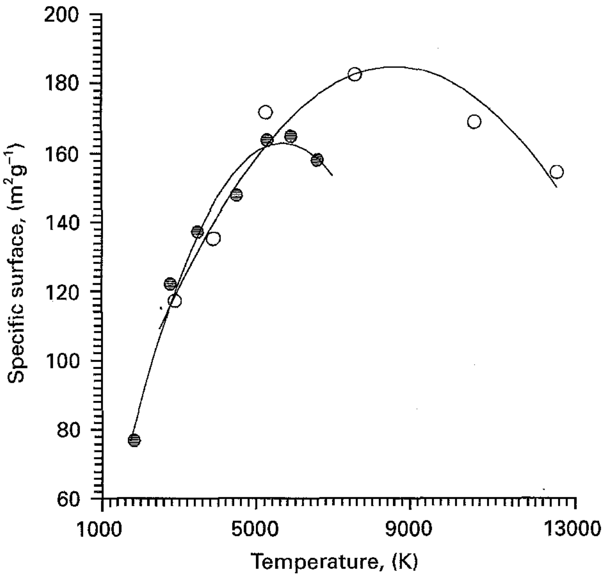

Figure 8 Dependence of the UDMN specific surface (S) on the average temperature at plasma-forming gas (Ar) flow-rate of $1700 \, l \, h^{-1}$ and powder-carrying gas (N_2) flow-rate of $210 \, l \, h^{-1}$ for: ● – WW PCR with calorimetric measurements; ○ – WW PCR without calorimetric measurements (no forced water-cooling).

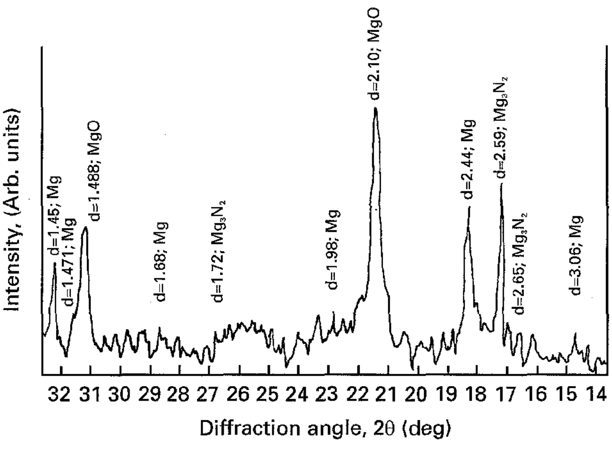

Figure 9 X-ray pattern of a UDMN sample (Table III, sample No. 4) prepared in a WW PCR without calorimetric measurements (no forced water-cooling).

The electron-microscope photographs of PCS UDMN (Fig. 10) illustrate the high-degree of dispersity of the ultradispersed particles (UDP).

4. Conclusion

We present thermodynamic calculations of the equilibrium constant of the synthesis reaction of magnesium nitride from elemental magnesium and nitrogen

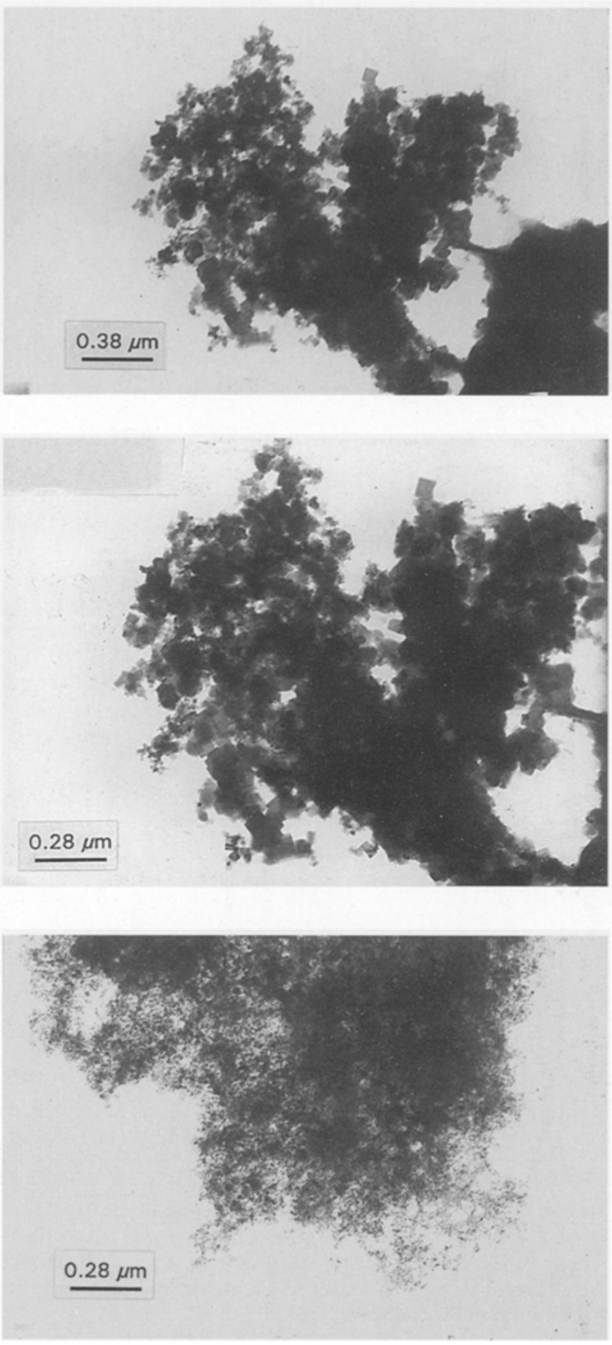

Figure 10 Electron-microscope photographs of plasma-chemically-synthesized UDMN: (a) sample No. 6, Table II, magnification 28 000, (b) sample No. 6, Table II, magnification 36 000, (c) sample No. 5, Table III, magnification 36 000.

within the temperature range 298–1800 K (above 1800 K Mg_3N_2 disintegrates) accounting for the aggregation state of the components. We show that, as a result of the exothermic behaviour of reaction (2), the particle temperature begins to exceed that of the plasma jet at a concentration of the magnesium particles in the plasma above 6.2%. This experimental fact is also probably the cause of the high degree of nitride formation (up to 73%). When using a CW PCR, we synthesized an ultradispersed product containing up to 56% Mg_3N_2 with a specific surface of up to 33 $m^2 g^{-1}$, while operating a WW PCR we obtained UDP with Mg_3N_2 content of up to 73% with specific surface value reaching 184 $m^2 g^{-1}$. We thus experimentally demonstrated the predominant influence of the radial temperature gradients in the PCR on the synthesis of UDMN with a maximal degree of nitride formation and maximal specific surface. The UDMN exhibits high chemical activity so that it must be stored in a dry atmosphere in order to prevent its hydrolysation by water vapour (reaction (1)) and its oxidation by oxygen. Slow annealing at 900 K diminishes considerably its chemical affinity to water vapour.

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