Mendeleev Commun., 2001, 11(4), 159–161

Chemical reactions between metals and active gases in the electric explosion of wires for the production of nanoparticles

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10.1070/MC2001v011n04ABEH001432

Thermodynamic and kinetic peculiarities of chemical reactions have been investigated for the electric explosion of metals in active gases.

When high-density current ($i = 10^6$–10^8 A cm^{-2}) is passed through a metal wire, an electric explosion of the wire occurs. This is a quick pulsed process characterised by unstable conditions and rapid changes in the thermodynamic parameters of the system.[1] The electric explosion of wires in inert atmospheres is used for preparing metal nanopowders. The nanopowders of chemical compounds can also be prepared using active gases.[2–7] Although the use of the electric explosion of wires is of practical interest for producing powders, the mechanisms of the process in chemically active gases have not been adequately studied. Only the mechanisms of chemical reactions in low-temperature plasmas were considered in the literature.[8,9] However, the reaction conditions in the electric explosion of wires are essentially different from ordinary plasma-chemical conditions.

We studied the chemical composition and properties of powders prepared by the electric explosion of aluminium and copper wires (0.37×10^{-3} and 0.38×10^{-3} m in diameter, respectively) in the atmospheres of pure gaseous O_2, N_2, NH_3 and CO_2 and in their mixtures with argon and measured the velocities of expansion of metal vapours. The electric explosion of wires was performed at input energies higher than the sublimation energies of the metals by a factor of 2.1–2.4 delivered in a time of 1.6×10^{-6} s. The powders were collected in special containers using a filter. The samples were stored and analysed in an inert atmosphere.

To examine the effect of thermodynamic conditions on the yields of the reactions, the experiments were performed at gas concentrations sufficient for 100% conversion of metals into their compounds.

The reaction

$$2Cu + CO_2 \longrightarrow Cu_2O + CO, \qquad (1)$$
$$\Delta H^0 = 110 \text{ kJ mol}^{-1},\ \Delta S^0 = 10 \text{ J mol}^{-1}\text{ K}^{-1}$$

was taken as an example of the electric explosion of wires with $\Delta H > 0$ and $\Delta S > 0$ at $P(CO_2) = 10^5$ Pa. The forward reaction is possible only at high temperatures. At the standard states of the reactants, the equilibrium temperature is $T_{\text{equil}} \approx 10^4$ K. It was determined by chemical analysis (titration with $K_2Cr_2O_7$) that the powder contained 10% Cu_2O (the balance copper). Thus, the effective temperature at least in a part of the reaction zone was $\geq 10^4$ K. Electron microscopy (JEM-100CX II microscope) showed that the number of faceted particles increased in comparison with the electric explosion in argon. However, the specific surface area remained almost unchanged (5–6 m^2 g^{-1}, the average number particle size was 115 nm).

As examples of the electric explosion processes with $\Delta H < 0$ and $\Delta S < 0$, the following reactions were studied:

$$2Al + N_2 \rightleftharpoons 2AlN; \qquad (2)$$
$$\Delta H^0 = -287.5 \text{ kJ mol}^{-1},\ \Delta S^0 = -104 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$2Al + {}^3\!/_2O_2 \rightleftharpoons Al_2O_3; \qquad (3)$$
$$\Delta H^0 = -1657 \text{ kJ mol}^{-1},\ \Delta S^0 = -302 \text{ J mol}^{-1}\text{ K}^{-1}$$

with equilibrium temperatures of 2760 and 5470 K, respectively.

Unlike reaction (1), these reactions go forward at $T < T_{\text{equil}}$; however, at $T > T_{\text{equil}}$, the compound decomposes and a part of the metal remains unoxidised under conditions of quick cooling. In general, the powders obtained consisted of faceted particles and their specific surface area was 1.5–3 times higher than that in the case of the electric explosion of wires in argon (23–48 m^2 g^{-1} and up to 18 m^2 g^{-1}, respectively). Grey powders were obtained in reaction (2), and they contained up to 5% Al. Evidently, this is due to the instability of AlN at $T > 2760$ K and a sufficiently high rate of 'congelation' of aluminium in a nitrogen atmosphere. In reaction (3), the reaction products are white and do not contain aluminium, as found by chemical analysis (volumetric analysis). Thus, either the electric explosion temperature does not reach 5470 K or the rate of product quenching is insufficiently high for the 'congelation' of aluminium in an oxygen-containing atmosphere.

The reaction with $\Delta H < 0$ and $\Delta S > 0$

$$Al + NH_3 \longrightarrow AlN + {}^3\!/_2H_2; \qquad (4)$$
$$\Delta H^0 = -241 \text{ kJ mol}^{-1},\ \Delta S^0 = 5 \text{ J mol}^{-1}\text{ K}^{-1}$$

is thermodynamically unidirectional. In the electric explosion of wires, it gives a greyish product in 100% yield, judging by the results of chemical analysis. Aluminium traces are responsible for this colour; evidently, this is also due to the instability of AlN at $T > 2760$ K. Thus, the electric explosion of wires can be used as a preparative method for reactions like (4) if the products are stable and for reactions like (2) and (3) if the products are stable and $T_{\text{equil}} > 5500$ K.

The yields of reactions (2), (3) and (4) were measured at variable concentrations of active gases in their mixtures with an inert gas and at variable total pressures of the gas mixtures. At a total pressure of 2×10^5 Pa, the yields of reaction (3) in Ar + O_2 and N_2 + O_2 gas mixtures were equal to 100% at O_2 concentrations of 20 and 4%, respectively. In reaction (4), 100% yield was achieved at 50% NH_3 in argon. Reaction (2) in pure nitrogen at 2×10^5 Pa afforded AlN in 65% yield (Figure 1, curve *3*), and the AlN yield approached 100% only at $P(N_2) = 1.5\times10^6$ Pa (as found by photocolorimetry using Nessler's reagent).

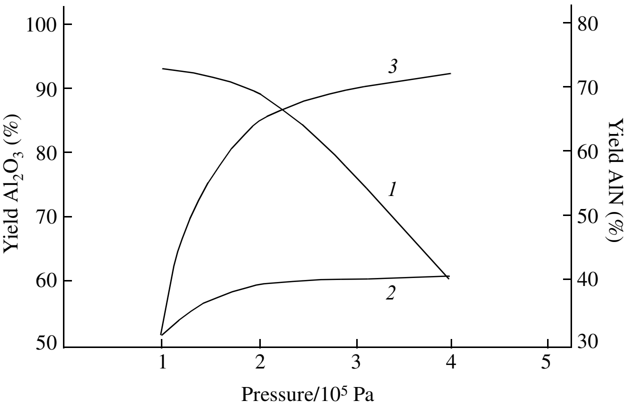

Figure 1 Yields of (*1*) Al_2O_3 ([O_2] = 12%) and (*2*) AlN [$P(N_2) = 10^5$ Pa] as functions of the pressure of gas mixtures and (*3*) yield of AlN as a function of N_2 pressure.

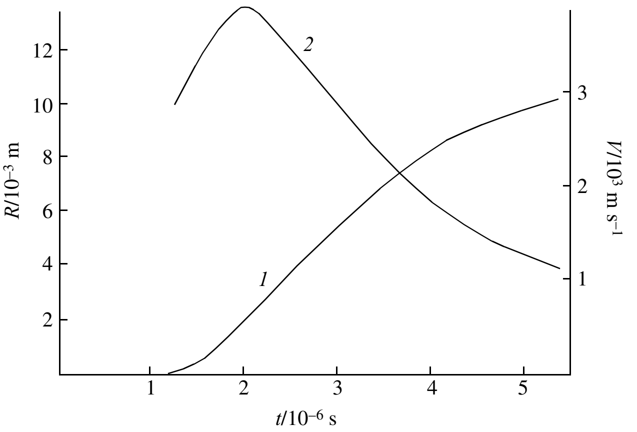

Figure 2 The time dependence of the (*1*) radius and (*2*) velocity of dispersion of the products of electric explosion of wires.

Figure 1 also demonstrates the yields of aluminium oxidation and nitridation (curves *1* and *2*, respectively) as functions of the inert gas pressure at a constant O_2 concentration (12%) and a constant partial pressure of N_2 (10^5 Pa). These plots are opposite to each other; *i.e.*, both catalysis and inhibition of the reactions by an inert gas (Ar) take place.

It is also of interest that nanopowders obtained in reactions (2)–(4), which contained the metal mixed with the oxide or the nitride remain active towards air (pyrophoric), water, acids, and alkalis. This fact suggests that no continuous oxide or nitride films are formed on the aluminium surface during the electric explosion in active gases.

Either a metal vapour or a vapour-droplet mixture may be the products of the electric explosion of wires. We assume that the explosion product is a metal vapour; that is, full evaporation of the conductor substance takes place during the explosion or immediately after it. Generally, the phase state of explosion products (a vapour or a vapour-droplet mixture) is not important, and this assumption allows us to simplify the consideration. We also suggest that a reaction between the metal and the ambient gas proceeds within a definite volume of a gas cylinder, which is smaller than the volume of the explosion chamber. The temperature of the cylinder is the same throughout the volume (it decreases with expansion), and the chemical reaction takes place on the mutual diffusion of explosion products into the gas atmosphere. Thus, the cylinder radius r_s is determined by the temperature at which the reaction stops, T_s. The limiting radii were calculated from the active gas concentration at which 100% conversion is achieved following the reaction stoichiometry: $r_s(O_2 + Ar) = 1.34\times10^{-2}$ m, $r_s(NH_3 + Ar) = 0.7\times10^{-2}$ m and $r_s(N_2) = 0.13\times10^{-2}$ m.

Because the process is essentially nonequilibrium, only apparent temperatures of the reaction ending can be considered. To evaluate these temperatures, we measured the velocity of expansion of explosion products by the velocity photoscanning method at a normal pressure of the gas atmosphere and the energy content $E = 2.1E_s$ (Figure 2), where E_s is the sublimation energy of the metal. It was found that the velocity initially increased ($V_{max} = 3.7\times10^3$ m s^{-1} at $t = 2.1\times10^{-6}$ s) and then decreased down to 10^3 m s^{-1} at 6.5×10^{-6} s.

We assume that the electric energy is consumed mainly for the evaporation of the metal and for the one-dimensional motion of the vapour. Then, during the expansion, the vapour mixes with the ambient gas and the energy of the one-dimensional motion is uniformly redistributed over all degrees of freedom. In the presence of an active gas, the metal vapour reacts with it. Two stoichiometrically equivalent patterns of the reaction are possible: (i) the expansion of the vapour cylinder, the mixing of the vapour with the ambient gas and the chemical reaction occur simultaneously; (ii) the expansion of vapour goes faster than the mixing; the vapour ‘piston’ compresses the ambient gas and the reaction proceeds in a thin cylindrical layer of the compressed mixture near to the explosion products–active gas contact surface.

For the mentioned above radius r_s, the measured velocities V_s of vapour expansion, in accordance with Figure 2, are as follows: $V_s(O_2) = 10^3$ m s^{-1}, $V_s(NH_3) = 2\times10^3$ m s^{-1} and $V_s(N_2) = 3.5\times10^3$ m s^{-1}. The effective temperatures of one-dimensional motion calculated for these velocities using the molecular-kinetic theory[10] are ~1320, ~5300 and ~16200 K, respectively, which, after division by the degree-of-freedom number of the relevant gases (C_v/R) and addition of the initial temperature (~300 K) become as follows: $T_s(O_2) \approx 560$ K, $T_s(NH_3) \approx 1400$ K and $T_s(N_2) \approx 3540$ K. For the vapour and gas reactions under the given conditions (reaction time of ~10^{-6}–10^{-5} s and cooling rate of ~10^8 K s^{-1}), these data can be considered as realistic.

This model fits well the data on the catalysis and inhibition of reactions in the electric explosion of wires. Thus, an increase in the pressure of the O_2 + Ar mixture at a constant concentration of O_2 decreases the reaction yield (Figure 1, curve *1*). In our opinion, this is caused by the reaction in a gas phase according to pattern (i), and an increase in the pressure diminished the expansion radius of the explosion products and the explosion products–active gas contact surface area. In the case of nitrogen, the cylinder radius is small, the density of products is high and the pressure in explosion products essentially exceeds the pressure of the gas atmosphere. Therefore, an increase in the ambient gas pressure does not result in any detectable limitation of the expansion velocity of explosion products. Probably, the formation of a chemical compound takes place according to pattern (ii) in a narrow cylindrical layer of the explosion products–ambient gas contact surface. An increase in the pressure results in an increase in the reacting gas concentration and an increase in the chemical reaction yield (Figure 1, curve *3*). The increase in the AlN yield with increasing *P*(Ar) at constant $P(N_2)$ (Figure 1, curve *2*) may be caused by the formation of long-living species Ar* (up to ~10^{-5} s),[11] which increase the size of the reacting gas cylinder at the expense of excitation transfer to N_2. Probably, similar reasons cause a relative decrease in the limiting concentration of O_2 in a mixture with N_2, as compared to an O_2 + Ar mixture. At high temperatures, N_2 reacts with aluminium vapour with formation of AlN particles, which are stable and, consequently, are oxidised in an even greater volume.

It should also be noted that an appreciable distinction exists between the maximum apparent temperatures evaluated by different methods and for different reactions: 2.3×10^3 K from the yield of reaction (2) and 3.7×10^3 K from the contact surface velocity. These discrepancies are associated with both inaccuracy in estimations (changes of ΔH^0 and ΔS^0 with temperature were not taken into account) and nonequilibrium processes. In particular, local energies of collisions, which correspond to $T_{max} \sim 1.6\times10^4$ K in our case, rather than average energies can be important for the activation of elementary reactions.

We are grateful to Mr. Frederick Tepper (Argonide Corp., Sanford, US) and Dr. David Ginly (NREL, Golden, US) for helpful discussions. This work was supported by the DOE IPP programme (subcontract no. AAX-0-29631-01).

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Received: 30th January 2001; Com. 01/1758