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REDUCTION OF ALUMINUM OXIDE IN A NONEQUILIBRIUM HYDROGEN PLASMA

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A new method is proposed and experimental investigations are carried out aimed at reducing aluminum oxide in a nonequilibrium hydrogen plasma of a combined glow discharge (CGD) at a pressure of 1315.8–13,158 Pa, a discharge current of $5 \cdot 10^{-2}$*–3 A, and a hydrogen flow rate of* 10^{-6}*–*10^{-4} *nm*^{3}*/sec. A high degree of conversion of the aluminum oxide (60%) with an energy consumption of 20 kW·h/kg of* Al_2O_3 *is attained. Reduction of metals from oxides and other compounds in a CGD nonequilibrium hydrogen plasma can be used for producing rare-earth and high-purity metals.*

The isolation of free aluminum in plasma reduction or dissociation of Al_2O_3 is a very difficult problem [1]. We can note three main problems that arise when this process is realized in a quasiequilibrium plasma: 1) the difficulty of introducing a substance into a high-temperature discharge zone; 2) insufficient duration of stay of the particles in this zone (10^{-3}–10^{-1} sec); 3) the release of reaction products and inhibition of reverse reactions. According to the literature data, the yield of the product obtained in this manner amounts to 30%; the aluminum is contaminated by lower oxides (AlO) [2, 3].

To solve this problem, a new method of introducing a substance in the solid phase into the plasma was proposed [4]; the essence of this method is as follows: cylindrical pellets 2 with a hole on the axis manufactured by the method of pressing from a powder of reduced-metal oxide are installed into tube 1 (of quartz or ceramics) between the hollow cathode 3 and anode 4 in the region of a positive discharge column. This configuration forms a combined glow discharge (Fig. 1) [5].

The processes in a capillary discharge at atmospheric pressure in the gas phase in plasmachemical reactions were investigated earlier in [6].

Experimental Procedure. The reduction of aluminum oxide (alumina)was studied on a setup (Fig. 2) that incorporated: the plasmachemical reactor with a combined glow discharge 1, the high-voltage power supply of the discharge 2, the system of gas preparation 3, the pumping system with a fore pump 4, the radio-frequency mass spectrometer 5, the spectrograph for recording atomic emission spectra in the visible range 6, the unit of electrophysical measurements with recording on digital voltmeters 7, and the personal computer 8. The high-voltage power supply ensured measuring the current in the range of $5 \cdot 10^{-2}$–3 A at a no-load voltage to 5 kV. Commercial hydrogen with a 98% purity was used as the reducing agent. The volumetric flow rate of the gas R_v was varied in the range of 10^{-6}–10^{-4} nm^3/sec at a working pressure P of 1315.8–13,158 Pa in the plasmatron. The pressure of the plasma-generating gas was measured with an oil gauge. The composition of the reaction products was recorded by an MX-7304 radio-frequency mass spectrometer with a volume sensitivity of 10^{-2}%. The limiting residual pressure in the vacuum system of the mass spectrometer was $2.6 \cdot 10^{-4}$ Pa. The plasma composition at the outlet from the capillary was checked by photographing the spectrum on the spectrograph whose operating range was 250–800 nm. The discharge current, the voltage, and the gas temperature outside the capillary were determined using the unit of electrophysical measurements [7] that incorporated a Chromel–Alumel thermocouple covered with a quartz cap 2.5 mm in diameter [6], a high-voltage voltage divider, and a calibrated ohmic shunt for measuring the current. The diameter of the Chromel–Alumel wire

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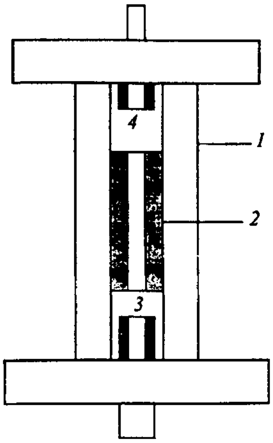


Fig. 1. Schematic of a plasmachemical reactor with a combined glow discharge.

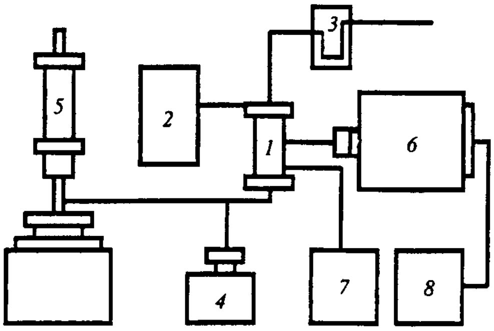
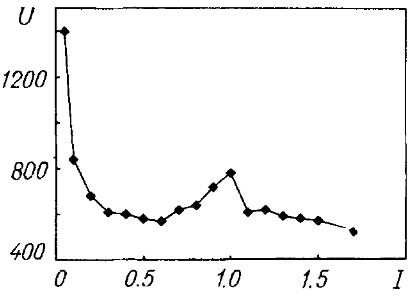


Fig. 2. Schematic of an experimental setup for investigating heterogeneous plasmachemical processes.

was 0.3 mm. The thermocouple was introduced through the hollow cathode, whose inside diameter was 10 mm, into the region of a positive column of the glow discharge. The variation in the plasma temperature due to the plasma being disturbed by the thermocouple was disregarded. The underestimation of the plasma temperature due to the cooling of the surface of the quartz cap at a gas temperature of up to 1200 K showed that this is a magnitude of about 1% and is included in the measurement error. The thermocouple can be cooled when the reduction reaction that occurs with the absorption of heat proceeds on the quartz-capillary surface. This process is fundamental in determining the upper bound of a temperature interval.

The signals were recorded on digital voltmeters. The measurement error was ±10% for the temperature, ±5% for the gas flow rate, ±2% for the pressure, ±1% for the current, and ±4% for the discharge voltage.

The body of the reactor 1 (Fig. 1) was manufactured of quartz glass 50 mm in diameter to ensure a residual air pressure of about 10 Pa in the reactor and thermal decoupling of the sealing system of the electrodes. To ensure long-duration contact of the particles with the plasma, use was made of specimens in the form of cylinders 11.5 mm in diameter with a 3-mm axial hole; the specimens were manufactured by the method of pressing from the powder of aluminum oxide 2 and were installed between the hollow cathode 3 and the hollow anode 4 in the region of the positive column of the glow discharge. Furthermore, the employment of these cylinders with the capillary from a powder of reduced material ensured a low heat removal from the reaction zone, since the thermal conductivity of the powder pressed at low temperature of 0.36 W/(m·K) is two orders of magnitude lower than the thermal conductivity of the dense sintered oxides of 30 W/(m·K) [9]. Realization of the reaction in the capillary with the walls of reduced oxides excludes contamination of the products obtained by the wall material. The capillary diameter was selected from the conditions of implementation of the process of oxide reduction: the temperature on the interior capillary surface must, at least, exceed



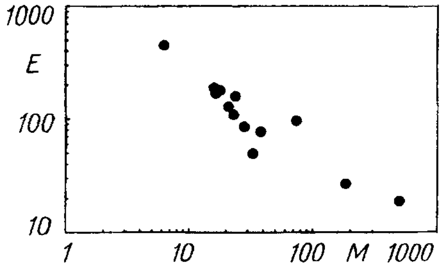


Fig. 3. Volt-ampere characteristics of a combined discharge in hydrogen at a pressure of P = 2631.6 Pa and a hydrogen flow rate of $R_v = 10^{-5}$ nm^3/sec; the capillary length is 10^{-1} m. The recording time is 34 mm. U, V; I, A.

Fig. 4. Energy consumption vs. mass of the reduced aluminum oxide per unit time. E, kW·h/kg; M, mg/min.

the boiling point of aluminum (2457 K) and, possibly, the boiling point of aluminum oxide (3000–3250 K) for the reaction in the gas phase. According to the data of calculation of the energy balance, the plasma temperature on the capillary axis must be no less than 3500 K. Since in the process of reduction of the aluminum oxide the capillary diameter increases, we must increase the current to maintain the conditions optimum for the reaction. In all the conducted experiments, the current was increased linearly with time. The duration of the process was varied in the range of 5–50 min.

The range of working currents was selected from the conditions of ensuring hydrogen temperatures in the capillary required for the reaction to occur and the operating regime of the electrode with a normal cathode and anode layer to be maintained [10]. The fulfillment of the latter condition is obligatory only to exclude contamination of the reaction products by the electrode material because of the strong erosion in the arc spot. In operation with the electrodes of the same material (Al), discharge regimes with higher currents can be realized. In a nonequilibrium hydrogen plasma, the translational temperature can be measured by contact methods only to 1200 K since at 1100 K the process of reduction of silicon oxide (the quartz cap on the thermocouple) begins [11]. The temperature in the interval of 500–1200 K was measured as a function of the discharge current in the range of 0.05–1 A, the discharge-tube diameter in the range of 10–50 mm, and the pressure in the range of 1315.8–13,158 Pa. As a result, we obtained the relations employed subsequently to calculate the gas temperature on the capillary axis. This enabled us to determine an initial capillary diameter of 3 mm in accordance with the possibility of increasing the discharge current up to 3 A.

Results and Their Discussion. The experiment was conducted with aluminum-oxide specimens of different length (5 to 200 mm). This permitted the determination of the voltage drop directly on the specimen with a capillary and, correspondingly, the electric-field strength in the capillary (20–40 V/cm) as a function of the discharge current. The current density in the capillary is an order of magnitude larger than the current density in the glow discharge at the outlet from the capillary and, correspondingly substantially lower is the electric-field strength. The volt-ampere characteristic of the combined glow discharge in hydrogen has an abnormal character (Fig. 3). The ascending portion of the volt-ampere characteristic is associated with the beginning of the active phase of the reaction and increasing isolation of the substance in the capillary, which requires an additional increase in the energy contribution. The volt-ampere characteristic shows that the rate of the reduction process begins to grow at a current of 0.6 A. According to the data of calculation of the hydrogen temperature in the capillary, this current corresponds to a hydrogen temperature of 2700 K. Further increase in the current to 1 A causes an increase in the hydrogen temperature to 3200–3530 K and intensifies the process of reduction of the aluminum oxide in the gas phase. This causes the capillary diameter to increase to 5 mm and the gas temperature to decrease to 2600–3000 K in spite of the current increase. The voltage decrease at a current larger than 1 A is, apparently, due to the decrease in the reaction rate [12]. In a slow process when practically the entire aluminum isolated in the reaction is ionized, ionic plasma spraying of a metal film onto the cathode surface occurs. With increase in the rate of the reaction occurring with a larger energy contribution and substantially higher flow rates of the hydrogen when only an insignificant portion of the reduced aluminum is transferred in the form of positively charged ions, deposition of pure aluminum on the hot cathode is hindered, which is, possibly, associated with the formation of aluminum hydride in these regimes. Spectrum recording permitted the determination of a qualitative composition of the plasma. Intense lines of the aluminum and a very weak molecular spectrum of the aluminum oxide were recorded on the spectrogram, which confirms the occurrence of the process of reduction of the aluminum oxide in the regimes, in which one was unable to obtain a metal coating on the electrodes.

The measurements showed that the reaction rate increased with the power released in the capillary and attained a value of $3 \cdot 10^{-2}$ kg/h for aluminum oxide. The energy efficiency of this process increases rapidly with reaction rate. Figure 4 presents the energy consumption as a function of the amount of the substance reduced per unit time. The minimum energy consumption was 20 kW·h/kg for aluminum oxide. Calculating the parameters of the nonequilibrium plasma in front of the capillary and inside it permitted the assumption that, under these conditions, the reaction of oxide reduction goes both in the gas phase and on the capillary surface. The occurrence of the reactions in the gas phase is facilitated by the warmup and evaporation of the interior capillary surface, while the heterogeneous processes in the condensed phase are favored by the relatively high diffusion coefficient of hydrogen atoms in the lattice [13]. Since the experimental determination of the reaction channel involves certain difficulties, we can only assume what processes are possible in the system considered. Since, under these conditions, the hydrogen practically totally dissociates into atoms (the degree of dissociation is close to unity) [12], the probability for the reaction to occur with the participation of excited atomic hydrogen is rather high:

$$\mathrm{Al_2O_3} + 6\mathrm{H}^* = 2\mathrm{Al} + 3\mathrm{H_2O}\,, \quad \Delta G = -\,5719 \text{ kJ/mole}\,.$$

In the gas phase, the reaction can also occur with the participation of the ions and electron-excited molecules of hydrogen:

$$\mathrm{Al_2O_3} + 3\mathrm{H}_2^* = 2\mathrm{Al} + 3\mathrm{H_2O}\,, \quad \Delta G = -\,2045 \text{ kJ/mole}\,,$$

$$\mathrm{Al_2O_3} + 3\mathrm{H}_2^+ = \mathrm{Al}^+ + \mathrm{Al}^{2+} + 3\mathrm{H_2O}\,, \quad \Delta G = -\,1010 \text{ kJ/mole}\,,$$

where ΔG is the change in the Gibbs energy for these reactions at a temperature of 3000 K.

CONCLUSIONS

1. The use of a new method of introduction of a substance into a plasma enabled us to set up a fundamentally new plasmachemical reactor for carrying out heterogeneous reactions, in particular, the reaction of direct reduction of aluminum oxide in a nonequilibrium hydrogen plasma.
2. Direct reduction of aluminum oxide at relatively low temperatures (~3000 K) and low pressures in a nonequilibrium hydrogen plasma is realized. A rather high degree of conversion of the aluminum oxide (50–60%) is obtained. The energy consumption in the reaction attained 20 kW·h/kg of $\mathrm{Al_2O_3}$, the productivity was 0.03 kg/h.
3. Rapid removal of the reaction products from the capillary ensured a high reaction rate without much excess hydrogen with a water content in it of up to 2%. It is established that the energy consumption decreases when the reduction process is intensified.
4. This method of direct reduction of metals from oxides or other compounds (chlorides, fluorides) can be employed in producing rare-earth elements, high-purity metals, and other materials with simultaneous monitoring of the purity of materials with the aid of an emission spectral analysis.

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