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Chemical preparation of ultra-fine aluminium oxide by electric arc plasma

Aluminium oxide is extensively used in electronics, rocket production, atomic power energetics, the chemical industry, metallurgy and other branches of industry because it has a high boiling point, great mechanical stability and high dielectric parameters.

Al_2O_3 powder is usually prepared by alkali treatment of bauxite or by heating bauxite with soda. The Al_2O_3 thus prepared does not meet the requirements of modern technology since it contains different impurities and has particles of quite large size, $> 40\,\mu m$. Nowadays, the plasma-chemical method of preparation is in many cases the only one by which it is possible to obtain certain products with high dispersity and activity [1–3].

In the patent and general literature the preparation of Al_2O_3 under a plasma jet [4], high-frequency induction-coupled plasma [5–9] and glow discharge [10] is briefly mentioned. Usually the product has a specific surface 14 to 130 $m^2\,g^{-1}$ and a greater purity than that of reagents. The rate-determining step, as in the case of all heterogeneous plasma-chemical processes, is the evaporation of the refractory substances (Al_2O_3, Al) in the plasma jet. There are no data in the literature for direct preparation of Al_2O_3 from aluminium and oxygen under a plasma jet.

It is known [11, 12] that the reaction:

$$2\,Al + 1.5\,O_2 = Al_2O_3 + 1.67\,MJ\,mol^{-1} \quad (1)$$

is displaced to the right over a wide temperature range from 300 to 4000 K. The conversion of aluminium into aluminium oxide in this temperature range is practically complete. With the heterogenous oxidation process the reaction practically stops after protective filming of Al_2O_3 which hinders the diffusion of oxygen atoms to the aluminium. This restriction can be overcome if the process is realized at high temperature such that the reaction is carried out in the gas phase, i.e. using the high energy of the plasma.

The main purpose of the present short communication is to report the possibilities for the synthesis of a pure, highly-dispersed Al_2O_3, having a high specific surface and great chemical activity, from elementary aluminium and oxygen under a plasma jet.

The process flow diagram of the plasma reactor is shown in Fig. 1. Aluminium powder with an average particle size of 10 to 20 μm and specific surface, S, of 5 $m^2\,g^{-1}$, and oxygen (99% purity) are used as basic reagents. Argon is used for plasma-forming and as the powder-transporting gas. The specific surface is determined by the Kljatchko–Gurvitch method [13], based on low-temperature adsorbtion of air at 77.4 K. The quantity of non-reacted aluminium is defined complexonometrically [14] with complexon III by the method of residual titration. The degree of oxidation (in percentage) is determined by the difference in the general quantity of aluminium and the non-reacted aluminium related to the general quantity of aluminium. The preliminary tests are carried out using plasmatron with maximum effective power $W = 18$ kW at $0.708 \times 10^{-3}\,m^3\,s^{-1}$ flow rate of plasma-forming argon, $0.053 \times 10^{-3}\,m^3\,sec^{-1}$ flow rate of oxygen and $16.7 \times 10^{-3}\,g\,sec^{-1}$ consumption of aluminium powder. The temperature of the plasma jet and the reactor is determined on the basis of the energy balance.

The analysis of the prepared product shows

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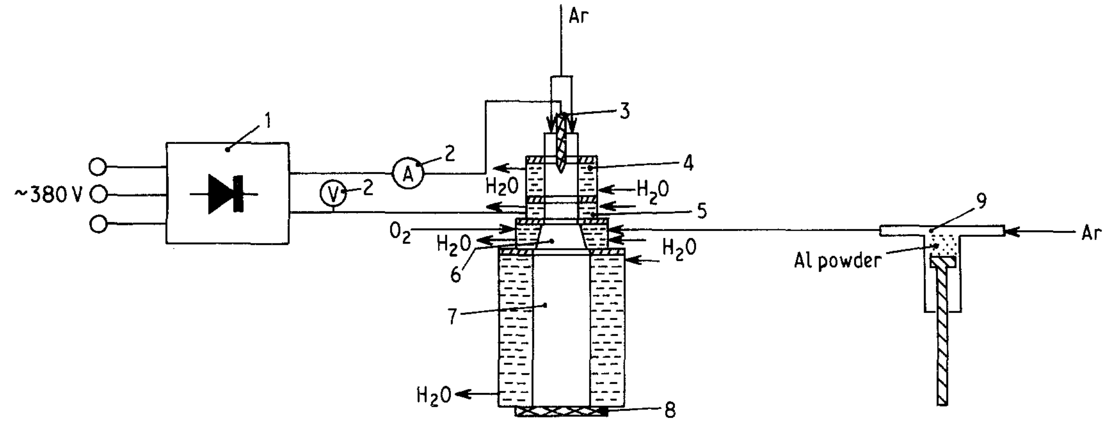

Figure 1 Process flow diagram of the plasma-chemical equipment. 1, rectifier; 2, electrical measuring instruments; 3, cathode; 4, plasmatron; 5, anode; 6, plasma-chemical reactor; 7, cooling equipment; 8, filter; 9, powder transportation equipment.

that by a temperature rise at the plasmatron nozzle outlet of 4000 to 10 000 K the degree of oxidation increases by up to 50% and the specific surface of product increases by up to $200\,m^2\,g^{-1}$. The low degree of oxidation is in contradiction with the thermodynamics and the kinetics of the process at high temperature. The causes for this are the non-homogeneous reagent mixing with the plasma jet and the high linear speed of the aluminium powder ($30\,m\,sec^{-1}$) as a result of which the duration of the contact with the plasma jet (3×10^{-4} sec) is less than the time needed for full evaporation (3×10^{-3} sec) [15]. Another cause of the incomplete aluminium evaporation is the high temperature gradients along the cold walls of the reactor.

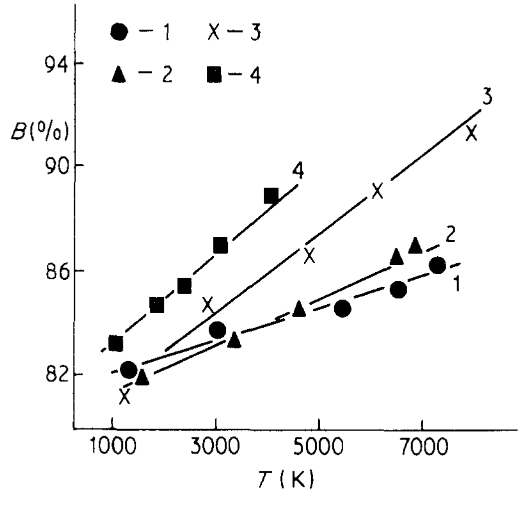

Figure 2 Dependence of the aluminium oxidation degree, B, (%) on the temperature in the plasma-chemical reactor, T, (K) and the flow rates of the plasma-forming argon, D_{Ar}, ($m^3\,sec^{-1}$) and oxygen, D_{O_2}, ($m^3\,sec^{-1}$) at an aluminium consumption of $G_{Al} = 6.67 \times 10^{-3}\,g\,sec^{-1}$. Curve 1, $D_{Ar} = 0.089 \times 10^{-3}\,m^3\,sec^{-1}$; $D_{O_2} = 0.079 \times 10^{-3}\,m^3\,sec^{-1}$. Curve 2, $D_{Ar} = 0.178 \times 10^{-3}\,m^3\,sec^{-1}$; $D_{O_2} = 0.079 \times 10^{-3}\,m^3\,sec^{-1}$. Curve 3, $D_{Ar} = 0.300 \times 10^{-3}\,m^3\,sec^{-1}$; $D_{O_2} = 0.079 \times 10^{-3}\,m^3\,sec^{-1}$. Curve 4, $D_{Ar} = 0.089 \times 10^{-3}\,m^3\,sec^{-1}$; $D_{O_2} = 0.158 \times 10^{-3}\,m^3\,sec^{-1}$.

For elimination of some of the faults mentioned, tests have been carried out with plasma-chemical equipment much the same as that in [16]. The results obtained (Fig. 2) show the increase in oxidation with temperature rise. It increases with the flow rates of the plasma-forming

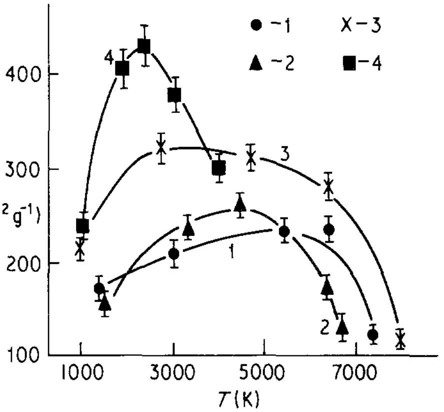

Figure 3 Dependence of the Al_2O_3 specific surface, S, ($m^2\,g^{-1}$) on the temperature in the plasma-chemical reactor, T, (K) and the flow rates of the plasma-forming argon, D_{Ar}, ($m^3\,sec^{-1}$) and oxygen, D_{O_2}, ($m^3\,sec^{-1}$) at an aluminium consumption of $G_{Al} = 6.67 \times 10^{-3}\,g\,sec^{-1}$. Curves 1 to 4 as in Fig. 2.

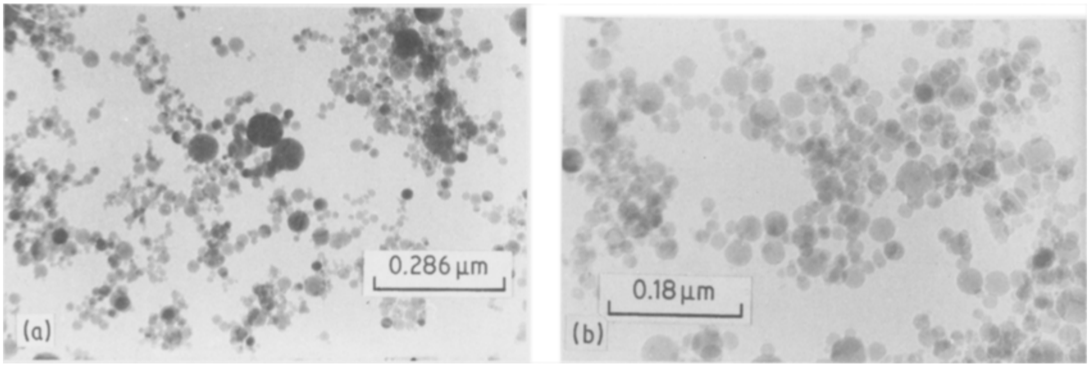

Figure 4 Electron micrograph of plasma-prepared Al_2O_3.

gas and also oxygen at constant temperature. These facts can be accounted for by the increase in the difference of the plasma jet temperature and the aluminium evaporation temperature (moving force growth), and with the improvement of heat transfer between the reagents and the plasma jet in the reactor which leads to a more complete aluminium evaporation. On the other hand, this more complete evaporation leads to formation of ultra-fine unreacted aluminium particles in the cooling equipment. These particles can react with the oxygen at low temperature because their size is approximately equal to that of the protective Al_2O_3 film. The continuing reaction of the aluminium particles and the oxygen after the reactor causes the degree of oxidation to be greater than the theoretical one at the reactor temperature. In accordance with the considerations mentioned it may be expected that the specific surface of the prepared Al_2O_3 will be increased with temperature. As it turns out, the relation $S = f(T)$ passes through a maximum (Fig. 3). It is possible that at higher temperatures of the plasma jet some of the prepared particles cannot be cooled enough (below the boiling point) causing them to stick together in the cooling equipment or to be baked on the filter. The increase in the specific surface with the increase in the flow rates of oxygen and argon is due to the more complete evaporation of aluminium which is a result of the better mixing of the reagents and the plasma jet. The shift of the maximum towards the lower temperatures is a result of the shortened time of passage in the cooling equipment; this time contributes to the recrystallization and baking of the ultra-fine particles. The X-ray diffraction analysis shows that the basic phase in the product is γ-Al_2O_3 and lines of Al and $Al_2O_3 \cdot H_2O$ are observed at the same time. The electron micrographs of the sample with the highest degree of oxidation and specific surface, with magnifications of 70 000 and 100 000 (Fig. 4) show that the particles have a regular spherical form with a size of 6 to 45 nm. The differential distribution of the particles by size is shown in Fig. 5.

It has been shown that the plasma-chemical synthesis of γ-Al_2O_3 from elementary aluminium and oxygen under electric-arc low-temperature plasma is possible. A product with high dispersion and specific surface, which depend on the parameters of the plasma-chemical process, is obtained. Its specific surface is considerably higher than that of those prepared by the known plasma-chemical and classical methods. By improving the mixing

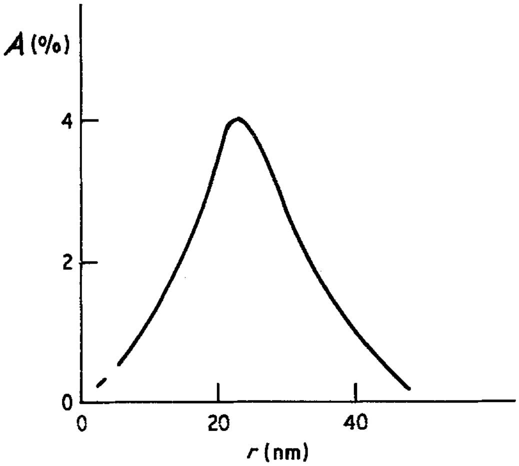

Figure 5 Differential distribution, A (%), of the Al_2O_3 particles by size, r (nm).

conditions between the reagents and the plasma jet, or with more complete evaporation of aluminium a more ultra-fine γ-Al_2O_3 powder is prepared. This can be utilized as an active catalyst, sorbent, catalyst carrier, for fine surface polishing, in powder metallurgy and for application of high-temperature and corrosion-resistant coating.

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Electrical resistivity and dielectric strength of plant fibres

Insulation resistance and dielectric strength of ligno-cellulosic materials such as wood give an indication of their dielectric constant, current leakages at certain voltages, moisture content and stability under electric fields. The study of electric properties of such materials also indicates their suitability as insulating materials for special applications such as suspension insulators, bushings, studs, sleeves, gaskets, spacer panels and switch boards. However, very little work has been reported [1, 2] on the electrical properties of natural fibres. In fact, there are no standards available for measuring the electrical parameters of these fibres.

In this communication we report the volume resistivity and dielectric strength of some natural fibres (coir, banana, sisal, pineapple leaf and palmyrah fibres) which are abundantly available renewable resources, with a view to stimulate new uses for these fibres. The electrical resistivity of these fibres was measured as a function of applied voltage for all fibres at 65% relative humidity (r.h.). For coir the resistivity was also measured as a function of retting (retting is a bio-chemical process in which coconut husks are soaked for a period of 8 to 10 months in saline water to facilitate the extraction of fibres). The resistivities and dielectric strengths of the fibres were also measured after dryheat at 110° C and after damp heat at 55° C with 95% r.h.

Coir fibres (both retted and unretted) were brought from Kovalam, near Trivandrum in India, while all the other fibres used in the present study were procured from cottage industries under

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