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Synthesis of nanometer alumina particles by plasma transferred arc alternative

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Abstract

The gas to particle conversion refers to the production of condensed particles from individual atoms or molecules in the gas phase. The particle formation is thus driven by the cooling of a supersaturated vapour. High temperatures and hence high energy sources such as hydrocarbon flames, laser beams or hot wall reactors are generally necessary. In the current work, a new and original method has been developed. A transferred arc is used to produce nanometric particles from the condensation of metallic vapours obtained by controlling the evaporation of the anode material.

Keywords: Nanoparticles; Al_2O_3; Powder-gas phase reaction

1. Introduction

Nanoparticles are viewed by many as fundamental building blocks of nanotechnology. They are the starting point for many "bottom-up" approaches for preparing nanostructured materials and devices. Major efforts in nanoparticle synthesis can be grouped into three broad areas: sol–gel processing,[1] ball milling [2] and gas phase synthesis.[3–4] Gas to particle conversion refers to production of particles from individual atoms or molecules in the gas phase. The particle primary size is driven by the cooling of a supersaturated vapour, while their further growth strongly depends on the properties of the flow into which they are imbedded. High temperatures and hence high energy sources such as, laser beams,[4] hot wall reactors or hydrocarbon flames are often necessary. In the current work, a transferred arc is used to produce nanometric alumina particles from the condensation of aluminium vapours obtained by controlled evaporation of the aluminium anode material, which becomes the solid precursor of the synthesis. This requires a good control of the heat transfer to the anode, which depends on properties of the cold boundary layer between the arc and the aluminium anode,[5] the arc root dynamic as well as the separation of evaporation/nucleation-growth steps. It can be achieved by the inclination of the torch assembly relatively to the normal to the main aluminium anode surface. That's why a new and original experimental set-up (Fig. 1) was built in order to control vapour production and its thermal history.

2. Experimental set up

As presented in Fig. 1, the transferred arc is stabilized by a secondary anode-nozzle (blown arc) and is transferred between a thoriated tungsten cathode and the aluminium anode which is the solid precursor to be vaporized. The blown arc, first started, increases the plasma flow velocity and ionizes the gap between the nozzle exit and the anode of the transferred arc. Thus, it reinforces the "stiffness" of the arc column, permitting its inclination, and allows increasing the distance between the stabilizing secondary anode-nozzle and the main anode keeping a good convective flow to it. The heat flux density transferred to the aluminium anode can be regulated with the help of the electrical resistor R, distributing the current between the stabilization anode-nozzle (blown arc) and the main aluminium anode. Besides the target is rotating, permitting the temperature control at the arc attachment, and thus, the vaporization flux. As the torch assembly is mounted on "ball bearings", the angle between the jet axis and the normal to the anode surface can be changed continuously from $\theta = 0^\circ$ to 85°, whereas the electrode gap can vary from 1 to 25 mm. Former experiments showed that it was possible to control the cold boundary layer properties closed to the anode surface by increasing the angle. It becomes possible to generate diffuse or constricted stable arc

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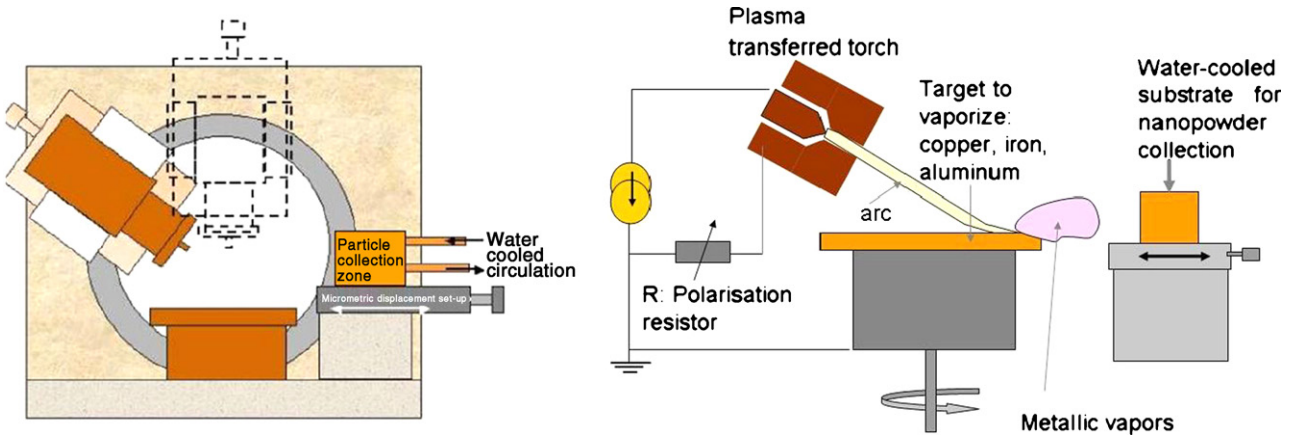

Fig. 1. New and original experimental set-up developed.

root, and so, to control vapour production. Beyond the modification of the heat transfer mechanisms and arc root stability, this inclination allows the orientation of the metallic vapours towards a pressure and temperature controlled zone. Hence, the control of vapours thermal history becomes possible.[6] The particles are collected onto a water-cooled substrate, mounted on micrometric displacement set-up in order to modify the residence time of particles imbedded in the flow. Ultra fine particles synthesized are characterized by controlling their size distribution, as well as their composition. Micro structural features of the particles were studied using Scanning Electron Microscopy (Philips XL 30). If the particles synthesized were too small to be visualized on SEM microscopy, the collected powder was dispersed ultrasonically in alcohol and then disposed on carbon coated copper grids for investigation by transmission electron microscopy (TEM JEOL 2010). The chemical composition of the particles was obtained by XRD. The diffraction pattern of the powder was recorded at a speed of $0.04^\circ\ s^{-1}$ using Cu Kα radiation.

3. Results

Synthesis of particles with given size and composition requires the control of the vapour flux and thermal history. Nevertheless, as experiments presented here were performed at atmospheric pressure, in air, the control of the chemical composition is not possible: oxides are necessarily formed. The experimental parameters are summarised in Table 1.

With such parameters, the arc root is constricted and stable. Due to the high power level transferred to the anode precursor, its vaporisation occurs. The vapours naturally follow the plasma flow towards the collecting substrate, as shown in Fig. 2. They are collected onto the water-cooled collecting substrate.

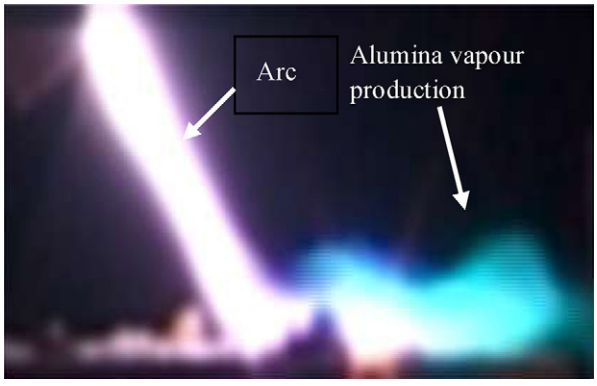

Fig. 2. Vapour production control and orientation.

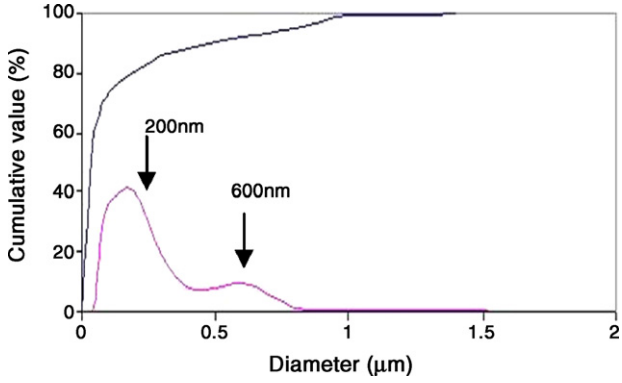

Fig. 3. Laser scattering technique result.

Particle size distribution of the processed powder is shown in Fig. 3. It is obvious from Fig. 3 that all particles are in the submicronic range. Two main peaks can be distinguished, one centred on 200 nm and the other on 600 nm. That can be explained

Table 1
Working parameters for alumina synthesis

Plasma gas	Intensity transferred (A)	Total voltage (V)	Gas flow rate (L/min)	Angle	Nozzle internal diameter (mm)	Collection distance	Rotating speed ($m\ s^{-1}$)
Ar	14 A	55 V	4	45°	2.5 mm	30 mm	$0.4\ cm\ s^{-1}$

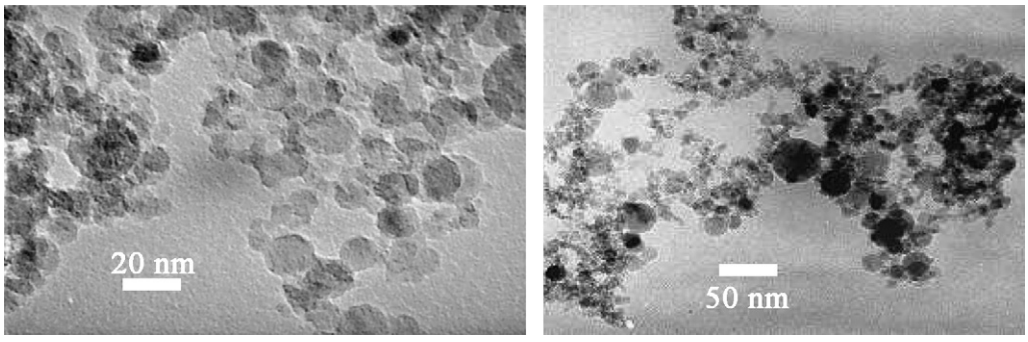

Fig. 4. TEM observation of the aluminium oxide particles synthesized (collection distance = 30 mm).

by the very good control of the vaporization process, avoiding droplet ejection, and by the dissociation of the vaporization and nucleation/growth steps. By the way, it must be underlined that the reproducibility of the experiments is achieved. As ultra fine particles have an inherent tendency to form agglomerates and aggregates, the results of particle size distribution studies by laser scattering mostly give the size distribution of these agglomerates. The actual size of the individual particles in the clusters can be determined by transmission electron microscopy (TEM). The micrographs obtained are presented on Fig. 4. The spherical or near spherical morphology of the particles is obvious, but they tend to form aggregates, whose compactness depend on ramifications orientation. TEM allows resolving the aggregates, into individual particles with size ranging from a few nanometers to about 40 nm. Aggregates are formed by sintering of primary particles during the synthesis process. These aggregates often have a fractal-like, highly branched structure and reach a size of about 300 nm in several dimensions. In some applications, such as catalysis, agglomerates with an open structure like those are desired. However, in many potential applications nonagglomerated spherical nanoparticles of uniform size are needed.

X-ray diagram showed in Fig. 5 proves that particles are well crystallized, even if some of them are not. X-rays diffraction results of the powder indicate that they are heterogeneous, comprising γAl_2O_3, αAl_2O_3 and not yet reacted aluminium. As no oxygen had been introduced in the plasma plume during the experiments, formation of aluminium oxide can be explained as follow. For appropriate working parameters, vaporization of aluminium precursor occurs. These vapours are naturally directed by the plasma flow towards the water-cooled substrate for collection. Nevertheless, due to viscous strength, air penetrates in the fringes of the plasma and diffuses inside its core, where O_2 is dissociated. Hence, atomic oxygen can react with atomic aluminium vapour to form aluminium oxide. The latter corresponds probably to the gas phase reaction of aluminium and atomic oxygen. Unfortunately, the quantity of oxygen entrained being uncontrolled, only part of the aluminium nanoparticles are oxidized. X-ray diffraction results indicate that the main phase is that of γ aluminium oxide. Presence of discontinuous rings, as well as broadened peaks from normal X-ray patterns, prove that the particles are crystallized and in nanometric range (below 80 nm). Vapours of aluminium react with oxygen to form aluminium oxide, which crystallizes in the metastable γ phase due to the rapid quenching associated with the process. The formation of the metastable γ phase, in preference to the thermodynamically stable α phase has also been observed in fine alumina powder prepared by other high temperature techniques, such as plasma spraying, arc discharge and electrodynamic atomization.[7] Also a few αAl_2O_3 particles are still detected. No real explanation can be proposed, due to the very complex physical phenomena involved in nucleation and growth of particles. As particles collected over the water cooled substrate are constantly heated by the plasma flow, they might, for example, crystallize in the metastable γ phase due to the rapid quenching and then, when submitted to a post thermal treatment, γ phase recystallises in the α phase.

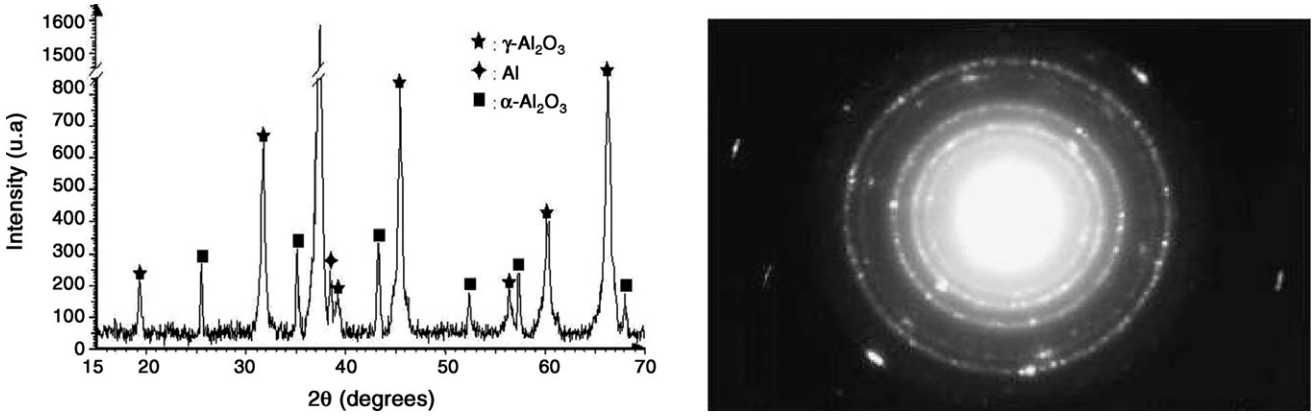

Fig. 5. XRD of powder synthesized.

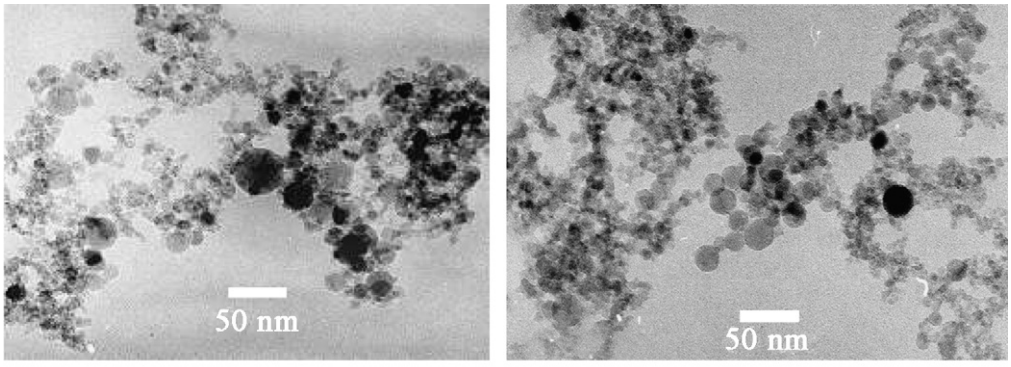

Fig. 6. Effect of plasma forming gas on powder properties (collection distance = 30 mm); (a) pure Ar as plasma forming gas; (b) Ar-H2 as plasma forming gas.

Plasma forming gases may be an important parameter in plasma arc techniques. For example, nitrogen can be used for nitride formation or hydrogen to reduce metal oxidation. Helium is supposed to be a good quenching gas, due to its low molecular weigh, could reduce the size as well as the degree of aggregation of the particles synthesized. That's why experiments were performed by shifting from pure argon-to-argon helium (75–25% weigh) as plasma forming gas in order to visualize its effect on alumina particles characteristics. All the relevant parameters are those presented in Table 1. TEM micrographs are presented in Fig. 6, for a collection distance of 30 mm. The particles obtained are quasi identical. Particles are clearly nanoparticle chain aggregates, composed of primary particles that are approximately 10 nm, even if particles with diameters reaching 30 nm can be observed, while XRD analysis shows that the γAl_2O_3 is mainly synthesized. Finally, adding helium in such proportion as plasma forming gas does not reduce the degree of dispersion and agglomeration, which is typical of many vapour phase processes. It might be interesting to use pure helium as plasma gas.

4. Conclusion

Synthesis of alumina particles with controlled size and composition requires both the control of the partial pressure in reactive species and their thermal history. In the current work, the aluminium anode of the transferred arc is considered as the solid precursor of the synthesis. Thermal vapour history is obtained by tilting the angle between the plasma jet and the anode precursor, made of the material to be vaporized. They are then naturally entrained and orientated by the plasma flow towards a collecting substrate. Alumina particles synthesized are clearly nanoparticle chain aggregates initially about few hundred nm long, composed of primary particles that are approximately 10 nm, even if particles with diameter reaching 60 nm can be observed. In some applications, such as catalysis, agglomerates with an open structure like those are desired. Shifting for pure argon to argon-helium (75–25 % w) as plasma forming gas tends to reduce slightly the degree of aggregation of primary particles. More experimental studies are needed, using a wider range of materials and operating conditions, with well-controlled geometries and flow regimes, for synthesizing particles with desired sizes and composition.

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