

Application of transferred arcs to the production of nanoparticles*

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Abstract: A brief review is given of the application of transferred arcs to the production of nanoparticles. The advantages and limitations of transferred arc reactors and the concept of the CRTP reactor are discussed. Examples are given of experimental and modelling work carried out at CRTP on the production of fumed silica from quartz and aluminum nitride from the reaction aluminum vapour and ammonia.

INTRODUCTION

For many years, a variety of different plasma processes have been used to synthesise ultra-fine particles. Both homogeneous and heterogeneous precursors have been used in combination with many different types of plasma generators including transferred arcs, non-transferred arcs, high frequency induction plasmas, and combinations of these. The particles produced are characterised by their small size (<1 µm), and may include pure metals, alloys, ceramics, and even composite materials. Each processing scheme has its own distinct advantages and limitations. This paper focuses on the use of transferred arcs in such syntheses. A very brief review is given of previous work. The remainder of the paper focuses on recent experimental and modelling work performed in the CRTP laboratories of McGill University.

Transferred arcs have been used since the early 1970s and 1980s to perform reductions, nitridations and other reactions. In most cases a small button of material was placed on the anode of a transferred arc under controlled atmosphere and a consolidated material or coarse powder was produced; the papers by O. Matsumoto and co-workers are typical of these efforts [1–3]. In the late 1980s and early 1990s, a number of workers synthesised ultra-fine particles in transferred arc reactors. Gauvin & Gans [4] produced fumed silica in a Plasmacan transferred arc reactor using continuous feeding of quartz. The arc was struck to a graphite anode and thus the product, which started to form within the plasma vessel, was contaminated with carbon. Etemadi [5] grew both AlN crystals and AlN ultra-fine particles in a free burning nitrogen arc struck to an aluminum anode. The powdered product had a broad range of particle sizes and was contaminated with aluminum, although more AlN was formed when ammonia was introduced to the chamber. Similar results, although at much higher power were reported by other workers [6,7]; the problem was always incomplete reaction and uncontrolled particle size and size distribution.

TRANSFERRED ARC ADVANTAGES AND LIMITATIONS

In the previous work, the transferred arc was used to volatilise at least one of the reacting species to allow it to react with a second; a rapid quench then produced the desired ultra-fine particles. When compared to other reactor systems, the transferred arc reactors, have a number of significant advantages. Because the

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arc is struck directly to the anode work piece, there is essentially unlimited temperature driving force for evaporation. Temperatures of more than 10 000 K are easily sustained at the arc root. The transferred arc system is also characterised by high energy efficiency. In principle, the only loss is at the cathode and this can be limited to of the order of five percent. The energy of the arc and anode losses as well as Joule heating within the anode can, in principal, all be used to evaporate the anode. Because transferred arcs can be operated over a broad range of gas flow rates including very low flow rates, this reduces the cost of operation and allows simple control over the concentration of the evaporated species in the exhaust gas. Finally, the plasma evaporator may be scaled up over a broad range of powers by increasing the current (100–2000 A).

The major limitations of transferred arc evaporators are practical ones, and most of these involve materials of construction. The intense arc radiation may lead to melting or other deterioration of the side-walls of the reactor. The high efficiencies described above are only possible with very high wall temperatures. To avoid conductive losses from the crucible, the crucible walls should be as hot as possible. This poses thermodynamic limits (reaction with the molten anode) as well as physical limits such as melting and dissolution of the crucible material in the molten anode. Reactor wall temperatures must be kept low enough to avoid melting and reaction with the volatilised species but hot enough to avoid condensation before the quench zone is reached. We have learned that these limitations can be formidable problems to overcome.

CONCEPTUAL DESIGN OF THE CRTP REACTOR

To minimise the problems encountered by earlier workers, the reactor system currently used at CRTP for the production of nanoparticles has the following features:

- 1 Separation of evaporation and reaction (or quench)
- 2 Transferred arc evaporation
- 3 Particle formation, in axial flow cylindrical reactor with radial injection of second reactant and/or quench

This has the great advantage of allowing separate optimisation of the two reactor sections, thus giving better control over conversion and particle size distribution. In what follows, some examples are given of recent research using this reactor concept for the production of fumed silica and aluminum nitride.

FUMED SILICA

Fumed silica is a speciality chemical consisting of interconnected amorphous particles of silica about 10 to 20 nm in diameter linked in a loose chainlike structure. It has wide uses in the chemical and pharmaceutical industries as a filler and thixotropic agent. It is currently made by the reaction of silicon tetrachloride in an oxygen/hydrogen flame. This process is well developed, but is expensive and environmentally problematic since it produces HCl. The proposed plasma process evaporates silica at the anode of a transferred arc evaporator to form SiO(g) and oxygen. A steam quench reforms the silica but in the desired particle size and amorphous form.

The general thermal plasma process was studied by a number of workers but has not yet found commercial application. Addona and co-workers [8,9] used a CRTP type reactor to carry out a combined experimental and modelling study of this system. The experimental apparatus is shown in Fig. 1. It consists of a water-cooled shell supporting a conventional thoriated tungsten cathode assembly and a graphite crucible anode which contains the molten silica. The inside of the vessel is heavily insulated to reduce heat losses and provision is made to continuously feed the granular silica. The evaporated silicon monoxide leaves in a side stream with the plasma forming gas where it is quenched by a large number of symmetrical radial steam jets. The fumed silica product is collected in a bag filter.

Modelling

The modelling work was aimed at examining the flow within the transferred arc evaporator and predicting the evaporation rates of silicon monoxide as a function of arc current and plasma gas flow rate. The model

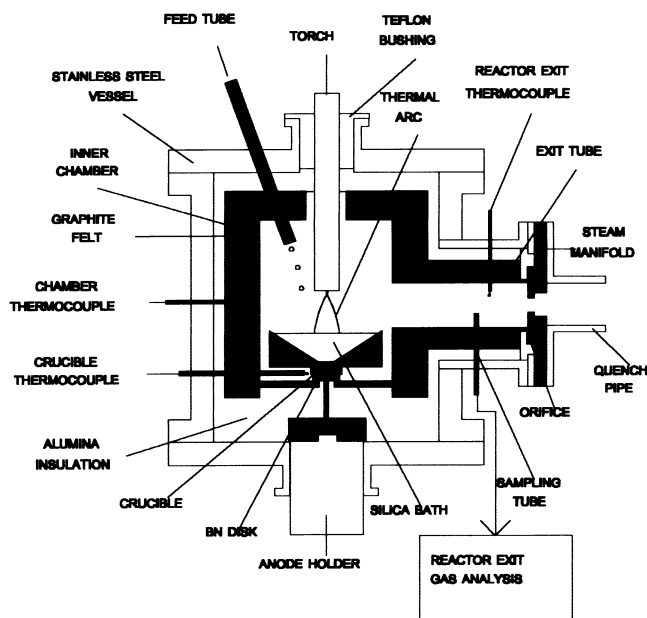


Fig. 1 Transferred arc silica evaporator from Addona [8,9].

developed combined an existing [10] 2-D model of a transferred arc and a model of the anode. The boundary conditions at the arc-anode interface were matched and the gas phase and anode conditions computed by an iterative procedure. The model allows computation of the temperature, velocity, and current density fields in both phases and has been solved both for pure argon and argon + hydrogen plasmas. The laminar flow in the molten anode is due to the combined effects of MHD pumping, buoyancy, shear from the plasma jet, and the Marangoni effect due to the variation of surface tension with temperature. The model assumes that the decomposition of silica is a heat transfer controlled process. Once the boiling point of the silica at the reactor pressure is reached, further addition of heat leads to decomposition to SiO and $1/2 \text{O}_2$.

Figure 2 shows the temperature distributions in the gas and anode, at an argon gas flow rate of 15 L/min and a current of 200 A. The highest gas temperatures (about 20 000 K) are reached near the cathode tip, while the gas temperature at the arc root is of the order of 12 000 K. A lower, but still high temperature stream of gas flows radially outward over the anode surface giving intense convective heating. It is clear from this figure that while the whole anode is molten, the highest temperatures are localised to just below the arc root. A more detailed temperature distribution of the anode is given in Fig. 3. This shows that vaporisation ($T \approx 3000 \text{ K}$) is limited to a diameter of about 10 mm below the arc root.

A distribution of the velocity vectors within the anode is shown in Fig. 4; the velocities are very low ($< 3 \times 10^{-4} \text{ m/s}$) with the highest velocities localised below the arc root where the forces are concentrated. The low velocities are attributed to the high viscosity of molten silica. It may be observed that the circulation is counter-clockwise relative to the axis of symmetry everywhere except directly under the arc root. This means that the Marangoni and MHD forces overcome the gas shear everywhere except under the arc root, where the flow is reversed.

Experimental

Figure 5 summarises the effect of both arc current and plasma gas flow rate on the rate of silica decomposition with an arc length of 20 mm. It may be seen that the decomposition rate is essentially independent of plasma gas flow rate, but that it increases with arc current as expected. The point at the highest current and gas flow rate is in error, because under these conditions, the crucible became sufficiently hot to react with the silica and provided an additional source of silicon monoxide at the expense of crucible deterioration. In a commercial process, it is unlikely that the plasma gas used would be argon. It would be better to use a reducing gas such as hydrogen, which lowers the 'boiling point' of the

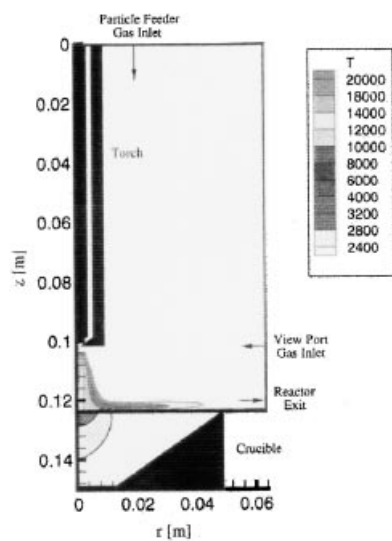


Fig. 2 Gas and silica temperature distribution [8].

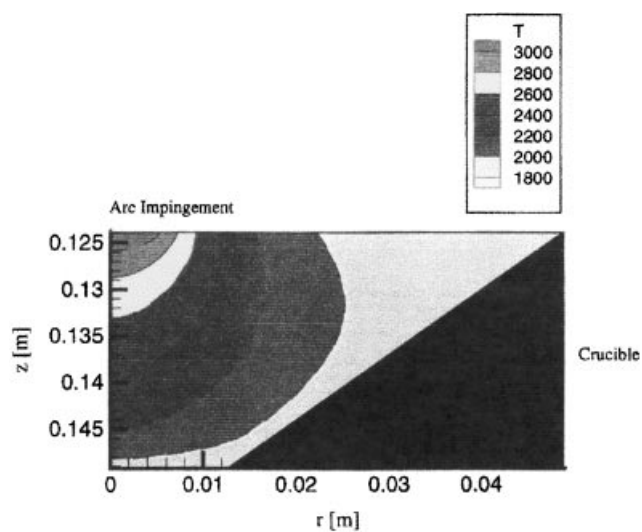


Fig. 3 Detailed molten silica anode temperature distribution [8].

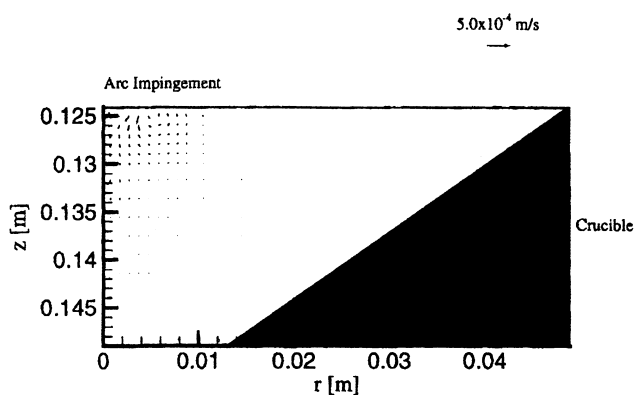


Fig. 4 Velocity distribution in molten silica anode [8].

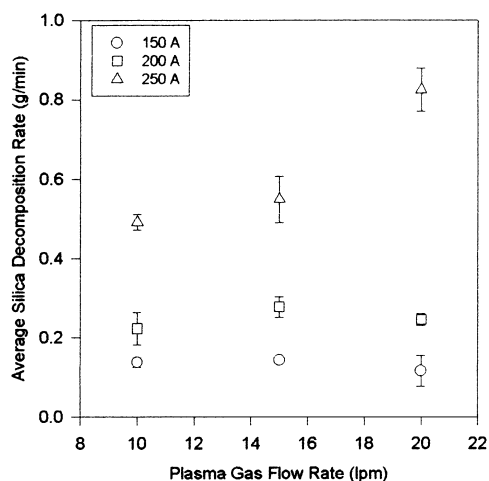


Fig. 5 Silica decomposition rate as a function of plasma flow rate and current [9].

silica and provides much better heat transfer properties. A test was performed of the effect of adding small quantities of hydrogen to the plasma gas.

The results are shown in Fig. 6, which shows the concentration of carbon monoxide in the exhaust gas from the reactor as a function of time; because the reactor interior was made of graphite, the oxygen from silicon monoxide production reacted with the reactor walls to produce CO. The CO flow rate is thus proportional to the silica decomposition rate. The arc voltage was increased by 42% and 28%, as the hydrogen content was raised to 3% and 1.3% respectively. An increase of hydrogen to 3% gave an increase in the decomposition rate of 7.5 times showing that both the production rate and efficiency of the process can be greatly increased with the use of hydrogen.

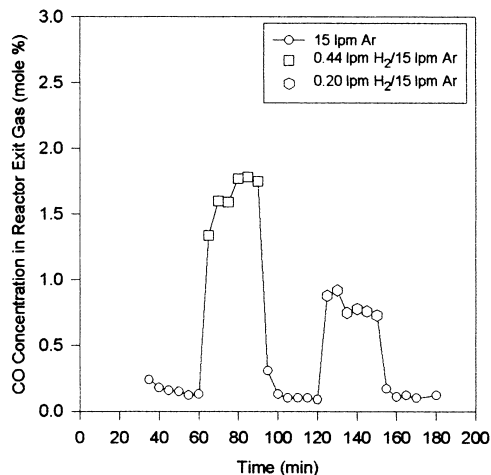


Fig. 6 Effect of hydrogen addition on silica decomposition rate [9].

The product quality was found to be almost identical to commercially available material (Aerosil[®] 200) in terms of surface area, appearance, hydroxylation etc., but lacked the thixotropic properties of that material. This was attributed to the fact that our research reactor lacked the agglomerator, which is included in the flow sheet of the commercial process.

ALUMINUM NITRIDE

Aluminum nitride has been studied by a number of workers and was chosen as a model system for study in the CRTP laboratories. It has potential applications as a substrate support in the electronics industry,

where its high thermal conductivity and high electrical resistivity are important properties. It may also be used as a high temperature structural ceramic or crucible material. The early work of Moura [11] used a side discharge reactor similar to that of Addona, with radial injection of ammonia into a stream of argon carrying aluminum vapour. He demonstrated the ability to achieve essentially complete conversion to AlN with a particle size of the order of 20 nm. da Cruz developed a co-axial reactor which allowed both radial and axial injection of the ammonia. Examples of his experimental and modelling work are summarised below.

Experimental

The experimental reactor developed by da Cruz & Munz [12] is shown in Fig. 7. The water-cooled shell is heavily insulated, and aluminum was evaporated from a graphite crucible, which served as the anode of a transferred arc system. In both systems, the reactant, ammonia was injected downstream of the transferred arc evaporator according to the CRTP concept. For radial injection experiments, the arc power was varied from 5.4–14 kW; both argon and argon containing 10% hydrogen were used. The conversion to aluminum nitride was incomplete due to premature condensation of the aluminum before ammonia injection. Perhaps more important, was the apparently contradictory effect of quench intensity on the surface area of the particles produced with these two plasma gases. Figure 8 shows that for Ar + H₂ plasma gas, the surface area per unit mass increases (particle size decreases) as the quench intensity is increased; this is as expected. In the case of pure argon plasma gas, the particle size increased as quench intensity increased which was certainly not expected. Although not shown here, it was also observed that for a non-reacting system with only aluminum and argon, the surface area was almost independent of quench intensity. All these results suggested that surface reaction was important in the nucleation and growth of aluminum nitride in this system.

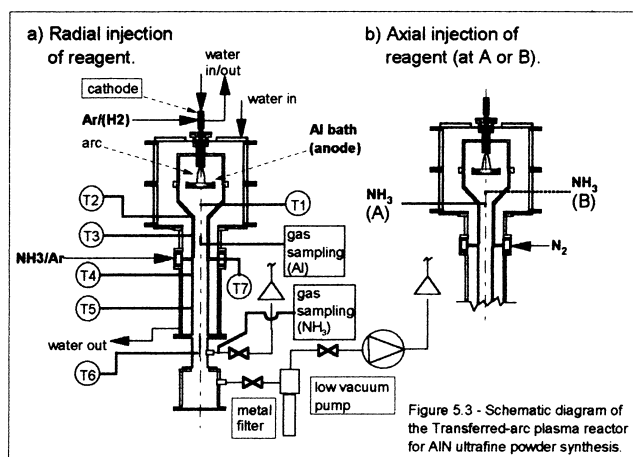


Fig. 7 Reactor developed by da Cruz & Munz for AlN production [12].

In the case of axial injection of ammonia, in an area of the reactor, which was at higher temperature, full conversion to aluminum nitride was achieved. It was found that the particle sizes were smaller when the injection was further downstream because these particles had less time to grow. The particle also increased in size as the reaction temperature increased. Overall, the mean particle diameter ranged from 10 to 52 nm, based on both surface area measurements and TEM measurements. Individual particles as large as 110 nm were detected. The crystalline structure of the particles was invariably hexagonal.

Modelling

A 2-D model was developed for the particle generator reactor. The temperature, velocity and species fields in the axial reactor with radial injection were calculated using the SIMPLER algorithm. This was combined with a moment based model for the nucleation and growth of aluminum nitride particles. A new model was developed for the nucleation of the aluminum nitride particles in this system; this considered

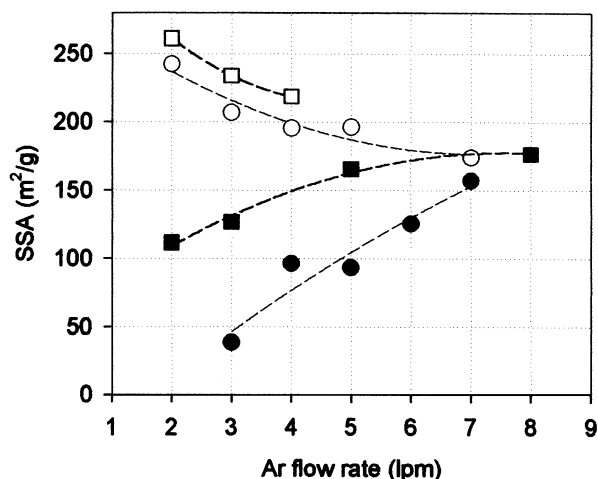


Fig. 8 Variation of particle surface area with quench intensity and plasma gas [12].

the effect of surface reaction on the surface of clusters of the new condensed phase. A cluster of x atoms of Al and y molecules of AlN was considered and allowed to interact with the gas phase according to the elementary reactions shown in Fig. 9. The results of prediction from this model were compared with the classical nucleation model which assumes only the nucleation of pure aluminum without surface reaction. A comparison of the two models for radial injection is shown in Fig. 10. It may be seen that while the classical model predicts the nucleation to be restricted to a very small low temperature region near the upstream wall and injection areas, the surface reaction enhanced nucleation model (SREN) predicts much higher peaks in nucleation and over a much broader region. These predictions were much closer to the experimentally observed trends, especially the apparently contradictory trends of particle size variation with quench intensity.

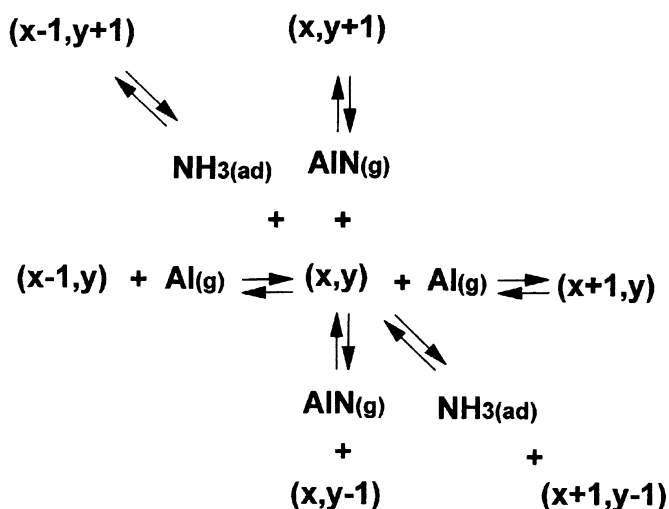


Fig. 9 Schematic illustration of elementary reactions on a cluster of x Al and y AlN [12].

The model allowed the prediction of the intensity of nucleation rate, gas phase reaction rate, condensation rate (Al, AlN) as well as surface reaction rate. A summary of the relative magnitude of these different components of the phase transition is shown in Fig. 11, also for radial injection. It may be seen that while the amount of nucleation (in $\text{kg}/\text{m}^3 \text{s}$) is small, it is very important in determining the final conversion and size distribution of the product. The gas phase reaction rate and subsequent aluminum nitride condensation rate are both also quite small. The larger terms are the aluminum condensation rate and the surface reaction rate, which are roughly equal in magnitude. By integrating over any chosen

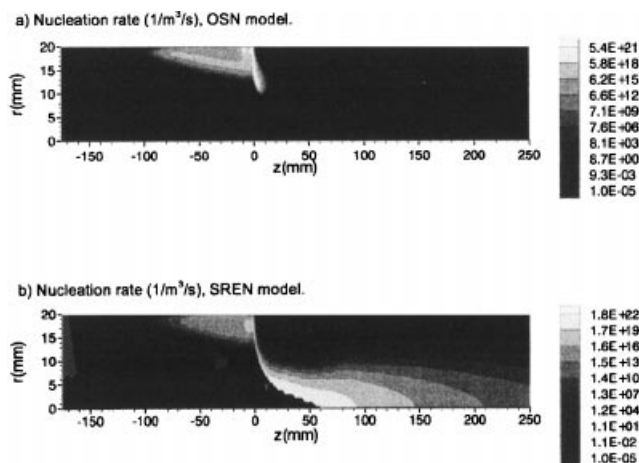


Fig. 10 A comparison of the nucleation rates in radial injection predicted by the one species nucleation model and the surface reaction enhanced nucleation model [12].

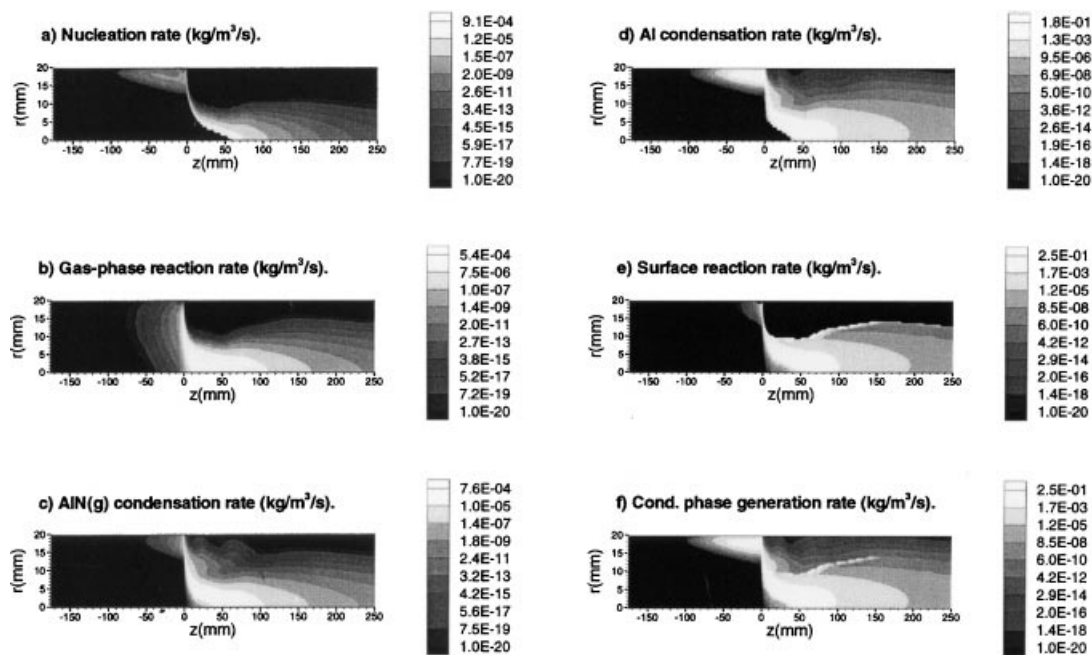


Fig. 11 Predictions of mass rates corresponding to the various phase transition mechanisms for AlN.

reactor cross-section, the model can be used to predict product composition and particle size distribution and thus used for reactor design and optimisation. A great deal of uncertainty in property values and elementary reaction rates makes the model more qualitative than quantitative at this point but correctly predicts many of the experimental observations and is useful in understanding the very complex phenomena taking place in these reactors.

FUTURE WORK

Future work in modelling will involve both the plasma evaporator and the axial reactor. The arc/anode model can be used for scale-up and optimization of the evaporator but must be modified to include the effect of metal on the arc properties as well as the mass flow rate of metal from the arc root. The nucleation and growth model can be applied to other systems and should eventually be integrated with

the arc/anode model into a single comprehensive model. Future experimental work will deal with other systems and better evaporator designs to avoid premature cooling of the plasma gas prior to injection and quench.

CONCLUSIONS

The work performed to date on very different systems has demonstrated that the use of transferred arc plasma evaporators followed by cylindrical reactors can be used to produce a variety of nanosized ceramic and metallic powders. A judicious blend of modelling and experimental work will minimize the risks inherent with scale-up and industrialization. Materials of construction continue to be a major problem with this as well as many other plasma systems.

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