SYNTHESIS REPORT

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SYNTHESIS REPORT

DEVELOPMENT OF A TWIN DC PLASMA ARC FOR THE PRODUCTION OF ULTRA FINE CERAMIC POWDERS, THEIR EVALUATION AND PROCESSING.

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ABSTRACT

The objectives of the programme were to develop the twin DC plasma arc technology and produce nanometre sized ceramic powders and coatings. Powders produced included Al_2O_3, ZrO_2, Y_2O_3, SiC, AlN and Si_3N_4 with particle sizes < 200 nm and some c 5 nm. Particles of composition ZrO_2 / Y_2O_3 were shown to be phase stabilised following plasma treatment.

The characteristics of the plasma arcs were defined and a model for the vapourisation and condensation of powders developed, which agreed with experimental findings.

Reactor designs were evaluated and a compact reactor developed enabling continuous collection of nanometre sized powders in a controlled atmosphere.

INTRODUCTION

Plasma arc technology has been applied to many different disciplines within the materials industries including tundish heating for steel, environmental waste ash treatment (arc furnace dusts, incinerator ashes) and glass fusing and melting.

Thermal plasma arcs are characterised by electrical conduction through a path created in a gas. The gas is excited sufficiently to allow dissociation into ions and electrons. The temperature for ionisation varies according to the gas species but is typically in the range 7000 to 15000 K for unconfined arcs. Two broad classifications of Thermal plasma systems exist: Transferred Arcs where ionised gas columns form an electrical bridge between the plasma torch electrode and a remote counter electrode; and the non-transferred arcs where the counter electrode is part of the plasma torch. The twin transferred arc plasma represents a third category, where two transferred arc jets may be joined to form an electrical bridge remote from the plasma torches. Figure 1 illustrates the three modes of operation.

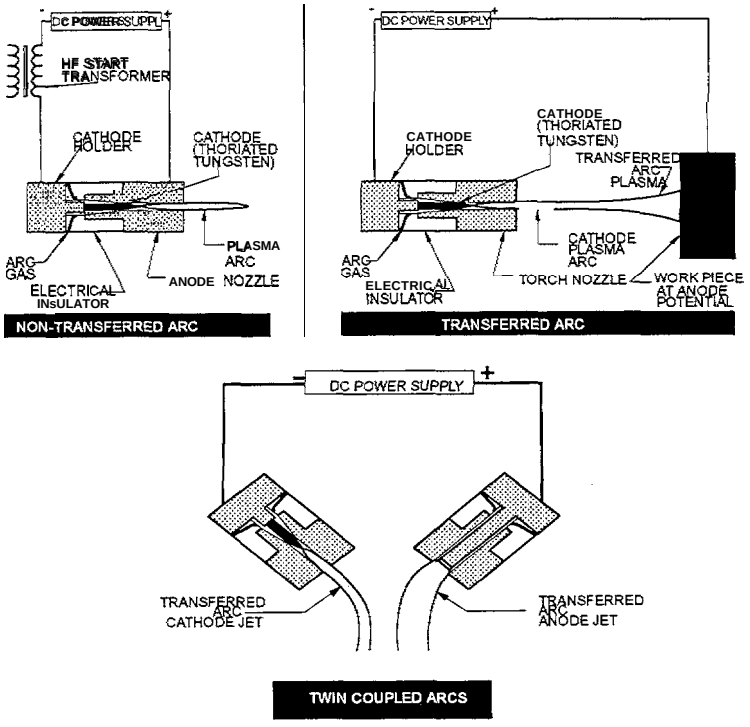

FIGURE 1. PLASMA TORCH TECHNOLOGY.

The Tetronics twin DC arc system maybe produced using the same power supply as is used for conventional non-transferred or transferred arc operation. The cathode plasma torch has a water cooled tungsten electrode whilst the anode plasma torch has a water cooled copper button electrode. Twin DC arc technology has two major advantages over competing technologies in material processing applications. The material to be treated only comes into contact with the arc and not the actual plasma torches, thus it is possible to produce powders with no contamination from the electrode material, i.e. tungsten or copper. Secondly, as the arcs couple either through the melt or above it thus completing the electrical circuit, there is no requirement for a return electrode connection in the vessel, thereby greatly simplifying hearth / reactor design.

The twin torch approach was believed to have application in the treatment of dispersed particulate feedstocks and allow the production of nanometre size powders for use in the formation of composite structures. [n twin torch DC plasma systems the arcs couple remotely from the material target making it possible to inject various powder combinations into the arcs. Thus, zirconia could be injected into one arc column and yttria into the other. Alternatively, materials such as alumina and zirconia could be premixed prior to entering the arcs and injected as one species to give a co-composite without the traditional problems of getting powder mixtures into a single transferred or non-transferred arc. The twin torch approach therefore simplified torch design and avoided erosion problems during injection.

The area of nanometre processing is one in which a great deal of research is being devoted and offers the possibility to form high compact densities at substantially lower firing temperatures than conventional micron sized powders. Due to the small particle size, compacts formed from nanometre powders are anticipated to possess enhanced physical properties such as increased fracture strength and toughness. Current work has already shown that nanometre inclusions of SiC within micron sized grains of Al_2O_3 substantially increases the fracture strength /1-3/, of alumina compacts from 350 MPa to > 1000 MPa.

In order to understand and control the behaviour of the plasma arcs, it was necessary to model their variance with gas composition, current and the vapourisation of particles within the arcs. Subsequently, to understand the appearance and formation behaviour of the particles collected, it was necessary to model the condensation of gaseous species as they exited the plasma arcs.

TECHNICAL DESCRIPTION

The powder production facilities were established at Tetronics, as illustrated in Figure 2. The reactors were water cooled to avoid overheating and to allow an energy balance to be established. Powders of varying particle size were injected into the plasma arcs and subsequently collected in a controlled atmosphere glove box. The bag-filters were double stitched, PTFE coated gortex bags capable of retaining particles at least 1 nm in diameter. The glove boxes were maintained under a nitrogen atmosphere, whilst powders were being collected and handled. This arrangement was proved to prevent contamination and surface hydrolysis due to moisture vapour leading to particle growth. Storage of the particles was in sealed canisters under a nitrogen atmosphere,

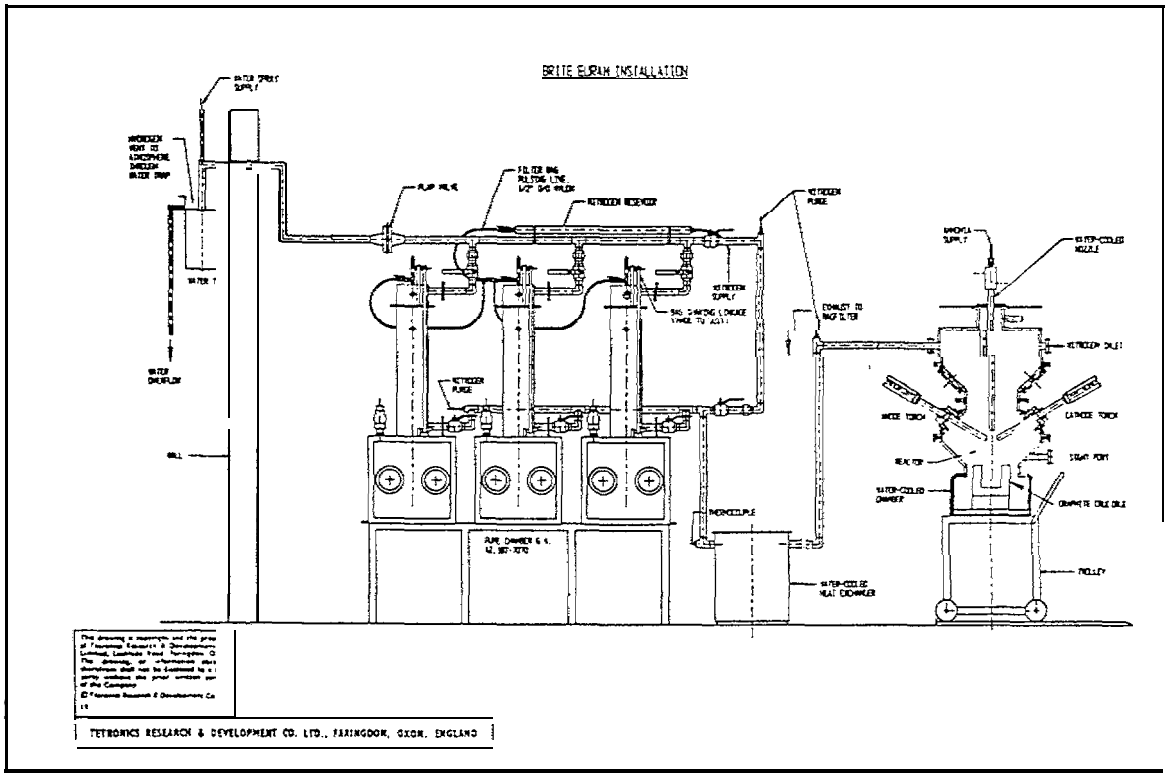

FIGURE 2: SEALED POWDER COLLECTION FACILITY.

Powders were injected either co-currently or counter-currently into the combined arc zone for in flight vapourisation evaluation. Powders produced by in-flight vapourisation were Al_2O_3, ZrO_2, Y_2O_3 and mixtures of these samples. The feed rate of these materials was varied between 60 g/hr and 2000 g/hr to determine the optimum conditions for commercial scale-up of nanometre size powders.

Impingement of the arc on precharged bulk materials was used to synthesise AIN, SiC, B_4C / SiC, Si_3N_4 / SiC and Si_3N_4 as follows:

AlN from liquid aluminium in the presence of nitrogen and ammonia.
Si_3N_4 from liquid silicon in the presence of nitrogen and ammonia.
SiC from silicon carbide granules in the presence of argon.
Si_3N_4 / SiC from silicon carbide granules in the presence of nitrogen and ammonia.
B_4C / SiC from silicon carbide granules and B_4C powder in the presence argon and nitrogen.

To achieve the in-flight vapourisation of powders or the sublimation of bulk materials contained within a graphite crucible, the input power and reactor gas exit temperature were continuously monitored and adjusted accordingly. Typical operating conditions were: DC current 300-800 Amps, Power 36-240 kW, gas exit temperature 300-500°C. The use of nitrogen as either a processor diluent gas was employed to verify the scale-up potential of the process.

Fine feed materials (< 10 μm diameter) were fed using carrier gas. Coaxial gas injection was employed to focus the injected feed on the combined plasma arc zone, as illustrated in Figure 3.

The arc characterisation studies were undertaken using an Optical Emission Spectroscopic (OES) Diagnostic technique based on the principal of local thermodynamic equilibrium (LTE) within the plasma arcs, /4-6/. This technique utilises the rapid decrease in plasma emissivity with temperature, at constant pressure and allows non LTE areas of the plasma arcs to be modelled as being within LTE, thus simplifying the calculations made. Hydrogen was injected as a standard into the argon / nitrogen plasma arcs and the spectral emissivities and half-widths calculated for the H_β line. From these values and knowledge of the position within the arcs where the measurement was made, a distribution of electron densities, gas composition and arc temperature within the plasma volume was developed. Following these spectroscopic diagnoses, the vapourisation of particles within the plasma arcs were modelled. Programmed were written which calculated the residence time of particles within the plasma arcs (dependent upon carrier and plasma forming gas velocities) and the heat absorbed and re-radiated by particles. The results of these models were subsequently validated by experiment. The condensation behaviour of particles was also determined and correlated with experimental findings.

Utilising the arc characterisation data a compact reactor was constructed, Figure 3. The plasma arc temperatures are superimposed on the diagram for reference.

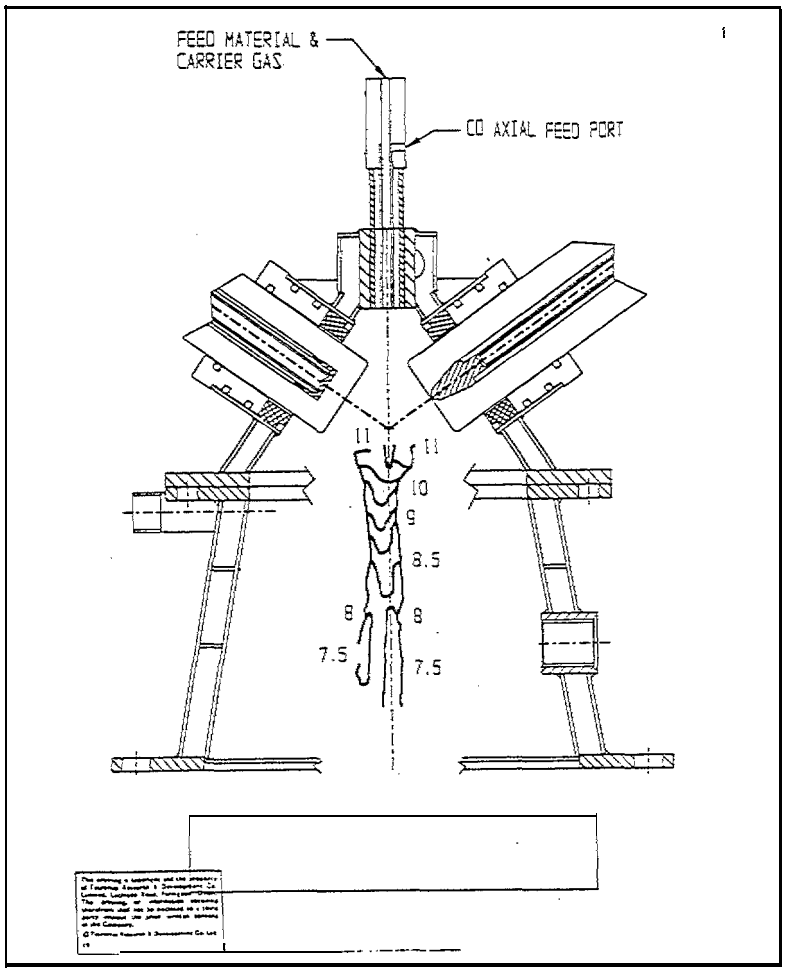

FIGURE 3: COMPACT REACTOR FOR POWDER AND COATING PRODUCTION WITH SUPERiMPOSED PLASMA GAS TEMPERATURE (KK).

Nanometre sized powder coatings were undertaken in the compact reactor used for the powder production with the additional involvement of a CNC controlled and a PLC programmed co-ordinate coating table which had been designed and built specifically for the program me. The coating table was located in an area of the plasma where the arc temperature was expected to be in the region of 7500 K. The cooling of the table was therefore designed to be of the order 50 kW. The table was pre-programmed to move in the x, y axes with a manual adjustment in the z-axis for height. Pre-plasma processed and raw powders were injected into the arcs at a rate of ≈ 60 g / hr and the condensed species removed from the table after the arc was extinguished.

The powders collected following plasma treatment were examined by the traditional techniques for specific surface area, particle size distribution, X-ray diffraction and SEM/TEM. Subsequently, the powders were processed by conventional die - pressing techniques into compacts for sintering trials. The very fine nature of some of the powders produced, did require the development of a novel filter pressing

technique to achieve good compact densification in the unfired state. Green densities as high as 60% of theoretical were achieved. The filter pressing technique allowed the green compact properties to be examined as a function of water removal and strain rate applied. The greatest influence on the green strength and structure of the pressed cakes was found to be the theological properties of the original material slips. These investigations involved theological processing and examining the influence of electrolyte addition on slip technology and subsequent material handling. Compacts were fired using normal atmospheric furnaces, hot presses and graphite induction furnaces for comparison between die pressing and filter pressing routes.

RESULTS

A representation of the plasma arc temperatures available within the twin torch columns can be seen in Figure 4. These results were obtained at 200 A, included torch angle of 110° with torch gas flows of anode 30 Nl/min argon, cathode 20 Nl/min nitrogen and 0.4 Nl/min hydrogen to both torches. The plasma temperature was estimated by measuring the half width of the H_β line.

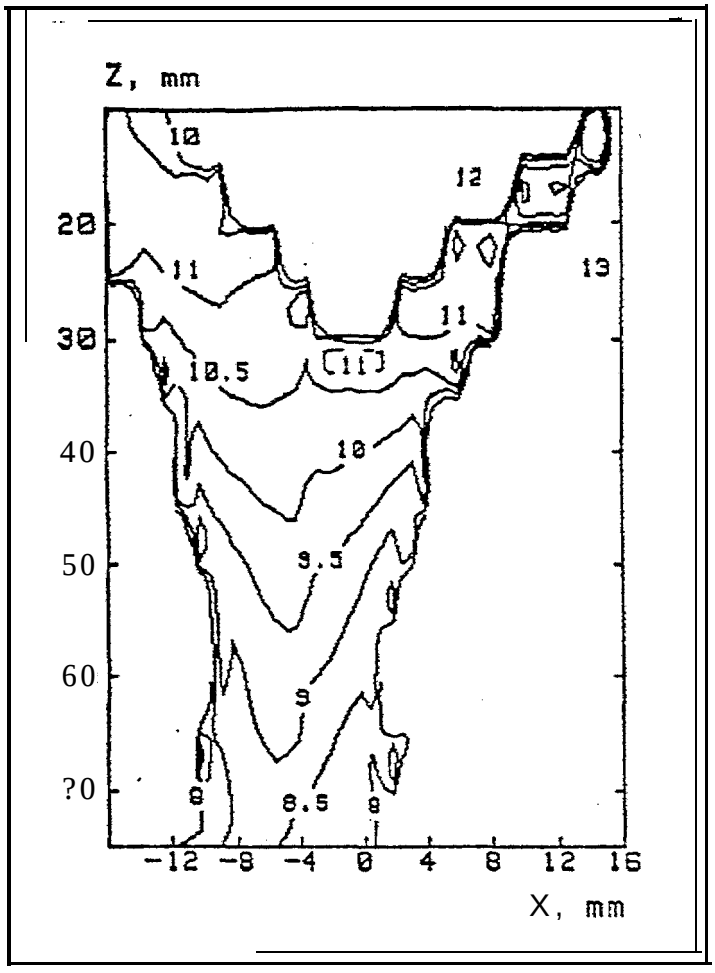

FIGURE 4. PLASMA TEMPERATURE (KK) IN TWIN ARC COLUMNS.

The maximum arc temperatures in the plasma columns occurred at the anode and cathode arc root spots, these being 13000 and 13500 K ± 500 K respectively. Injection of powder into the arcs caused a decrease in the temperature of the plasma by ≈ 3000 K. Variation of the electron density in the plasma arc coupling zone was achieved by injection of differing gases into the arc columns. This ability to vary the electron density in the plasma by the injection of secondary gases is a unique feature of the twin DC arcs. The exploitation of this phenomenon is continuing.

The vapourisation studies indicated that discrete particles of size < 10 μm were vapourised when injected into the plasma arcs. However, materials whose diameter was > 10 μm would only be partially melted but not vapourised. These results were validated by experimental findings.

The modelling of the condensation of particles from the plasma arcs, was undertaken by a Monte Carlo simulation. Under this simulation particles were introduced into a box and their motion within this environment was of a Brownian type. For the purposes of the model, particles were introduced one at a time into a hypothetical box. Once the particle had come to rest or left the defined box area, a further one was introduced. In such a manner, agglomerates of up to 1 μm were generated by 1000 particle events. Agglomerates actually observed in experimental trials were up to 5 μm in diameter, with a open pore structure.

Alum ina powders produced following plasma treatment were of the δ and 0-phase in preference to the original a-phase. The formation of these new phases is in accord with previous literature /7-8/. The new powders were of size c 200 nm in the baghouse, with a fraction of that collected, below 30 nm. Sintering of these materials produced poor densification behaviour, due to the phase transformation on firing to the smaller volume a-phase, and consequent non-uniform sintering. Agglomerates were formed by re-circulation of particles within the plasma flame and growth up to 5 μm was recorded. These particles were particularly interesting in that they were of a open pore structure and suitable for catalysis or filter applications.

Alumina particles of starting diameter >10 μm, were injected into the plasma arcs and in accord with the modelling data were sphereoidised rather than vapourised, as can be seen in Figure 5.

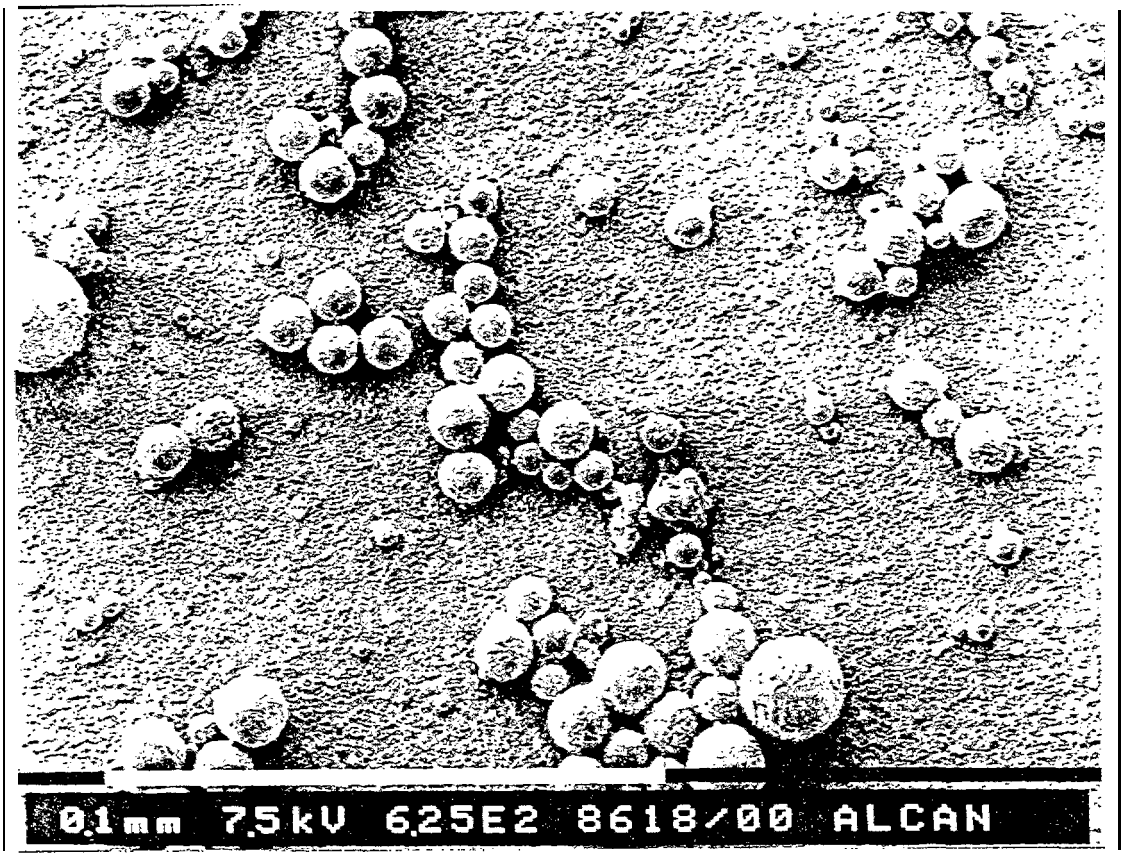

FIGURE 5: **Sphereoidisation** of Alumina Particles by the Twin Torch Plasma.

Zirconia / yttria mixes were processed, with good chemical homogeneity being achieved in the powders as collected in the baghouse facility. The average particle size of materials collected was 50 nm with a significant fraction less than 10 nm in size, as can be seen in Figure 6. As expected such fine particles were very surface active and prone to agglomeration through surface hydrolysis or as an effect of the energy available from the electron beam used in microscopic examination. The phases present were either cubic or monoclinic/tetragonal depending up on the initial dopant addition. Good sintering characteristics were achieved, but the limited amount of powder produced precluded any significant physical property studies being undertaken.

Sublimation of silicon carbide granules (4 mm size) yielded collection rates up to 1 kg / hour and particle sizes ≈ 300 nm. Dopants such as boron carbide were processed with the silicon carbide and no second phases were distinct in subsequent X-ray diffraction or electron microscopy studies. Sublimation of the silicon carbide in a ammonia / nitrogen atmosphere yielded a mix phase material containing both silicon nitride and silicon carbide.

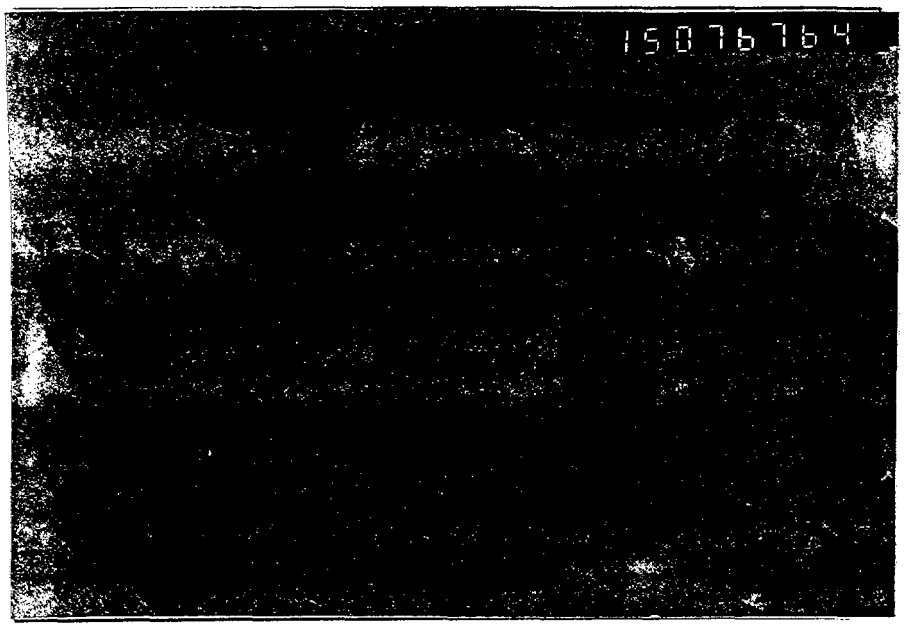

FIGURE 6: TEM of ZrO_2 / Y_2O_3 Powders **(Mag** 200000)

Silicon nitride was formed by volatalising silicon metal atoms from a melt in the presence of ammonia. In such a manner, particles of size 10 to 20 nm were formed. The low volatility of silicon yielded only small quantities of powders. The amount of nanometre size silicon nitride collected was not sufficient for mechanical property testing and examination.

Coatings prepared from these injected powders were formed on a water cooled copper substrate, Figure 7. The use of alumina materials, led to vitreous translucent coatings when the power was increased to the plasma arcs. The feeding of zirconia / yttria and pure yttria powders led to the production of semi-porous structures loosely bonded by fused agglomerates. Such structures may find application as filter media. The input power for the coating studies varied with the material being processed, but was in the range 40 to 100 kW.

The behaviour of nano-powders when dry pressed using a single action die was studied. It was established that dry pressing of nano-powders yielded very poor compact densities with many laminations being present. This was due to agglomeration and an increased surface to volume ratio of bridged particles. In order to overcome these difficulties a colloidal processing route, involving filter pressing, was used to prepare dense compacts. Filter pressing was achieved by using a load cell arid an Instron tensile testing machine and loading a wet compact at constant cross head rate to produce a specimen. The specimen was subsequently dried and fired. By the use of this technique, compact densities in the range 60-65 % of theoretical were achieved.

FIGURE 7: Silicon Carbide Coating Prepared by Twin Torch Plasma.

Studies into the colloidal processing of materials revealed the importance of the double layer thickness surrounding the particles and the influence the processing medium has on this value. Figure 8 illustrates the densification behaviour of a alumina powder processed at different pH values. The slips processed at pH of 1.9 when the particles were flocculated, i.e. the inter-repulsive forces between them were reduced to a minimum, produced the greatest compact density in the fired state.

Particles of diameter 1 µm with an associated double layer thickness of 10 nm would be little changed in diameter on processing in a liquid medium and hence there would be little influence on particulate packing density. However, when particles of diameter 10 nm, are processed a 10 nm double layer thickness would mean that the packing density is reduced by a factor of eight since the effective particulate diameter is doubled. This reduction in packing density leads to lower green compact densities and subsequent fired density. Therefore, time was spent in developing suitable wet processing rheology to fabricate compacts of high green density.

Green compacts have been fabricated with densities up to 70% of theoretical by filter pressing and correct rheological processing. The filter cakes were investigated and found to be homogeneously packed.

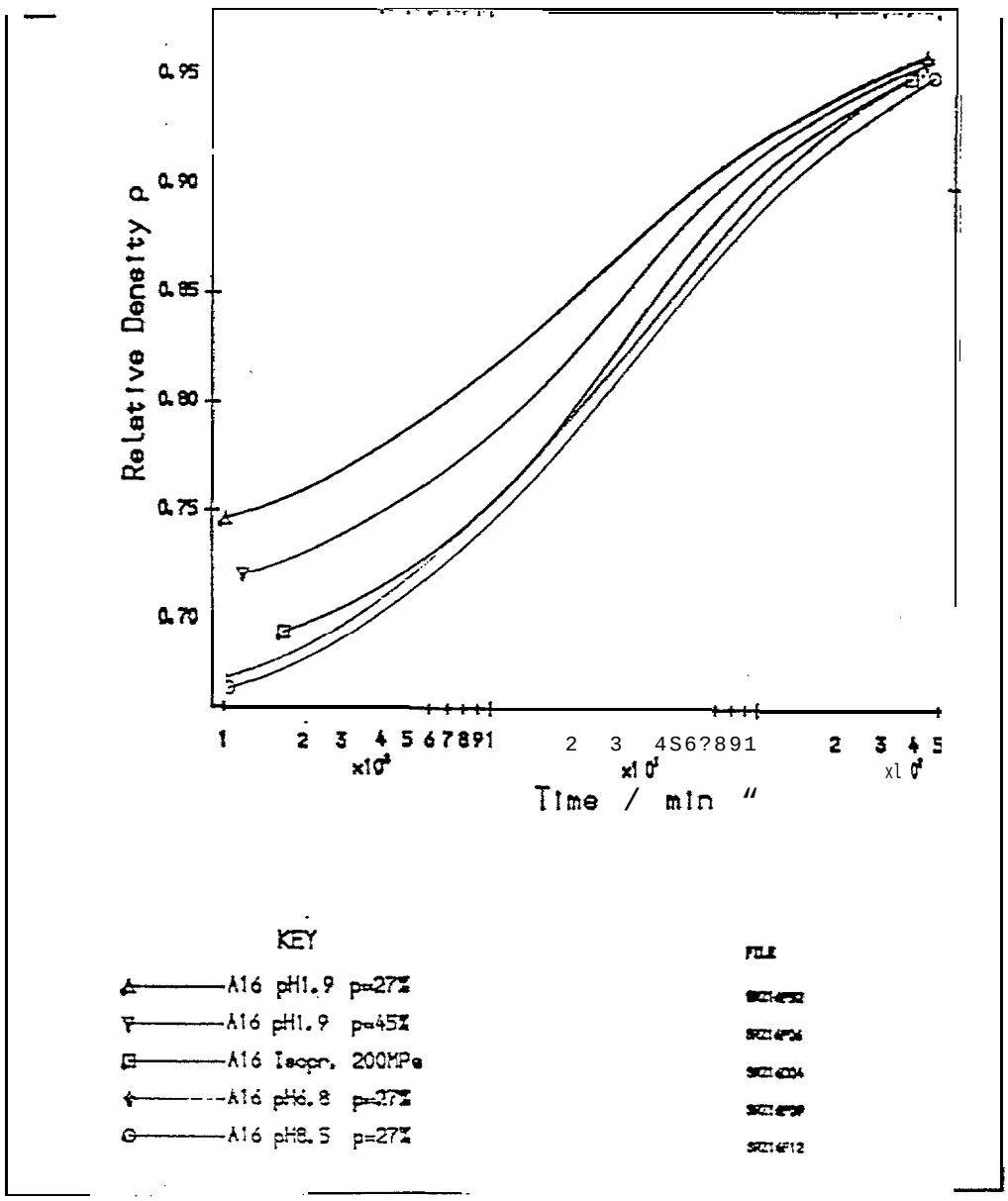

FIGURE 8: Effect of Processing on the Densification of Alumina Powder Compacts.

CONCLUSIONS

The modelling was verified by experimental findings and confirmed that discrete particles of size < 10 μm were completely vapourised in the plasma, whilst materials greater than this size were sphereoidised. Condensation of particles from the vapour state followed a Monte Carlo type simulation. Agglomerates of up to 1 μm in size could be developed.

Powders and composite materials have been fabricated from Al_2O_3, ZrO_2, Y_2O_3, SiC and Si_3N_4. The materials collected in a controlled atmosphere baghouse were of particle size < 100 nm with some particles < 10 nm. The phases present were indicative of the gas composition. The use of nitrogen to the plasma torches led to the formation of small amounts of oxy-nitride phase in alumina powders. Large amounts, up to 1 kg, of nanometre size alumina and silicon carbide powders were produced.

Coatings from the nanometre powders were prepared and evaluated at atmospheric pressure, Fusion of grains within these coatings were clearly visible, together with areas of transparent material in certain coatings. Those coatings not fused were semi-porous and may have application in filter/catalyst roles.

The twin arc has been evaluated and areas defined in terms of electron and ion concentrations. The bridging zone between the twin arc columns is anomalous and still requires further evaluation.

A wet filter pressing route for the formation of high density compacts based on nanometre size materials was developed. Compacts formed by this route had pressed densities in the range 55-65% of theoretical. Nanometre particles of alumina prepared by plasma were of the δ and θ phases. On subsequent heat treatment these alum ina powders reverted to the α-phase with an associated volume expansion. Poor fired densities were achieved. Grain growth in these compacts was indicative of coarsening processes, with the very fine grains disappearing very quickly. The compacts prepared from zirconia / yttria powders were very chemically homogeneous and the phases present reflected the initial dopant addition made.

Application of these materials is likely in the catalyst, filter and aggregate industries where the formation of open pore spherical agglomerates up to 5 μm in diameter will have potential for industrial commercialisation.

A small reactor unit has been developed forvapourising and condensing particles without re-circulation within the plasma arcs. The size of this reactor is idea! for academic / industrial application and accepts powder feed rates upto 300 g / hour in a wide variety of gaseous environments.

A new logic circuit based on IGBT technology has been developed with low loss switching at applications up to 200 kHz.

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