

SYNTHESIS OF NANO-CRYSTALLINE CERAMIC POWDERS BY CHEMICAL PROCESS

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ABSTRACT

Several processes were developed by our research group to synthesise nano-crystalline ceramic materials. Amongst them, the investigation of the new, simple and versatile technique to generate ultra fine powders of advanced ceramic oxides using a chemical pyrophoric reaction and sol-gel techniques are noteworthy. In the solution combustion technique, the role of pH on the morphology of the synthesised powder was attributed to the redox reaction. These pyrophorically generated precursors could also be utilised to synthesise nano-crystalline aluminium nitride powders at low temperatures using carbothermic process. An economically feasible alkoxide based sol-gel process for the production of high purity nano-crystalline alumina powders was established and several subsequent processes to generate nano-spheres to micro spheres were investigated. This increased the potential of these high pure nano-crystalline spherical alumina powders for practical applications in spray coating on industrial components, fabrication of envelope for sodium vapour lamp, hip joints and IC substrate.

Key Words : Nanocrystalline, Pyrophoric, Sol-gel, Alumina, AlN.

INTRODUCTION

Over the years, the research activities indicated the size-dependant variation of particulate and microstructural properties, particularly in the nanometer range as an important area for the development of new materials and material processes. This resulted in excellent new properties and increased the interest in nano-crystalline materials tremendously. The research activities were also directed towards understanding the surface characteristics of these ultrafine particles for efficient applications in devices and lowering the processing temperatures. The improvement of physical properties by consolidating the loosely agglomerated nano-crystalline ceramic material expected to result in significant payoffs to the industries. Problems such as decomposition of constituent phases that are frequently encountered in the sintering of nitrides, and deleterious interfacial interactions can also be solved by resorting to nano-particles as the starting materials. Moreover, smaller grain size should result in improved mechanical properties and super plastic behaviour for net shape forming. So far, several techniques were available for the synthesis of nano-crystals that include chemical processes (co-precipitation, sol-gel, freeze-drying, spray drying) and physical processes (laser ablation, microwave plasma synthesis and inert gas condensation). One of the concerns in all those techniques was the control of agglomeration, because an agglomerated powder was of little benefit during densification as coarsening prevails over sintering. It was well known that, chemically homogeneous single-phase powder with well-defined particle size distribution, as the starting material was must to achieve the desired properties in the sintered bodies.

In this paper, several chemical processes developed at National Metallurgical Laboratory, Jamshedpur for the synthesis of nano-crystalline ceramic powders are reviewed.

SYNTHESIS AND CHARACTERISATION

Solution combustion technique

A simple and versatile solution combustion process involving a pyrophoric chemical reaction was used to yield ultra-fine ceramic powders. In this process, clear aqueous solution of metal nitrates was prepared and calculated amount of citric acid was added. Subsequently, liquor ammonia was added to neutralize the pH of the solution at 7.0 and the final pH of the solution was adjusted by adding either dilute nitric acid or liquor ammonia as required. The beaker containing the complexed solution was placed on a hot plate and concurrently heated from the top by the radiation from an infrared lamp. During heating, the solution in the beaker was evaporated and a dried black coloured gel type mass was formed, which upon continued heating suddenly foamed up and caught fire, leaving a finely powdered mass in the form of a very low density sponge. The detailed process is given in the form of a flow sheet in figure 1. The as-prepared mass containing an intimate mixture of amorphous oxides and carbon were highly floppy and 3.5 – 6 g of powder occupied a volume of 250 c.c. The details of the process were also been reported elsewhere [1-3]. The powder was calcined to yield the nano-crystalline powders and also heated at 1230 to 1630°C for 90 minutes in nitrogen atmosphere to yield the nano-crystalline aluminium nitride powder [4]. The chemical pyrophoric reaction technique was also used to prepare a large number of ceramic powders.

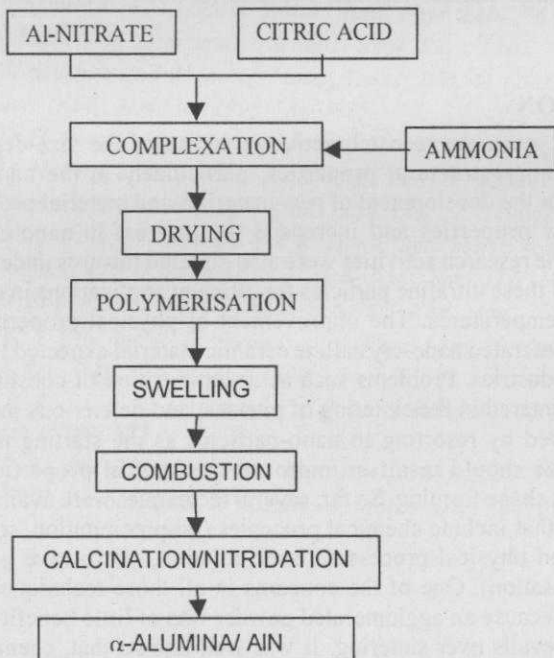


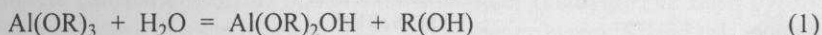
Fig.1 : Schematic of the nitrate-citrate process



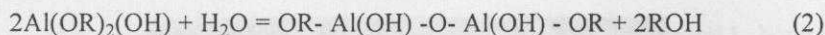
Fig. 2 : Photograph of the as-prepared powders

Sol-gel synthesis of alumina powders

Aluminium-isopropoxide was prepared by reacting aluminium metal with isopropyl alcohol in anhydrous condition and in the presence of trace amount of mercuric chloride and carbon tetrachloride at 80°C. The exothermic reaction generated sufficient amount of energy to maintain the temperature for the completion of reaction. Thus the energy requirement for the alkoxide synthesis was noticed to be negligible. The aluminum alkoxide was distilled out under low pressure (at 10 mm of Hg) and at a temperature between 150 to 250°C. Subsequently, the distilled aluminum alkoxide was hydrolyzed with excess of water at 80-90°C for sufficient time and stirred vigorously. Small amount of acetic acid was added to the hydrolyzed sol and the temperature was maintained at 80-90°C. The stirring was continued and after 3 to 4 h of peptization, a clear sol was prepared. The sol was further aged at 80 to 90°C for 4 to 6h to yield the gel. The hydrolysis and gelation could be explained by the following reactions.



This reaction of hydrolysis proceeded rapidly in presence of catalyst (acetic acid or nitric acid) with further hydrolysatation and subsequently polymerization took place as given below.



Assuming linear polymerization for simplicity, the final gel incorporating n aluminum ions could be formulated as,



The dried gel was rapidly heated for calcinations and desired phase formation. During heating all the organic residues were also burnt out at this stage. The dried gel was ground in high alumina ball mill to get very fine particles of transition alumina, which was calcined at 1200°C to prepare α -alumina powder and again reground. The details of the sol-gel process are schematically shown by a flow sheet in figure 3. During phase transformation to alpha alumina at 1200°C , considerable amount particle size coarsening took place. To reduce this coarsening, the seeds of nano-metric α -alumina particles (5wt%) were added to act as nucleation sites, which decreased the transformation temperature. The seed added sol was converted to gel, which was subsequently calcined to yield α -alumina powder.

It was noticed that the removal of solvent was a major problem in the sol-gel process. Therefore, we have adopted numerous drying techniques and processes to synthesize ultra fine alumina powder with improved physical and chemical characteristics and those techniques were direct decomposition of alkoxide, emulsification and spray drying process.

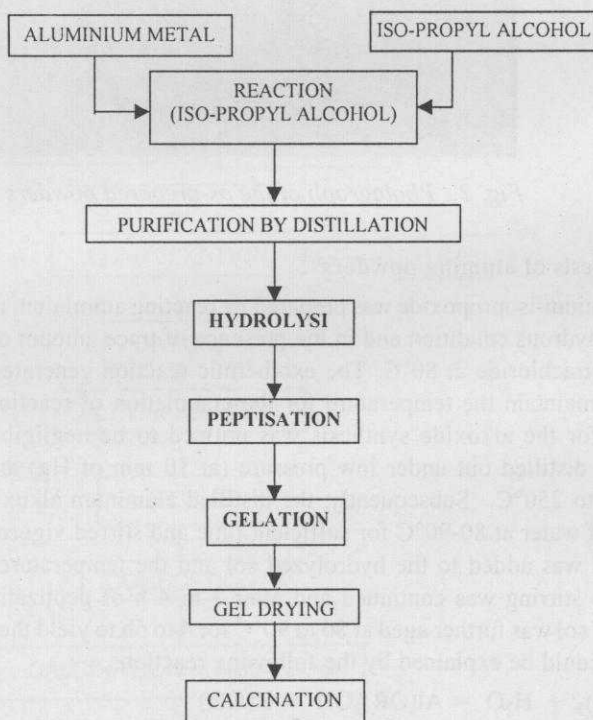


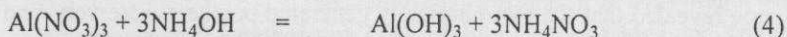
Fig. 3 : Schematic of the Sol-Gel process

In the solution combustion technique, the dried semi-solid gel type mass was collected prior to decomposition for all the pH's and investigated by the thermal analyzer (TG/DTA). The as-prepared powders were also calcined at various temperatures for a fixed period of 1h. The calcined powders were subsequently characterized by TEM and XRD analyser. Carbon-coated copper grids were used to support the ultrasonically dispersed calcined powders for the TEM observations and nickel filtered Co-K α radiation was used for the X-Ray diffraction analyses of the synthesised powders.

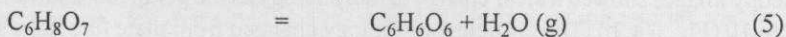
SOLUTION COMBUSTION TECHNIQUE

During heating, the solution containing aluminium nitrate-citric acid-ammonia transforms into a semi-solid black coloured gel type of mass, which on further heating auto-ignites to yield a charred mass. The appearance of the combustion decomposition is evident from the thermal analysis (TG/DTA) of the dried mass collected prior to pyrophoric decomposition, which showed an exothermic peak at 288.41°C with a concurrent weight loss of » 85%. A typical TG/DTA plot for the sample obtained for pH=10 is shown in figure 4. We observed that the combustion wave propagation from one point to the end point of the reactant and the combustion reaction completed within a few seconds. Therefore, this solution combustion process could be termed as solution combustion decomposition (SCD) technique. It is understood that the exothermic heat generated in this combustion technique is governed by a thermally induced redox reaction involving citrate and nitrates anions in the precursor, where, the nitrate ions act as oxidant and the citrate ions act as reductant [6]. The thermal analysis of the citric acid was investigated by Hon et al. [7] and they reported the appearance of one endothermic peak at ~300°C and one exothermic peak at ~470°C. The appearance of the exothermic peak at 288.41°C for sample prepared at pH=10 clearly indicated the nitrate-citrate redox reaction in this system.

The nitrate ions of NH₄NO₃ formed during addition of liquor ammonia by the following reaction



and the citrate ions took part in this redox reaction. During heating the citric acid melted at 173°C and converted to aconitic acid by the reaction



The aconitic acid then yielded itaconic acid (C₅H₆O₄ and CO₂) on further heating. The itaconic acid (m.p. 166°C), which upon continued heating underwent polymerization and swelled with the de-carboxylation releasing CO₂. The Al-hydroxide formed in the reaction 4, remained dispersed within the polymerized matrix and the heat liberated during exothermic redox reaction involving ammonium nitrate-citrate anions was sufficient for the complete calcinations of the compounds and water removal. The flash pyrolysis of NH₄NO₃ was known to yield nitrogen, H₂O and nascent oxygen [8] and this excluded the possibility of formation of NO_x and HCN species in the process, which made the process less hazardous. The decomposed mixture after the completion of exothermic reaction was found to be a foamy mass and 3.5 g of the powder was observed to occupy a volume of 250 cm⁻³.

The X-ray diffraction analyses of the as-prepared powder showed that the as-generated powders were amorphous in nature (Fig. 5a), which required to be calcined at elevated temperatures to yield α -alumina powder (Fig. 5d). A clear transition from amorphous state to nano-crystalline state could be noticed in the X-ray diffractogram of the powder calcined at 600°C (Fig. 5b), where small and broad peaks started appearing at $2\theta = 48^\circ$ and at $2\theta = 67^\circ$. The amorphous alumina powder after calcination at 700°C transform to γ -alumina and δ -alumina powder (Fig. 5c) and finally converts to α -alumina powder above 1100°C. Single-phase α -alumina powder was prepared after calcination at 1200°C for 1h. Since all the organic materials and ammonia related compounds are either volatilized or burnt off during calcination at elevated temperatures, the purity of the alumina powder could be controlled by the purity of starting chemicals.

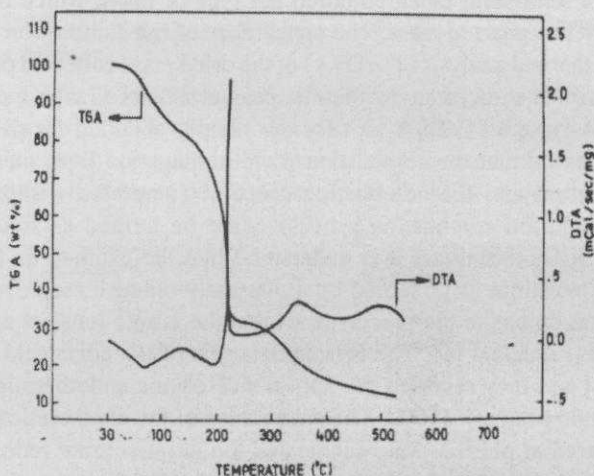


Fig. 4 : TG/DTA plot of the citrate precursor heated at 10°C/min (pH=10)

The microstructural investigations carried out by the transmission electron microscope revealed that the pyrophorically generated powders were very fine and sub-micrometer in size at least in one direction. A few representative TEM images of the alumina powder prepared at different pHs are shown in figure 6. The transmission electron microscopy images showed a clear change in morphology as the pH of the solution increases from 2 to 10 (Fig. 6 a, b). The particle morphology changed from plate like flake structures (observed at low pH of 2) to desegregated fine particulates at pH = 10. The citrate-nitrate stoichiometry in the precursor composition was the primary factor in controlling the reaction enthalpy in such a redox reaction [10]. At low pH, the increase of nitrate ions decreased the enthalpy of the exothermic reaction and the slow rate of decomposition of the precursor enabled the alumina particles to come closer to form flakes. Whereas, the sharp decomposition of the precursors at pH = 10 associated with a very sharp DTA peak led to generation of large amount of gases, which desegregated the precursor into ultrafine powders dispersed within the foamy structure. This pyrophoric process could be used for the generation of a large number of ceramic oxides that included YSZ, aluminates, cuprates etc. Ultra fine alumina powders could also be prepared using ethylene glycol and urea instead of citric acid (Fig. 7).

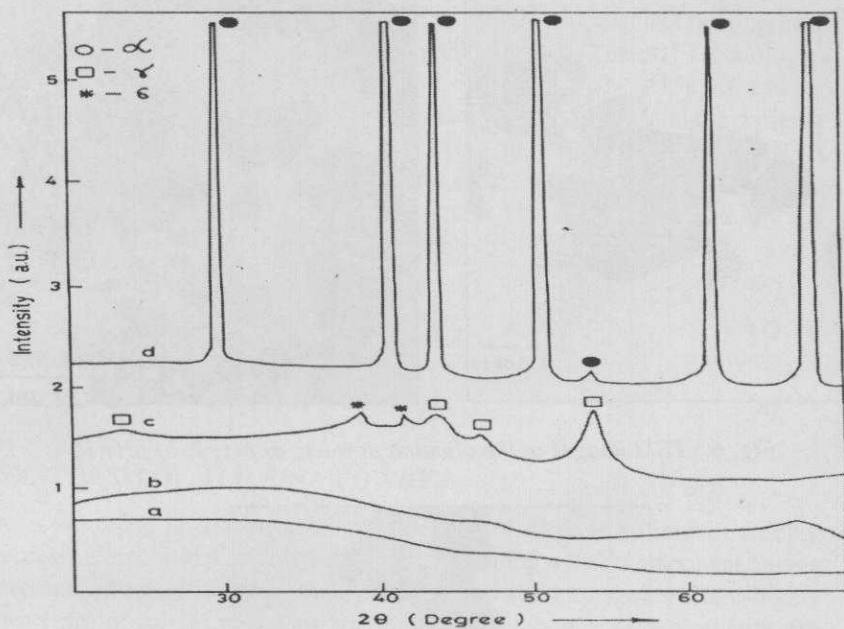


Fig. 5 : XRD patterns of the alumina powder:

a) as-prepared and after calcination at: b) 600°C, c) 700°C and d) 1100°C

SYNTHESIS OF AlN POWDERS

Aluminium nitride is an excellent electronic substrate material with high thermal conductivity comparable to that of BeO and also has excellent dielectric properties, good thermal compatibility with Si, high temperature machinability, and high mechanical strength and non-reactivity. The commercial AlN powders are normally synthesized by either carbothermal [11] or direct nitridation of Al [12]. The decomposition of organometallic compounds [13], reduction and nitridation of Al-polynuclear complex [14], chemical vapour decomposition [15], plasma synthesis [16] and self-propagating high temperature synthesis [17] are the other important processes. We have synthesised a new precursor for the carbothermal reduction and nitridation of alumina using the chemical pyrophoric reaction described above, in which the inorganic material was trapped in the polymer matrix and during pyrophoric decomposition the polymer was charred and the nano-sized Al₂O₃ particles produced were uniformly dispersed in the carbon matrix. The carbon content in the hygroscopic precursor mixture was estimated to be 50% by weight. The thermo gravimetric (TG) and differential thermal analysis (DTA) of the pyrophorically synthesised precursor in flowing N₂ atmosphere up to 1573 K indicated that the decomposition was associated with 3 steps of weight losses [Fig. 7]. Processes that might account for the weight loss between room temperature and 1073 K were due to desorption of water and hydroxides and removal of volatile organic materials. The weight loss at ≈ 1273 K (Point A in figure 8) was due to formation of γ-AlON, which was observed in XRD analyses of the samples nitridated in this temperature region and the formation of AlN was indicated by the weight loss at ≈ 1473 K (Point B in figure 8).

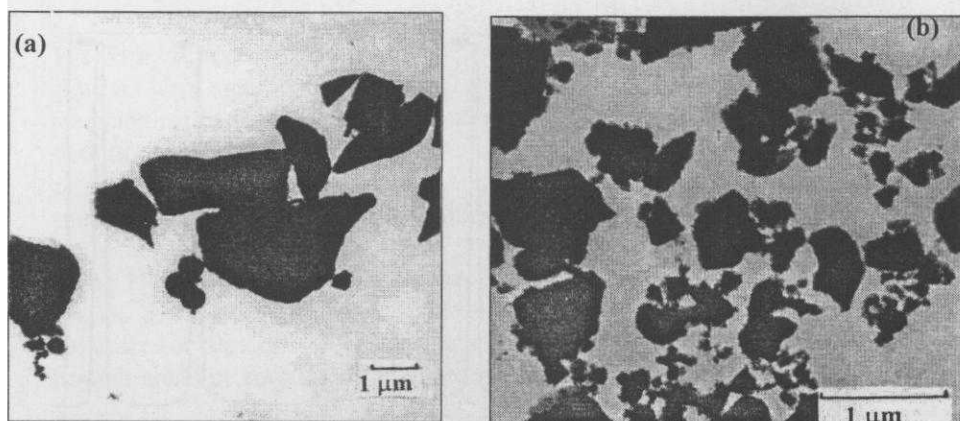


Fig. 6 : TEM images of the alumina powder: a) pH=2, b) pH=10

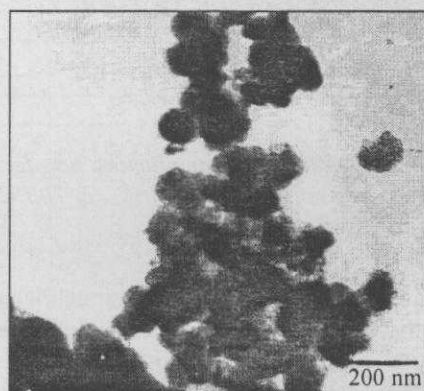


Fig. 7 : TEM image of the alumina powder prepared by the glycol-urea route

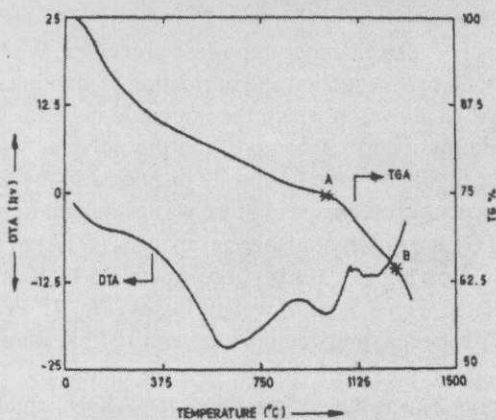
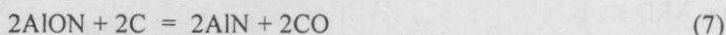
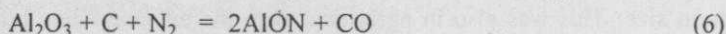
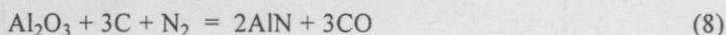


Fig. 8 : TG/DTA plot for the pyrophorically generated precursor in nitrogen

The XRD analyses of the precursors nitrated at various temperatures ranging from 1503 to 1903K for 90 minutes in flowing N₂ in a graphite furnace (Thermal Technologies Inc. USA) and decarburised at 973 K indicated the formation of AlN at 1503 K and the complete conversion above 1673 K. The X-ray diffractograms also indicated the presence of a considerable amount of γ -alumina and γ -AlON in the temperatures below 1673 K. A typical XRD pattern of the single phase AlN powder synthesised at 1773 K is shown in figure 9. The presence of AlON in the low temperatures between 1503 K and 1603 K clearly indicated the nitridation reaction to proceed in the following manner.



The complete reaction can be written as,



SOL-GEL SYNTHESIS OF ALUMINA POWDER

The term sol refers to a suspension or dispersion of discrete colloidal particles, while a gel represents a colloidal or polymeric solid containing a fluid component having an internal network structure wherein, both the solid and fluid components are highly dispersed. Two types of sol-gel processes are reported in literature. In one process, the cations first form a sol of hydroxides and the discrete colloidal particles slowly coalesce together to form a rigid gel. Since the particles are very fine, these gels can be calcined at much lower temperatures than the conventionally derived powders to obtain a homogenous product. The method is however limited to two component systems because of the solubility products of the alkoxides. In other process, the cations are either complexed with organic acids (viz., citric acid) which undergoes subsequent polymerization leading to gel formation or made to react with each other through the reactive groups (viz., ethoxy- or methoxy-) to form long chain compounds and subsequent gel formation. In the sol-gel process atomic level mixing of the constituents occur leading to formation of single-phase products much more easily than by other processes. Varying the precursors, solvent, pH of the sol, calcination temperature and processing environment, the purity, microstructure and properties of the product can be controlled. The sol-gel process for production of alpha alumina powder was developed by B.E.Yoldas [18], where, aluminum alkoxide was hydrolyzed with excess amount of distilled water at 80 - 90°C for sufficient time and stirred vigorously. Then the prepared sol was peptized with small amount of either acetic acid or HNO₃ or HCl and subsequently aged to form a transparent gel. The gel on subsequent calcination gives ultra fine powders of alpha alumina. The alkoxide based sol-gel process also suffers due to high cost of the starting organometallic compounds and considerable amount of particle coarsening when nano-metric gel was calcined to form alumina, which no longer remained nano sized.

We have developed the alkoxide-based sol-gel, in which the more than 90% alcohol was recovered to reduce the cost of production. The chemical analyses of the prepared alkoxide showed a purity >99.96%. Whereas, the alumina powder prepared by the calcination and grinding techniques showed induction of impurities. Therefore alternate processing of the sol and gel was adopted to avoid the grinding steps and increase the

purity of the final powder. The XRD analyses of gel dried at different temperatures (100-500°C) showed extensive line broadening, which indicated the crystalline sizes were of the order of 10 nm. Typical XRD pattern of the gel dried at 100°C is given in figure 11. The SEM micrograph of the said powders revealed that the particles sizes vary from submicron sizes to 50µm and the shapes of the particulates were irregular. These particulates when studied by TEM exhibited the morphology of nano-structured agglomerated particles (Fig. 12), which suggested that though the particulate sizes were in the micrometer range, the crystallites present within those particulates were nanometer in size. This was also in agreement with the extensive line broadening noticed during XRD study.

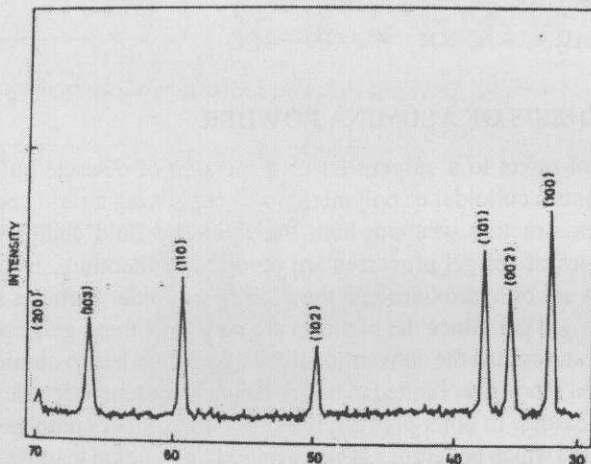


Fig. 9 : XRD pattern of AlN powder prepared at 1500°C



Fig. 10 : TEM image of AlN powder prepared at 1630°C

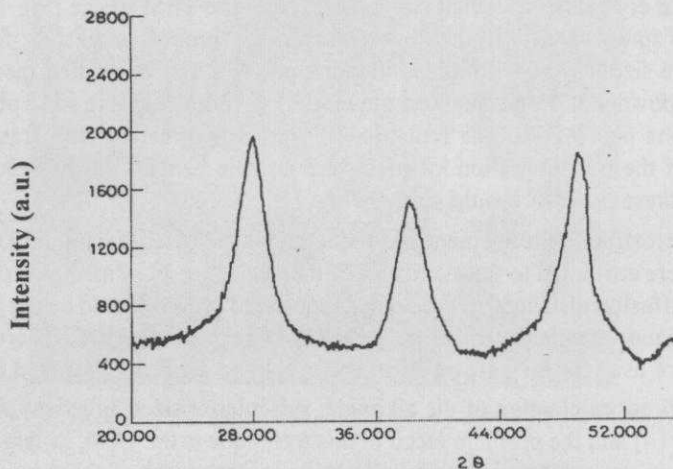


Fig. 11 : XRD pattern of alumina gel dried at 100°C

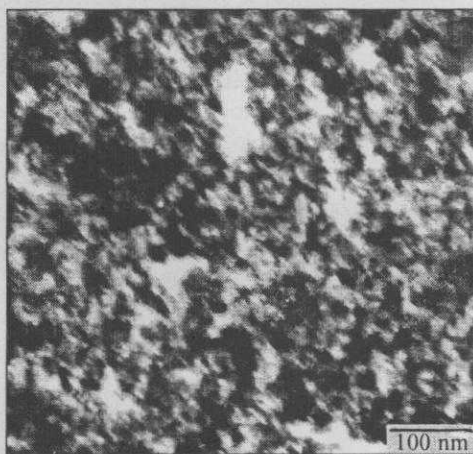


Fig. 12 : TEM image of the alumina gel dried at 100°C

From the XRD patterns, it was found that the dried gel on calcination at 1200°C showed 100% conversion to alpha phase and the diffraction line also become sharper indicating increase in crystallite sizes. The SEM investigations of the powder revealed the morphology of non-spherical irregular fragmented crystal/ particulates with wide range of particles sizes due to particle coarsening, which was observed from the decrease of X-ray line broadening.

As mentioned earlier, the seeding with nano-sized α -Al₂O₃ powder was investigated to improve the chemical and physical properties of the particles. The TG/DTA experiments of the seed added gel revealed the phase transformation temperature at 1030°C, indicating a decrease of 170°C with the seeding, and the incubation time is also reduced from hours to a few minutes. The addition of seed not only lowers the phase transformation temperature

also control the crystallite sizes that can be seen from the TEM image (Fig. 13). The X-ray diffraction lines were noticed to be comparatively broader indicating formation of finer crystallite sizes in the seed added alumina powder. The controlled morphology of the α -alumina powder in the seeding technique was known to be due to solid phase epitaxy growth on alpha phase [19]. The reduction of the transformation temperature and the acceleration of the transformation kinetics were notable benefits of the seeding. It was expected that these powders would sinter below 1200°C [20].

The microstructure refinement and reduction of the α -Al₂O₃ sintering temperature to <1200°C were attributed to the avoidance of the development of microstructure and the reduction of diffusion distance [20]. Though nano-sized powder could be prepared by the seeding technique, the shapes of these particles were non-spherical. Therefore, other techniques were used for the generation of spherical powders and discussed below.

In the direct calcination of the alkoxide, sub-micron sized spherical powders was prepared (Fig. 14) and the problem faced in this technique is the yield, as large portion of the Al-oxide vapour generated during calcination, escaped out of the furnace. Another drawback of the route is the high cost of production due to non-recovery of alcohol and low yield. Only advantage is that this route could produce uniform, spherical and high purity powders. In emulsification technique, nearly spherical and fine alumina powders were prepared (Fig. 15 a, b). The TEM and SEM images revealed that the shape of the droplets formed during emulsification was the final shape of the calcined particles. Therefore, the control of droplet morphology is an important factor in this method. A large numbers of ultra fine crystals within these calcined particles were also noticed. From the several techniques used for emulsification, the oil emulsification is found to give better powder in terms of size and shapes (Fig. 15b).

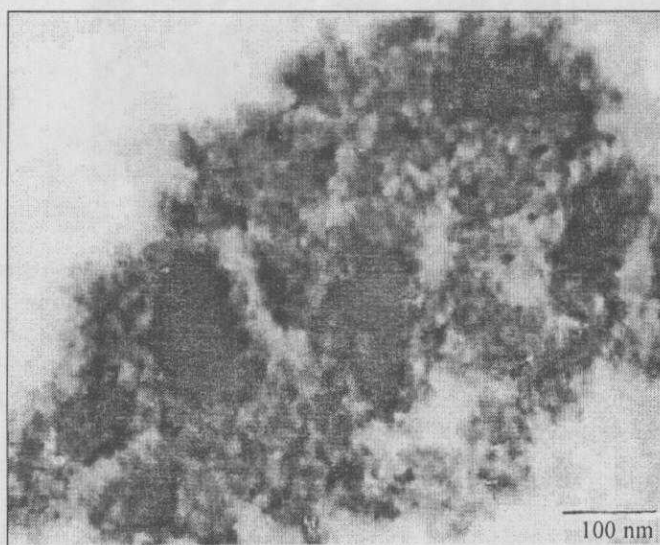


Fig. 13 : TEM image of seeded alumina powder

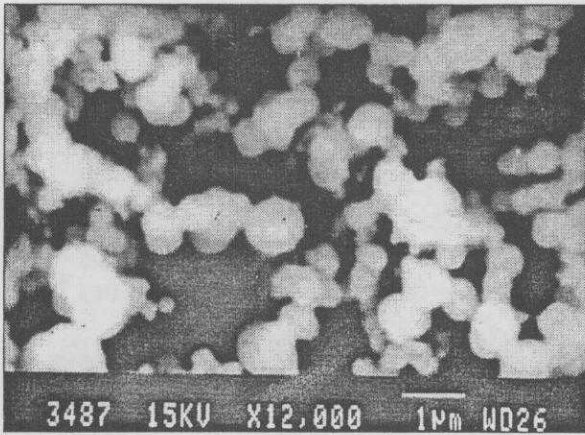
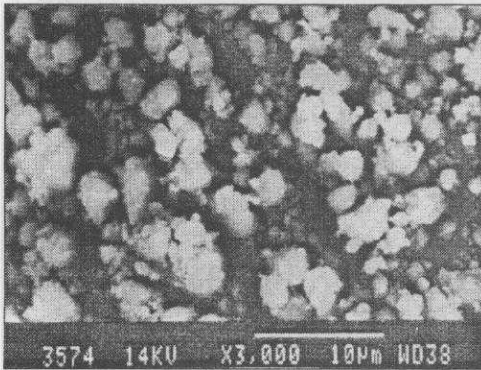
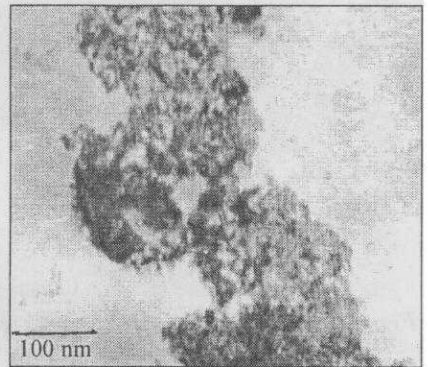


Fig. 14 : SEM image of the alumina powder prepared by direct calcination route



(a)



(b)

Fig. 15 : Alumina powder prepared by the oil emulsification technique: a) SEM image and b) TEM image showing the large number of particles within the calcined particles

The SEM and TEM images showed that spherical and hollow alumina powders could be prepared using spray drying technique by changing the sol characteristics (Fig. 16). It was noticed that if the sol was viscous and the droplet sizes were big, it resulted in the formation of hollow spheres. Using finer droplets of low viscous sol solid spheres could be prepared. These spherical alumina powders also found to be polycrystalline in nature containing nano-sized alumina crystals (Fig. 17). As-prepared spray dried powders were boehmite and on calcination it converted to α -alumina powder, which remained spherical and free flowing. During calcination, the hollow spherical alumina powders were observed to convert in the ring shaped morphology, which could be used as nano-filters. The average particle size of the spray-dried powder was found to be $\sim 10 \mu\text{m}$. These powders were directly used for plasma and thermal spray coating on steel substrate. A few SEM images of the coated surface is shown in figure 18.

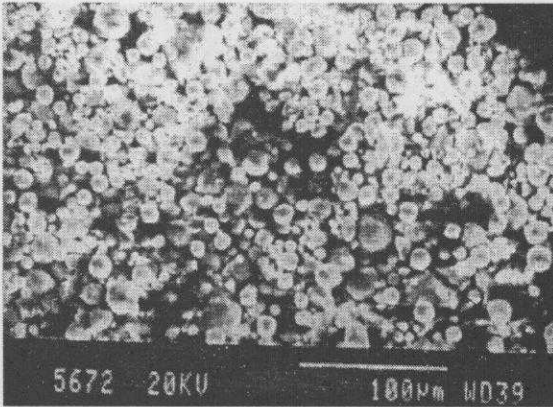


Fig. 16 : SEM image of the spray dried powder showing spherical morphology

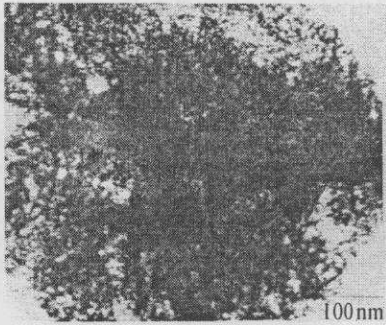


Fig. 17: TEM image of the spray dried powder showing nano-crystallinity

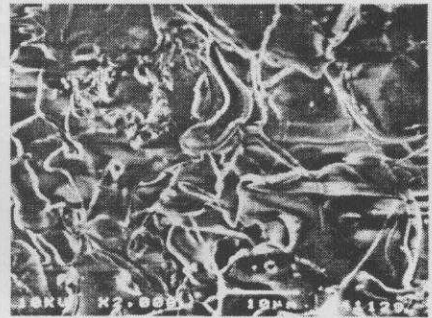


Fig. 18 : SEM image of thermal spray coating on stainless steel

CONCLUSIONS

A systematic investigation on the synthesis of nano-crystalline alumina powder by a chemical pyrophoric reaction using ammonia-citric acid route and by varying the pH of the precursor solution is carried out. The pH of the precursor solution plays an important role in controlling the morphology of the synthesised powder due to increase of nitrate ion concentration at low pHs. The sluggish decomposition of the precursors at low pH (2) yielded flaky powders, whereas, the rapid decomposition at high pH =10 produced fine desegregated powders. The as-prepared amorphous powders yielded the nano-crystalline alumina powder after calcination at elevated temperatures. A new precursor for the synthesis of nano-crystalline AlN powders has been developed. In this process, single phase AlN powder has been prepared at ≈ 1673 K. Particle sizes are observed to be less than 100 nm. Systematic studies on the preparation of nano-crystalline alumina powders by an economically viable sol-gel process were carried out. Several processes were developed to prepare spherical powders, which could be used directly for spray drying on industrial components.

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