Reactive Plasma Synthesis of Nanocrystalline Ceramic Oxides

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Abstract. Reactive plasma synthesis is an attractive route to synthesize nanocrystalline materials. A 40 kW DC non-transferred arc plasma reactor has been designed and developed in our laboratory for synthesis of nanocrystalline materials. The main components of the plasma reactor include a 40 kW DC plasma generator or plasma torch, water-cooled reactor segment, product collection facility, DC power supply, cooling-water system and exhaust gas vent. The system has been used to synthesize nano-crystalline oxides of aluminium, titanium and zirconium. Aluminium metal powder was used as the starting material to synthesize alumina. The hydrides of Ti and Zr were used as the precursor for synthesis of nanocrystalline titania and zirconia respectively. The precursor powders were injected into the thermal plasma jet and were allowed to react with oxygen injected downstream the jet. The precursor powder particles were oxidized ‘in-flight’ to form nano-sized powder of the respective metal, which deposited on the walls of the reactor and collector assembly. Various analytical tools were used to characterize the products.

1. Introduction

Thermal plasma technology is being increasingly applied to variety of materials processing applications. This technology has been successfully applied to synthesize nano-crystalline ceramic oxides. Ultrafine oxide powders of specific ceramic materials are also used for catalytic applications. The conventional method of producing fine oxide powders involves controlled precipitation and pyrolysis of suitable salts [1]. The main limitation of high temperature decomposition route is the evolution of environmentally unacceptable and corrosive gas. Controlled precipitation of hydroxides from solutions of nitrates, sulphates or other salts followed by thermal treatment is another method. This method involves large volume of solutions also calcination step can induce grain growth. Nanocrystalline ceramics oxides have also been synthesized by sol-gel method. The sol gel method is however limited to oxides only. Further, it involves a large quantity of solution and also longer processing time.
Thermal plasmas, by virtue of their inherent potential, are effective media for the synthesis of nanophase materials.[2,3] High temperature gas phase chemistry in the plasma environment provides an attractive route to synthesize a variety of ceramic materials. Thermal plasma processes are characterized by high enthalpy, high temperature and high reactivity, which make them versatile. The high quench rate associated with the process suppresses grain growth resulting in ultrafine particles. The processing time is relatively short, compared with other competitive techniques. The present paper deals with preparation and characterization of nano-crystalline oxides of aluminium, titanium and zirconium.

2. Experimental setup
The plasma reactor consists of a double walled water cooled reaction chamber. At the top a flange mounted 40 kW DC plasma torch is used as the plasma source. This flange also has provisions for injecting reactive gases and shield gases at desired positions to enhance the reaction. The reaction chamber is mounted on a water cooled chamber into which the reacted materials in vapour form enter for sudden expansion and cooling resulting in nano sized powder. The fine powder will get deposited to the side walls of the chamber, which can be removed later. Suitable filter assemblies and exhaust systems are also incorporated in the system. Temperature along the length of reactor can be monitored using thermocouples. The control console houses all controls and indicators for operating parameters of plasma as well as the cooling water for reactor. Proper filter and exhaust is attached to the system. Schematic diagram of the experimental setup is shown in figure 1.

![Schematic diagram of the experimental setup](image)

Fig. 1. Schematic of Plasma Reactor for synthesis of Nanocrystalline Ceramic Oxides
1. Plasma Torch  2. Reaction Chamber  3. Collection Chamber  4. Exhaust system  
5. Control Console  6. Power Supply  7. Cooling water circulator  8. Gas supply  9. Powder feeder

3. Experimental Procedure
Powder of aluminium, titanium hydride and zirconium hydride were used as feed stock powders. The powder was sieved using standard test sieves to get 38-75 micron size powder for experiments. Synthesis of nanocrystalline ceramic oxides has been done using a 40 kW DC non-transferred arc plasma torch based reactor system. The powder was injected into the plasma jet by means of a volumetric turn table powder feeder. Oxygen was used as the reactive gas and was injected in to the reaction chamber at radial distance of 50mm around the flame through equi-spaced shield gas holes.
The feed stock powder was injected into the plasma after establishing a stable flame. The powder particles melt and vaporize and the molten droplets and the vapour react with oxygen forming ceramic oxides. The operating parameters were optimized to melt and evaporate the powder. The vapour then reacted with the shield gas was then quenched to form fine nano crystalline ceramic oxides. The powder gets deposited at the cold boundary of the reactor walls and was later taken out. Typical operating parameters are given in Table 1.

| Parameter                     | Operating range |
|-------------------------------|-----------------|
| Power input (kW)              | 12-16           |
| Primary Plasma gas (Argon) LPM| 25-30           |
| Secondary Plasma gas (Nitrogen) LPM | 1-3     |
| Powder Carrier gas (Argon) LPM | 10-15         |
| Shield gas (Oxygen) LPM       | 30-40           |
| Powder flow rate (g/min)      | 2-5             |

4. Results and discussion

4.1 Nano-crystalline TiO₂

Phase structure of the synthesised powder was ascertained by X-ray powder diffraction technique. X-ray powder diffraction patterns were recorded using a Ni-filtered copper Kα radiation. Diffraction pattern of a typical sample of plasma synthesized titanium dioxide is shown in Fig.2. It is evident from the figure that the precursor powder is completely converted into titanium dioxide. The average particle size, calculated using Scherrer formula, gave an average value of 20 nm. The diffraction pattern clearly shows the presence of both the metastable anatase phase as well as the thermodynamically stable rutile phase. Anatase phase is seen to be the major fraction (more than 70%) of the synthesized powder. Formation of metastable phase is not uncommon in plasma processing [4]. This is due to the high quench rate associated with the process. Thermal treatment of the powder at 700°C resulted in the conversion of anatase to rutile.

Process parameters had a significant effect on the extent of conversion of precursors to the oxides. In particular it was observed that the input power to the plasma torch, feed rate of the precursor powder and the reactive gas concentration strongly influenced the in-flight oxidation process. It was found that when the process was carried out at 10 kW and lower input power, the product was mixed with a large fraction of the unreacted material. This is due to the fact that at lower power to the torch, the plasma temperature is lower and therefore, results in incomplete conversion. Similarly, large feed rate of more than 10g/min of the precursor powder resulted in incomplete oxidation. Complete conversion of the metal/hydride powder to nao-phase oxide material was possible above 16 kW input power and a feed rate of 5 g/min.

Figure 3 shows the SEM photograph of synthesized Titanium oxide and Figure 4 shows the TEM photograph of synthesized particles. The SEM picture shows clusters of nano-particles, which are clearly resolved into individual nao-sized particles.
Fig. 2 Typical X-ray diffraction pattern of plasma synthesized TiO$_2$

Fig. 3 SEM photograph of a typical sample of plasma synthesized titanium oxide showing clusters of nanoparticles.

4.1 Nano-crystalline aluminium oxide

Figure 4 is the scanning electron micrograph (SEM) of a typical sample of alumina powder collected from the main chamber of the reactor. It is seen that all the particles are below 80 nm and that about 70% of the particles are below 30 nm. Individual particles are not discernible, but agglomerates consisting of nanosized particles can be seen. Transmission electron micrograph (TEM) of a typical sample is shown in figure 4. The clusters are resolved to individual particles with size ranging from few nanometers to about 30 nm. Spherical morphology of the particles is also evident from the figure.
The first step leading to the alumina formation is the interaction of molten droplets of aluminium with oxygen. Oxidation to aluminium to alumina is highly exothermic, the standard enthalpy of formation of aluminium oxide from the elements being -1675.7±1.2 kJ mol⁻¹ [5]. The enthalpy of formation increases with temperature and is -2243.73 kJ mol⁻¹ at 300 K. The heat released during oxidation, coupled with the high temperature in the plasma medium leads to the dissociation of aluminium oxide and formation of sub-oxides of aluminium which recombine with oxygen to form nano crystalline aluminium oxide.

![Fig. 3 SEM photograph of a typical sample of plasma synthesized aluminium oxide](image)

Fig. 3 SEM photograph of a typical sample of plasma synthesized aluminium oxide

![Fig. 4 TEM photograph of a sample of plasma synthesized aluminium oxide showing resolved individual nanoparticles.](image)

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5. Conclusions
Nanocrystalline ceramic oxides have been synthesized by reactive thermal plasma synthesis in an indigenously developed thermal plasma reactor. Ti metal, Al metal, TiH2 and ZrH2 powders were used as the precursor materials, which were injected into the plasma jet and allowed to react with oxygen introduced as a reactant gas to form nano-sized powder. Results of electron microscopy revealed that more than 70% of the particles were below 30 nm.

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