Phase controlled structure formation of the nanocrystalline zirconia using thermal plasma technique

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Abstract. Nanocrystalline ZrO₂ powder was synthesized by dc transferred arc thermal plasma reactor by homogeneous gas phase condensation mechanism. ZrO₂ is an oxide ceramic with a high melting point, good chemical resistance and high mechanical strength. When doped with certain oxides, ZrO₂ shows high ionic conductivity. ZrO₂ is also recognized as a superior thermal barrier material. Thermal plasma synthesis of oxide nano materials shows pressure dependent crystalline phase and crystallite size. The X-ray diffraction analysis clearly shows that as the ambient oxygen gas pressure increases from 100 Torr to 1000 Torr the abundance of tetragonal phase goes on increasing. The morphology of the as synthesized ZrO₂ powder was found to be spherical and independent on the ambient gas pressure as seen from the Scanning Electron Microscopy studies. The specific surface area of powder was calculated using the nitrogen gas adsorption Brunauer, Emmett, Teller surface area analysis technique and found no much variation.

1. Introduction

Nanometric ZrO₂ (Zirconia) particles are of technologically important class of materials with wide range of applications [1]. Zirconia occurs in three different polymorphic forms: monoclinic (M), Tetragonal (T) and cubic (C) phases. The monoclinic phase is thermodynamically stable at temperature T< 1170 °C, and transforms into the tetragonal phase above 1170 °C, at about 2370 °C it further transforms into the cubic phase [2]. These high temperature phases are of technological importance. Normally these high temperature phases are not stable at room temperature. To stabilize them at room temperature one needs to add some stabilizers such as yttria, calcia or magnesia in zirconia. Several studies have examined the stability of zirconia particles; a general conclusion might be that the observed phase stability largely depends on the techniques used to produce the materials and the size of the resulting particles [3].

The 8 mol% yttria stabilized zirconia is used as an electrolyte in solid oxide fuel cells [4]. Also it is used as an oxygen sensor [5]. Tetragonal zirconia exhibits high mechanical strength and toughness. Tetragonal zirconia is used as ceramic biomaterials, high temperature ceramic, used in high temperature turbine engines. Tetragonal zirconia exhibits high mechanical strength and toughness. The tetragonal zirconia is one of the most important thermal barriers coating material because it has low thermal conductivity and a thermal expansion coefficient that is well matched with that of the nickel alloys used in high temperature turbine engines. Tetragonal domains are also useful as ion conductors in high temperature sensors and in catalytic processes [3]. Thus the phase controlled study of zirconia becomes necessary. In this article, we report the synthesis of metastable tetragonal zirconia.

We found that the metastable zirconia structure can be formed without addition of a stabilizing dopant. The tetragonal phase in zirconia synthesized by dc transferred arc thermal plasma reactor (DCTATPR) was found to be dependent on operating parameters i.e. ambient oxygen gas pressure.
2. Experimental Procedure
In a DCTATPR 99 % pure zircaloy, in the form of sheets were placed over water cooled graphite anode and was melted and evaporated with the help of thermal plasma operated at 7-9 kW power in the pure oxygen ambient. As a result of homogeneous gas phase condensation, tiny particulates of zirconia were found to deposit over the water-cooled hemispherical dome. The collection criterion was so chosen that the particulates, before their deposition over the hemispherical dome, could travel almost equal distances from the plasma zone in order to suffer almost equal number of collisions. Sufficient time was allowed for the chamber to cool down to the ambient temperature after each synthesis run. This helped in settling down the particulates over the reactor chamber walls. ‘Figure 1’ shows the schematic of the DCTATPR. The as-synthesized zirconia powder was collected from the dome and characterized with the help of X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The details of the basic working mechanism for the system have been given in reference [6].

3. Results and discussion
3.1. X-Ray Diffraction Studies
‘Figure 2(a)’ shows the XRD pattern of the powders synthesized at different ambient oxygen gas pressure viz 100 Torr, 250 Torr, 500 Torr, 760 Torr, 1000 Torr along with the standard XRD patterns of, monoclinic ZrO$_2$, tetragonal ZrO$_2$ and hexagonal graphite. The most intense peak observed at $2\theta = 28.2^\circ$ corresponds to the (111) plane of monoclinic ZrO$_2$; whereas the peak observed at $2\theta = 30.2^\circ$ corresponds to (111) plane of tetragonal ZrO$_2$. These peaks were found suitable for comparing the relative abundance of two phases in the as synthesized nano ZrO$_2$. The XRD analysis clearly shows that as the ambient oxygen gas pressure increases from 100 Torr to 1000 Torr, the purity of tetragonal phase increases. The zirconia synthesized at 100 Torr shows a monoclinic phase, while those synthesized at other operating pressures (250 Torr to 1000 Torr) show the mixed phases of monoclinic and tetragonal zirconia. It is also worth noticing that the relative concentration of tetragonal phase with respect to the monoclinic phase increases with increasing ambient. Moreover abundance of the tetragonal phase increases dramatically with increase in ambient pressure in reaction chamber from 100 Torr to 500 Torr and remains fairly constant for the pressure above 500 Torr. The intensity of the two peaks (‘M’ for monoclinic and ‘T’ for tetragonal ZrO$_2$) have been shown together for the samples synthesizes at the different operating pressures from 100 Torr to 1000 Torr in ‘figure 2(b)’. It is very interesting to notice that the relative intensity of the two phases of the zirconia changes systematically for these samples. The intensity of the peak ‘T’ shows an increase with increasing operating pressure,
whereas the intensity of the peak ‘M’ shows an exactly opposite trend. The relative intensity ratio defined by \( F = \text{Intensity of ‘T’/ Intensity of ‘M’} \) is then plotted in ‘figure 2(b)’ to indicate the abundance of one phase relative to the other. A small peak observed at \( 2\theta = 26.5^{\circ} \) corresponds to the (111) plane of hexagonal graphite which is used as a substrate holder and enters into the as synthesized product as a contaminant.

A steady increase in this ratio, from 0.15 to 4.54 indicates that the ambient pressure during the synthesis, imparts a strong control over the crystalline phases. From ‘figure 2(a)’ it is also seen that a higher (above 500 Torr) ambient pressure helps in the formation of tetragonal, whereas lower (100 Torr) ambient pressure favors the growth of monoclinic.

**Figure 2(a).** XRD spectra for ZrO\(_2\) prepared by thermal plasma and **Figure 2(b).** Peak intensity ratios of major lines of tetragonal and monoclinic phases determined from the corresponding XRD patterns as a functions of the operating pressure.

The change in the crystalline phase based on the operating pressure in the reactor can be understood from the cluster chemistry in the vapor phase condensation. The process starts from the evaporation of the anode (zircaloy in the present case) as a consequence of the plasma interaction. These vapors fill the space above the anode surface and diffuse out into the plasma zone, followed by the chemical reactions with oxygen, which enters and surrounds the plasma.

Larger supercooling arises, from our observations of the expanded plasma plume, near the substrate as the pressure is decreased. On account of the sub atmospheric pressures the plasma near the boundaries starts deviating from the LTE (local thermodynamic equilibrium) conditions. As a consequence; the temperature associated with the plasma plume also decreases with decreasing operating pressure. The growth occurring at the boundary, at low pressure (100 Torr), therefore, seems to stabilize into the monoclinic phase which is well known low temperature stable phase. The high temperature vapor phase condensation, as in the present case, results from the homogeneous nucleation followed by quenching due to high collision rate.

When the operating pressure in the reactor increases the plasma near the boundaries starts approaching LTE conditions. Hence the temperature near the plasma plume increases. The tetragonal zirconia is a high temperature phase and, therefore, the fraction of tetragonal phase in the powder increases.

### 3.2. Powder Morphology

The morphology of the ZrO\(_2\) synthesized at different operating pressures viz 100 Torr, to 1000 Torr is shown in ‘figure 3’. The average particle sizes and morphology of the as synthesized samples [A to E] inferred from the SEM micrographs and the fraction of the crystalline phases [7], as inferred from the
XRD, is presented in table 1 along with the yield of the powder. It is seen from SEM pictures that the average grains are spherical in shape with average size of 130 nm of all the operating pressure in the present studies. There is no significant change in grain size with change in operating pressure. The specific surface area of powder was calculated using the nitrogen gas adsorption BET surface area analysis technique and was found to be 5.39 m$^2$/gm for 100 Torr, 18.09 m$^2$/gm for 250 Torr and 9.57 m$^2$/gm for 500 Torr of ambient gas pressure. The result of the specific surface area was found to be controlled by the shape and size of the particles.

Figure 3. SEM images of ZrO2 prepared by thermal plasma

Table 1: The particle sizes, morphology, the crystalline phases, specific surface area and the yield of the powder for zirconia synthesized at different ambient gas pressures.

| Nomenclature of the sample | Ambient gas pressure (Torr) | Average particle size (nm) | Crystalline phase | Specific surface area (m$^2$/gm) | Yield of the powder gm/hr |
|---------------------------|----------------------------|---------------------------|-------------------|----------------------------------|--------------------------|
| A                         | 100                        | 150                       | 93.44             | 6.56                             | 12.4276                  | 2                        |
| B                         | 250                        | 130                       | 76.63             | 23.37                            | 13.3687                  | 3                        |
| C                         | 500                        | 130                       | 39.60             | 60.40                            | 22.3655                  | 8                        |
| D                         | 760                        | 130                       | 38.13             | 61.87                            | 11.4528                  | 3                        |
| E                         | 1000                       | 130                       | 38.13             | 61.87                            | 12.0701                  | 4                        |

4. Conclusions
The paper reports the influence of the operating pressure in a dc arc plasma reactor on the formation of crystalline phase of ZrO$_2$. The relative abundances of the tetragonal and monoclinic phases were seen to be affected by the ambient pressure. The tetragonal phase was found to be prominent at 500 Torr and above whereas the monoclinic phase was the major phase at 100 Torr. Moreover, the variation of the ratio of the relative concentration of tetragonal to that of monoclinic was found to increase with the increase in the ambient gas pressure up to 500 Torr and above 500 Torr to 1000 Torr the variation in relative the relative concentration was found to be nearly same. The crystalline phase formation of the as-synthesized ZrO$_2$ is explained on the basis of different oxygen content available at different ambient pressures. The formation of monoclinic clusters is favored at larger supercooling and they act
as nucleating sites for the further growth. A detailed analysis of the reaction products was carried out with the help of X-ray diffraction and SEM investigations.

5. References
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