Synthesis of Nano-ZrO_2 by Reactive Plasma processing

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Abstract. A novel technique, reactive plasma processing was utilized to produce nano-crystalline Zirconia from zirconium hydride. XRD result showed mixture of monoclinic and tetragonal phases. TEM analysis reveals 95% of the particles were in the range 18-23 nm.

Keywords: Nano-crystalline Zirconia, Zirconium hydride, Plasma processing.
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INTRODUCTION

Zirconia exhibits three crystallographic phases: monoclinic, tetragonal and cubic. They are stable from room temperature to 1175˚C, 1175-2370˚C and 2370-2750˚C [1]. Stabilizing the high temperature phases at room temperature in pure zirconia is of fundamental interest in Materials Science. This can be achieved only by synthesis of nano-materials

In this work nano ZrO_2 was synthesized by reactive plasma processing (RPP). It is a novel technique, which takes the advantage of high temperature and high enthalpy of the thermal plasma jet to effect 'in-flight' chemical reactions in the presence of reactive gas to synthesize nano-sized powders of advanced ceramics [2].

PLASMA REACTOR AND SYNTHESIS

The plasma reactor includes a 40KW DC non-transferred arc plasma torch, water-cooled reactor segment, product collection facility, DC power supply, powder feeder, water cooling system, gas feeding system and exhaust gas. The DC non-transferred arc plasma torch is mounted on the reactor, which is a double-walled stainless steel cylindrical vessel 300 mm in diameter and 600 mm in length. The torch electrodes and reactor are cooled by water. The powder is injected into the plasma jet through a side port provided at the anode of the plasma torch. A mixture of argon and nitrogen was used as the plasma gas. The powder feed rate and carrier gas flow rate were monitored and controlled. Details of the reactor set up are described elsewhere [3].

The precursor material used was ZrH_2 powder of 99.8% purity. ZrH_2 powder (38-53μm size) stored in a powder feeder, was injected into the plasma jet by using Argon as the carrier gas. Oxygen gas was introduced 10mm downstream of the exit of the plasma torch. ZrH_2 dissociates to form Zr particles and hydrogen gas in the plasma jet that are subsequently converted to ZrO_2 and water vapor, which escapes along with the exhaust gas stream. The nano-crystalline ZrO_2 thus formed settles on walls of the reactor and collection chamber. The resultant powder was scraped from the walls of the reactor and different segments of the collection chamber and characterized by XRD, TEM and Raman spectroscopy.

CHRACTERIZATION

XRD pattern of the synthesized sample was recorded using Ni- filtered Cu k-α radiation. The crystallite size, D was evaluated based on the Scherrer equation [4].

$$D_{hkl} = \frac{0.94\lambda}{B_{hkl} \cos\theta} \qquad (1)$$

Where λ is X-ray wavelength, B is full width at the half maximum and θ is the Bragg angle.

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RESULTS AND DISCUSSION

X-ray diffraction pattern of reactive plasma synthesized nanocrystalline ZrO_2 is shown in fig.1. It is evident from the figure that the precursor powder (ZrH_2) is completely converted into zirconium oxide, because all the diffraction peaks of the pattern could be indexed to monoclinic or tetragonal phase of zirconium oxide. Based on the relative intensities of the XRD peaks percentage of m-ZrO2 and t-ZrO2 are found to be 56 and 44 respectively. The average crystallite sizes calculated, using Scherrer formula, from (-111) line of monoclinic phase and (101) line of tetragonal phase were 34 nm and 19 nm respectively. It shows that monoclinic phase of zirconia exists in crystallite sizes above 20 nm whereas metastable tetragonal phase exists below 20nm. Raman spectrum of the sample also confirmed the findings of XRD results.

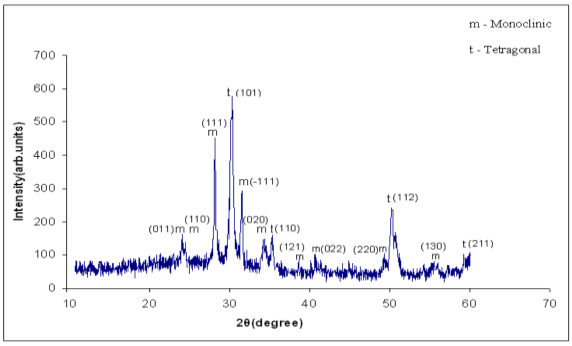

FIGURE 1. X-ray diffraction pattern of reactive plasma synthesized nanocrystalline ZrO_2

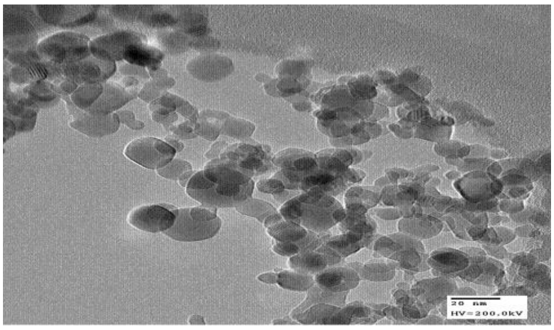

FIGURE 2. TEM photographs of reactive plasma synthesized nanocrystalline ZrO_2

The occurrence of metastable tetragonal phase is attributed to the critical crystallite size effect reported by Garvie [5]. Garvie experimentally showed the existence of a critical size of ~ 30 nm, below which the metastable tetragonal phase is stable and above which the monoclinic phase is stable. The observed phase structure and crystallite size are found to agree with the above report [5].

TEM photograph shown in fig.2 clearly resolves the individual nano particles. It is seen from the figure that 95% of the particles are between 18 – 23 nm. However a few particles below 10nm and above 35 nm are also observed. When zirconium hydride particles enter the plasma jet, they dissociate into Zr and H and the Zr particles melt. The molten droplets of Zr react with oxygen gas leading to the formation of zirconium oxide. This formed zirconium oxide further melts and dissociates into ZrO(g), Zr vapour and oxygen due to the high temperature of the plasma medium and highly exothermic nature of the formation reaction of ZrO_2 [6]. As zirconium vapour and ZrO(g) move downstream, they react with oxygen and form ZrO_2 molecules, which condense on the cold wall of the reactor as nano sized spherical particles. The high quench rate which controls the crystallite growth rate, favours the formation of metastable tetragonal phase as a consequence of critical size effect.

CONCLUSION

Synthesis of nanocrystalline ZrO_2 powder by reactive plasma processing was reported in this work. Zirconium hydride was used as precursor material which was injected into the plasma jet and allowed to react with oxygen to form nano-sized ZrO_2 powder. TEM result clearly shows individual particles in the range of 18-23 nm. The exothermic nature of the formation of ZrO_2 and high temperature of the plasma medium favours the formation of metastable tetragonal phase, which is confirmed by XRD and Raman spectroscopy.

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REFERENCES

1. Shukla, S.; Seal, S. Int. Mater.Rev. 50, 45-64,(2005).
2. M. Vijay, P.V. Ananthapadmanabhan, K.P. Sreekumar, Applied Surface Science 255, 9316–9322, (2009).
3. Ananthapadmanabhan PV, Sreekumar KP, Venkatramani N, Taylor PR. J. Alloys Cpds 70,244, (1996).
4. J.I. Langford, A.J.C. Wilson, J. Appl. Cryst. 11, 102-113, (1978)
5. Garvie.C., J. Phys. Chem. 69, 1238, (1965).
6. P.V. Ananthapadmanabhan, T.K. Thiyagarajan, K.P. Sreekumar, N. Venkatramani, Scripta Materialia 50,143-147, 2004