



Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

Reinforcement of alumina with carbon nano cones and characterization[☆]

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ARTICLE INFO

Article history:

Received 3 March 2019

Received in revised form 17 May 2019

Accepted 20 May 2019

Available online xxxxx

Keywords:

Reinforcer

XRD

SEM

DRS

Crystallite size

Band gap

ABSTRACT

Pure alumina powder is synthesized by solid state reaction method, wherein aluminium nitrate nano hydrate is annealed for 3 h at 1000 °C in muffle furnace. Carbon nano cones, as a reinforcer, are added to pure alumina in different weight proportions such as 0.5%, 2.5% and 4% and annealed at 1000 °C for 3 h in nitrogen atmosphere. The synthesized samples were characterized using XRD, SEM and DRS techniques to estimate crystallite size, interplanar distance and band gap. SEM reveals the surface morphologies of all samples and a rough estimate of crystallite sizes varying from few nm to 15 μm.

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Peer-review under responsibility of the scientific committee of the Exploring Nanostructures for Enhanced Power Conversion Efficiency of Solar Cells Conference.

1. Introduction

The conventional engineering ceramics like zirconia (ZrO₂), silicon nitride (Si₃N₄) and alumina (Al₂O₃) have low density, high stiffness and excellent thermo stability. But their brittleness remains an issue and it prevents them for structural applications [1]. However, working on the improvement of fracture toughness, nano crystalline ceramics has shown normally a meek or at times descent improvement [2–4]. In addition, the concept of tuning the mechanical properties of ceramics by introducing flakes, particulates and fibres as a second phase in the ceramic matrix has become a renowned approach for more than a decade [5,6].

Alumina is a prominent member in the family of engineering ceramics and highly preferred for catalytic support [7–10] in many industrial applications. The other interesting properties such as

high electrical resistivity [11,12], high elastic modulus [13], wear resistance [14–16], high hardness [17], chemical inertness [14] makes it desirable for numerous applications. Various methods and procedures have been discussed in the literature for reinforcement of alumina using carbon nano tubes (CNTs) [18–21], carbon nano fibres (CNF) [22–24] and graphene [25–27]. The uniform dispersion of reinforcing particulates/fibers, the nature of interface between alumina and re-inforcer etc. are the major factors in improving the mechanical properties. It has been shown that the addition of 2 wt% MWCNTs with alumina improved the fracture toughness by 94%, whereas, composite of Al₂O₃-5 wt% CNTs yielded only 65% [28]. Hence it is imperative to confine the concentration of the reinforcing material in the optimal range, and for the present work, we tried in the range of 0–4 wt% of carbon nano cones. In our previous attempt of synthesizing alumina-carbon composites [29], it has been observed that doping alumina with carbon nano cones had a very little impact in showing any predominant changes in XRD and Raman spectroscopy. The expected level of changes in micro level characteristics such as interplanar distance, lattice strain and crystallite size were remained a concern. The extent of deformation caused to the lattice of alumina by carbon nano cones might be meagre in the previous case. Further,

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agglomeration of the nano particles was another concern in estimating the average crystallite size. Hence, we changed the methodology and experimental conditions in the present case of synthesizing carbon nano cones reinforced alumina powder and its characterization.

It is expected that the introduction of particulates of carbon nano cones as a second phase will tune the micro structure of alumina. This tuned micro structure will improve the mechanical properties such as hardness and fracture toughness for specific applications.

2. Experimental methods

Pure alumina is synthesized by solid state reaction method [30]. In this process, aluminium nitrate nano hydrate (purity $\geq 95\%$, Merck Pvt. Ltd) is annealed for 3 h at 1000 °C in the muffle furnace (specs: Technico Muffle furnace having alumina tube with metal hinges) to obtain alumina powder. The sample prepared is labelled as AP (alumina pure). The procedure followed for reinforcement of alumina is as follows:

Carbon nano cones of 0.0094 g (0.5%) are added to pure alumina of 1.8706 g (99.5%) and grinded using mortar & pestle set up. This process ensures proximity and good contact area between the reacting species for enhancing the reaction rate of the solid state reaction to some extent.

The grinded mixture is carefully loaded in a quartz boat and introduced into the muffle furnace (specs: Technico Tube furnace having alumina tube with metal hinges), wherein the temperature profile is suitably set to anneal it at 1000 °C for 3 h in nitrogen atmosphere. The whole process takes nearly 11 hrs to remove the samples from the muffle furnace. Similarly, nano cones of 0.047 g (2.5%) and subsequently 0.0752 g (4%) are also added with pure alumina, by maintaining the total weight of 1.88 g. The same procedure is repeated to get the reinforced powder samples in the corresponding cases and they are labelled as ACC1, ACC3 and ACC5 respectively for convenience. Detailed analyses of the reinforced powders using characterization tools such as X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), and scanning electron microscopy (SEM) are presented.

3. Results and discussion

The characterization results of the pure and reinforced samples are presented below.

3.1. X-ray diffraction analysis

The x-ray diffraction peaks of the pure and reinforced samples are recorded using the instrument Rigaku Smart Lab XRD in the 2 theta range from 20° to 80°, with Cu K- α radiation of wavelength 1.5406 Å. The peaks of the pure alumina are positioned at 2 theta values of 25.92, 35.49, 38.11, 43.69, 52.89, 57.83, 61.59, 66.84, 68.53 and 77.30, thereby confirming the alpha phase of alumina. Debye-Scherrer method [31] is applied to estimate the average crystallite size for all the cases and the results are tabulated below in Table 1.

Table 1
Estimated average crystallite sizes for carbon reinforced alumina.

S.No	Sample	Average crystallite size (nm)
1	AP (Pure Alumina)	36.47
2	ACC1 (0.5% carbon)	36.85
3	ACC3 (2.5% carbon)	39.47
4	ACC5 (4.0% carbon)	37.28

Fig. 1 show, the peaks for pure as well as the reinforced samples of varying carbon nano cones content of 0.5% to 4%. Interestingly, Fig. 2 reveals shifting of peaks and variation of intensity due to the subsequent enhancement of carbon content as we move from the bottom. Here the shifting is towards the lower side of theta values that confirms the gradual increase of interplanar distance, when the doping is increased from 0.5% to 4% and the same is revealed from Table 2 shown above.

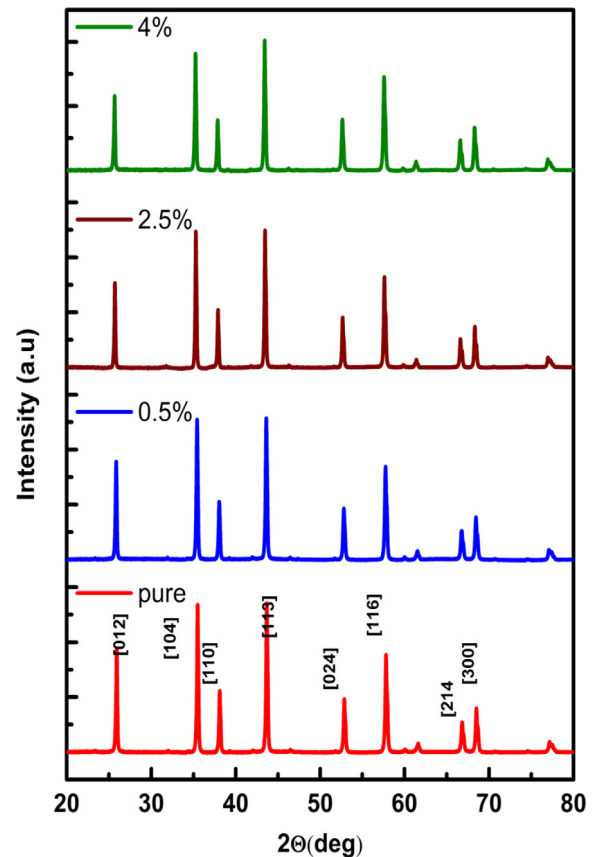


Fig. 1. XRD scans of pure and carbon reinforced alumina.

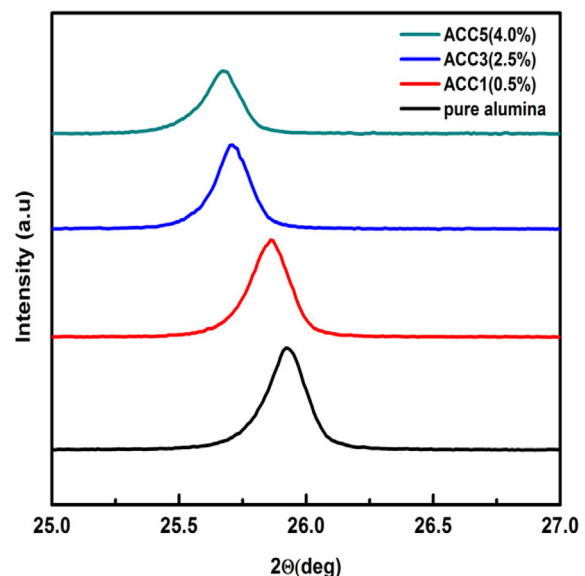
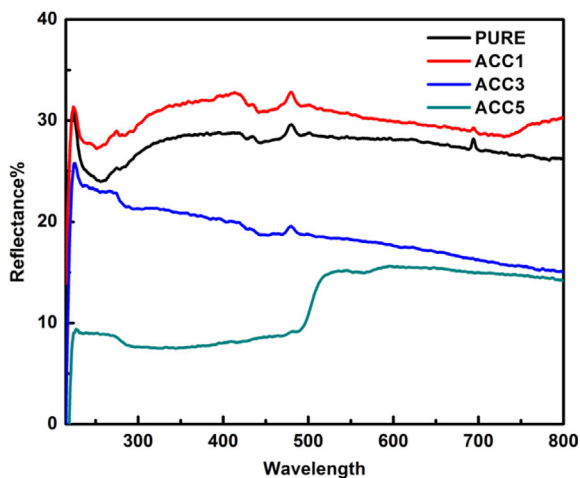


Fig. 2. (0 1 2) peak shift in carbon reinforced alumina.

Table 2

Estimated interplanar distance (d) for alumina composites.

Sample	2 θ	θ	θ (rad)	hkl	d (nm)
Pure	25.92	12.96	0.2260	(0 1 2)	0.343
ACC1	25.85	12.92	0.2255	(0 1 2)	0.344
ACC3	25.70	12.85	0.2242	(0 1 2)	0.346
ACC5	25.66	12.83	0.2238	(0 1 2)	0.347

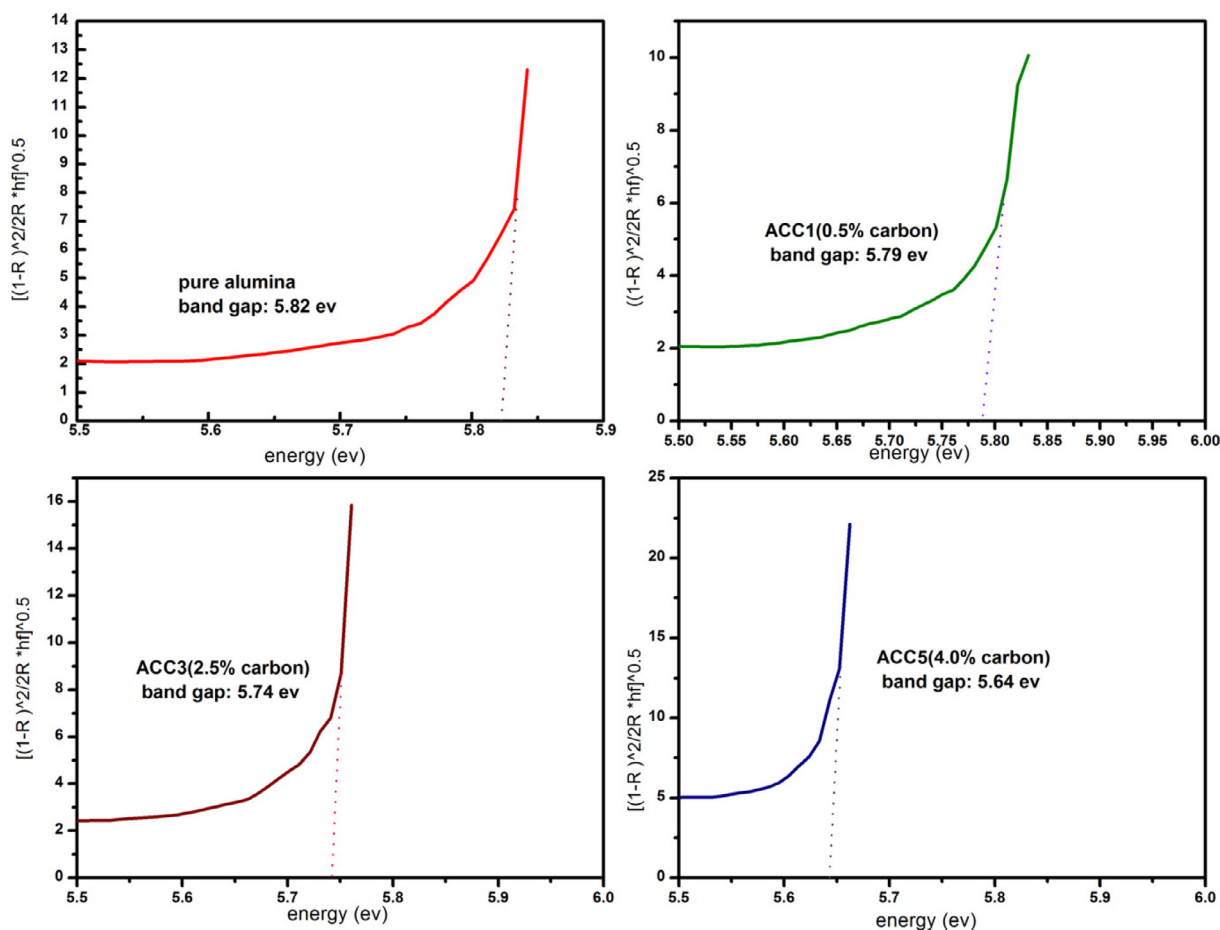
**Fig. 3.** Diffuse reflectance spectra of pure and carbon reinforced alumina.

3.2. DRS analysis

The diffuse reflectance spectra of the pure and reinforced samples were recorded using UV-Vis spectrophotometer (JASCO V650). The reflection spectra obtained in each case is shown in Fig. 3. As the composition varies, the composite samples are well differentiated in the plot. The optical band gaps of the samples are also worked out by plotting modified Kubelka-Munk function, $[F(R) \cdot h\nu]^{1/2}$ versus energy $[F(R) = (1-R)^2/2R]$ for all the cases and are shown in Fig. 4, [32]. They are found to be 5.82 eV, 5.79 eV, 5.74 eV and 5.64 eV for the cases of pure, ACC1, ACC3 and ACC5 respectively. In other words, they are showing a decreasing trend as we move on to the successive cases. It may be attributed to the increase in lattice parameter as we increase the doping.

3.3. Scanning electron microscopy

The surface morphologies of the respective samples are analyzed using SEM; VEGA TESCAN 3 and shown in Fig. 5.

**Fig. 4.** Kubelka- Munk bandgap plots for (a) Pure Alumina; (b) ACC1; (c) ACC3; and (d) ACC5.

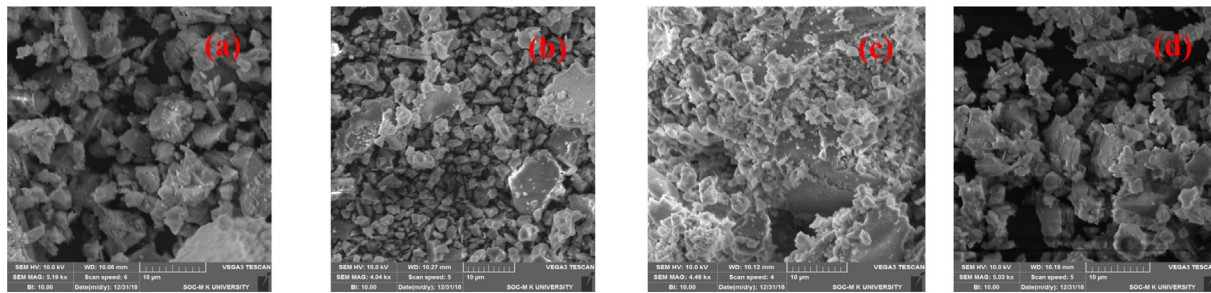


Fig. 5. SEM morphological images of (a) Pure Alumina; (b) ACC1; (c) ACC3; and (d) ACC5.

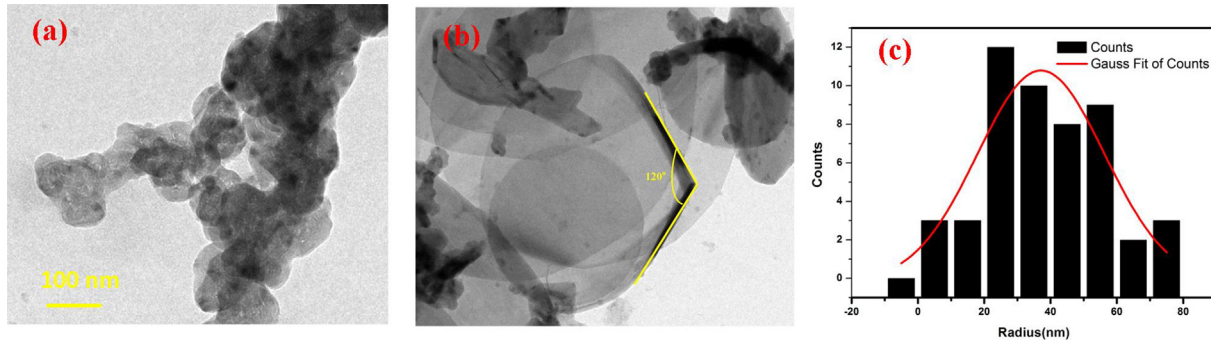


Fig. 6. TEM characterization of carbon nano cones (a) Top view; (b) Apex angle (120°); (c) Radius distribution (avg. radius: 37 nm).

Agglomeration of particles is found in all cases and the average particle size varies roughly from few nm to 15 μm .

3.4. Transmission electron microscopy

TEM characterization of the nano cones is illustrated in Fig. 6. Using ImageJ software, the apex angle and the average top end radius were calculated and found to be 120° and 37 nm respectively.

4. Conclusions

Pure alumina was synthesized and it has been reinforced successfully with carbon nanocones under the preferred methodology and experimental conditions. The impact of reinforcement is observed in the shifting of XRD peaks towards the lower side of 2θ values and variation of intensity from case to case. Accordingly, the increasing trend of interplanar distance of (012) is confirmed as we increase the doping. Debye-Scherrer method shows the increasing trend of average crystallite size, when starting from pure case till it reaches 2.5% of carbon nano cones. When the carbon content is increased further to 4%, average crystallite size decreases from 39.47 nm to 37.28 nm. This is one aspect, where further research is required to assess the possible reasons for this trend. DRS analysis shows that band gap decreases, when the carbon content is increased and is attributed to increase in lattice parameter. SEM reveals the morphological variations from case to case and of course, the problem of agglomeration needs further attention. To sum up, it is expected that the micro structural variations discussed above would be well reflected in the mechanical properties such as hardness, fracture toughness etc. and the same is left for our future studies.

Acknowledgements

Authors extend their sincere thanks to Dr. B.I.Ravi, Addl. Dir. (Sust), CVRDE (DRDO), India for valuable suggestions and constant

encouragement; Dr. Jean Patrick Pinheiro, from Institute for energy technology, Norway, for providing carbon nano cones for the study. Author JM is thankful to DST-PURSE programme at Madurai kama-raj university, India for SEM analysis.

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