

## **Effect of Nano Carbon and Resins with Magnesia on Formation of Multi Walled Carbon Nano Tube**

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**Abstract:** Nano composites with magnesia refer to a broad range of composite materials with magnesia acting as the matrix and carbon nano material acting as the filler. The effect of the resins like epoxy and phenol formaldehyde in the formation of the CNTs in the nano composite was studied. The reinforcement of carbon nano particle in the MgO matrix along with the resins in the reduced atmosphere at high sintering temperature at 1100°C, 1300°C and 1500°C for 3hrs were observed. Characterization was done by using XRD, Raman spectroscopy, SEM and FESEM. MgO with epoxy resin and carbon nano particle exhibited proper distribution of carbon on magnesia which was fully coated with carbon. The MgO with nano carbon and phenyl formaldehyde fired upto 1300°C also showed proper distribution of carbon on magnesia grain with some graphitization of carbon which was confirmed by X-ray diffraction. The diffraction pattern and spectra from the Raman spectrophotometer of the magnesia composition with phenyl formaldehyde resin fired at 1500°C in reducing atmosphere suggest well distributed coating of carbon and formation of multi walled carbon nano tube. From the scanning electron microscopy of this composition reconfirmed proper distribution of MWCNT above magnesia grains. The field emission electron microscope confirmed the nucleation of MWCNT in the presence of the phenol formaldehyde resins and nano carbon particle above magnesia grains at higher temperature in reduced atmosphere due to higher resin carbon and increase in the rate of diffusion in the matrix.

**Key words:** nano carbon, magnesia, composites, filter.

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### **1. Introduction**

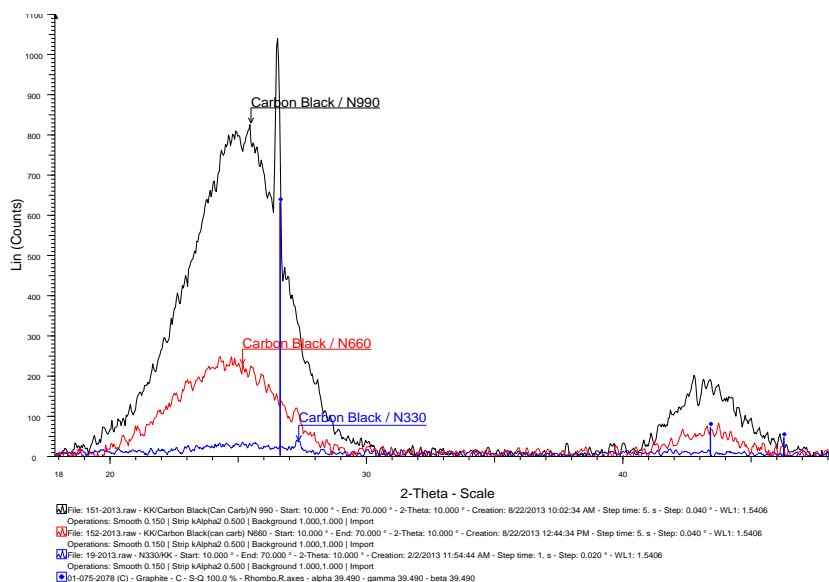
Nano composites with magnesia refer to a broad range of composite materials with magnesia acting as the matrix and carbon nano material acting as the filler [1]-[3]. Due to unprecedented improvement observed in properties of the nano composites, research interest in this area has grown exponentially in recent years. In designing better nano-composites for advanced technological applications, some of the major challenges are: understanding the structure-property relationships, interaction and integrity of the two components at the interface, the role of nano fillers and resins in enhancing the properties of the resulting material route. The effect of the resins like epoxy and phenol formaldehyde in the formation of the CNTs in the nano composite is the need for development of new generation material specially carbon containing refractory.

Phenol formaldehyde (PF) resin is an established binding material for making carbon containing magnesia carbon bricks. Epoxy (EP) resin is water soluble and for making carbon containing castables

water based resin is required for initial strength of the castables. The effect of these two types of resins (EP & FP) on formulation of multi walled carbon nano tubes containing compacts of MgO was studied [4]-[6].

## 2. Experimental

Nano carbon black of three grades (N330, N660 & N990) which have different particle sizes were analyzed with Bruker D8 Advance X-Ray Diffractometer on 40V & 40mA current using copper target as shown in Fig. 1 [7].



Comparative XRD of different grade of carbon black  
 Fig. 1. XRD of different grades nano carbon black

The XRD of different nano carbon grades have graphite like structure and exhibit an increase in intensity with increase in particle size. The nano carbon black of N330 grade was used to study the effect of resins on MgO due to its high surface area and lower particle size (30nm approx). Composites were prepared by grinding and mixing the raw materials (MgO powder, Nano carbon powder, Epoxy resin and Phenol formaldehyde in different stoichiometric proportion respectively as depicted in the Table 1.

Table 1. Compositions with Different Resins and Nano Carbon

| Sample No. | Composition of the sample.             |
|------------|--|
| A          | MgO + Nanocarbon                       |
| B          | MgO + Nanocarbon + Epoxy resin         |
| C          | MgO + Epoxy resin                      |
| D          | MgO + Nanocarbon + Phenol formaldehyde |
| E          | MgO + Phenol formaldehyde              |

All the mixed compositions were milled in Retsch make centrifugal ball mill for 2 hours in sintered alumina pot with highly sintered alumina balls of 9 moh hardness to minimize the contamination from grinding media at 100 rpm by rotating alternately in clock wise and anti-clockwise direction. The different powder mixes were uniaxially pressed into pellets of 30 mm diameter and about 5.50 mm thick under a specific pressure of 1500kg/cm<sup>2</sup> in a 100T Carver lab press. All the samples were dried in a oven at 110°C for 8 hours.

The specimens were sintered in reducing atmosphere at 1100°, 1300° and 1500°C for a period of 180 minutes after raising the temperature at the rate of 3°C per minute in 1800°C Naskar chamber furnace. Finally the soaked samples were furnace cooled. The physical parameters like bulk density and apparent

porosity were measured by using Archimedes' principle in water.

A series of XRD phase investigation of magnesia with nano carbon and different resins were carried out with BRUKER D8 Advance equipment. The phases present in each of the compositions were identified with the help of Diffrac plus Eva software. For characterization of the formation of carbon nanostructure not mentioned clearly by the XRD, Raman spectrophotometer was used as it is a vital tool based on the vibration of the molecule. The pieces of the samples were mounted in the holder in an upright position such that the inner surface of the sample is irradiated with the light. The microstructure of green and fired samples with nano carbon and different resins at 1500°C for 3 hrs in reducing atmosphere were also taken. The microstructure and morphology of the products were observed by using a Scanning electron microscope (SEM, Zeiss) equipped with an energy dispersive spectroscopy (EDS, Oxford INCA). After seeing the encouraging result of formation of crystalline structure were also taken from field emission scanning electron microscope (FESEM, Zeiss) of fired sample at 1500°C for 3 hrs in reducing atmosphere with different resins and nano carbon.

### 3. Results & Discussions

The resins play a great role in bricks containing carbon and the effect of epoxy resin and PF resin has different characteristics. The bulk density may vary with change in resins. Fig. 2a shows a plot of bulk density and Fig. 2b shows the apparent porosity for different samples at different sintering temperatures.

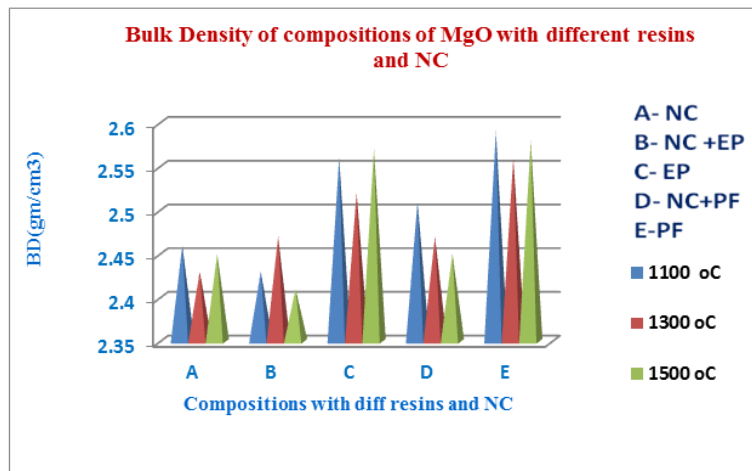


Fig. 2a. Bulk Density of Different Compositions Fired at Different Temp.

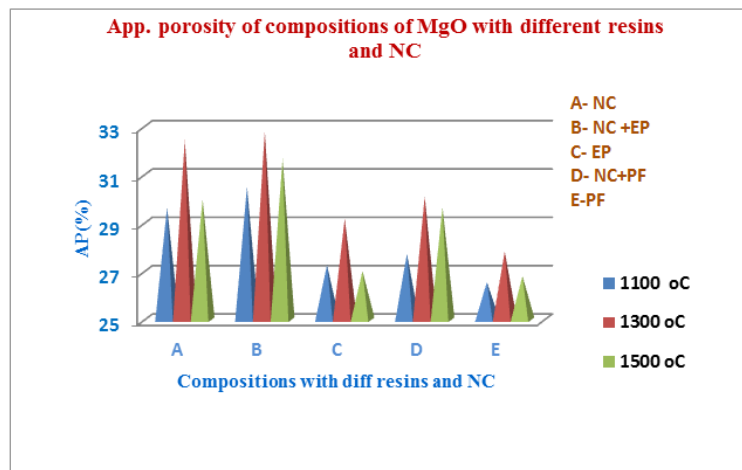


Fig. 2b. Apparent porosity of different compositions fired at different temp.

The surface area of nano carbon is very high as stated earlier so the bulk density of nano carbon is very low. Thus the bulk density of compositions with nano carbon was less compare to without nano carbon due to its very high surface area. The retention of carbon is more in phenolic resin at higher temperature which may form nano carbon chain in reducing atmosphere. This formation and retention of carbon may not be with epoxy resin and nano carbon in reducing atmosphere at higher temperature. The formation of carbon chain may increase density in the composition with phenol formaldehyde resin with nano carbon. The density may also increased due to some sintering and crystallization of phenolic resin with nano carbon at 1500°C in reduced atmosphere. This result in increase in density and decrease in the porosity at higher temperature with composition of phenolic resin and nano carbon.

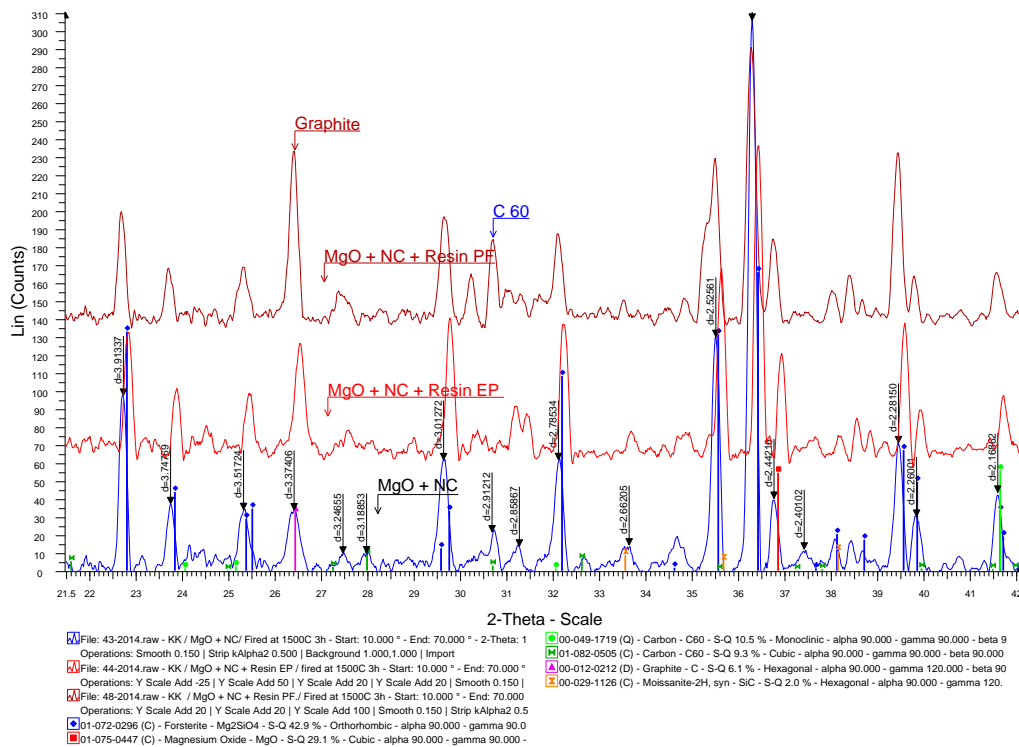


Fig. 3. XRD of different resins with MgO and Nanocarbon sintered at 1500°C / 3hrs.

A comparative study was carried with the diffraction pattern of the samples available from the X-Ray Powder Diffractometer for the phase analysis illustrating the effect of resins as binding material along with the matrix constituents MgO and Nanocarbon in the samples at the sintering temperature 1500°C for 3hrs in reduced atmosphere, depicted in the Fig. 3. Comparison of the diffraction pattern of all the three samples (Mgo+NC, Mgo+NC+Resin EP, and Mgo+NC+Resin PF), showed a sharp peak of carbon nanotube around 26.4°. The peaks of graphite and carbon nanotube occur at the same 2-theta scale. The graphitization of the amorphous carbon (carbon black) along with the binder resulted in the formation of carbon nano tube in the reduced atmosphere at higher temperature.

The sample with the resins as a binding material have an intense peak with epoxy resin but it is more prominent in the sample MgO+NC+Resin PF. This indicates the crystallization of amorphous carbon. The graphitization and crystallization of the amorphous carbon results in the increase of hardness in the nano composite indicating a strong bond between the grains may be due to the formation of CNT. The formation of CNT at lower sintering temperature is not favourable in the reducing atmosphere. But at the higher temperature, there is growth of the CNT in the nano composite.

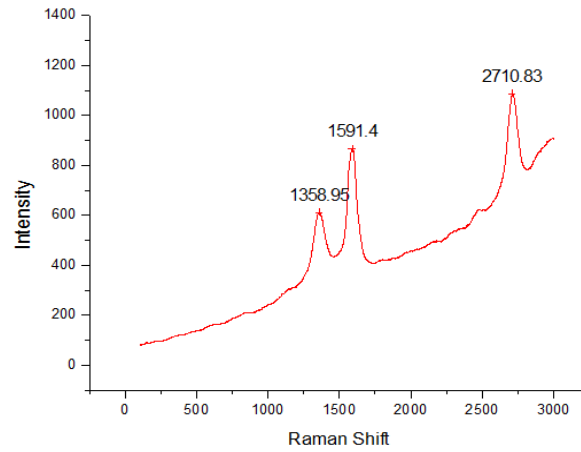


Fig. 4(a). Raman Spectra of the samples – MgO+NC+ EP resin.

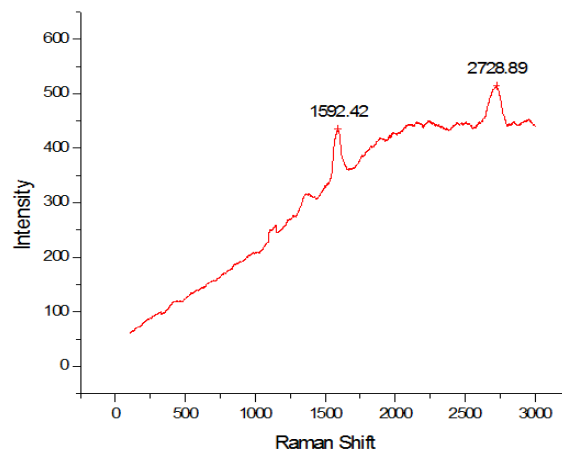


Fig. 4(b). Raman Spectra of the samples MgO+NC+ PF resin

Fig. 4a depicts the formation of G', G and D peaks at 2710.83  $\text{cm}^{-1}$ , 1591.4  $\text{cm}^{-1}$  and 1358.95  $\text{cm}^{-1}$  respectively, which are in accordance with the graphitic raman spectral peaks (G'-2700  $\text{cm}^{-1}$ , G -1582  $\text{cm}^{-1}$  and D -1354  $\text{cm}^{-1}$ ). However Fig. 4b has only G' and D peaks with the lowering in the intensity of the peaks. In the absence of radial breathing mode, there is a formation of the Multiwalled Carbon Nanotube (MWCNT) whereas in presence of breathing mode formation of single wall carbon nano tube. Hence, more the formation of MWCNT in the matrix, harder the nano composites.

Scanning electron microscope of the green compact confirm the proper coating of carbon and distribution of carbon in the compacts of both epoxy and PF resin having compositions as shown in Fig. 5a & Fig. 5b.

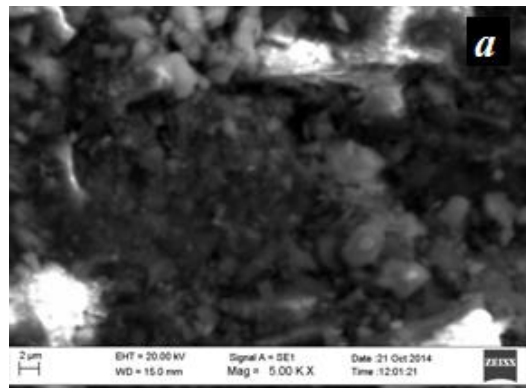


Fig. 5(a). SEM of green compositions with Epoxy resin and nano carbon

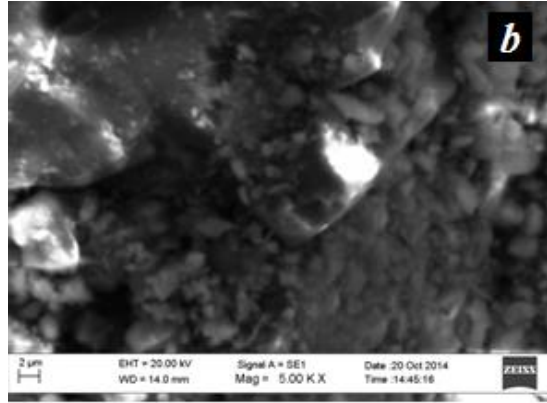


Fig. 5(b). SEM of green compositions with PF resin and nano carbon

Proper distribution of carbon was also seen in the compositions fired in a closed compact box of graphite bed at 1500°C for 3 hours. Localised oxidation of some layer was observed in the epoxy resin based composition as shown in Fig. 5c. However in PF resin fired in reducing atmosphere at 1500°C, the microstructure showed the magnesia grain encapsulated with some crystalline carbonaceous material which may be multi walled nano tubes formed above the grain as shown in Fig. 5d.

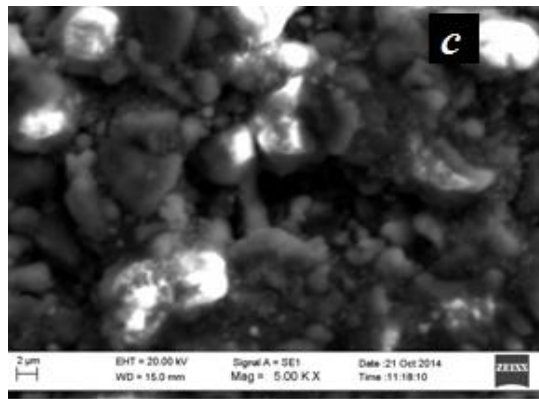


Fig. 5(c). SEM of composition with Epoxy resin and nano carbon fired at 1500°C/3hrs

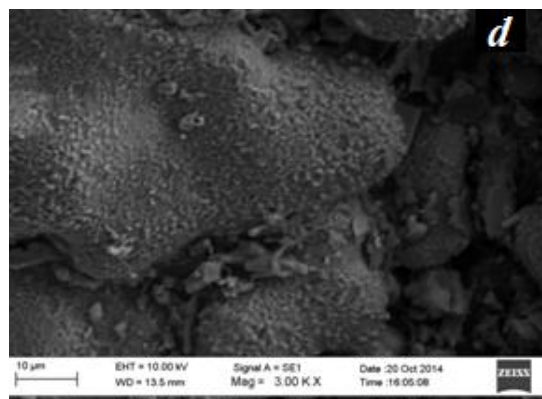


Fig. 5(d). SEM of composition with PF resin and nano carbon fired at 1500°C/3hrs

The FESEM of both epoxy and phenol formaldehyde resins also show proper distribution of carbon when fired at 1500°C in reduced atmosphere with epoxy resins and phenol formaldehyde resins. The composition with epoxy resin has well distribution of nano carbon particle above the magnesia grains but no nucleation or nano tube formation is indicated as shown in Fig. 6(A).

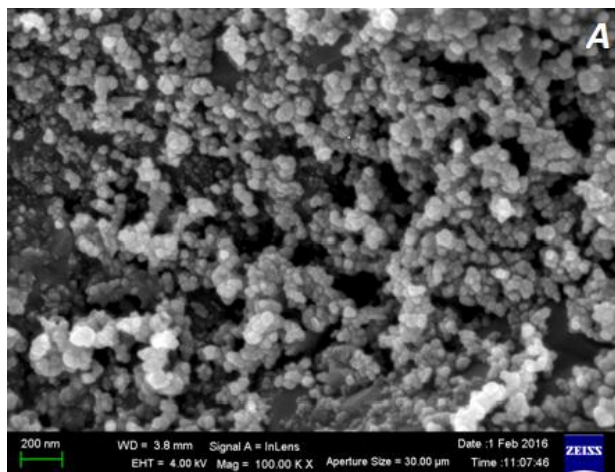


Fig. 6(A). SEM of composition with Epoxy resin and nano carbon fired at 1500°C/3hrs

The composition with phenol formaldehyde resin has well distribution of nano carbon particle above the magnesia grains and has nucleation of carbon nano tubes above the surface of magnesia grains as shown in Fig. 6(B). The nucleation of CNT is in a bunch and it is around 200nm size. Big nano tube of around 700nm size formation is also indicated.

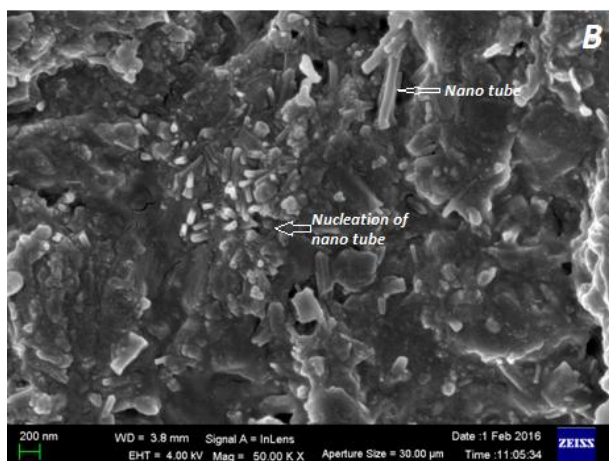


Fig. 6(B). SEM of composition with PF resin and nano carbon fired at 1500°C/3hrs

The XRD and Raman spectra of compact containing Epoxy resin not show any formation of nano tube but the compacts with PF resin and nano carbon black confirm the presence of MWCNT in the matrix. Thus it appears that phenyl formaldehyde resin and nano carbon black combination form in situ nano carbon tubes in the composition. The PF based composition may have more mechanical strength and have better erosion resistance compare to epoxy resin based composition which can be explored further. The PF resin and nano carbon coated magnesia composition is suitable for making new generation low carbon containing materials for preparation of steel vessels which may give longer life. This can also be used in manufacturing of trough / runner castables and carbon containing masses.

#### 4. Conclusions

- The Magnesia grains coated with nano carbon black with phenyl formaldehyde resins have better bulk density and lower apparent porosity at higher temperature (1500°C) compared to coated magnesia with epoxy resins.
- XRD studies showed more graphitization with PF resin at higher temperature.

- Raman spectra of compositions with PF resins also confirmed formation of in situ MWCNT with PF resins at higher temperature. Further, validation of the observation was obtained by SEM.
- The FESEM of composition with epoxy resin confirm well distribution of nano carbon above the surface of grains whereas with composition with phenol formaldehyde established the nucleation of carbon nano tube of around 200nm and a tendency of formation of more bigger nano tube in the matrix.

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