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Production of nano structured silicon carbide by high energy ball milling

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Abstract

In this paper, an attempt has been made to modify the micro sized Silicon carbide powder into nano structured Silicon carbide powder using High Energy Ball Mill. Ball milling was carried out for the total duration of 50 hours. The sample was taken out after every 5 hours of milling and it was characterized for its crystallite size, lattice strain, and percentage of crystallinity by using X-Ray Diffractometer. It was found that for the 50 hrs, milling the crystallite size was reduced from 120 nm to 26 nm and the percentage of crystallinity got reduced from 74% to 49%. The size, shape and texture of the fresh as well as nano structured Silicon carbide powder were studied using Scanning Electron Microscopy (SEM). The fresh Silicon carbide powder particles were mostly angular in shape. The shape of the 50h milled particles is irregular and the surface morphology is rough.

Key words: Nano powders, High Energy Ball Milling, X-ray and SEM analysis.

1. Introduction

Nanoscience and nanotechnology has become the buzz-word in recent years. It has appeal of miniaturization: also, it imparts enhanced electronic, magnetic, optical and chemical properties to a level that cannot be achieved by conventional materials (Bhusha, 2004; Kohlar et al., 2004). A variety of ways have been reported to synthesize nano level materials such as plasma arcing, chemical vapor deposition, electro deposition, sol-gel synthesis, high intensity ball milling etc (Guozhong Cao, 2004). Among these methods, high-energy milling has advantages of being simple, relatively inexpensive to produce, applicable to any class of materials and can be easily scaled up to large quantities (Baraton, 2003). In this mechanical treatment, powder particles are subjected to a severe plastic deformation due to the repetitive compressive loads arising from the impacts between the balls and the powder. This produces novel crystalline and amorphous materials with crystallite sizes at the nanometer scale (Koch, 2006).

Metal matrix composites are advanced materials resulting from a combination of two or more materials in which tailored properties are realized. It is well known that the particle- reinforced metal matrix composites have excellent mechanical properties due to the addition of the high strength and high modulus particles like TiC, Al_2O_3, SiC, TiB_2 etc. However the ductility of the MMCs deteriorates with high ceramic particle concentration (Akio et al., 1999). It is of interest to use nano sized ceramic particles to strengthen the metal matrix, so called metal matrix nano composites (MMNC) while marinating good ductility (Akio et al., 1999, Mussert et al., 2002). Currently, there are several fabrication methods of MMNCs, including mechanical alloying with high energy milling (Chen et al., 1997), ball milling (Utriga Filho et al., 2003), nano sintering (Groza, 1999) vortex method (Akio et al., 1999), spray deposition, electrical plating, sol - gel synthesis, laser deposition etc.

Casting, as a liquid phase process, is capable of producing products with complex shapes. It will be attractive to produce as-cast lightweight bulk components of MMNCs with uniform reinforcement distribution and structural integrity. Habibnejad-Korayem et al. (2009) reported the enhanced properties of Mg based composites reinforced with Al_2O_3 nano particles by vortex method. Mazahery et al. (2009) developed the high performance A356 – nano Al_2O_3 composites by vortex method. Ansary Yar et al. (2009) studied the microstructure and mechanical properties of aluminium alloy matrix composite reinforced with nano particle MgO by vortex method. Habibnejad-Korayem et al. (2010) carried out the study on tribological behaviour of pure Mg and AZ31 magnesium alloy strengthened with Al_2O_3 nano particles by vortex method. Yang et al. (2004) studied the effect of nano sized SiC particles reinforced in molten aluminium alloy by ultrasonic dispersion. Lan et al. (2004) reported the studies on microstructure and microhardness of SiC nano particles reinforced magnesium composites fabricated by ultrasonic method.

From the above and currently available literature conclusion can be drawn that very limited literature is available in the production and characterization of nano structured reinforcements by high energy ball milling method; for instance the production of nano structured silicon carbide powder. Hence, in this paper an attempt has been made to modify the micro sized silicon carbide into nano-structured silicon carbide using high-energy ball mill. Later this nano structured silicon carbide will be used as reinforcement for the production of metal matrix nano composites.

2. Experimental Procedure

2.1: High Energy Ball milling

Silicon carbide (SiC) powder used for this study was procured from M/s Madras metallurgical laboratory, Chennai with an initial particle size of 12 µm. The reduction in particle size of SiC from micron level to the nano level was carried out using a high-energy planetary ball mill (Model: Retsch, PM 100, Germany) in a stainless steel chamber using tungsten carbide and zirconia balls of 10 mm Φ and 3 mm Φ ball sizes respectively. The total duration of milling was 50 hours. The rotation speed of the planet carrier was 200 rpm. The ball mill was loaded with ball to powder weight ratio (BPR) of 10:1. Toluene was used as the medium with an anionic surface active agent to avoid agglomeration. The milled sample powder was taken out at a regular interval of every 5 hours of milling and dried with mechanical drier.

2.2: X-Ray Diffraction studies

The fresh as well as milled silicon carbide powder was characterized with an X-Ray Diffractometer (Model: 2036E201; Rigaku, Ultima IV, Japan). JADE software was used to investigate the structural changes and phase transformations of powders occur during mechanical milling. Sample preparation of XRD is done as per the standard practice. Sample packing was carried out by filling the silicon carbide powder on a glass slit of 12 X 12 X 2 mm size. Precautions were taken to have a tight powder packing on the glass slit and no manual contamination with the powder specimens. The X-ray diffraction measurements were carried out with the help of a Goniometer model 2036E201 using Cu K_α radiation (K_α= 1.54056 A^0) at an accelerating voltage of 40 kV and a current of 20 mA. In this test the sample was in stationary condition, only the arms of the X- ray tube was rotating in the opposite direction up to 90 ^{0} of 2θ during the test. The samples were scanned in the range from 3^0 to 90^0 of 2θ with a scan rate of 2 ^{0}/ min. The analysis was carried out to find out crystallite size, peak height, crystallinity and also amount of induced strains in the milled silicon carbide.

2.3: Morphology studies

Scanning electron microscopy (Model: SEM–Quanta 400, FEI -Netherlands) with EDAX energy dispersive X-ray spectroscopy (EDS) was used in order to evaluate the morphological changes of certain phases observed in the fresh as well as nano structured silicon carbide particles.

3. Results & Discussion

3.1: Crystallite size and Lattice strain

Figure 1 shows the scanning electron micrograph of the fresh silicon carbide. From this figure it is evident that majority of the silicon carbide particles are angular in nature. The X-ray diffraction (XRD) pattern of silicon carbide in initial stage is shown in figure 2, which shows the phases present in the silicon carbide and are largely silicon carbide (SiC), moissanite (3C-SiC) and quartz (SiO2).

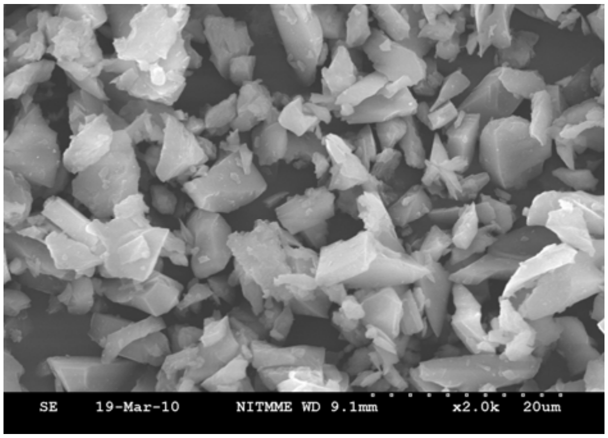


Figure 1: SEM micrograph of initial Silicon Carbide used in the study

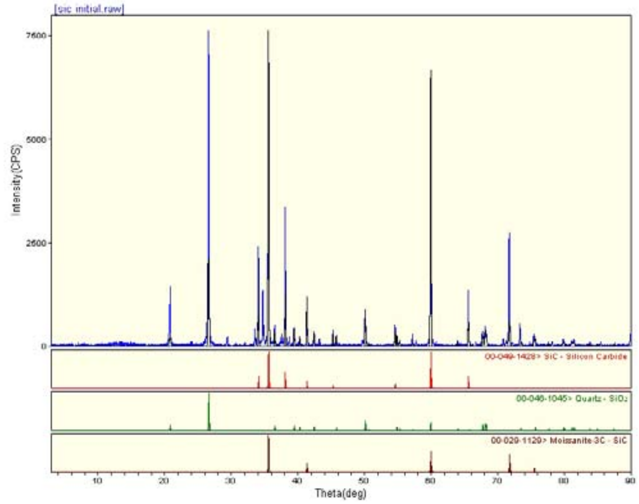


Figure 2: X-ray diffractogram of initial Silicon Carbide

The average crystallite size was calculated from the full width at half maximum (FWHM) of the X-ray diffraction peak using Scherer's equation (Cullity, 1978).

$$D = (k\ \lambda) / (B \cos\theta)$$

Where D is the particle diameter, λ is the X – Ray wavelength, B is the FWHM of the diffraction peak, θ is the diffraction angle and K is the Scherer's constant of the order of unity for usual crystals. The existence of stress in the materials results in lattice distortions of crystals; consequently, the diffraction peaks of the crystals are broadened. The relationship between the half width of the broadened diffraction peaks, B_d and the distortion of lattice, $(\Delta d/d)$ was described by Yang et al. (2000). The lattice distortion $(\Delta d/d)$ can be obtained from the following equation.

$$(\Delta d/d) = B_d / (4 \tan\theta)$$

Where $B_{d,}$ is half width of the broadened diffraction peaks, θ is half of the diffraction angle.

During ball milling the intense mechanical deformation experienced by the silicon carbide powder leads to generation of lattice strains, crystal defects and this plus the balance between cold welding and fracturing operations among the powder particles is expected to affect the structural changes in the powder. The measurement of crystallite size and lattice strain in the mechanically milled powders is very important since the phase constitution and transformation characteristics appear to be critically depending on them (Suryanarayana, 2001). Figure 3 illustrates the variation in crystallite size and lattice strain of the silicon carbide with the milling time. A steady decrease in the crystallite size is observed and it was found that the crystallite size get reduced from 108.36 nm to 26.34 nm for 50h milling time. The relative lattice strain is increasing with increasing the duration of milling time. This lattice strain was increased from 0.15 to 0.278 for as received and 50 h milled silicon carbide respectively.

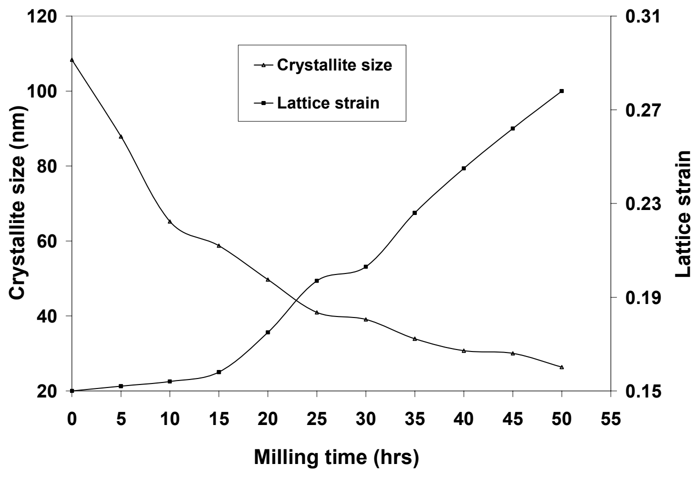
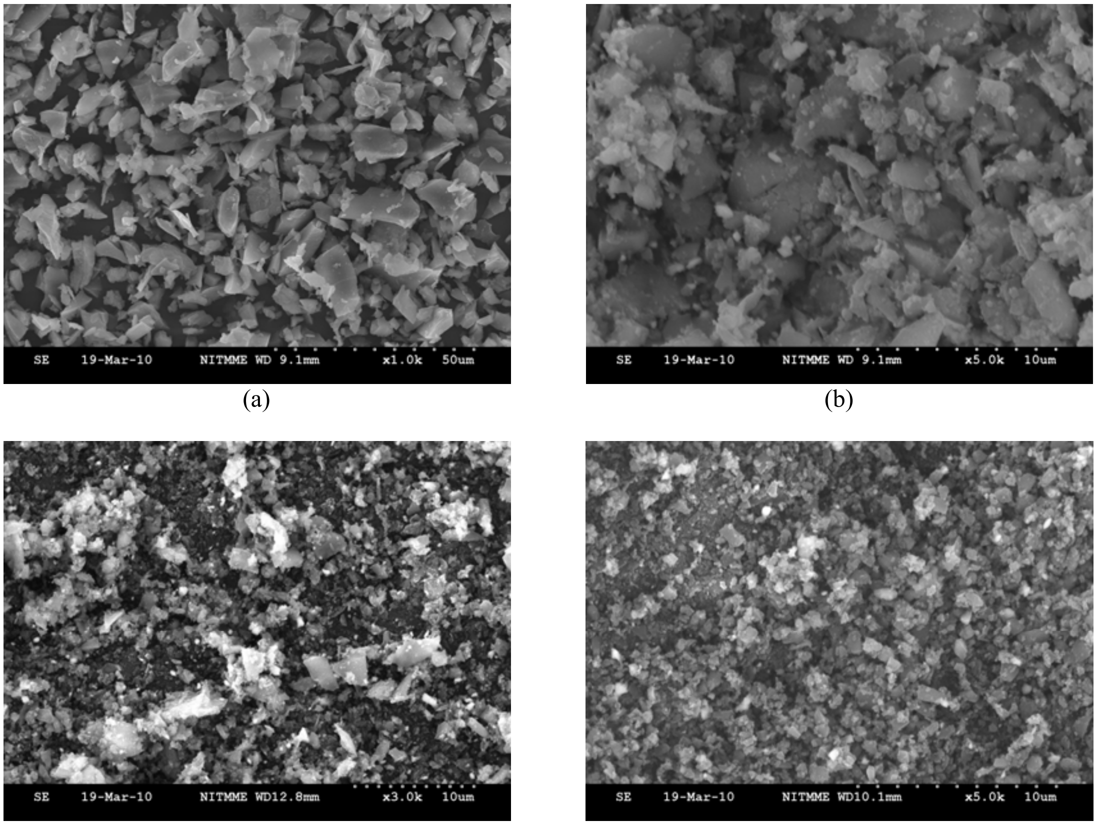


Figure 3: Variation of crystallite size and relative strain as function of milling time.

The size, shape and texture of the initial as well as nano structured silicon carbide were studied using Secondary Electron Imaging mode of Scanning electron microscopy (SEM). Figure 4 (a) shows the SEM image of initial silicon carbide. The initial silicon carbide particles are mostly angular in shape. Figure 4 (b) shows the SEM image of 15h ball milled silicon carbide. Here the angular structure of initial silicon carbide has been destroyed; and in this 15h, milling stage the silicon carbide is in cold welding condition hence the particles appears like enlarged flakes. The flake shaped particles are further crushed by intense impacts of the balls; hence the decrease in particle size occurs with increasing milling time as shown in Figure 4 (c & d), the SEM images for 30h and 50h ball milling times respectively. The final shape of the particles is mostly sub-angular and the surface morphology is rough.



(a) (b)

(c) (d)

Figure 4: The scanning Electron microscope photographs of Initial and Ball milled SiC powder (a) 0 h (b) 15 h (c) 30 h (d) 50 h.

The X-Ray diffractogram of the 50 h ball milled silicon carbide was shown in Figure 5. From this figure there is a confirmation of small tungsten carbide contamination in the milled silicon carbide sample. This entry might be from the tungsten carbide balls which were used as milling media during milling; also from Figure 5, it clearly observed that the intensity of the peaks in the XRD pattern got reduced and the peak broadening increased as the duration of milling increases. Three major phases were identified for all the milling times; which are silicon carbide (SiC), moissanite (3C-SiC) and quartz ($SiO2$).

Diffraction peak positions are accurately measured with XRD, which makes it the best method for characterizing homogeneous and inhomogeneous strains. Homogeneous or uniform elastic strain shifts the diffraction peaks positions. From the shift in peak positions, one can calculate the change in d-spacing, which is the result of the change of lattice constants under a strain. Inhomogeneous strains vary from crystallite to crystallite or within a single crystallite and this cause a broadening of the diffraction peaks that increase with $\sin\theta$ (Cao, 2004). The displacement of SiC (111) XRD peaks during ball milling process is represented in figure 6. This figure illustrate that with increasing milling time the peak height intensity shift slightly to the lower heights and increasing the peak broadening. This is the indication of high energy milling decreases the crystallinity of the silicon carbide, thus increasing the amorphous phase in it.

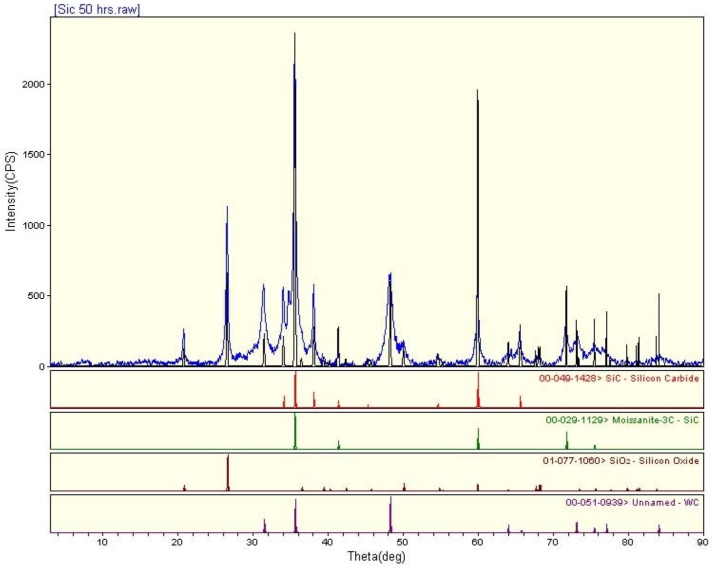


Figure 5: X- Ray diffraction patterns of 50 h milled silicon carbide show the tungsten carbide contamination in the milled silicon carbide.

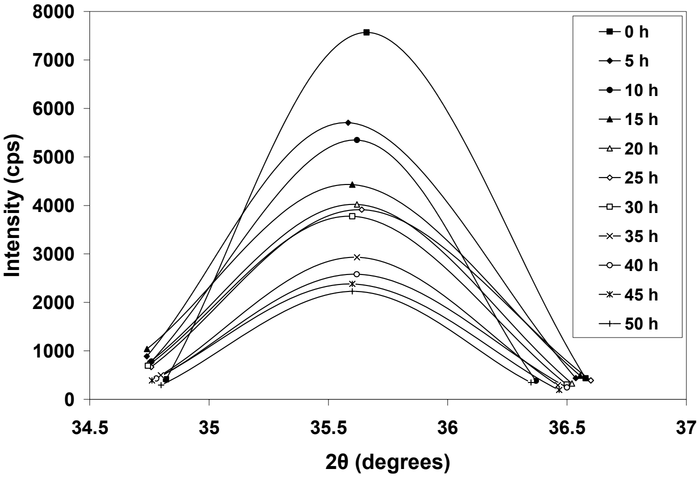


Figure 6: Displacement of SiC (111) XRD peaks at different milling times

3.2: Crystallinity

Crystallinity refers to the degree of structural order in a solid. Crystallinity is usually specified as a percentage of the volume of the material that is crystalline. A perfect crystal would extend in all directions to infinity, so no crystal is perfect due to its finite size. This deviation from perfect crystallinity leads to a broadening of the diffraction peaks. Deviations from ideal crystallinity, such as finite crystallite size and strain (at the atomic level) lead to broadening of the diffraction lines. By analyzing this broadening it is possible to extract information about the level of crstallinity of a material. Various sources of line broadening are Instrumental broadening, Crystallite size broadening and Strain broadening.

In the present analysis the percentage of crystallinity was obtained from JADE software available in X-Ray Diffractometer (Model: 2036E201; Rigaku, Ultima IV, Japan). These values were calculated based on Pseudo – Voigt function at the peak heights of various milling times. The results of XRD analysis of fresh as well as ball milled silicon carbide were used for crystallinity measurements. The decrease in crystallinity of silicon carbide with ball milling time is shown in the figure 7. This decrease was observed from 74% to 49% for as received and 50h ball milled powder respectively. While increasing the milling time decreases the crystallinity of the silicon carbide, thus increasing the amorphous domains in it.

As the milling time increases, particle size is decreasing and the specific surface area increases; and also surface roughness of the silicon carbide increases. The increased surface roughness supports the higher surface energy of the ball milled silicon carbide. This favours the generation of Vander Waal's interactions (Bhowmick et al., 1995). The increased surface roughness supports the increased wettability of the surface and also is expected to promote its compatibility with the polymer or metal matrices when it is used as reinforcing nano structured filler. This change is beneficial for the applications such as particulate nano filler in polymeric or metallic matrices. Hence, the enhanced amorphous and rough surface content is very encouraging as it may lead to better compatibility with various metallic and polymeric matrices.

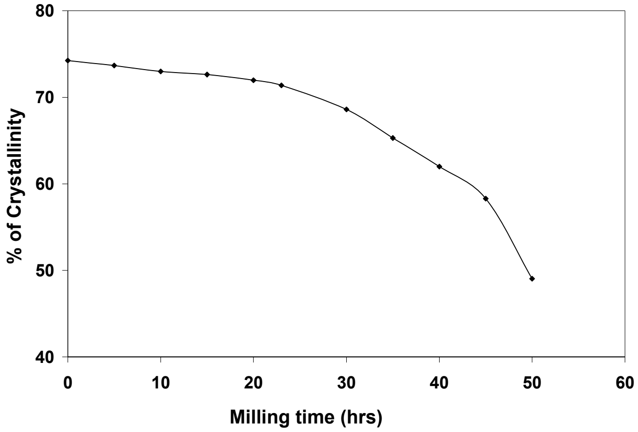


Figure 7: Variation in % crystallinity with milling time.

4. Conclusions

The size reduction of Silicon carbide from micrometer level to nano meter levels (from 120 nm to 26 nm) has been achieved by high-energy ball milling for the period of 50hrs. The percentage of crystallinity reduces from 74% to 49%. The silicon carbide becomes more amorphous and the crystallite size reduces drastically. The lattice strain was increased with increasing the milling time. The SiC phase is the maximum sufferer during milling; hence, with increasing the milling time SiC peak height shifts to the lower levels and also broadening of the diffraction pattern occurs. Currently the author is utilizing this nano-structured silicon carbide for synthesis of Aluminium- Silicon Carbide metal matrix nano composites (MMNC). The work is on progress and the results will be presented in the next publication.

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