



Research Paper

EXPERIMENTAL INVESTIGATION OF SILICON CARBIDE REINFORCED MoSi_2 CERAMIC NANOCOMPOSITE PREPARED BY MECHANICAL MILLING

M Jinnah Sheik Mohamed^{1*} and N Selvakumar²

*Corresponding Author: **M Jinnah Sheik Mohamed**, ✉ jsm_designer@yahoo.co.in

Nanocomposites can be considered as such strategic materials endowed with designed performance properties that reach far beyond those of conventional composites. The ceramic matrix nano composites provide greater deal of interest due to their unique and outstanding physical characteristics. In this present research, It is considered to mix the pure Molybdenum (Mo), Silicon (Si) and Carbon (C) powder in different proportions and continuously ball milled at high temperature for 60 h, as a result reduction of particles took place and SiC of 5% and 20% by weight with MoSi_2 Ceramic Nanocomposite were obtained. The above compositions were obtained by adjusting the weight of each elements based on molecular weight of each constituent in chemical reaction. In this work, experimental characterisation for these particles was investigated using Raman Spectroscopy, FTIR, SEM, AFM and Particle size analyser. Phase purity and grain size were determined by X-ray Diffraction analysis. Nanoindentation experiments were performed with Berkovich indenter for determining hardness from Force-displacement data.

Keywords: Nanocomposites, Ceramics, Characterization, Nanoindentation, MoSi_2 -SiC

INTRODUCTION

Nano Composite (NC) is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nm, or structures having nano-scale distances between the different phases that make up the

material (Suryanarayana, 2001). In mechanical terms, NC differs from conventional composite materials due to its exceptionally high surface to volume ratio of the reinforcing phase. Ceramic Matrix Composites (CMC) are engineered combinations of two or more

¹ Department of Mechanical Engineering, National College of Engineering, Maruthakulam, Tirunelveli, Tamil Nadu, India 627151.

² Department of Mechanical Engineering, Mepco Schlenk Engineering College, Sivakasi, Tamil Nadu, India 626005.

materials in which tailored properties are achieved by bringing the combined advantages of both reinforcement and the ceramic matrix into full play, which gives high degree of freedom in material design (Kristoffer *et al.*, 2008; and Renjie *et al.*, 2011). Mechanical Alloying (MA) is a solid-state powder processing technique involving repeated welding, fracturing and rewelding of powder particles in a high-energy ball mill (Chandradass *et al.*, 2008).

Transition carbides such as silicon carbides provide unusual unique properties which make it very interesting and important for several industrial applications. They have excellent high temperature strength, good corrosion resistance, chemically stable property and are extremely hard material and possess high Young's modulus. Among the hard alloys and refractory carbides, grains of SiC can be bonded together by sintering to form very hard ceramics which are widely used in applications requiring high endurance, such as car brakes, car clutches and ceramic plates in bullet-proof vests and in high-temperature/high-voltage semiconductor electronics. Naturally, reinforcements in the CMC contribute higher strength when compared to the parent material (Sajjad *et al.*, 2011).

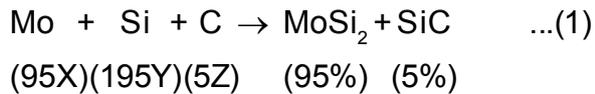
The MoSi₂ offers significant potential for high temperature structural applications because of their high melting point (2030 °C) and ability to undergo plastic deformation above 1000 °C. It possesses outstanding oxidation resistance up to the temperature as high as 1700 °C. Molybdenum disilicides find its place in military applications which require stronger steels with greater resistance to corrosion (Shakhtshneider *et al.*, 2009). It is

extensively used for heating elements in furnaces, power generation components, high temperature heat exchangers and filters, aircraft engine hot section components, etc. (Vikas *et al.*, 2007). In this study, the powder form of Mo, Si and C are added in two different proportions to obtain 5% and 20% of SiC by weight ratio with MoSi₂ powder by adjusting the molecular weight of each constituent in chemical reaction. Experimental characterisation is done using Fourier Transform Infrared spectroscopy, X ray Diffraction analysis, Scanning Electron Microscopy, Atomic Force Microscopy, Raman Spectroscopy and Particle size analysis.

MATERIALS AND METHODS

Synthesis and Processing

The composite is prepared in three different proportions with Molybdenum, Silicon and Carbon which forms MoSi₂ as primary matrix and SiC as secondary matrix. The raw materials used for this study are procured in research grade from Alfa Aesar, Hyderabad. In this present study, elemental powders of Mo (99.9%, 1-2 µm), Si about 20 µm and fine Carbon black (99.9%, 45 µm) are mixed in the desired proportions in a Glove box (Model: M Braun, AB Star-Germany) under argon gas atmosphere and sealed in a cylindrical WC vial together with 50 WC balls of 10 mm in diameter so as to obtain SiC of 5% and 20% by weight with MoSi₂ powder composite (Das *et al.*, 2007). The above compositions are obtained by adjusting the weight of each elements based on molecular weight of each constituent in chemical reaction using Equation (1).



The ball/powder weight ratio is maintained at the level of 20:1. The ball milling experiments are carried out using high-energy ball mill (Model: Pulversitte 6, Fritsch Germany) at a rotation speed of 300 rpm for 60 hrs of high temperature milling to attain the final by-product. The milling experiments are interrupted at a regular interval of 15 min. for cooling after 5 hrs of continuous milling. The reduction of particle size by means of chemical reaction has been performed (Rosales *et al.*, 2007; and Zhong, 2008). By this method, particles are synthesized which comprises of SiC reinforced MoSi₂. The milled powders are taken out from the vial for further experimental characterization.

Characterization Technique

FTIR Analysis

The Fourier Transform Infrared (FTIR) spectra were collected for the powders using a Bruker Optics GmbH FTIR spectrometer, (Model: ALPHA, Germany). The functional group of the samples were recorded by using FT-IR. Spectra were obtained at 4 cm⁻¹ resolution, averaging 24 numbers of scans.

Raman Spectroscopic Analysis

Raman spectroscopy was carried out to find the vibrational, rotational and other low-frequency modes in a system (Model: Nexus 670, TEC, USA). This analysis was used to analyse the composition (Mo, Si, C) of samples after every processing step.

XRD Analysis

X-Ray powder Diffraction (XRD) patterns were obtained for the powder samples using Siefert x-ray diffractometer using Cu-K α radiation (λ

= 1.54060 Å) at 60 kV over the range of $2\theta = 10^\circ - 90^\circ$ with a step size of 0.01708 and step time of 15.5076 s. Phase purity and grain size are determined by XRD analysis. The average grain size of the composites is calculated by using the Debye Scherrer equation.

SEM Analysis

Scanning Electron Microscopy (SEM-EDX PHILIPS XL 30) was used for investigation of microstructure and elemental analysis of the sample obtained at different conditions. The morphology of the synthesized MoSi₂-SiC composite and different phases were observed by scanning electron microscopy. Prior to examination all samples are ion sputtered with gold to enhance the charging of particles.

AFM Analysis

AFM is very important characterization technique to observe the morphological configuration and also the structural analysis in the order of nano range. The topography of the NC is analysed with the AFM (Model: XE 70, Park Systems-S. Korea). The surface roughness and particle size are examined by using AFM analysis.

Nano Hardness Analysis

Nanoindentation tests are performed at different indentation loads in the range of 2-4 nN with Berkovich diamond indenter in contact mode of AFM (Model: XE 70 Park Systems-S. Korea) and thus hardness are determined from Force-Displacement (F/D) curve.

RESULTS AND DISCUSSION

FT-IR Spectroscopic Analysis

Infrared Spectroscopy is a versatile and common method for characterization of

chemical bonds. This technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region. Figure 1a shows the details about the vibrational frequencies of MoSi₂-5% SiC composite recorded in solid mode of FT-IR spectrometer. This predicts that characteristic peaks are obtained in the region

of 1030 cm⁻¹ and 807 cm⁻¹. The peak at 1030 cm⁻¹ is attributable to the MoSi₂ and the peak at 807 cm⁻¹ is assigned to SiC (Wei *et al.*, 2009; and Poornaprakash *et al.*, 2011). The increase in % of SiC influences the absorption peaks of MoSi₂ and SiC (1030 cm⁻¹ and 807 cm⁻¹) which are slightly shifted as found in Figure 1b.

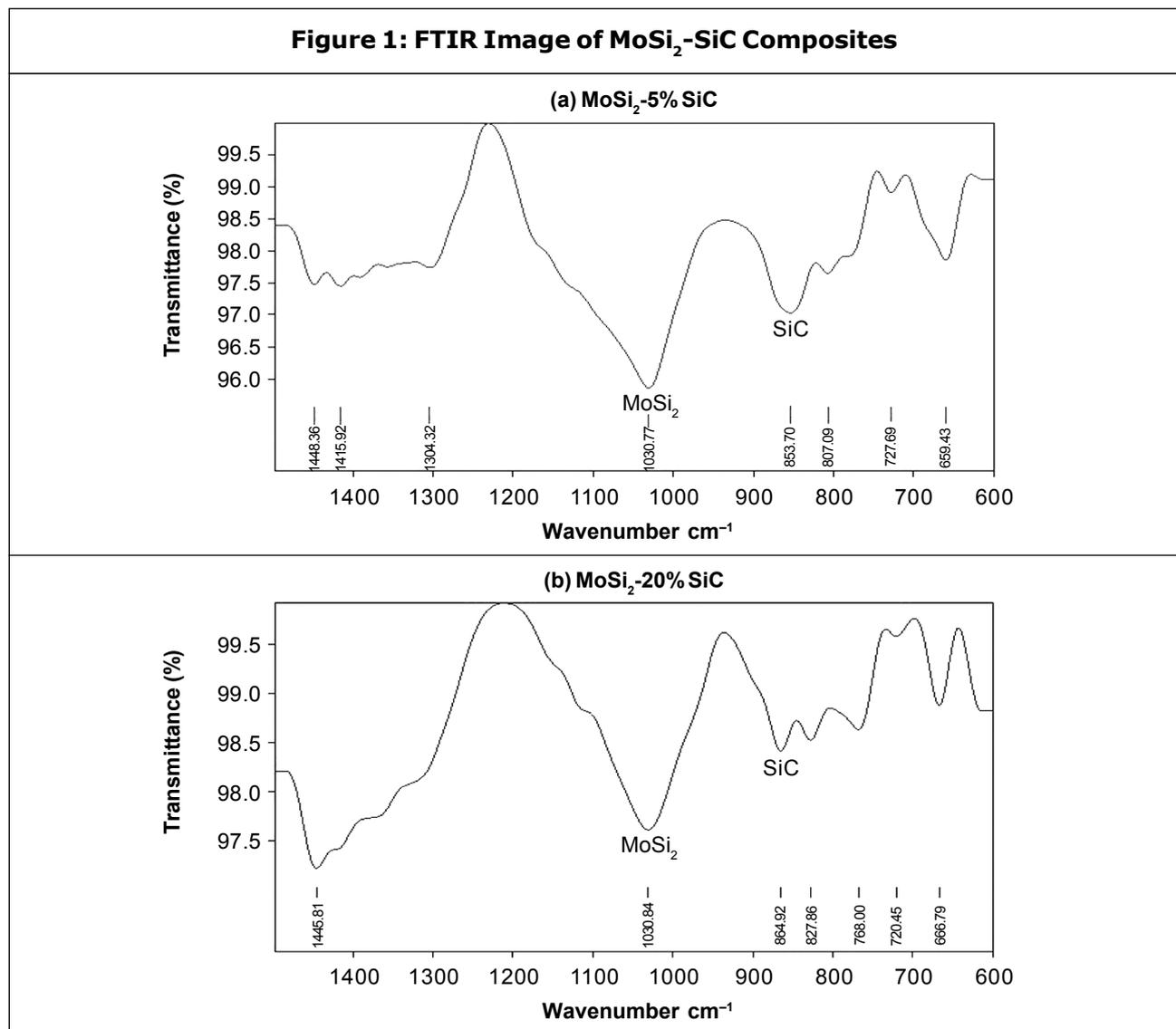


Figure 1b predicts that vibrational frequency of MoSi₂ is obtained in the peaks of 1027 cm⁻¹ and for SiC peak is 848 cm⁻¹ for MoSi₂-20% SiC. Thus FT-IR images confirmed the

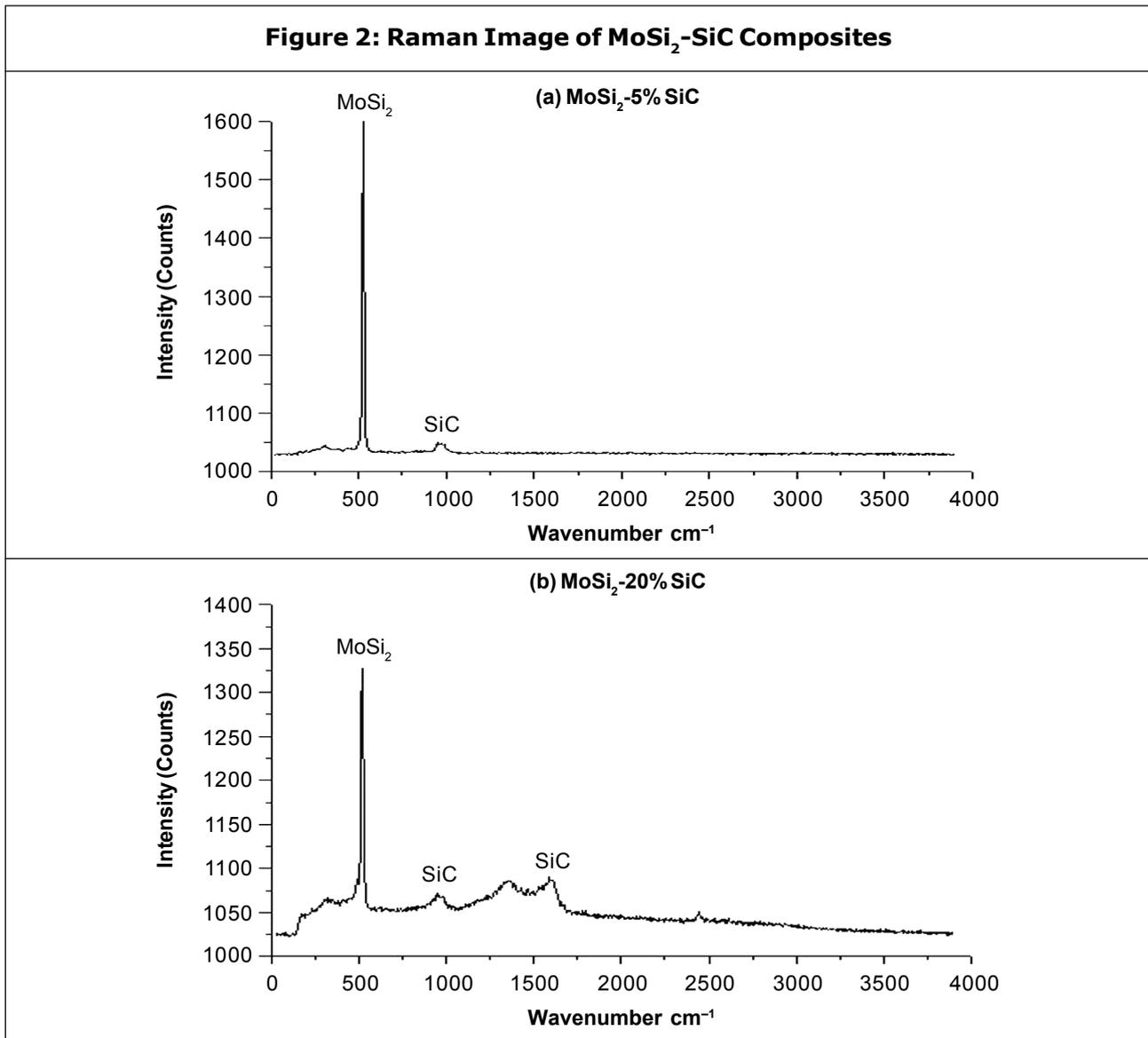
formation MoSi₂ and SiC when individual elemental powders are milled in desired proportions as per the procedure described in the materials and methods section.

Raman Spectroscopic Analysis

Raman Spectroscopy predicts molecular vibrational information that is inactive in the infrared region because of molecular symmetry. It uses visible or UV radiation rather than IR radiation. Figure 2 predicts that Raman shift for MoSi₂ is obtained in 502 cm⁻¹. But

while increasing the weight percentage of SiC, intensity of Raman shift increases as shown in the figure. Figures 2a-2b shows the intensity of SiC in ordinate axis for MoSi₂-5% SiC is 1045 counts and increases gradually up to 1084 counts for MoSi₂-20% SiC (Kin-Tak *et al.*, 2010).

Figure 2: Raman Image of MoSi₂-SiC Composites



The scattered intensities of peak height on the spectrum are then converted into scattering coefficient by dividing the recorded height of the sample peak by

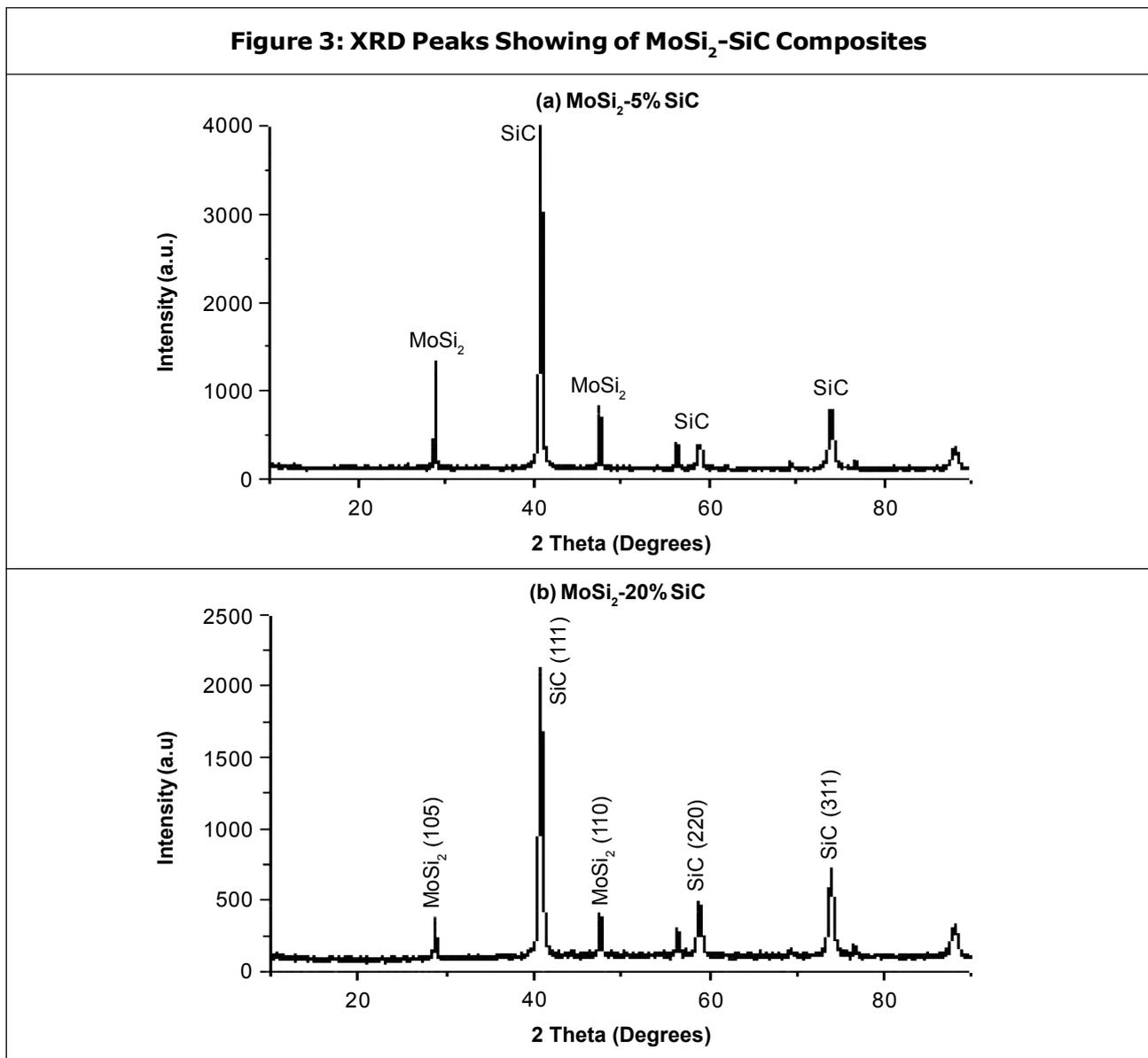
average height of the dual traces of MoSi₂ peak. By standard reference, peaks are obtained in cells of the same value (502 cm⁻¹).

X-Ray Diffraction Analysis

The XRD patterns of MoSi₂ and SiC NC are represented (Figure 3). A single distinct peak appears at 2θ = 41.4° which indicates the crystallinity of SiC that is resembled with JCPDS file No. 29-1129 (Naveen *et al.*, 2010) and no other peaks appearing over the scan range from 30° and 45°. According to XRD pattern, the peaks corresponding to SiC are appeared additionally at 2θ = 59.1° and 74.5° (Figure 3). It is observed that peak

appears at 2θ = 29.8° and 49° which is identified as the MoSi₂ reflection and clear that the 2θ peak characteristics for MoSi₂ and SiC are obtained in the same position for 5% and 20% SiC combinations. Also, from XRD pattern of the composites, the crystalline size of the samples is calculated using Debye Scherer Equation (2).

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad \dots(2)$$



where λ is the wavelength of X ray radiation, θ is diffraction angle, β is angular width at half maximum intensity. The particle sizes are calculated based on Equation (2) as 9.94 nm and 11.83 nm for 5 % and 20% SiC and MoSi₂ combinations respectively.

Characterization in Scanning Electron Microscopy

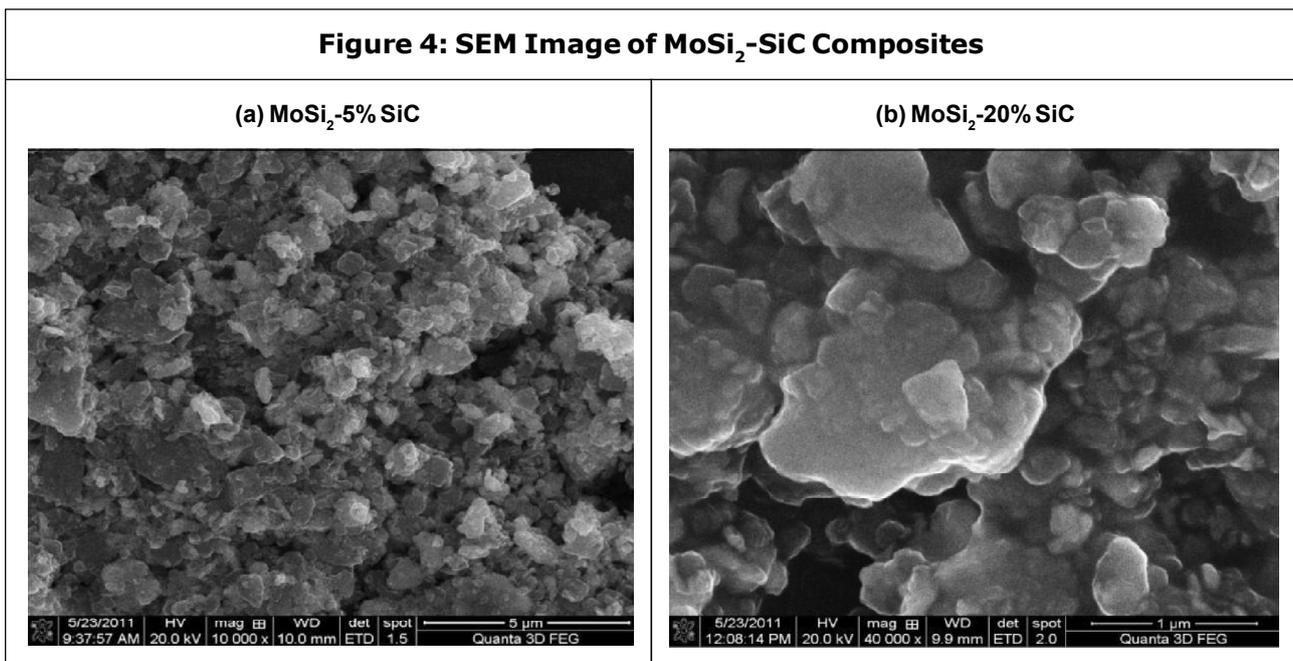
The samples are prepared for SEM investigation with ion sputtering by gold coating. Figures 4a-4b shows the SEM images of Nanocomposites in which MoSi₂-SiC are identified as two flattened different phases. This is because of crushing the base powder along with secondary particles for

prolonged time. Figure 4a provides the image of MoSi₂-5% SiC Nanocomposite and represents clear visibility of individual powder particles.

Figure 4b shows the SEM image of MoSi₂-20% SiC composite powder which is milled in high energy ball mill for about 60 h. The grey spots on the MoSi₂ granule show the deposition of SiC on the MoSi₂ matrix. The shape of the MoSi₂ particle is appearing like amorphous rock and flaky shape (Yuriy *et al.*, 2011).

The increase in % of SiC by weight increases the particle sizes of composites because of constant milling time and hard nature of SiC.

Figure 4: SEM Image of MoSi₂-SiC Composites



Topography of Nanocomposite Using AFM

AFM is very important characterization technique to observe the morphological configuration and also the structural analysis in the order of nano range. Figure 5a exhibits the AFM image of MoSi₂-5% SiC composite

in two dimensional formats. Particle distribution found in 10 × 10 μm area is explored by drawing a line profile across the 2D image which is represented as red line. Vertical line drawn is indicated by the green line. The surface roughness (Ra) found on red and green line is 11.675 nm and 9.600 nm respectively (Pavel *et al.*, 2010).

Figure 5a: AFM Topography of the MoSi₂-5% SiC Composite

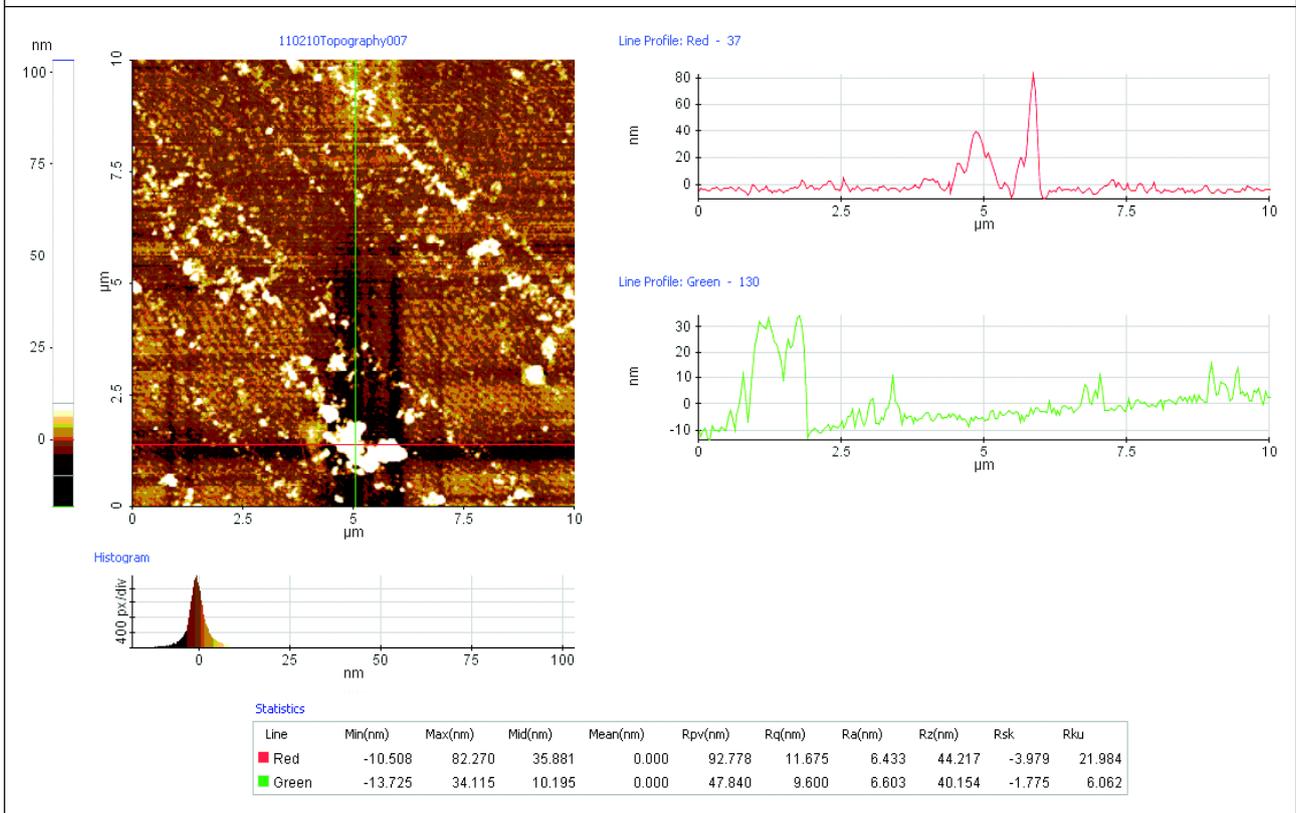
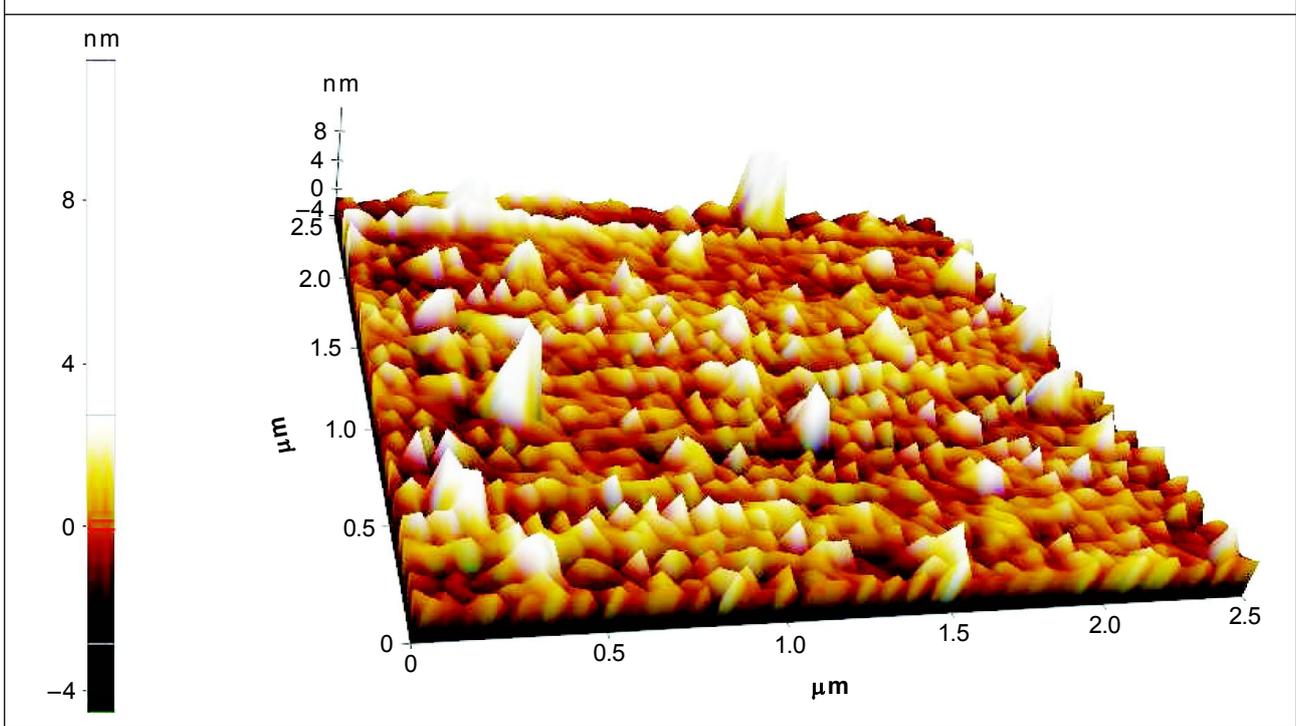


Figure 5b: 3D Image of AFM Topography



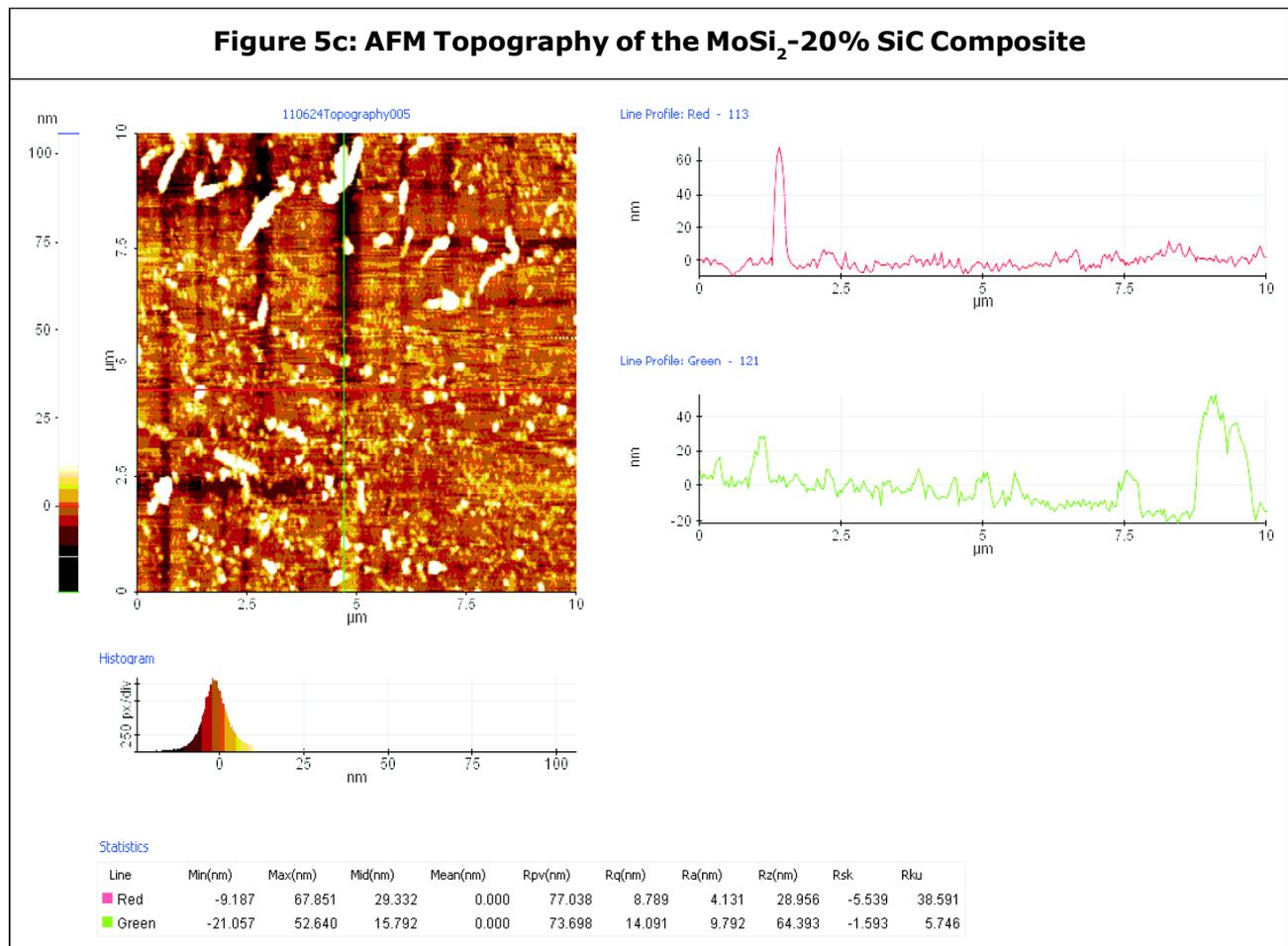


Figure 5b exhibits the three dimensional image of AFM topography of 5% SiC Nanocomposite and predicts that size of the particle is around 8 nm. Figure 5c shows the AFM image of CMC containing MoSi₂-20% SiC composite of scan size of 10 × 10 μm observed that the surface roughness and particle size are attained to the maximum of 14.091 nm and 12 nm respectively.

Particle Size Analysis

After the completion of ball milling, the samples are loaded into the sonicator with required solvent for about 10 min to prevent particle agglomeration. Afterwards the suspension is loaded into the particle size analyser. Figures 6a-6b shows that coarse

particles are existed for higher amount of SiC content. This is due to the high hardness and strength of secondary particle and also due to constant prolonged milling time of composites (Darryl *et al.*, 1996; and Morris *et al.*, 1997).

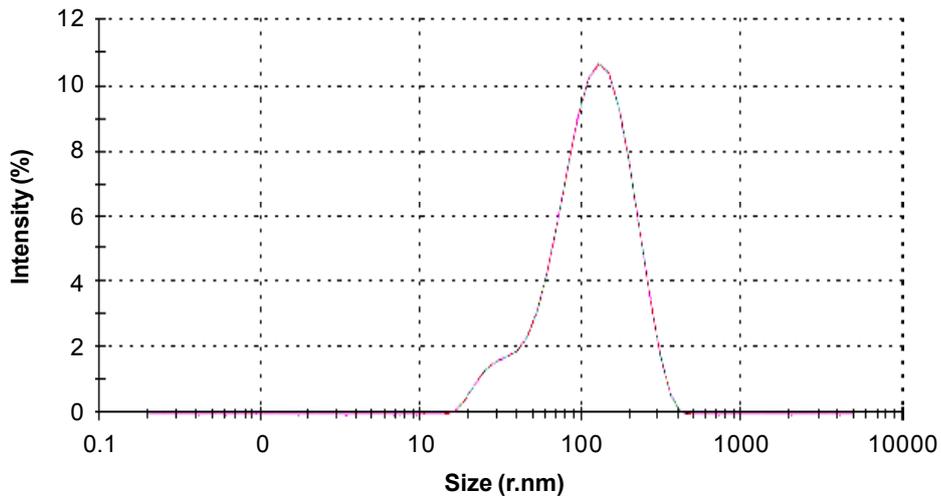
F/D Curve Analysis

Nanoindentation is another method to characterize the mechanical properties of materials on a very small scale. Features less than 100 nm across, as well as thin films less than 5 nm thick can be evaluated using this approach. Nanoindentation enables the user to perform indentation test to measure material properties, such as nanoscale hardness and elasticity. Single indentation

Figure 6: Nano Particle Analysis of MoSi₂-SiC Composites

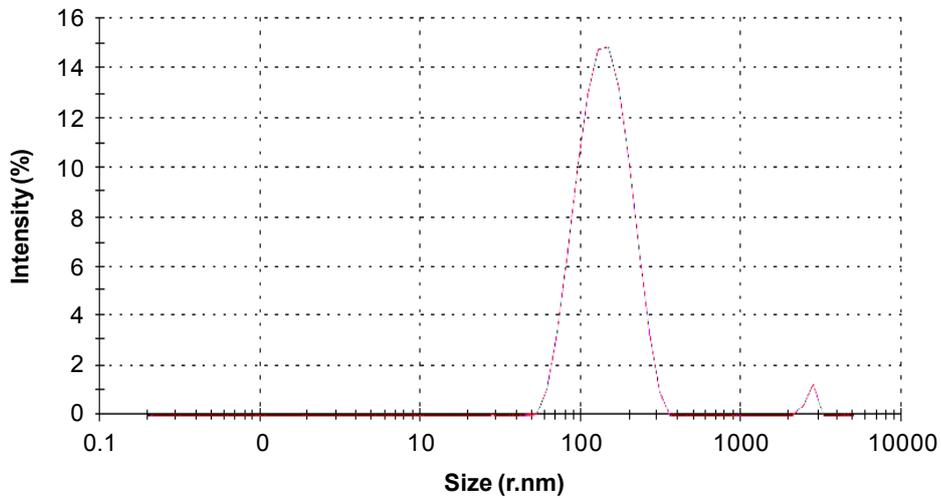
	Diam. (nm)	% Intensity	Width (nm)
Z-Average (r.nm): 96.55	Peak 1: 128.100	100.0	67.430
Pdl: 0.273	Peak 2: 0.000	0.0	0.000
Intercept: 0.807	Peak 3: 0.000	0.0	0.000
Result Quality: Good			

**(a) MoSi₂-5% SiC Composite
Size Distribution by Intensity**



	Diam. (nm)	% Intensity	Width (nm)
Z-Average (r.nm): 139.3	Peak 1: 146.100	98.3	51.280
Pdl: 0.263	Peak 2: 2694.000	1.7	159.000
Intercept: 0.838	Peak 3: 0.000	0.0	0.000
Result Quality: Good			

**(b) MoSi₂-10% SiC Composite
Size Distribution by Intensity**



cycle consists of loading, holding and unloading processes. A whole indentation measurement process consists of a single cycle or many cycles with gradually increasing loads. For indentation, the probe is forced into the surface in contact mode of AFM. The depth of the indentation is measured from the AFM image to evaluate hardness. F/D curve obtained during indentation also provides indications of the sample material's mechanical properties (John, 1995).

The F/D curve is also plotted as shown in Figures 7a and 7b. From these results, the hardness (H) can be calculated by using the formula (3).

$$H = \frac{P}{24.5 (h_c)^2} \quad \dots(3)$$

where P : maximum applied load; h_c : penetration depth (Mittraa *et al.*, 1997). It is deduced from Table 1 that, increasing Wt. % of SiC produces more amount of secondary matrix and thereby increases hardness.

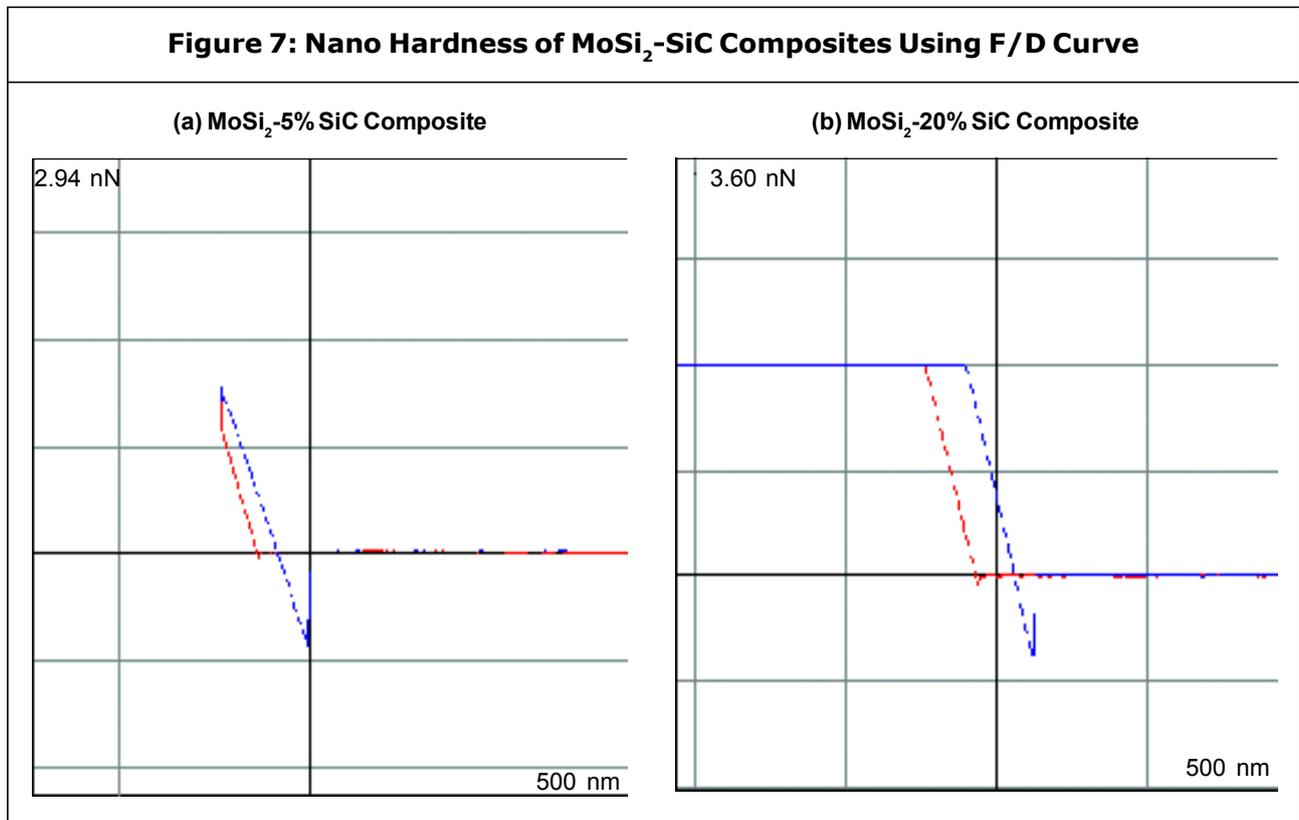


Table 1: Nano Hardness of Various Composites

S. No.	Nanocomposite	Load P , nN	Displacement h_c , nm	Hardness, kPa
1.	MoSi ₂ -5 SiC	2.94	88.99	15.16
2.	MoSi ₂ -10 SiC	4.00	82.66	23.89
3.	MoSi ₂ -15 SiC	3.00	57.49	49.39
4.	MoSi ₂ -20 SiC	3.60	136.62	78.72

CONCLUSION

The synthesis of MoSi₂-SiC NC is achieved by mechanical milling approach and characterisation are thus performed using FT-IR, XRD, SEM, AFM, Raman Spectroscopic and particle size analysis.

- From the different characterization it is deduced that the formations of MoSi₂ and SiC in various compositions are confirmed based on the functional group present in absorption spectra of FT-IR analysis when individual elemental powders of Mo, Si and C are milled in desired proportions.
- In SEM investigation, while increasing the % SiC by weight, the particle size of the nano composite also increases because of constant milling time of composites and hard nature of secondary matrix (SiC) than primary matrix (MoSi₂). When the SiC content increases from 5 to 20%, the particle size reduction takes more time and hence the particle sizes and roughness values are coarser.
- XRD analysis confirmed the crystalline size of the NC as 9.94 nm and 11.83 nm for 5% and 20% SiC respectively. Particle distribution is explored by AFM and surface roughness is calculated as 11.675 nm for MoSi₂-5 SiC composite.
- Nanohardness of two different combinations of NC such as 5% and 20% SiC is evaluated by performing nanoindentation test in contact mode AFM using F/D curve analysis. By increasing Weight percentage of SiC produces more amount of secondary matrix and thereby increases hardness.

- All these facts are substantiated from various results like SEM, AFM, XRD, etc. This high temperature withstanding capability of composite finds its applications in automobile and aerospace industries. 🌀

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