

Development and Characterization of Boron-Nitride Reinforced Nickel Matrix Composites

Atteeq Uz Zaman¹, Awais Khan¹, Fatima Zaman¹, Muhammad Moheen Khan¹, Umar Farooq¹, Tauheed Shehbaz¹ and Muhammad Ramzan Abdul Karim^{1,*}

¹Faculty of Materials and Chemical Engineering, Ghulam Ishaq Khan Institute of Engineering Sciences and Technology, Topi-24360, Swabi, Pakistan.

Abstract. In this work, pure nickel was reinforced with various contents of h-BN (4 & 8wt.%) and SiC (2, 4, 6 & 8wt.%) prepared via PM route. The synergistic effect of h-BN and SiC on mechanical and microstructural behaviour was investigated. The microstructure and crystal structure were characterized by scanning electron microscope and X-ray diffractometer. The density and microhardness were evaluated via He pycnometer and microhardness tester. SEM results revealed that the exfoliation reduced the particle size of h-BN from approximately 105 nm to 30-40 nm. Furthermore, the addition of h-BN and SiC improved the mechanical properties of the composite. The maximum hardness value of 420 HV was obtained for Ni-8BN-6SiC. This improvement in hardness was attributed to uniform dispersion and high hardness of h-BN and SiC. However, more addition of SiC (>6 wt.%) deteriorated the hardness of the composite due to generated porosity.

Keywords: Nickel metal matrix composite, h-BN, exfoliation, nanosheets, powder metallurgy, strength, hardness.

1 Introduction

Since recent years have shown a growing interest in the fabrication of advanced materials with improved mechanical, thermal, and electrical properties. Metal matrix composites (MMCs) are one of the class materials that have gained significant attention due to the higher strength-to-weight ratio, stiffness, low coefficient of thermal expansion and wear resistance compared to conventional metals. Owing to its superior properties, MMCs are widely utilized in various applications such as defense, automobile, aerospace, marine transport, rail transport, space, electronic and infrastructural sectors [1][2]. In MMCs, nickel, copper, titanium, magnesium, and aluminium are primarily employed as a matrix with a combination of TiC, SiC, BN, Al₂O₃, B₄C, AlN and Si₃N₄ etc as reinforcement materials. Among various types of MMCs, nickel-based MMCs have emerged as promising candidates attributed to its superior properties such as excellent corrosion and oxidation resistance, thermal stability, wear and mechanical properties. Consequently, Nickel (Ni) and its alloys are frequently used for the fabrication of pressure vessels, engine components and gas turbines. However, the mechanical properties of nickel-based MMCs are limited by the intrinsic brittleness of the reinforcing phase which can lead to premature failure and reduced durability. To address this problem, researchers have focused by incorporating ceramics reinforcement materials in nickel matrix.

In previous studies, the addition of nitrides such as aluminium nitride (AlN), boron nitride (BN) and titanium nitride (TiN) improved the mechanical properties of MMCs. Amongst, BN is an excellent ceramic reinforcing material for MMCs due to its low density, high thermal shock resistance, excellent strength, chemical inertness, improved thermal conductivity, superior molten metal erosion, ablation resistance, outstanding machinability and good lubrication properties [3]. On the other hand, silicon carbide (SiC) was extensively utilized in ceramics reinforcing materials for its exceptional combination of superior properties for example high compressive strength, extreme hardness, high thermal conductivity, low coefficient of thermal expansion and chemical inertness [4]. Recently, the fabrication of nickel composites using merely SiC and BN is unable to meet the specified requirements. Therefore, a novel strategy was carried out by using binary reinforcement (h-BN & SiC) to prepare a hybrid composite of MMCs.

Today, numerous studies have been conducted on MMCs and their fabrication. Stark et al [5]. used cold-spraying to form a coating for aluminium substrates with h-BN as the filler material in a nickel matrix. The effect of filler material (BN) on the tribological properties of nickel was evaluated. The experimental findings demonstrated a significant enhancement in the hardness, strength and friction coefficient of both the coatings and the underlying substrate[6]. Hussain et al. [7] utilized a powder metallurgy approach to synthesize a novel composite material known as 3Di-hBN-Cu-Ni. Through a metal-organic chemical vapour deposition process, they successfully created three-dimensional interconnected hexagonal boron nitride (3Di-hBN) layers surrounding the grains of a Cu-Ni matrix. The experimental results revealed that the incorporation of 3Di-hBN had a positive influence on the mechanical properties of the composite. Specifically, the composite exhibited improved yield strength, ultimate tensile strength (UTS), and fracture toughness when compared to the Cu-Ni alloy. The presence of the 3Di-hBN layers at the interfaces of Cu-Ni grains played a crucial role in enhancing the overall performance of the composite. These layers facilitated load transmission, dislocation strengthening, and grain refinement mechanisms, allowing the composite material to effectively withstand applied loads. Tantawy et al. [8] reported the fabrication of Ni and Cu composites with varying contents of boron nitride contents via water atomization technique. The mixtures were compacted under an applied pressure of 400 MPa and sintered for 2 hours at 1000°C in a controlled atmosphere. This study yielded that the

increase in BN content led to a reduction in the relative density of the composites. However, this increase in BN content improved the hardness, saturation magnetization, and electrical resistivity.

Furthermore, Extensive research has been performed on various methods for reducing the size of hexagonal boron nitride (h-BN) sheets. Cao et al. [9] explored the method of liquid phase exfoliation to break down bulk layered structures of h-BN. By utilizing a mixture of ammonia water solution and isopropyl alcohol, they successfully obtained a powder consisting of exfoliated boron nitride nanosheets (BNNSSs) that exhibited exceptional stability in isopropyl alcohol solution.

In this work, the Powder metallurgy route was used to prepare Ni-reinforced h-BN and SiC metal matrix composite. The synergistic effect of h-BN and SiC on the mechanical properties of the Ni matrix composites was evaluated.

2 Material and experimental conditions:

2.1 Materials

Commercially available nickel powder of average particle size ranging from 2 to 50 microns with 99.9% purity (Sigma-Aldrich, USA) was employed as a matrix. Hexagonal boron nitride (1-2 μm, 99% purity) and silicon carbide (3-5μm, 99% purity) were utilized as reinforcement supplied from China. Table 1. Provides the detailed properties of materials investigated for studying the influence on mechanical and microstructural properties of Ni-based composites.

Table 1: Details properties of Ni, h-BN and SiC.

Materials	Density (g/cm ³)	Hardness (HV)	Fracture Toughness (MPa.m ^{1/2})	Ultimate Tensile Strength (MPa)	Thermal Conductivity (W/m. K)	Compression Strength (MPa)	Specific Heat (J/kg.k)
Ni	8.91	362	150	345 to 1000	91	935	460
SiC	3.21	2342	6.4	390	120	130	750
h-BN	2.1	3800	5	100000	751	1551.32	700

2.2 Exfoliation:

To facilitate the liquid phase exfoliation process, a synergistic combination of two liquids, ammonium and isopropyl alcohol (IPA) was employed. For the exfoliation of h-BN, a solution of 100 ml with a 28% ammonia concentration and IPA in a 3:2 ratio (60 ml ammonium and 40 ml IPA) was prepared. Two samples of 25ml and 75ml were collected from the solution to check the exfoliation of h-BN after 19 and 35 hrs, respectively. The exfoliated samples were then centrifuged for 30 minutes and, subsequently, dried for 15 hrs at 80°C in a vacuum oven.

2.3 METHODS:

The fabrication of Ni-BN and Ni-BN-SiC composites was carried out using the powder metallurgy (P/M) method. Initially, nickel powders were mixed with ethanol in a mechanical mixer, while h-BN and SiC were subject to ultrasonication for 1 hr. Subsequently, the h-BN and SiC slurry was added to the nickel-ethanol mixture and was then ball milled for 24 hrs with the milling speed of 150 rpm to achieve homogeneity among the particles. The resulting mixture was vacuum dried for 20 hrs for the removal of ethanol. The composite powder obtained was compacted in the cylindrical dia under a pressure of 60 MPa, to form green cylindrical samples with dimensions of 2 mm thickness and 13.5 mm diameter. Finally, the compacted samples were sintered in a tube furnace under argon conditions at an optimal sintering temperature of 1100°C for a duration of 1 hr. The details of the prepared compositions in this study are given in Table 2.

Table 2: Details compositions of the all the specimens.

Materials	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
	(Ni-4BN-2SiC)	(Ni-4BN-4SiC)	(Ni-8BN-6SiC)	(Ni-8BN-8SiC)	Ni-8BN
Ni	94%	92%	86%	84%	92%
SiC	2%	4%	6%	8%	0%
h-BN	4%	4%	8%	8%	8%

2.4 Characterization

Different characterizations have been performed to study the microstructure and mechanical properties of Ni matrix composites. Scanning Electron Microscopy (SEM, Carl Zeiss Evo 15) equipped with Energy Dispersive X-Ray (EDX) was used to determine the specimen morphology, size of the grains, and distribution of h-BN and SiC in the Ni matrix. To probe the crystalline plane and phase of the sintered specimen, X-Ray Diffraction (XRD, Proto Manufacturing Ltd, Canada) was employed. The green and sintered densities of the composites were determined via Helium pyrometry (IQIPyc, USA). The particle size of the powder before and after exfoliation for different time periods was determined by a particle size analyzer (Shimadzu). Additionally, to determine the impact on the mechanical properties of nickel reinforced with SiC and h-BN, the hardness of Ni matrix composite was determined via a microhardness tester (Tukon Model 300).

3 Results and Discussion:

3.1 Effect of Exfoliation of h-BN

In this work, the exfoliation of the h-BN powder was performed for different periods of time and compared with unexfoliated h-BN powder.

1. Series 1 is the unexfoliated sample.
2. Series 2 comprised the batch exfoliated for 19 hrs.
3. Series 3 underwent exfoliation for 35 hrs.

The progression from series 1 to 3 demonstrated a noticeable decrease in the mean particle size of h-BN from 105 nm to 34 nm. This confirms the effectiveness of liquid phase exfoliation in reducing the sheet thickness of hexagonal boron nitride (h-BN) samples. Table 3 presents the variation in sheet thickness after different durations of exfoliation. Series 1 represents the initial state of the particles without any exfoliation, while Series 2 represents the sample after 19 hrs of exfoliation, and Series 3 after 35 hours of exfoliation. In Series 1, the particle size of unexfoliated h-BN was relatively thick (tens to hundreds of nanometers) and stacked layers of h-BN were bonded together by weak Van der Waals, making it least favourable for the research due to the sample's inhomogeneity (Figure 1a). Series 2 exhibited a reduction in sheet thickness and improved uniformity in particle size distribution. However, Series 3 exhibited optimal results, with a thickness range of 30-40 nm and a more homogeneous appearance. The successful liquid phase exfoliation using an ammonium and IPA solution achieved the desired thinness of h-BN sheets. Nevertheless, Figure 1 (b) indicated some agglomeration of nanosheets after exfoliation. The clustering of h-BN can be prevented by dry milling or ball milling the sample before uniaxial compaction, ensuring homogeneity throughout the sample.

Table 3: Mean particle size in nanometers of samples exfoliated for defined durations.

Sr.	Samples	Mean Particle Size (nm)
1	Series 1 (unexfoliated)	105.1
2	Series 2 (19 hrs, 48 mins exfoliation)	63.5
3	Series 3 (35 hrs exfoliation)	34.2

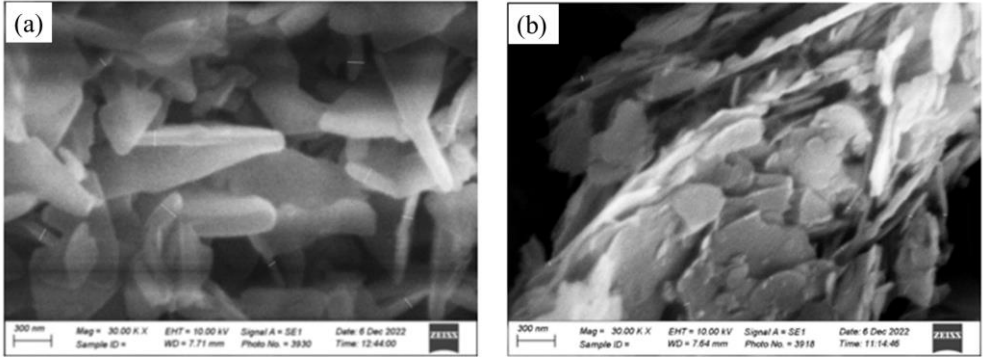


Figure 1: SEM images of (a) unexfoliated h-BN particles (b) exfoliated h-BN particles for 35 hrs.

3.2 Density measurement.

The densities of the composites measured before and after sintering are summarized in Table 4. As evident from Table 4, it can be observed that the green and sintered densities of the composites decreased with the addition of h-BN and SiC reinforcement. The highest sintered density of 7.67 g/cm³ was obtained for Ni-4BN-2SiC composites. However, further increase of h-BN and SiC contents resulted in a decrease in density and reached the value of 6.60 g/cm³ for Ni-8BN-8SiC composites. This reduction in the density of the composite was ascribed to the lower density of h-BN (2.7 g/cm³) and SiC (3.21 g/cm³). Furthermore, the formation of void spaces or pores between the particles led to a decrease in the composite density.

Table 4. Green and sintered densities of composites

Composites	Theoretical density	Green density	Sintered density
Ni-8BN	8.63	5.07	7.02
Ni-4BN-2SiC	8.71	5.26	7.74
Ni-4BN-4SiC	8.65	5.37	7.81
Ni-8BN-6SiC	8.46	5.64	7.93
Ni-8BN-8SiC	8.40	5.41	7.54

3.3 XRD analysis:

The XRD pattern of the Ni-BN-SiC composites as depicted in Figure 2. The XRD results, as shown in Figure 2, revealed distinct peaks at 2 θ equal to 64°, 47° and 35° confirm the

presence of SiC in all composites. Furthermore, h-BN peaks appeared at $2\theta = 28^\circ, 42^\circ$ and 56° . In addition, the peaks present at $2\theta = 44^\circ, 52^\circ$ and 77° endorse the existence of Ni. Importantly, no reaction peaks were observed, indicating that Ni, SiC and h-BN did not undergo any chemical reaction to form a new phase. However, some new peaks were detected, indicating the presence of oxygen which might be due to the oxidation of the sample during the exfoliation or sintering processes.

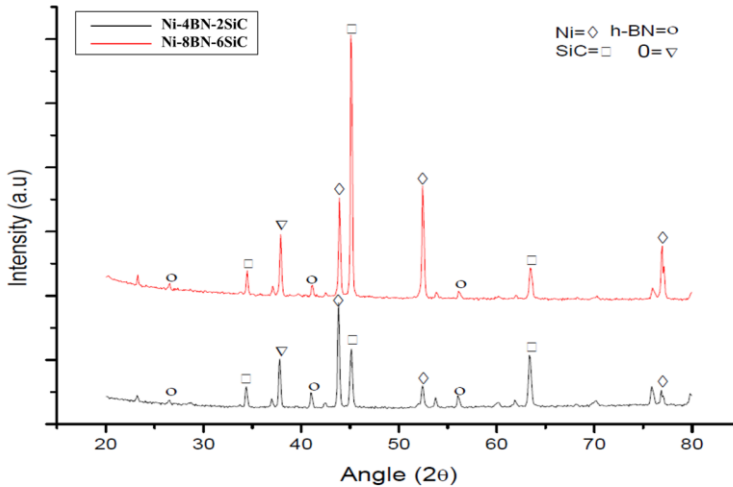


Figure 2: XRD pattern of (a) Ni-4BN-2SiC (b) Ni-8BN-6SiC.

3.4 Hardness Tests:

The variation in hardness of the Ni-BN-SiC composite is illustrated in Table 5. The results revealed that the composite incorporated merely 8 wt.% h-BN showed a hardness of 115 HV. However, the addition of dual reinforcement (h-BN and SiC) significantly improved the hardness of the composite. The composite incorporated with 4wt.% h-BN and 2wt.% SiC exhibited the microhardness of 154 HV. However, it reached the maximum value of 420 HV with the addition of 8wt.% h-BN and 6wt.% SiC. The enhancement in the hardness of the composite was attributed to the high hardness of SiC. In addition, further increments of SiC (> 6wt%) deteriorate the hardness of the composites attributed to the porosity.

Table 5: Micro-hardness values of different compositions

Compositions	Micro-Hardness
Ni-8BN	112
Ni-4BN-2SiC	154
Ni-4BN-4SiC	293

Ni-8BN-6SiC	420
Ni-8BN-8SiC	407

3.5 Microstructural analysis via SEM

Figure 3. demonstrates the SEM images of Ni-BN-SiC composites. SEM analysis of Figure 3 (a, b), revealed that all specimens have a strong neck and well-bonded microstructure. Moreover, h-BN and SiC were uniformly dispersed throughout the matrix as confirmed by EDX mapping (Figure 4). However, the composite containing 8wt.% h-BN and 8 wt.% SiC exhibited some void spaces and porosity Figure 3 (c, d). The degree of porosity increased with the increment of mass fraction SiC, as the excess SiC particles that remain unreacted create pores in the composite, with the volume of the pores expanding owing to the pressure of gas increasing within the pores [10]. In addition, EDX mapping (Figure 4) disclosed the presence of oxygen which was ascribed to the oxidation of during the exfoliation of the sample.

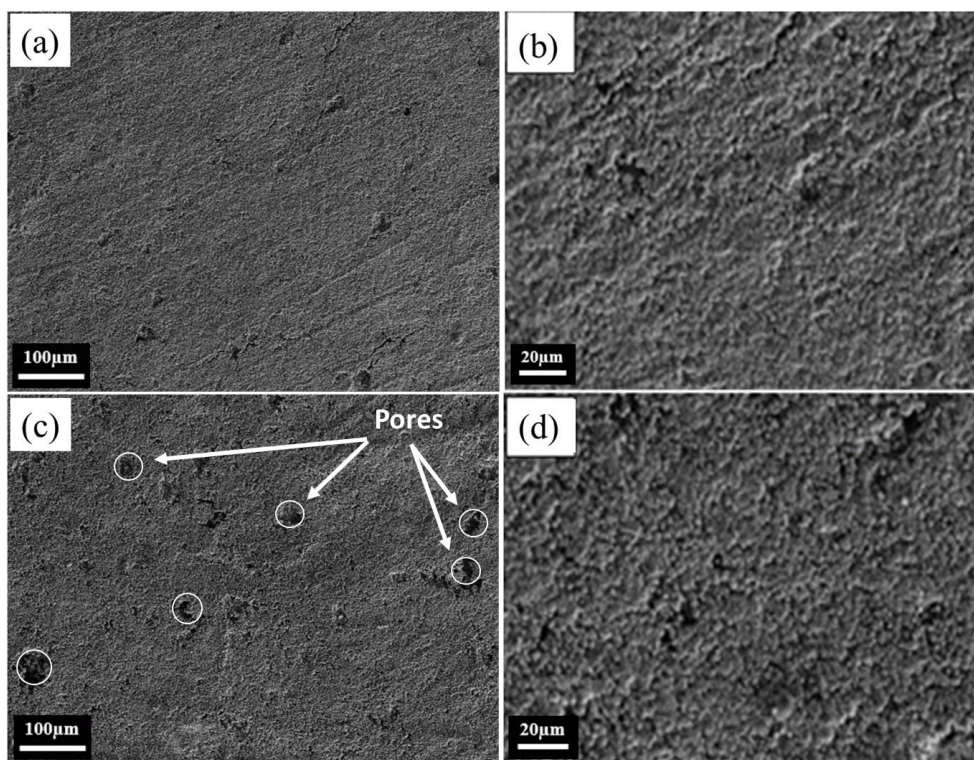


Figure 3: SEM micrographs of Ni-BN-SiC composite: (a, b) Ni-4BN-2SiC (c, d) Ni-8BN-8SiC.

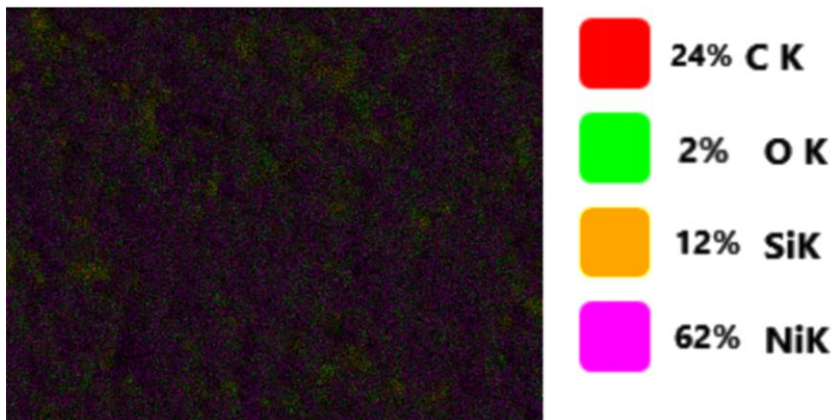


Figure 4. Elemental Mapping of mapping of Ni-4BN-2SiC

4. Conclusions:

The present study successfully employed powder metallurgy to fabricate various compositions of nickel composites with hexagonal boron nitride (h-BN) and silicon carbide (SiC).

1. The exfoliation process resulted in a significant reduction in the size of h-BN particle from 105 nm to 34 nm using a 3:2 solution of ammonium and IPA.
2. SEM analysis revealed the uniform dispersion of h-BN and SiC within the Ni matrix composite.
3. XRD characterization confirmed the presence of Ni, h-BN and SiC. No new phase was observed in the crystallographic analysis.
4. Hardness tests demonstrated that the nickel composite with 8% h-BN and 6% SiC exhibited the highest value of up to 420 HV, indicating enhanced mechanical properties.

Overall, this study demonstrates the fabrication and characterization of nickel composites with hexagonal boron nitride and silicon carbide which exhibited their enhanced properties and potential for a wide range of applications.

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