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Fabrication and Applications of Fullerenes Based Metal Nanocomposites: A Review

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Abstract

Several fabrication methods have been proposed to develop the metal matrix nano composites (MMNC) reinforced by carbon nano-materials (mostly the nanotubes, and graphene) by means of the liquid-state and the solid-state techniques. The spraying processes, the squeeze casting, the disintegrated melt deposition processes, the milling fabrication, and the friction stir processing have been used to fabricate the composite. However, the metal matrix nano composites, containing the fullerenes as reinforcement, are less known, although the properties of these objects with the predominant sp² bonding also extend their use in the composites. Fullerenes are hollow carbon molecules in the form of a sphere (buckyballs). Buckyballs can be essentially regarded as graphite layers, i.e., graphene sheets, wrapped into a spherical shape. Considering the staggering cost and limited availability of purified single walled carbon nanotubes (CNTs) and graphene, fullerenes with a spherical structure offer an interesting alternative to CNTs and graphene since they are available in abundance and at a much feasible cost. Furthermore, fullerenes offer a high degree of purity and maintain their quality even during the subsequent reproduction cycles. Thus currently, the fullerenes are widely investigated and have the potential for various technical applications. A significant potential application of fullerenes would be as reinforcement in metallic alloys used in structural parts. It should be noted that buckyballs, such as C₆₀ fullerenes, may be considered as fascinating reinforcements in comparison to CNT or graphene, due to their zero-dimensional

geometry. They can be easily dispersed and are scarcely damaged during severe mechanical dispersion processes carried out in metal matrix composites (MMCs). Fullerene has a great impact on Tribology applications due to its lubricating behavior. The spherical morphology and strong intermolecular bonding make fullerene as a lubricant material for industrial applications. This article will showcase in-depth analysis on collective information of fullerene based nano composites.

Keywords: Composites, Carbon, Fullerene, Processing, Properties

1. Introduction

Fullerenes are allotropes of carbon in which the molecules of carbon atoms are well connected by single and double bonds. It is observed that the Fullerenes molecules may be in various shapes and sizes. The reported shapes of Fullerenes molecules are in the form of hollow sphere, ellipsoid and tube shapes. The empirical formula for the Fullerenes molecules is denoted as C_n or Cn and n denotes the number of carbon atoms. The first ever literature established by Kroto et al¹ in 1985 which relates to C_{60} Buckminster fullerenes molecules. This unique molecule was established through vaporization of carbon from solid graphite disk through focused pulsated laser. A cluster of carbon atoms in 60 numbers was observed, thus coined as C_{60} . The C_{60} are closed Fullerenes or it can be called as Buckyballs. The name Buckyballs was inspired from the soccer ball since it resembles the molecular structure¹. Later the Fullerene family was extended with other forms of molecules based on shape, like Buckytubes (Carbon Nano Tubes) which are cylindrical shaped Fullerene. The existence of icosahedral symmetry in C_{60} and highest binding energy per carbon gained attention to the scientist for further research².

The increased demand for lightweight materials with high specific strength, stiffness and better tribological properties in the automotive, aerospace and defense sectors have accelerated the development and use of metal matrix nano composites (MMNCs)³⁻⁶. As material cost became a more significant consideration, the emphasis shifted toward particulate-reinforced materials, with the goal of a lower cost, high volume product that could be used in automotive and commercial aerospace applications. In past few decades, the studies related to Fullerene and Fullerene based nanocomposites established their potential usages in many applications, especially as thin films, organic polymers, and organic-inorganic nanocomposites in microelectronics and optics applications are few of them⁷.

2. Fabrication Techniques for Fullerene Based Nanocomposites:

The fabrication of nanocomposites can be established through various methods, like solid state methods, liquid state methods, deposition and spraying are few of them. The mostly reported Fullerene based nano composites are fabricated by solid state processing route such as Powder Metallurgy (PM) and Friction Stir Processing (FSP).

One of the early stage literatures related to synthesis of Fullerene based nanocomposites was demonstrated by Gurav et al⁸. The studies focused on the synthesis of Fullerene-Rhodium nanocomposite powders by aerosol decomposition method (See Figure: 1). Two types of solution of precursor was prepared, first contained mixed Fullerene extract in toluene and second contained mixed Fullerene extract and [(1, 5-COD) RhC1]₂ rhodium-based compound in toluene for study purpose. The synthesis of nano crystalline composite particles of Fullerene-Rhodium nano-composites demonstrated through evaporation of precursor solution which then undergone precipitation and subsequent decomposition under specific environmental conditions. In last, the powders were collected and further investigated for their features⁸. Choi et al.⁹ fabricated aluminum based fullerenes reinforced nanocomposites. The fabrication route involved in two steps, one was shattering fullerenes using two different control agents and second was disbursement of shattered fullerenes in aluminum powder using high energy ball milling and further considered for the investigation (See Figure 2(a-c)). Zuev and Ivanova¹⁰ fabricated Polymide-6 (PA6) based nanocomposite which reinforced with fulleroid fillers. The mechanical and electrical performances of the fabricated nanocomposites were evaluated.



Figure 1. Schematic of generation of fullerene-rhodium Nano composite powders via aerosol decomposition (Reprinted with permission from Ref. 8)



Figure 2. Step wise (a-c) ball milling following by hot rolling process to fabricate fullerene based metal Nano composite (Reprinted with permission from Ref. 9)

El-Shamy et al.¹¹ fabricated a hybrid nanocomposite films based on Polyvinyl alcohol/ carbon quantum dots/fullerene or (PVA/CQDs/C60) through a novel casting method (See Figure 3). This method includes, dissolving particulates CQDs/C60 in deionized water then added to PVA solution at specific temperature and time frame. As soon as some portion of the water evaporates, the solution was casted and dried¹¹. A nanocomposite of fullerene reinforced with Nafion was fabricated by Jung et al.¹² wherein a solution recasting method was considered. C₆₀ and DuPontTM Nafion PFSA (perfluorosulfonic acid) polymer dispersions are prerequisites for the fabrication processes. Vacuum dried Nafion PFSA polymer under specific temperature and time was further used. The Nafion PFSA polymer dispersed in Dimethylacetamide (DMAc) solution (stirred about 6hr at 80°c) and subsequently C₆₀ were dispersed in ortho-dichlorobenzene at various concentrations 0.1% wt. and 0.5% wt. (stirred about 24hr for stable dispersion and then dried in a casting mold at 120°C for 12 h¹².



Figure 3. Casting technique to manufacture fullerene based Nano composite¹¹

Santana et al.¹³ studied the phase transformations during milling and sintering process of Al- C_{60} and Fe- C_{60} . The conventional high energy SPEX mill was used for milling of Al- C_{60} and Fe- C_{60} with specific process parameters and Spark Plasma Sintering (SPS) ¹⁴ techniques was used for sintering process (See Figure 4). The microstructural studies were established during these two processes for understanding the influences of the milling and sintering for nanocomposite¹³.



Figure 4. Spark plasma sintering process (Reprinted with permission from Ref. 14)

An extensive method like powder metallurgy, sputtering and a thin film deposition method¹⁵ (See Figure 5) was studied¹⁶. Tin-Fullerene based nanocomposites were routed through powder metallurgy; where in the tin powder and fullerene were mechanically mixed and further sintered in three stages. While in sputtering method, the same powder metallurgy procedure was used except the sintering step. In thin film deposition method, the evaporation of tin and the sublimation of Fullerenes were used to obtain thin film. For both sputtering method and deposition method, a system was developed for synthesis of nanocomposites as shown in Figure 6¹⁶.



Figure 5. Thin film deposition method¹⁵



Figure 6. Schematic of the Nano composite deposition system used to produce materials by vapor condensation and in situ compaction (rf sputtering method) (Reprinted with permission

from Ref. 15)

Friction stir processing (FSP)¹⁷ was invented as grain modification technique^{18–21} derived from friction stir welding^{22–27}. Later, FSP is applied as composite manufacturing technique with a concept of particles insertion and subsequent distribution in base material to produce metal matrix type composite structure^{28–30, 3-6}. Figure 8 shows FSP of composite manufacturing method, wherein a non-consumable rotating tool is used. Figure 7 (a) and (b) show popular preprocessing steps to fill the particles/powder of materials to be inserted in the cavity. After filling powder in the slots or holes, the non-consumable tool is plunged and moved transversely as shown in Figure 7 (c) that in turn helps to mix the powder with plasticized material through stirring action of tool. Distribution of powder in matrix material can be governed by viscoelastic effect of materials subsequently alters the properties of the processed zone. The particles are usually in nano and/or micro size that are mixed with matrix under the effect of stirring and mixing. In fullerene-based composites fabricated by friction stir processing, the fullerene nano sized particles are reinforced into substrate material with stirring mixing process using non consumable tool.



Figure 7. Friction stir processing for composite manufacturing (a) preprocessing by slot method, (b) preprocessing by hole method and (c) processing with non-consumable tool



Figure 8. Materials flow with different rotational speeds for fullerene/Al FSP, (Reprinted with permission from Ref. 37)

With reference to the nature and structure of fullerene such as smallest size among all carbon allotrope and hardest reinforcement nano particle, the fabrication of fullerene-based composites using FSP is an effective solution^{31–36}. Fullerene/Aluminum (Al)³⁷ and Fullerene/Magnesium (Mg)³⁸ nano-composites were fabricated using FSP. The composite region fabricated by FSP

causes onion ring like features resulted from stirring effects, wherein the fullerene particles are distributed within those onion rings. The stirring effect causes severe deformation in base/substrate material with grain refinement. However, being one of the hardest materials, the deformation of fullerene can be avoided and that in turn lead to successful dispersion in base/substrate material. The distribution of fullerene in base material is greatly governed by the material flow under the effective viscoplastic conditions that is consequently controlled by processing parameters such as rotational and travel speeds, tool design and preprocessing insertion methods. However, limited studies were performed on these parameters. Morisada et al.³⁸ investigated material flow and subsequent mixing between fullerene particles (C60: 80 vol% and C70: 15 vol%) and AA5083 base material under the effect of rotational speeds (varied from 500 to 2000 rpm with an interval of 500 rpm) with groove (of $1 \text{ mm} \times 2 \text{ mm}$) type preprocessing step. Figure 8 shows variations in materials flow with mixing between fullerene and Al material under different rotational speeds with constant parameters such as triangular shape to trapezoidal shape stir zone with distinct materials mixing for rotational speed 500 rpm to 2000 rpm. The degree of desperation and continuous dynamic deformation increases with an increase in rotational speed during fabrication of fullerene/AA5083 that in turn resulted with more effective onion ring features and mixing between fullerene/AA5083 under trapezoidal stir zone shape. Increased rotational speed lead to increased heat input, which enhances viscoplastic behavior adequate for stirring-mixingprocessing. Besides, low rotational speed increases flow resistance due to low heat input that in turn results in inadequate material flow and absence of onion ring features. This resistance to material flow restricts movement of fullerene materials and subsequently causes consolidation in restricted zone, which can be interpreted as non-uniform distribution of fullerene particles in substrate material. Processing conditions must be adequate (with favorable heat input to lead effective viscoplastic conditions) in order to drive fullerene distribution in work piece material. The uniform dispersion of fullerene in Al matrix is also governed by revolution pitch of tool (combination of travel and rotational speeds) and the amount of fullerene the reinforcement in the Al groove. The density of onion ring is governed by revolution pitch. The dense onion ring (i.e. small revolution pitch) with full dispersion of fullerene in Al matrix results in uniform distribution. However, micro locations within stir zone region ways show non uniform distribution of fullerene in metal matrix material due to complex stirring mixing phenomena. In fullerene/AA5083 composite fabricated by FSP, micro level materials mixing is shown in Figure 9, wherein single

and aggregated fullerene molecules were observed in AA5083 matrix. Similar materials mixing between fullerene and Mg alloy of AZ31 was observed as shown in Figure 10. The grain size of the base material was greatly refined to 100 nm and 200 nm in case of fullerene/AZ31 and fullerene/AA5083 composite fabricated by FSP respectively³⁸. Morisada and Fuji³⁸ claimed that matrix grain diameter was reduced 1/800 as compared to base material microstructure. Morisada et al.³⁷ mentioned that grain growth is restrained by peening effect of fullerene particles that are dispersed in the Al matrix grain boundaries, which does not allow grain growth after dynamic recrystallization usually occur in FSP region.



Figure 9. Materials mixing between Fullerene/AA5083 (TEM images), (Reprinted with permission from Ref. 37)



Figure 10. Materials mixing between Fullerene/AZ31 (TEM image), (Reprinted with permission from Ref. 38)

Powder metallurgy (PM)³⁹⁻⁴¹ is well established fabrication method to manufacture nanocomposite materials^{42,43}. The homogenous dispersion of the fullerene particles is necessitated to achieve the best possible surface properties within the structural component. However, fullerene tendency of agglomerate leading to restricted intermixing over the entire surface area of metal. This in turn promotes the stress concentration while in service, which may result in premature failure of the component. Therefore, in order to obtain improved homogeneous mixing to form composite material, semi powder metallurgy (SPM) technique is found suitable in comparison to the conventional PM route^{44–46}. The schematic of SPM is shown in Figure 11, wherein the fullerene and metal powder were exposed separately to ethanol environment by employing mechanical agitator for an hour. This is to achieve homogenous dispersion of fullerene into the metal matrix. The aforementioned process is defined as ultrasonication. The same ultrasonic process is continued for another half an hour after mixing fullerene into metal solution. Then, magnetic stirring is applied with vacuum distillation to extract the ethanol from the composite powder. The same powder is kept into oven under argon vacuum environment for 12 hour⁴⁴⁻⁴⁶. The dried composite powder then pressed by hot press test machine for 2 hour⁴⁴⁻⁴⁶. Argon environment is exploited to ensure oxidation free material⁴⁴⁻⁴⁶.



Figure 11. Schematic of SPM (Reprinted with permission from Ref. 45)

3. Performance of Fullerene and Fullerene Based Nanocomposites

The lattice fringe observed from transmission electron microscopy (TEM) bright field micrograph evaluation indicates the presence of (002) d spacing of C_{60} for Fullerene nanocomposite. The similar observation also found in Fullerene-Rhodium nanocomposite. The TEM and X-ray diffraction (XRD) data confirm the presences of particles in nanometer scale for C_{60} and Rhodium. Thus, aerosol decomposition method is a good candidate for synthesis of nanocomposite materials⁸. The experiment conducted⁹ for fabricated three different samples. Sample A is fullerene dispersed aluminum nanocomposite, Sample B routed with stearic acid as an agent during the planetary ball milling process and Sample C routed with ethyl alcohol during the planetary ball milling process. The results show that the addition of agent significantly influences the hardness value and grain sizes. It is observed that hardness value increased for sample B then sample C and finally the in-situ sample A. Besides, the grain size reduced for sample B and sample C (See Figure 12). In general, the addition of stearic acid improved the hardness, reduces the grain sizes and thus, improves the tribological properties of nanocomposites.



Figure 12. HV values of Fullerene based Aluminum Nanocomposites (Reprinted with permission from Ref. 9)

The frictional coefficient studies resulted that a 2-time reduction of coefficient of friction observed for composites infused with fulleroids fillers than in-situ PA6. Furthermore, lowest coefficient of friction observed for PA6/fullerene C60 composite (0.002%wt) (See Figure 13). The current

voltage characteristics of the fabricated nanocomposites were evaluated and resulted a decrease in the resistivity in accordance with increase in fullerenes soot concentrations (See Figure 14)¹⁰.



Figure 13. Frictional coefficient results (1) insitu PA6 (2) PA6/fullerene C60 composite (0.002 wt%) and (3) PA6/fullerene soot composite (0.11 wt%)¹⁰ (reprinted with permission)



Figure 14. Volume resistivity Vs Concentration of fullerene Soot's¹⁰ (reprinted with permission)

The mechanical properties of pure Nafion, 0.1% fullerenes-Nafion and 0.5% fullerenes-Nafion were compared¹². The results show that pure Nafion failed at lower stress value itself and whereas 0.1% fullerenes-Nafion and 0.5% fullerenes-Nafion failed at higher stress values (Figure 15). The fullerene–Nafion exhibited significant improvements in mechanical stiffness and strength¹². The

TEM results confirmed fine dispersion of fullerenes for milling process and the phase transformations to carbide and diamond phases are observed through XRD diffraction images (See Figure 16). Furthermore, during sintering the nanostructure is retained in Fe-fullerene composite C_{60}^{13} .



Figure 15. Stress Strain curve for pure Nafion, 0.1% fullerenes-Nafion and 0.5% fullerenes-Nafion¹²



Figure 16. XRD diffraction images for Fe-C₆₀ and Al-C₆₀¹³ (reprinted with permission)

The performance of fullerene based nano composites fabricated by FSP is majorly measured with hardness variations in processed region and base materials. The dispersion of fullerene particles in base material greatly increases the hardness of processed zone. Morisada and Fuji³⁸observed that the hardness of processed region by FSP of fullerene/AZ31 is approximately increased 3 times

than the base material (i.e. AZ31) hardness (see Figure 17) due to uniform dispersion of fullerene C_{60} and grain refinement. Similar increase in hardness (around 2 times higher than base material of AA5083) is observed in case of fullerene/AA5083 nanocomposites of FSP³⁷. Higher fullerene concentration and uniform distribution of the same in matrix material increases the hardness of the processed zone due to particle reinforcement in matrix and reduction in grain size caused by strong stirring action.



Figure 17. Hardness distribution of AZ31 processed by fullerene reinforcement FSP, normal FSP and non-processed material, (Reprinted with permission from Ref. 39)

Fullerene/magnesium composites fabricated by SPM process⁴⁴⁻⁴⁶ showed limited work to identify the effect of fullerene quantity on the mechanical properties such as hardness and compression strength⁴⁴. The effect of fullerene on the corrosion^{44, 46} and wear properties⁴⁵ of the fullerene/magnesium composite was considered in the performance after fabrication. The Figure 18 shows that the dispersion of the fullerene is the function of the quantity. The agglomerate nature of the fullerene is reflected as the quantity of fullerene increases in the metal matrix composite. Interestingly, the effect of homogenous dispersion on to the mechanical properties is not seen significant. However, the hardness was increased with an increase in the fullerene quantity^{44, 45} (see Figure 19). The large surface area of fullerene lead to severe interfacial within the magnesium metal matrix. This is ultimately generating a diversified energy field within the pure material.

Hence, dislocation movement through low angle and high angle grain boundaries were possibly presented due to continuous change in the atomic orientation while processing and dispersion of fullerene particles (in case of SPM process). This in turn, promotes the higher dislocation density and restricted movement of dislocation within the composite material that led it to higher hardness within the processed region. Furthermore, the restriction of dislocation movement promotes its migration to all the possible direction that enhances the capacity to absorb the external energy applied on the composite, which in turn further increases the hardness of the material. However, the hardness slightly decreases when quantity of fullerene increases from 0.5% to 1%. This may be attributed to agglomerate nature of fullerene. As seen in Figure 20, quantity of fullerene particle at some areas are higher that suggest the heterogeneous dispersion, which in turn may promote the deformation of composite material leading to reduction in the hardness. On the other hand, reduction in hardness can also be explained through the weak Vander walls bond and agglomeration of fullerene particle. Interestingly, same author reported⁴⁴⁻⁴⁶ two different hardness values of composite at 0.5% fullerene addition. The difference in the value is significant. The reason of such a large variation is not reported and cleared by the previous author even after similar manufacturing conditions. The same may be attributed to the size of specimen fabricated i.e. 15 mm diameter and length^{44, 45} compared to 25 mm diameter and 20 mm length⁴⁶. The degree of fullerene dispersion is different with the size and it may affect the properties.



Figure 18. (a) HAADF TEM, (b) HRTEM images of HPT-processed Al/C₆₀ nanocomposite. The arrows in a show fullerene within the Al matrix³⁶



Figure 19. Hardness test results⁴⁴



Figure 20. SEM micrographs of A) Mg B) Mg – 0.25 wt.% Fullerene C) Mg – 0.50 wt.% Fullerene D) Mg – 1 wt.% Fullerene⁴⁵ (reprinted with permission)

Apart from drastic variations in hardness, the fullerene-based composites fabricated by SPM process affects wear properties. Wear rate of pure magnesium increases with an increase in the fullerene quantity till 0.5% fullerene addition⁴⁵. On the other hand, rate of wear is slightly decreases in case of 1% fullerene added to Mg metal matrix. This is attributed to the aforementioned agglomerate nature of fullerene. In the mentioned case variation in were rate is not significant but it cannot be negligible at all. However, strong bond and large interfacial area due to lower density (i.e. after addition of fullerene into pure magnesium) resist the wear. Furthermore, corrosion resistance is decreased with addition to fullerene material. This is because of galvanic couple generated between fullerene rich and fullerene free grain boundaries. This in turn, the site of energy diversification prone to corrosion. Hence, the study on homogenous dispersion of fullerene particle within metal matrix is vital as far as corrosion properties are concern. Similarly, compression strength of pure magnesium increased with an increase in the fullerene quantity at the time of fabrication. However, the experimental work is done only for 0.25% and 0.5% fullerene addition. The reported decrease in the density may be responsible for the higher compression strength⁴⁴. Reduction in the density of fullerene material promotes the large interfacial area and therefore the load transfer from pure magnesium to hard fullerene can be absorbed through the adequate dislocation mechanisms. This subsequently results in high compressive strength. The Table 1 shows the summary of reported material systems and methods for fabrications of fullerene-based nanocomposites.

Period	Composite System	Techniques Used	Researchers
1993	Fullerene-Rhodium	Aerosol	Abhijit S. Gurav, ZhibangDuan, Lumin Wang, Mark I, Hampden-
	1 unocompositos	Decemposition	Smith, andToivo
			T. Kodas [8]
1995	Fullerene-reinforced	Powder metallurgy	E. V. Barrera, J. Sims, and D. L.
	aluminum	and casting	Callahan [47]
1997	Fullerene composite	Liquid	Shunichiro Tanaka [48]
		chromatography,	
		purverizing,	
1999	Metal-Fullerene	Mechanical alloving-	Umemoto Minoru ZhiGuang
1)))	Wietai-i unerene	Rall Milling	Liu K Masuyama and Koichi
		Dun Mining	Tsuchiva [49]
2004	Hollow fullerene-	Using foaming	Reshef Tenne Rehovot
	like	agents and	(IL),Rapoport, Lod (IL); Mark
	Nanoparticles as	compaction,	Lvovsky, Herzliya (IL), Yishay
	solid lubricants In	impregnation	Feldman, Ashdod (IL); Volf
	composite metal		Leshchinsky, Rishon Letzion
2006	matrices	F : .:	(IL) [50]
2006	C60/AZ31	Friction Stir	Y. Morisada, H. Fujii, I.
2007	Fullerone/A 5082	Friction Stin	Nagaoka and M. Fukusumi [38]
2007	composites	Processing	1. Monsada, n. rujii, 1. Nagaoka K. Nogi M. Fukusumi
	composites	Tiocessing	[37]
2008	Mixing of metals	Electromagnetic field	Enrique V. Barrera,
	and polymers with	induced and acoustic	Yildiz Bayazitoglu [53]
	fullerenes	mixing	
	Nanofibers	~	
2010	Electro-active nano-	Solvent recasting	Jung-Hwan Jung, Sridhar
	composite actuator	method	Vadahanambi, Il-Kwon Oh [12]
	reinforced Nation		
2010	Al or Fe Matrix	Spark Plasma	Francisco C. Robles
2010	reinforced with	Sintering, mechanical	H.A.Calderon [52]
	fullerene	alloying	
2011	Composites of Fe-	Mechanical milling	I. I. Santana, F. C. Robles
	C ₆₀ and Al C ₆₀	and Spark Plasma	Hernandez, V. Garibay Febles
		Sintering	and H. A. Calderon [13]
2014	Aluminum-based	Ball-milling	Kwangmin CHOI, Jiyeon SEO,
	nanocomposite	technique	Donghyun BAE, Hyunjoo CHOI
	fullerence		נאן
2017	Fullerene-Reinforced	High-energy	Hamed Asgharzadeh Hamid
2017	Aluminum Matrix	mechanical milling	Faraghi, Hyoung Seon Kim [36]
	Nanocomposites	and hot extrusion or	
		high-pressure torsion	
		(HPT)	

Table 1: Summary of various reported materials system based on Fullerene nano composites

4. Conclusions:

- 1. Addition of acidic agents in Fullerene during the ball milling process and subsequent usage for fabrication of metal nanocomposite will influence the hardness and grain sizes in a greater manner.
- 2. Methods like powder metallurgy, RF sputtering and thin film depositions are good candidates other than casting and steady state process technologies.
- 3. The FSP composites based on fullerene compounds have a greater influence in increasing the hardness behaviors of the composite materials.
- 4. The fulleroids dispersion in PA6 shows significant reduction in coefficient of friction and also the electrical volume resistivity also found in decreasing mode as the fullerene soot concentration progresses. Also, reinforcement with certain polymers (e.g.Nafion) shows improvement in mechanical properties.
- 5. The milling and subsequent sintering unaltered the nanostructure specifically for Fe- C_{60} , this infers the milling and subsequent sintering can be a potential candidate for the process.

5. Future Directives:

- Adoptions of fullerenes in metal matrix composites are of greater impact in their tribological and electrical properties. Organic nanocomposites are supporting the electronic sector also. Thus, furthermore studies are to be kicked off for specific application with various environmental conditions.
- The material processing techniques are influencing the material properties for fullerenebased composites. Thus, rigorous studies are required to know the synergy between the process parameters and properties.

References

- 1. Kroto, Harold W., James R. Heath, Sean C. O'Brien, Robert F. Curl, and Richard E. Smalley. "C60: Buckminsterfullerene." nature 318, no. 6042 (1985): 162-163.
- 2. Kuzmany, Hans, Michael Matus, Bernhard Burger, and Johannes Winter. "Raman scattering in C60 fullerenes and fullerides." Advanced Materials 6, no. 10 (1994): 731-745.

- 3. Kumar, Ajay, Rishi Raj, and Satish V. Kailas. "A novel in-situ polymer derived nano ceramic MMC by friction stir processing." Materials & Design 85 (2015): 626-634.
- 4. Kumar, Ajay, Devinder Yadav, Chandra S. Perugu, and Satish V. Kailas. "Influence of particulate reinforcement on microstructure evolution and tensile properties of in-situ polymer derived MMC by friction stir processing." Materials & Design 113 (2017): 99-108.
- 5. Madhu, H. C., P. Ajay Kumar, Chandra S. Perugu, and Satish V. Kailas. "Microstructure and mechanical properties of friction stir process derived Al-TiO₂ nanocomposite." Journal of Materials Engineering and Performance 27, no. 3 (2018): 1318-1326.
- Kumar, P. Ajay, H. C. Madhu, Abhishek Pariyar, Chandra S. Perugu, Satish V. Kailas, Uma Garg, and Pradeep Rohatgi. "Friction stir processing of squeeze cast A356 with surface compacted graphene nanoplatelets (GNPs) for the synthesis of metal matrix composites." Materials Science and Engineering: A 769 (2020): 138517.
- 7. Innocenzi, Plinio, and Giovanna Brusatin. "Fullerene-based organic- inorganic nanocomposites and their applications." Chemistry of materials 13, no. 10 (2001): 3126-3139.
- Gurav, Abhijit S., Zhibang Duan, Lumin Wang, Mark J. Hampden-Smith, and Toivo T. Kodas. "Synthesis of fullerene-rhodium nanocomposites via aerosol decomposition." Chemistry of materials 5, no. 2 (1993): 214-216.
- Kwangmin, C. H. O. I., S. E. O. Jiyeon, B. A. E. Donghyun, and C. H. O. I. Hyunjoo. "Mechanical properties of aluminum-based nanocomposite reinforced with fullerenes." Transactions of Nonferrous Metals Society of China 24 (2014): s47-s52.
- 10. Zuev, Vjacheslav V., and Yulia G. Ivanova. "Mechanical and electrical properties of polyamide-6-based nanocomposites reinforced by fulleroid fillers." Polymer Engineering & Science 52, no. 6 (2012): 1206-1211.
- gamal El-Shamy, Ahmed. "Novel hybrid nanocomposite based on Poly (vinyl alcohol)/carbon quantum dots/fullerene (PVA/CQDs/C60) for thermoelectric power applications." Composites Part B: Engineering 174 (2019): 106993.
- 12. Jung, Jung-Hwan, Sridhar Vadahanambi, and Il-Kwon Oh. "Electro-active nano-composite actuator based on fullerene-reinforced Nafion." Composites science and technology 70, no. 4 (2010): 584-592.
- Santana, I., and H. Calderon. "Phase Transformations Induced by Mechanical Milling and Sintering in the (Fe, Al)-Fullerenes Composites." Microscopy and Microanalysis 17, no. S2 (2011): 1828-1829.
- 14. Hu, Zheng-Yang, Zhao-Hui Zhang, Xing-Wang Cheng, Fu-Chi Wang, Yi-Fan Zhang, and Sheng-Lin Li. "A review of multi-physical fields induced phenomena and effects in spark plasma sintering: Fundamentals and applications." Materials & Design (2020): 108662.
- 15. Jilani, Asim, Mohamed Shaaban Abdel-Wahab, and Ahmed Hosny Hammad. "Advance deposition techniques for thin film and coating." Modern Technologies for Creating the Thinfilm Systems and Coatings 2 (2017): 137-149.

- Barrera, E. V., J. Sims, D. L. Callahan, V. Provenzano, J. Milliken, and R. L. Holtz. "Processing of fullerene-reinforced composites." Journal of materials research 9, no. 10 (1994): 2662-2669.
- Flak, Richard August, Scott M. Packer, Russell J. Steel, Monte E. Russell, and Brian E. Taylor.
 "Friction stirring and its application to drill bits, oil field and mining tools, and components in other industrial applications." U.S. Patent Application 13/281,868, filed November 1, 2012.
- 18. Gupta, Kapil. Surface Engineering of Modern Materials. Springer, 2020.
- 19. Hutchings, Ian, and Philip Shipway. Tribology: friction and wear of engineering materials. Butterworth-Heinemann, 2017.
- Bose, Susmita, Samuel Ford Robertson, and Amit Bandyopadhyay. "Surface modification of biomaterials and biomedical devices using additive manufacturing." Acta biomaterialia 66 (2018): 6-22.
- Vyas, Hardik, and Kush P. Mehta. "Effect of Multi Pass Friction Stir Processing on Surface Modification and Properties of Aluminum Alloy 6061." In Key Engineering Materials, vol. 813, pp. 404-410. Trans Tech Publications Ltd, 2019.
- 22. Mehta, Kush P., and Vishvesh J. Badheka. "A review on dissimilar friction stir welding of copper to aluminum: process, properties, and variants." Materials and Manufacturing Processes 31, no. 3 (2016): 233-254.
- Mehta, Kush P., and Vishvesh J. Badheka. "Hybrid approaches of assisted heating and cooling for friction stir welding of copper to aluminum joints." Journal of Materials Processing Technology 239 (2017): 336-345.
- 24. Mehta, Kush P., Pierpaolo Carlone, Antonello Astarita, Fabio Scherillo, Felice Rubino, and Poojan Vora. "Conventional and cooling assisted friction stir welding of AA6061 and AZ31B alloys." Materials Science and Engineering: A 759 (2019): 252-261.
- 25. Mehta, Kush P., Rahul Patel, Hardik Vyas, Shabbir Memon, and Pedro Vilaça. "Repairing of exit-hole in dissimilar Al-Mg friction stir welding: process and microstructural pattern." Manufacturing Letters 23 (2020): 67-70.
- Mehta, Kush P., and Vishvesh J. Badheka. "Effects of tilt angle on the properties of dissimilar friction stir welding copper to aluminum." Materials and Manufacturing processes 31, no. 3 (2016): 255-263.
- Patel, Nirav P., Parth Parlikar, Rahul Singh Dhari, Kush Mehta, and Milap Pandya. "Numerical modelling on cooling assisted friction stir welding of dissimilar Al-Cu joint." Journal of Manufacturing Processes 47 (2019): 98-109.
- 28. Rathee, Sandeep, Sachin Maheshwari, Arshad Noor Siddiquee, and Manu Srivastava. "A review of recent progress in solid state fabrication of composites and functionally graded systems via friction stir processing." Critical Reviews in Solid State and Materials Sciences 43, no. 4 (2018): 334-366.
- 29. Sharma, Vipin, Ujjwal Prakash, and BV Manoj Kumar. "Surface composites by friction stir processing: A review." Journal of Materials Processing Technology 224 (2015): 117-134.

- Arora, H. S., H. Singh, and B. K. Dhindaw. "Composite fabrication using friction stir processing—a review." The International Journal of Advanced Manufacturing Technology 61, no. 9 (2012): 1043-1055.
- 31. Bhavani, Kalli Sai, Tummala Anusha, and Pradeep Kumar Brahman. "Fabrication and characterization of gold nanoparticles and fullerene-C60 nanocomposite film at glassy carbon electrode as potential electro-catalyst towards the methanol oxidation." International Journal of Hydrogen Energy 44, no. 47 (2019): 25863-25873.
- 32. Miyazawa, K., H. Satsuki, M. Kuwabara, and M. Akaishi. "Microstructural analysis of highpressure compressed C 60." Journal of Materials Research 16, no. 7 (2001): 1960-1966.
- 33. Guo, Zhenghong, Yanqun Pan, Ruifeng Guo, and Zhengping Fang. "Fabrication of fullerene decorated by iron compound and its effect on the thermal stability and flammability for highdensity polyethylene." Fire and Materials 44, no. 4 (2020): 506-515.
- Lavrentiev, V., M. Motylenko, M. Barchuk, C. Schimpf, I. Lavrentieva, J. Pokorný, C. Röder, J. Vacik, A. Dejneka, and D. Rafaja. "Structure assembly regularities in vapour-deposited gold–fullerene mixture films." Nanoscale Advances 2, no. 4 (2020): 1542-1550.
- 35. Sizonenko, O., S. Prokhorenko, A. Torpakov, D. Żak, Y. Lypian, R. Wojnarowska-Nowak, J. Polit, and E. M. Sheregii. "The metal-matrix composites reinforced by the fullerenes." AIP Advances 8, no. 8 (2018): 085317.
- 36. Asgharzadeh, Hamed, Hamid Faraghi, and Hyoung Seop Kim. "Fabrication of fullerenereinforced aluminum matrix nanocomposites." Acta Metallurgica Sinica (English Letters) 30, no. 10 (2017): 973-982.
- Morisada, Y., H. Fujii, T. Nagaoka, K. Nogi, and M. Fukusumi. "Fullerene/A5083 composites fabricated by material flow during friction stir processing." Composites part A: Applied Science and manufacturing 38, no. 10 (2007): 2097-2101.
- 38. Morisada, Y., and H. Fujii. "Nanocomposites fabricated by the friction stir process." Welding International 22, no. 1 (2008): 11-15.
- 39. Cavaliere, Pasquale, ed. Spark plasma sintering of materials: advances in processing and applications. Springer, 2019.
- 40. Pardhi, Yogiraj, ed. Metallurgy: Advances in Materials and Processes. BoD-Books on Demand, 2012.
- 41. Olevsky, Eugene A., and Dina V. Dudina. "Other Field-Assisted Sintering Techniques." In Field-Assisted Sintering, pp. 401-414. Springer, Cham, 2018.
- 42. Manohar, Guttikonda, Abhijit Dey, K. M. Pandey, and S. R. Maity. "Fabrication of metal matrix composites by powder metallurgy: a review." In AIP Conference Proceedings, vol. 1952, no. 1, p. 020041. AIP Publishing LLC, 2018.
- 43. Sivasankaran, S., K. Sivaprasad, R. Narayanasamy, and P. V. Satyanarayana. "X-ray peak broadening analysis of AA 6061100- x- x wt.% Al2O3 nanocomposite prepared by mechanical alloying." Materials Characterization 62, no. 7 (2011): 661-672.

- 44. Turan, Muhammet Emre, Yavuz Sun, and Yasin Akgul. "Mechanical, tribological and corrosion properties of fullerene reinforced magnesium matrix composites fabricated by semi powder metallurgy." Journal of Alloys and Compounds 740 (2018): 1149-1158.
- 45. Turan, Muhammet Emre, Yavuz Sun, and Yasin Akgul. "Improved wear properties of magnesium matrix composite with the addition of fullerene using semi powder metallurgy." Fullerenes, Nanotubes and Carbon Nanostructures 26, no. 2 (2018): 130-136.
- 46. Turan, Muhammet Emre, Yavuz Sun, Fatih Aydin, Huseyin Zengin, Yunus Turen, and Hayrettin Ahlatci. "Effects of carbonaceous reinforcements on microstructure and corrosion properties of magnesium matrix composites." Materials Chemistry and Physics 218 (2018): 182-188.
- 47. Barrera, E. V., J. Sims, and D. L. Callahan. "Development of fullerene-reinforced aluminum." Journal of materials research 10, no. 2 (1995): 366-371.
- 48. Tanaka, Shun-ichiro. "Fullerene composite." U.S. Patent 5,648,056, issued July 15, 1997.
- 49. Umemoto, Minoru, Zhi Guang Liu, K. Masuyama, and Koichi Tsuchiya. "Ball milling of fullerene and mechanical alloying of fullerene-metal systems." In Journal of Metastable and Nanocrystalline Materials, vol. 2, pp. 93-102. Trans Tech Publications Ltd, 1999.
- 50. Tenne, Reshef, Lev Rapoport, Mark Lvovsky, Yishay Feldman, and Volf Leshchinsky. "Hollow fullerene-like nanoparticles as solid lubricants in composite metal matrices." U.S. Patent 6,710,020, issued March 23, 2004.
- 51. Robles-Hernández, Francisco C., and H. A. Calderon. "Nanostructured metal composites reinforced with fullerenes." Jom 62, no. 2 (2010): 63-68.
- 52. Sizonenko, O., S. Prokhorenko, A. Torpakov, D. Żak, Y. Lypian, R. Wojnarowska-Nowak, J. Polit, and E. M. Sheregii. "The metal-matrix composites reinforced by the fullerenes." AIP Advances 8, no. 8 (2018): 085317.
- 53. Barrera, Enrique V., and Yildiz Bayazitoglu. "Containerless mixing of metals and polymers with fullerenes and nanofibers to produce reinforced advanced materials." U.S. Patent 7,323,136, issued January 29, 2008.