OPTIMIZATION OF PROCESSING PARAMETERS ON PHYSICAL AND MECHANICAL PROPERTIES OF COPPER-CNT NANOCOMPOSITES

V VEERANAATH

Department of Mechanical Engineering, Faculty of Engineering and Technology, SRM Institute of Science and Technology, Kattankulathur, Tamil Nadu, India

ABSTRACT

Attracting materials like Carbon NanoTubes (CNTs) are proved to be a more promising candidate as the nanodispersion in metal-based nanocomposites. CNTs reinforced in the copper metal matrix is one of the utmost demanding nanocomposites in many industrial applications because of its enhancement in characteristics. But, the hindrance to the enhancement in the properties is the agglomeration of nanoparticles to form clusters and poor interfacial attractions between the constituents. Powder metallurgy is the most common and advantageous fabrication method for these metal matrix nanocomposites. Ball milling and Ultrasonication techniques are methods employed of mechanical blending to evade the growth of clusters. The microstructures of the samples show that the CNTs are homogeneously distributed in some cases which are studied using SEM analysis. The influences of the reinforcement content and manufacturing constraints on the various properties like density, hardness, and Coefficient of Friction (COF) are analyzed and studied. The optimum values of the reinforcement content and process parameters on various outputs are determined using Taguchi and Grey Relation Analysis and ANOVA study is also used to evaluate the role of the governing constraints on the output responses.

KEYWORDS: Nanocomposites, Nanoparticles, Mechanical, Parameters

Original Article

Received: Apr 12, 2020; **Accepted:** May 03, 2020; **Published:** May 22, 2020; **Paper Id.:** IJMPERDJUN202065

INTRODUCTION

Metal Matrix NanoComposites (MMNCs) are nowadays gaining a lot of curiosity among the manufacturing and speculative investigators because of its wide range of applications. Linked to old-fashioned composites, these nanocomposites yield improved hardness, density, and wear rates along with the friction effect [1]. A wide diversity of metals like aluminum, copper, magnesium, etc. are employed as the binding base metal in MMNCs among which copper is considered to be an interesting candidate as the binding matrix. The cause behind the familiarity of copper is the improved characteristics. And so, even the mechanical features of the copper can be further improved by reinforcing a metal or a ceramic in the copper base which makes it suitable for applications with great scope [2]. Researchers used large number of reinforcements like alumina, silicon carbide, carbon nanotubes, Titanium carbide, Boron carbide, etc. to improve the characteristics of metal matrix alloy. However, Carbon NanoTubes (CNTs) have a special distinction as reinforcement in copper alloy because of its noteworthy properties like high aspect ratio, load-bearing capacity, and conductivity [3]. Thus, by reinforcing CNT in the copper alloy, the nanocomposites which are produced have a great space in growing market demands. There are many fabrications available to produce Cu-CNT nanocomposites namely powder metallurgy, stir casting, metal disintegration, etc. Every processing technique has its own merits and demerits. But the powder metallurgy method through mechanical

alloying route yield more merits compared to others. But the challenges and the problems faced in this method are agglomerations of nanodispersions to form clusters and poor interfacial attractions which may upset the characteristics of the nanocomposites [4]. Many researchers around the universe have tried a lot of means to reduce agglomerations, improve the bonding characteristics, and learn the influence of nanodispersions content on various properties which are focused below.

Ali Samer Muhsan et al. [5] fabricated copper-CNT nanocomposites by fabrication technique name metal injection moulding to homogeneously disperse nanotubes in the matrix which is proved effective using SEM images of the sintered samples. The thermal properties exhibited an upstanding improvement in addition of 1 vol% of MWCNT which again quoted it as a positive technique for processing. Walid M. Daoush et al. [6] used electrodeless incorporation of the base metal over the exterior of the reinforcement followed by compaction and sintering steps. It was also observed that this method is extra appropriate for the high content of nanotubes in copper as the enhancement in electrical properties is observed. Guiderdoni et al. [7] fabricated CNTs with different numbers of CNT walls and reinforced the same in the copper followed by consolidation in sintering at a high vacuum atmosphere. The double-walled CNT exhibited an improvement in hardness and wear rate in the study. Koti et al. [8] fabricated uncoated and nickel-coated reinforcements using a powder metallurgy route and used TEM images to study the dispersion of reinforcement in the base metal. An improvement in wear rate and friction characteristics were obtained in addition of CNT. Rajyashree et al. [9] highlighted the advantages of electrodeless incorporation of Copper CNT samples to guarantee good interactions. Yan et al. [10] studied the tensile behavior of the various samples in different kinds of nanotube arrangements. Despite these efforts, many researchers focused on it and there is a large area of scope to overcome the limitations faced in the powder metallurgy fabrication process.

Thus, this paper is mainly focused on the fabrication of copper-CNT nanocomposites with powder metallurgy techniques via mechanical alloying processes of ball milling and ultrasonication techniques. The developed nanocomposites were done by employing SEM images to study the dispersion of reinforcements. The effects of reinforcement content and process parameters like processing times on the various outputs like hardness, density, and COF were studied and optimized using Taguchi and Grey Relation Analysis techniques along with ANOVA analysis.

MATERIALS AND METHODS

Copper (Cu) powders with a purity of 99.15%, the mean size of 25 μ m and density 8.16g/cm³, and CNTs of purity 96%, 10-30nm in diameter, and 10-35 μ m were used in this study. The processing techniques include functionalization of CNTs, blending of CNTs, and copper via ball milling and ultrasonication and consolidation. The first stage of functionalization of CNTs is very mandatory to remove unwanted impurities and to attach certain functional group molecules in CNTs to make it easily disperse. The CNTs were functionalized by acid treatment in a magnetic stirrer for 8 hours in a nitric acid solution which is then centrifuged at 10000rpm for 12minutes at 20°C, filtered, and then finally dried at 100°C for 3 hours to get in powder form. Then the functionalized CNTs and copper powders are blended in planetary ball milling setup at 250rpm for different times of 60, 120, and 180min with a ball to powder ratio of 10:1. Ethanol is used as a stabilizing agent during the process and WC balls and jars are used for the process. Then the blended samples are then further subjected to the ultrasonication process using probe method for further reducing the agglomeration of reinforcements and dismantling the clusters. The ultrasonication is done for different times of 10, 15, and 20minutes to analyze the influence of the same on various output responses. In the last stage, the blended powder solution is consolidated by drying the same in the oven and

then compacting and sintering in spark plasma sintering process at a pressure of 50MPa in a high vacuum state. L9 orthogonal array of design of experiments are taken for the study whose parameter selection is revealed in table 1 wherein the ball milling period and ultrasonication time are varied along with the reinforcement content of 10, 20, and 30 vol % of the sample. The SEM images were used to study the distribution of the consolidated specimens. The Vickers hardness test is employed to evaluate the microhardness of the specimens, the samples' density is measured based on Archimedes principle and the COF is determined from sliding wear tests by using the formula $\mu = F/N$ where F is the force induced due to friction and N is the applied load.

Table 1: Parameter Selection

Parameter	Level 1	Level 2	Level 3
CNT, vol %	10	20	30
Ball Milling Time (min)	60	120	180
Ultrasonication Time (min)	10	15	20

RESULTS AND DISCUSSIONS

The various outcomes of the L9 orthogonal experiments namely hardness, density, and COF of the fabricated samples are presented in table 2.

Table 2: Output Responses of L9 Orthogonal Array of Experiments

Exp. No.	CNT, vol %	Ball Milling Time (min)	Ultrasonication Time (min)	Density (g/cu.cm)	Hardness (Hv)	Coefficient of Friction
1	10	60	10	8.33	83	0.52
2	10	120	15	8.15	86	0.54
3	10	180	20	8.26	85	0.57
4	20	60	15	7.33	76	0.48
5	20	120	20	7.78	73	0.45
6	20	180	10	7.42	74	0.49
7	30	60	20	7.15	71	0.41
8	30	120	10	7.23	69	0.42
9	30	180	15	7.30	68	0.47

From table 2, it is clear that the maximum density is observed as 8.33g/cu.cm when compared with pure copper alloy on adding 10 vol% of CNT because of the dense nature of the reinforcements. But however, on further adding of nanotubes, the dense performance of the nanocomposites reduced on increasing the CNT content which may due to the fact of dispersion of CNTs which is shown in SEM images in figure 1. Similarly, the microhardness of the samples is also improved considerably in addition of CNTs because of the load-standing capacity of the reinforcements and again the same trend is found in hardness also as the density is due to relative density. But the minimum COF is obtained at 30 vol% of CNT content which may due to reduced wear rate and less force induced in friction. The influence of the various input factors on the responses like is given by mean effect plots of the same as revealed in figure 2. From the SEM images of the sintered nanocomposites, it is clear that the CNTs which are marked in red circles are uniformly distributed in most of the experiment cases but in some places agglomeration and formation of clusters also observed which may be the main reason behind the negative effect on the characteristics of the nanocomposites.

Figure 1: SEM Images of Cu-CNT Nanocomposites
(A) Experiment No. 1 (B) Experiment No. 4.

Figure 2: Mean Effect Plots of the Output Responses (A) Density (B) Hardness (C) Coefficient of Friction.

From the mean effects plots shown in figure 2, it is very evident that all the output responses vary inversely with reinforcement content, that is, the properties fall with a rise in reinforcement content because of the formation of CNT clusters on increasing the content. But for the ball milling period, the density values increase up to 120 minutes, and after which it started to reduce which may due to damage of CNTs which may lessen the characteristics of the same. Similarly, the hardness value also reduced with a rise in the ball milling period as the extensive ball milling might have reduced the length to diameter proportion of the reinforcement which in turn affects the load-standing capacity. And the COF might

increase after 120 minutes of ball milling because of the reduction in wear rate. On considering ultrasonication time, the hardness and COF reduced after 15 minutes of ultrasonication as more ultrasonication might have damaged the CNT further to reduce the length to diameter proportion and other characteristics of the same.

OPTIMIZATION

Taguchi Analysis

In single-objective Taguchi analysis, each output response is analyzed individually to find the best conditions for each response under the various factors. It is done by taking the S/N ratio into account and by removing the various noise factors. Here in this study, the input factors are reinforcement CNT content, ball milling time, and ultrasonication time. The main effect plots of S/N ratios of various output reactions are presented in figure 3.

**Figure 3: Analysis of S/N Ratios of the Output Responses
(A) Density (B) Hardness (C) Coefficient of Friction.**

The optimum or near optimum conditions of input constraints are predicted relating to the case which has a high S/N ratio. In this study, “Larger the better” norms are nominated for hardness and density responses and “Smaller the better” norms for the COF. From figure 3a, it is predicted that maximum density will be obtained at 10vol% of CNT, 120min of ball milling and 20min of ultrasonication, from figure 3b, the maximum hardness is predicted at 10vol% of CNT, 60min of ball milling and 15min of ultrasonication and from figure 3c, the minimum coefficient friction is predicted 30vol% of CNT, 120min of ball milling and 20min of ultrasonication as the corresponding S/N values are found to be maximum. The interaction plots of various output responses with the input factors are shown in figure 4.

Figure 4: Interaction Plots of the Output Responses
(A) Density (B) Hardness (C) Coefficient of Friction.

From the interaction plots of density, hardness, and COF, it is commonly found that there is no much relationship between CNT, vol% and the ball milling period, and CNT, vol% and sonication time but there are more interactions or relation between the ball milling and sonication time as this time has more effect on damaging the CNTs. The damage of CNTs may reduce the aspect ratio which may, in turn, affect the physiognomies of the reinforcement.

Table 3: ANOVA Analysis of Density with R-Sq = 94.86

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
CNT, vol %	2	1.66336	92.18%	1.66336	0.83168	17.95	0.053
Ball Milling Time (min)	2	0.02042	1.13%	0.02042	0.01021	0.22	0.819
Ultrasonication Time (min)	2	0.02802	1.55%	0.02802	0.01401	0.3	0.768
Error	2	0.09269	5.14%	0.09269	0.04634		
Total	8	1.80449	100.00%				

Table 4: ANOVA Analysis of Hardness with R-Sq = 97.49

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
CNT, vol %	2	366.889	96.32%	366.889	183.444	38.4	0.025
Ball Milling Time (min)	2	1.556	0.41%	1.556	0.778	0.16	0.86
Ultrasonication Time (min)	2	2.889	0.76%	2.889	1.444	0.3	0.768
Error	2	9.556	2.51%	9.556	4.778		
Total	8	380.889	100.00%				

Table 5: ANOVA Analysis of Coefficient of friction with R-Sq = 99.12

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
CNT, vol %	2	0.0186	81.58%	0.0186	0.0093	93	0.011
Ball Milling Time (min)	2	0.0032	14.04%	0.0032	0.0016	16	0.059
Ultrasonication Time (min)	2	0.0008	3.51%	0.0008	0.0004	4	0.2
Error	2	0.0002	0.88%	0.0002	0.0001		
Total	8	0.0228	100.00%				

Tables 3, 4, and 5 presents the ANOVA outcomes of the output responses of density, hardness, and COF respectively. It is recognized that in the situation of density, the major contribution of 92.18% to the output is from CNT, vol%, and similarly for hardness and COF also, the major contribution of 96.32% and 81.58% is from CNT, vol% only. This proves that output responses are more dependent on CNT, vol % rather than the other two dispensation constraints of ball milling and ultrasonication duration as the addition of CNT and agglomeration of the same affects the responses much.

Confirmation experiments are performed to confirm and authorize the predicted results of the Taguchi analysis. So, the experiment is repeated on the ideal conditions of each output response, and individual nanocomposites are built. The predicated and actual values of the confirmation experiments are shown in table 6 below.

Table 6: Confirmation Experiments – Taguchi Analysis

Response	CNT, vol %	Ball Milling Time (min)	Ultrasonication Time (min)	Optimal Conditions			
				S/N Ratio		Output Response	
				Predicted	Experimental	Predicted	Experimental
Density (g/cu.cm)	10	120	20	18.475	18.413	7.66	8.34
Hardness (Hv)	10	60	15	38.676	38.68	76.11	87
Coefficient of friction	30	120	20	7.683	7.74	0.483	0.56

GREY RELATION ANALYSIS

Grey Relation Analysis (GRA) is used for the optimization of multiple output cases wherein the constraints are complicated and by utilizing a concept called grey which shows the deprived and unclear information. Grey relation analysis includes the normalization of the test results, calculating the deviation and grey relational coefficient from which ranking is done. The GRA of the test results is revealed in table 7 and 8. The normalization of the test results is revealed in Table 7. Deviation, Grey relational coefficient, and rank with Grey Relational Grade (GRG) are revealed in table 8. The mean effects plot of the GRG is revealed in figure 5. Interaction plots of GRGs are revealed in figure 6. ANNOVA analysis of the GRG is presented in table 9.

Table 7: Grey Relational Analysis - Experimental Values & Normalization

CNT, Vol %	Ball Milling Time (min)	Ultrasonication Time (min)	Experimental Values			Normalization		
			Density (g/cu.cm)	Hardness (Hv)	Coefficient of Friction	Density (g/cu.cm)	Hardness (Hv)	Coefficient of Friction
10	60	10	8.33	83	0.52	0	0.1667	0.3125
10	120	15	8.15	86	0.54	0.1525	0.0000	0.1875
10	180	20	8.26	85	0.57	0.0593	0.0556	0
20	60	15	7.33	76	0.48	0.8475	0.5556	0.5625
20	120	20	7.78	73	0.45	0.4661	0.7222	0.7500
20	180	10	7.42	74	0.49	0.7712	0.6667	0.5000

Table 7 Contd.,

30	60	20	7.15	71	0.41	1.0000	0.8333	1.0000
30	120	10	7.23	69	0.42	0.9322	1	0.9375
30	180	15	7.3	68	0.47	0.8729	1.0000	0.6250

Table 8: Grey Relational Analysis – Deviation Sequence, Grey Relational coefficient & Grade

Deviation Sequence			Grey Relational Coefficient			GRG	Rank
Density (g/cu.cm)	Hardness (Hv)	Coefficient of Friction	Density (g/cu.cm)	Hardness (Hv)	Coefficient of Friction		
1	0.8333	0.6875	0.3333	0.375	0	0.3765	7
0.8475	1.0000	0.8125	0.3711	0.3333	0.3810	0.3618	8
0.9407	0.9444	1	0.3471	0.3462	0.3333	0.3422	9
0.1525	0.4444	0.4375	0.7662	0.5294	0.5333	0.6097	4
0.5339	0.2778	0.2500	0.4836	0.6429	0.6667	0.5977	5
0.2288	0.3333	0.5000	0.6860	0.6000	0.5000	0.5953	6
0.0000	0.1667	0.0000	1.0000	0.7500	1.0000	0.9167	1
0.0678	0.0556	0.0625	0.8806	0.9000	0.8889	0.8898	2
0.1271	0.0000	0.3750	0.7973	1.0000	0.5714	0.7896	3

Figure 5: Mean Effect Plots of the GRG.

Figure 6: Interaction Plots of the GRG.

Table 9: ANOVA Analysis of GRG with R-Sq = 99.46

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
CNT, vol %	2	0.383142	97.53%	0.383142	0.191571	179.45	0.006
Ball Milling Time (min)	2	0.005407	1.38%	0.005407	0.002703	2.53	0.283
Ultrasonication Time (min)	2	0.002142	0.55%	0.002142	0.001071	1	0.499
Error	2	0.002135	0.54%	0.002135	0.001068		
Total	8	0.392826	100.00%				

From table 8, it is more evident that the conditions of 30 CNT, vol %, 60 min ball milling time, and 20 min ultrasonication time has produced a high rank based on GRG out of the nine experiments. Figure 5 shows the mean effect variation of the GRG with the processing constraints and through which also, the same conditions are observed. The interaction plot shown in figure 6 exhibited that there is more relational or interconnection between ball milling and ultrasonication duration on the grade. As like the output responses, for the GRG also, the more contribution of 97.53% is from the CNT content only, as shown in table 9. The validation experiment of the above-foretold condition is given in table 10.

Table 10: Confirmation Experiment – Grey Relational Analysis

Output	Prediction	Experiment
Density (g/cu.cm)	7.66	8.24
Hardness (Hv)	76.11	77.13
Coefficient of friction	0.483	0.513

CONCLUSIONS

- This paper is mainly concentrated on the fabrication of Copper-CNT nanocomposites by employing hybrid ball milling and ultrasonication approach and the analysis of the influence of the various processing constraints and reinforcement content on various output responses. The output responses like density, hardness, and friction fall

with a rise in reinforcement content which may be due to the development of CNT clusters on increasing the content.

- From Taguchi analysis, the optimal experiment inputs for best outputs responses were analyzed and confirmation tests were done and the same was validated.. There are also lot of interactions between the input factors of ultrasonication and ball milling time observed in the analysis. And from ANOVA analysis of the results of the Taguchi analysis, it is proved that the output responses are more dependent on CNT content than the other processing constraints. Grey relational analysis is used for multiple objective studies wherein the optimum result is predicted at the case of 30 CNT, vol%, 60 min ball milling time, and 20 min ultrasonication time based on grade and ranking. Confirmation experiments are also done to validate the same. From ANNOVA analysis, again 97.53% dependence is on CNT content.

REFERENCES

1. Benyamin Abbasipour, Behzad Niroumand, Sayed Mahmoud Monir Vaghefi, Mohammad Abedi (2019). Tribological behavior of A356–CNT nanocomposites fabricated by various casting techniques. *Precision Engineering*, 29, 1993-2004
2. REDDY, A. CHENNAKEESAVA. "Low and High Temperature Micromechanical Behavior of BN/3003 Aluminum Alloy Nanocomposites." *International Journal of Mechanical Engineering and Technology* 6.4 (2017): 27-34.
3. Dawid Janas, Barbara Liszka (2017). Copper matrix nanocomposites based on carbon nanotubes or graphene, *Materials Chemistry Frontiers*
4. M.R. Akbarpour, H. Mousa Mirabad, S. Alipour, H.S. Kim (2019). Enhanced tensile properties and electrical conductivity of Cu-CNT nanocomposites processed via the combination of flake powder metallurgy and high-pressure torsion methods, *Materials Science & Engineering A*, 773
5. Habeeb, Majeed A. "Effect of Nanosilver Particles on Thermal and Dielectric Properties of (PVA-PVP) Films." *International Journal of Applied and Natural Sciences* 2.4 (2013): 103-108.
6. Bruno Faria, Cátia Guarda, Nuno Silvestre, José N.C. Lopes, Diogo Galhofo (2018). Strength and failure mechanisms of cnt-reinforced copper nanocomposite, *Composites Part B*, 145, 108-120
7. Belekar, RAJU M., P. S. Sawadh, and R. K. Mahadule. "Synthesis and structural properties of Al₂O₃/ZrO₂ nano composite prepared via solution combustion synthesis." *International Journal of Research in Engineering & Technology*, 2, 145 152 (2014).
8. Ali Samer Muhsan, Faiz Ahmad, Norani M. Mohamed, Puteri Sri Melor Megat Yusoff, Muhammad Rafi Raza (2013). Uniform Dispersion of Multiwalled Carbon Nanotubes in Copper Matrix Nanocomposites Using Metal Injection Molding Technique, *International Journal of Manufacturing Engineering*, 2013
9. Bhattacharya, S. S., and S. B. Chaudhari. "Study on structural and thermal properties of polypropylene silica nanocomposite filaments." *International Journal of Textile and Fashion Technology* 5.1 (2015): 15-22.
10. Walid M. Daoush (2008). Processing and Characterization OF CNT/Cu Nanocomposites by Powder Technology, *Powder Metallurgy and Metal Ceramics*, 47
11. Ch. Guiderdoni, E. Pavlenko, V. Turq, A. Weibel, P. Puech, C. Estournes, A. Peigney, W. Bacsa, Ch. Laurent (2013). The preparation of carbon nanotube (CNT)/copper composites and the effect of the number of CNT walls on their hardness, friction and wear properties, *Carbon*, 58, 185 –197

12. Vishwanath. Koti1, R. George, Praveennath G. Koppad, K. V. Shivananda Murthy, Ali. Shakiba (2018). *Friction and Wear Characteristics of Copper Nanocomposites Reinforced with Uncoated and Nickel Coated Carbon Nanotubes*, *Materials Research Express*
13. Rajyashree M. Sundaram, Atsuko Sekiguchi, Mizuki Sekiya, Takeo Yamada, Kenji Hata (2018). *Copper/carbon nanotube composites: research trends and outlook*, *Royal Society Open Science*, 5
14. Yuping Yan, Yinxiang Lei, Sheng Liu (2018). *Tensile responses of carbon nanotubes-reinforced copper nanocomposites: Molecular dynamics simulation*, *Computational Materials Science* 151, 273–277

AUTHORS PROFILE

V. Veeranaath is currently working as Assistant Professor in Department of Mechanical Engineering, Faculty of Engineering and Technology, SRM Institute of Science of Technology for the past 5 years. I completed B.Tech (Mechanical Engineering) in Pondicherry Engineering College and M.Tech (Computer Integrated Manufacturing) in SRM University. My research interests are Tool Engineering, Optimization and Nanocomposites. I am a Life time member in International Association of Engineers (IAENG) and Associate Member in Institution of Engineers (IEI).