

Preparing and Investigation a New Nanofluid for Employing in Machining Process: Synthesis and Characterization of Graphene Oxide Nanoparticles

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ABSTRACT

The quality of machined workpieces, particularly precious metals, is the main goal of every machining process. A suitable cutting fluid can substantially affect the machining outcome. The present study is novel in that it uses nanofluids in the machining process to mitigate the adverse effects of high temperatures and fraction. Graphene oxide (GO) nanoparticles were synthesized using the modified Hummers method. FTIR, FESEM and XRD tests were used for GO characterization and also for atomic, surface and chemical analyses. The studied workpiece was a bronze shaft, $\varnothing 20$ mm. Different nanofluid solutions (0.25 and 0.5 vol%) were applied to reduce the machining loads and increase the workpiece flatness. The results were then compared with those from a base water-oil (90-10 vol%) cutting fluid (Behran, Iran). The NP characterization confirmed the satisfactory quality of the particles. It also showed that the effect of NP on the machining forces is substantial. Accordingly, the largest reduction in the mean machining force was achieved when using the 0.5% nanofluid solution (28.34% less than the base fluid). The surface roughness of the bronze shaft was lower when using the 0.5% nanofluid (0.57 μm) instead of the base fluid (0.668 μm). Finally, it can be concluded that this nanofluid can be an alternative to the base fluids in the machining process.

1-Introduction

The essential research on improved accessories and feedstocks is driven by the need for new technologies. Most industries seek to manufacture their products at the lowest cost and the highest quality to dispose of operations with non-value added processes [1]. Nanotechnology is an efficient science capable of effecting drastic changes in different industries [2]. A literature review showed that the use of nano-scaled high-tech materials can improve the performance of different mechanisms including machining [3], energy storage [4], solar systems [5], photo catalytic properties [6], and surface properties of different tools [7]. The use of nanofluids (NFs) as an applied branch of nano

science is central to improve the quality and efficiency of thermal and lubrication systems. The term nanofluid (NF) was coined by Choi in 1995 [8] and refers to the suspension of NPs (1-100 nm) in a base fluid.

Because of their better thermophysical properties, the academic focus on carbon NPs [9] has been greater. A great deal of research has been carried out on graphite nanoparticles [10], graphene nanoplates [11], carbon nanotubes [12], graphene oxide (GO) nanoplates [13], fullerene [14], and carbon fibers in making NFs with industrial applications. Given the thermophysical properties of GO nanoplates, their synthesis and mass production are very important subjects. In graphite, graphene layers

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are held stacked on one another by a strong steady force, which makes it difficult to cleave graphite to obtain single-layer materials. Graphite oxidation is an effective technique to split graphene layers. In this process, ECCOH, EOH, and epoxide functional groups are placed between the sheets to develop hydrophobicity, which in turn leads to the detachment of nanoplates in water under ultrasonic treatment [15, 16].

The desirable properties of NFs improve the heat transfer rate and make them a good candidate, as a smart fluid [17], for industrial applications related to heat transfer systems. There are numerous reports regarding the great potential of NFs for lubrication and heat transfer purposes [18-21]

The use of cutting fluids with higher heat transfer potential in the machining process can ensure desirable qualitative properties including the required surface flatness and dimensional tolerances/geometry, reduced machining forces, and longer tool life [22, 23].

Generally, cutting tools experience wear under extreme temperatures, pressures, and sliding speeds, as well as thermal and mechanical shocks. Tool wear deforms its geometry, which in turn affects surface flatness and machining forces [24, 25].

Cooling has always been a major challenge in the machining process [26, 27]. A practically proper approach to increase the heat transfer from the machining area is to use nanofluids. In this relation, the use of fluids containing nanoparticles is a modern cooling approach for machine tools. The improved heat transfer of machining fluids can remove the adverse effects of the heat generated during the process [28].

Different theoretical and empirical studies have particularly focused on the thermal properties of fluids containing solid nano-fluids. Most of them have reported that conduction and convection coefficients were substantially improved during the NF heat transfer [29, 30].

In 2008, cutting nano-fluids were first used in a grinding process. The study first analyzed the kinetics of Al_2O_3 - and ZnO -containing NFs. It was reported that the highest improvements in the thermal conductivity of NFs were 20 and 65% compared with the water-oil base fluid. Shen et al. later used the above-mentioned NF in a grinding process. Their results showed that the

grinding forces and the surface flatness were improved by the NF application [31].

Verma et al. used molybdenum disulfide nanoparticles to improve the properties of the base fluids containing a paraffin, triglyceride (canola oil), or lecythis oil base. Their research was focused on a ball bearing, and their results showed that the NF highly reduced friction and wear [32].

Setti et al. used water- Al_2O_3 NF for grinding Ti-6Al-4V. In this experiment, the grinding forces and surface integrity were measured by using different NF concentrations (vol%). The results showed a better surface quality and reduced grinding forces for this alloy [33]. In another study on heat-treated AISI D2 steel, water NF and CNTs were used. It was reported that the surface roughness of the workpiece was improved whereas the scale of the surface properties was reduced from micro to nano [34]. Najiha et al. investigated the effects of the water-TiO₂ NF on the machining of an aluminum alloy. The experiment was conducted using different nanoparticle volume fractions. Finally, the authors reported that the NF performed satisfactorily as a coolant and a lubricant. Given this literature review, it can be stated that the application of NFs in machining processes can improve cooling and lubrication of the tools during the process [35].

Research has supported that the application of NFs as a cutting fluid in machining can increase heat transfer, reduce machining forces, and improve surface flatness of the workpiece. This study aimed at synthesis and characterization of NPs and also their application in water-oil/GO NFs in the machining process. Given the layered structure of NPs, which improves tribological properties, and also their thermal properties, it was predicted that the machining result would considerably outperform the output from the application of the base fluid.

2- Materials and methods

2-1- The study workpiece

A 500 mm long bronze shaft (\varnothing 20 mm) was used for the experiments. Research shows that the structure and mechanical properties of bronze are very similar to those of gold. Since the application of NFs in the machining process of economically precious gold bars can improve the quality of the process, this study used bronze

shafts that have highly similar characteristics to gold. Once the operational conditions are determined by experimentation, the possibility of applying these findings to the machining and making of gold jewelry can be facilitated. At the same time, the findings can be directly applied to the machining of bronze pieces.

2-2- Synthesis of graphene oxide nanoparticles

Graphene oxide (GO) nanoparticles (NPs) were synthesized using the modified Hummers method [36, 37]. Accordingly, at the start of the synthesis process, 69 ml of highly concentrated H_2SO_4 was added to a mixture of 3 gr of graphite powder and 1.5 gr $NaNO_3$. The reactive solution was then cooled down in an ice bath. A 9 gr batch of $KMnO_4$ was then gradually added to the reactive solution within 2 hours at $35^\circ C$. Another 9gr batch of $KMnO_4$ was then added at once. The resulting solution was kept for 4 hours in a $35^\circ C$ bath and was then cooled down to the room temperature. For fast oxidation of the reactive solution, a 400cc mixture of ice and then 3cc H_2O_2 were also added. The synthesis was completed at this point. The synthesized product was washed using 200 ml of distilled water, 200 mLit of 30% HCl, and 200 ml of ethanol at each step to extract the NPs by a centrifuge. Finally, the remaining NPs were coagulated in ether and were then passed through filter papers. The resulting nanomaterials were dried at $40^\circ C$ in an oven.

2-3- Making of and stability of water-oil/GO NF

The NF production process of the study had two phases [38]. The synthesized GO NPs were added to the base fluid through two processes (*i.e.* magnetic and ultrasonic) to make the nanofluid. The mass of the nanoparticle was determined by Eq. (1).

$$\varphi = \frac{\left(\frac{m}{\rho}\right)_{GO}}{\left(\frac{m}{\rho}\right)_{GO} + \left(\frac{m}{\rho}\right)_{bf}} \quad (1)$$

The above equation shows the volume fraction of NPs. Here, φ is the volume fraction of NPs,

and ρ_{bf} and ρ_p are the densities of the base fluid and NPs, respectively.

The required amount of NPs was measured by a digital balance (± 0.0001 g) once the GO NPs were obtained. A magnetic stirrer (RET Basic) was used to mix the NPs with the base fluid. An ultrasound probe was finally used to uniformly distribute the NPs in the base fluid. The ultrasound device (UP400St) had 400W power operating at a frequency of 24 kHz.

3- Machining system and variables

A TN50D lathe machine was used to analyze the effect of water-oil/GO NF on the machining process. The process forces were measured by a dynamometer (Kistler), which was connected to the experimental setup. A SV-2100 Column Roughness Meter was also used to examine the surface quality of the workpiece. The variable experimental conditions were provided based on the field studies and the system capacity using the fixed forward speed of 0.11 mm/rev, cutting speed of 710 mm/min, and cutting depth of 1 mm. A SANDVIK cutting tool was selected based on technical handbook recommendation and field studies. The study base fluid was a mixture of water and Behran cutting oil at a volume fraction of 90-10. The applied nanofluid contained the base fluid and GO particles at volume concentrations of 0, 0.25 and 0.5%. Fig. 1 shows the different equipment and materials used in the study.

4- Results and discussion

4-1- GO characterization

The GO nanoparticles synthesized by the modified Hummers method were characterized using field emission scanning electron microscopy (FESEM), X-ray diffraction analysis (XRD) and fourier-transform infrared spectroscopy (FTIR). The results are given in Figs 2 -4.

FESEM images show the surface structure of GO nanoplates (Fig. 2). These nanoparticles have a plate-like structure. The wrinkles on the NP layers can be due to the chemical synthesis and formation of the functional groups on their surface, which are inevitable during the process [39].

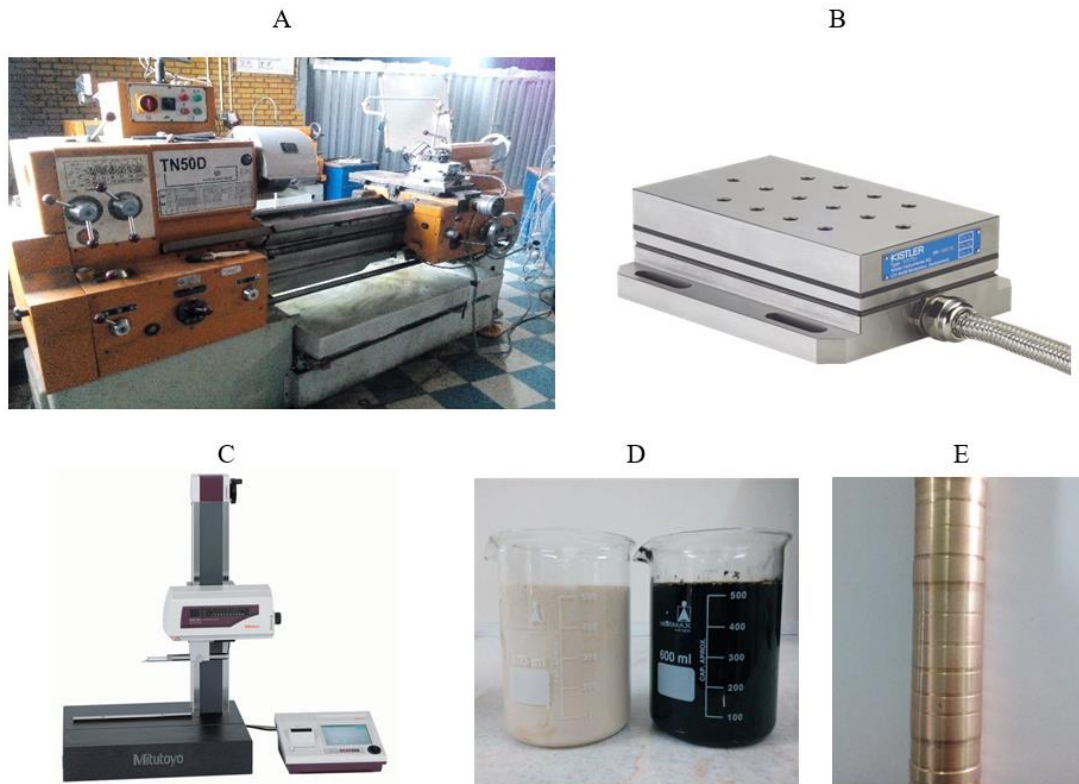


Fig. 1. Experimental setup and materials:
 A: Machining tool, B: Dynamometer, C: Roughness, D: Nanofluid, E: Bronze rod.

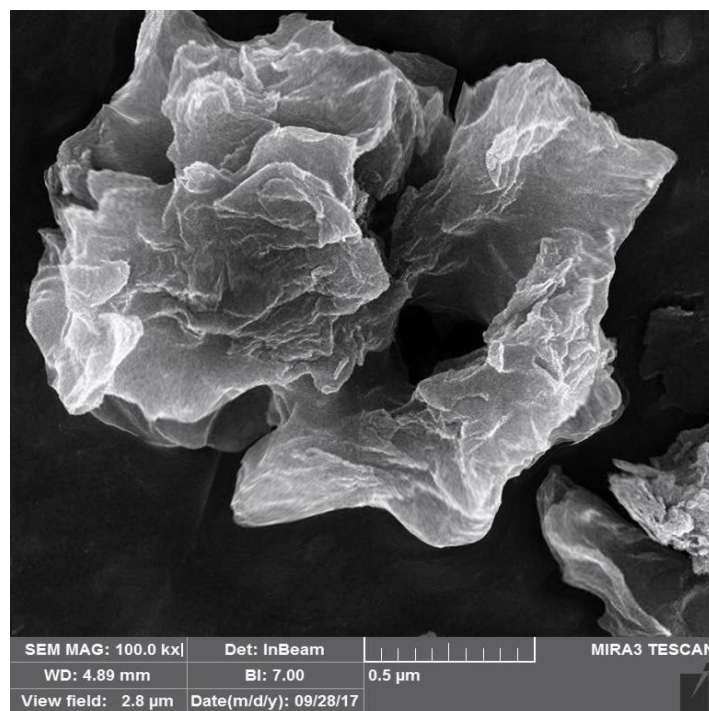


Fig. 2. SEM and XRD images of GO nanoplates.

Fig. 3 shows the XRD test results for GO nanoparticles in 2θ angle. Naturally, due to different atomic layout and order, different materials have different unique diffraction patterns [40]. The study results verify the atomic structure of nanoparticles, and the peak for GO nanoparticles is at the 11.15° angle.

The FTIR test results of graphene oxide nanoparticles within the $1400\text{-}3850\text{ cm}^{-1}$ range by passing the beam through the subject are given in Fig. 4. The FTIR spectrum of the synthesized GO had two strong peaks at 1719 cm^{-1} and 1733 cm^{-1} corresponding to the vibrational dual bond C=O. The strong 3412 cm^{-1} peak also indicated the presence of the O-H bond [41].

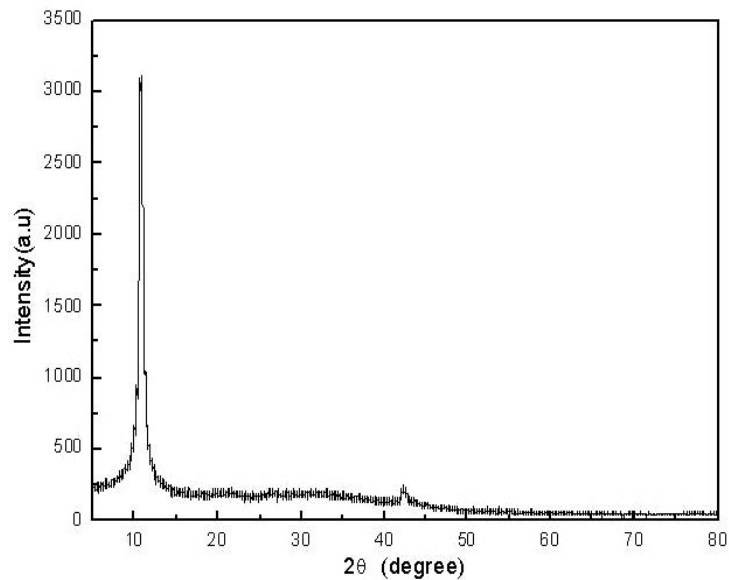


Fig. 3. XRD image of the GO nanoparticles.

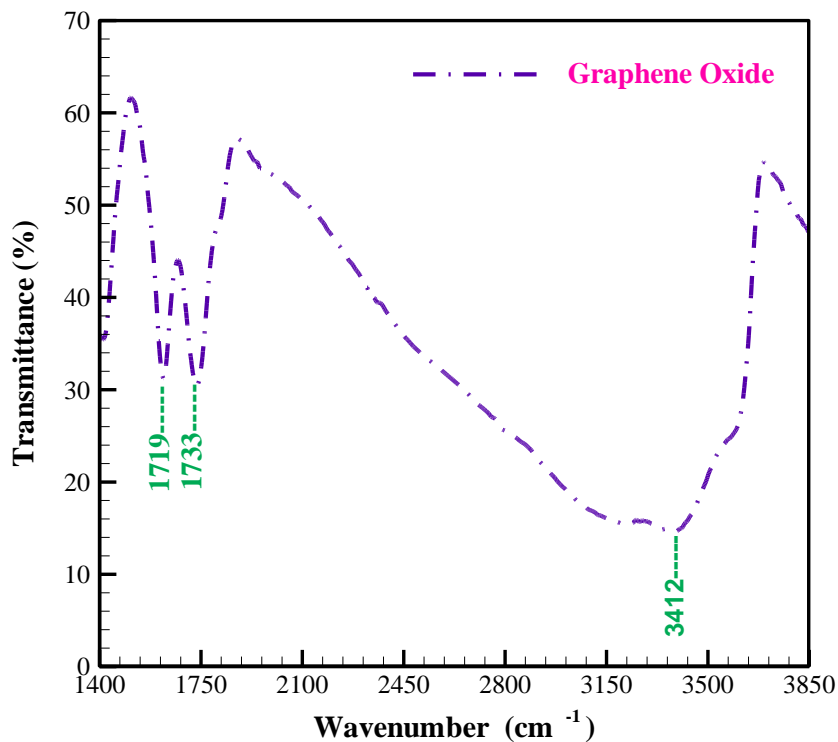


Fig. 4. FTIR results for the GO nanoparticles.

4-1- NF effect on bronze shaft surface roughness

Figure (5) shows the effect of the GO-containing NF flow on the mean surface roughness (Ra) of the machined workpiece. According to the results, surface roughness of the sample machined with the NF flow is much lower than that of the sample machined with the base cutting fluid (water-oil, 90-10 vol%). The most important factors contributing to the improved surface quality can be the high thermal conductivity, anti-friction, and anti-wear properties of the GO nanofluid.

The GO nanoparticles in the cutting fluid reduced the friction coefficient between the tool and the chip by preventing the direct contact between the surfaces. As a result, the formation of the built-up edge (BUE) as a source of the increase of roughness became less likely. Moreover, reduced friction at the tool-chip interface improved the chip flow, which in turn reduced the workpiece and tool vibrations. The roughness from these sources was thus reduced.

4-2- NF effect on the machining forces

Results of the machining forces under different NF concentrations are given in Fig. 6. The mean machining force was determined by Eq. (2) using data from the dynamometer.

$$F_m = \sqrt{(F_f)^2 + (F_t)^2 + (F_c)^2} \quad (2)$$

Where F_m or the mean machining force is determined from the equation, F_c is the cutting force, F_f is the friction force, and F_t shows the thrust force determined by the dynamometer. As shown, the application of the nanofluid reduced the mean machining force in all cases. The most important reason behind this reduction can be the high thermal properties and the antifriction characteristics of the GO-containing nanofluid. Accordingly, the nanoparticles inside the base fluid can penetrate into the tool-chip interface to reduce the gap across the interface, which in turn increases the local forces. As a result, nanoparticles are sintered due to high pressure and temperature and form a porous film that bears a fraction of the forces and prevents direct contact. During this process, the mean machining force is reduced as the temperature and the coefficient of friction are lowered. The use of GO in the base fluid, in order to improve the properties such as heat transfer and flow model, can boost the performance in the manufacturing industry and the machining process in particular.

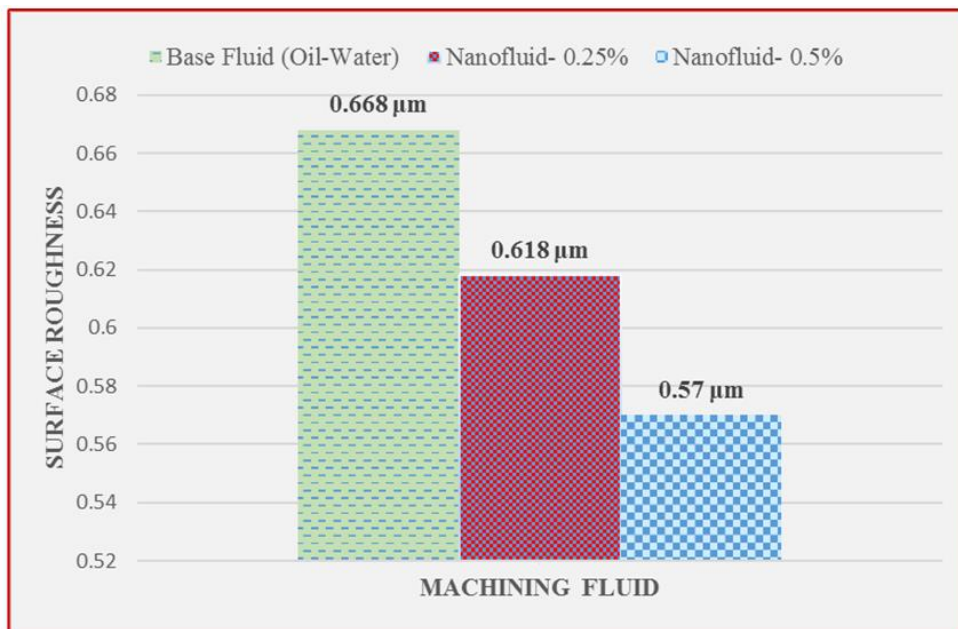


Fig. 5. The effect of the GO nanofluid on the surface roughness.

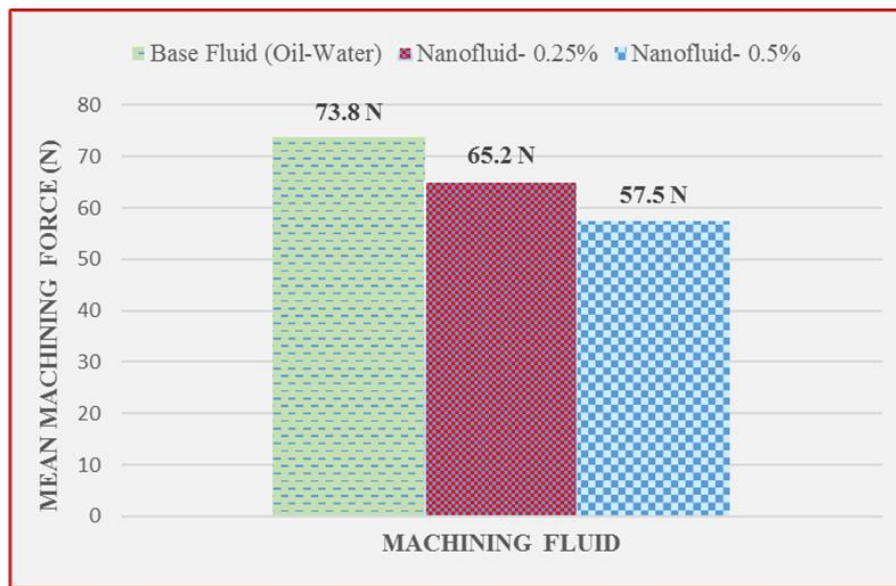


Fig. 6. The effect of the GO nanofluid on the mean machining forces.

5- Conclusion

In this experimental study, GO nanoparticles were first synthesized using the modified Hummers method. The characterization of graphene oxide particles was carried out using XRD, FTIR and FESEM tests. The nanofluid was then made using a water-oil (90- 10 vol%) base fluid and two nanoparticle concentrations (0.25 and 0.5 vol%) through a two-phase method. A machine lathe coupled with a dynamometer was used for the experiments. The findings are as follows:

1. The characterization of the nanoparticles synthesized using the modified Hummers method confirmed the good quality of particles in terms of atomic, structural and chemical structures.
2. The production of the GO-containing nanofluid by mechanical and ultrasonic methods had satisfactory results as they showed lasting stability.
3. The surface roughness of the workpiece was reduced when using an NF flow containing GO nanoplates, which is due to the higher heat transfer rate as well as its antifriction and antiwear properties. Accordingly, raising the NF concentration up to 0.5 vol% invariably provided better conditions in terms of the surface flatness of the workpiece.
4. The GO nanoparticles penetrated into the machining interfaces and formed a porous

medium considering the local conditions. This film minimized the direct contact between the surfaces and thus reduced the mean machining force.

5. A comparison of the differences between the use of the NF and the base fluid showed that the NF effect on reduced machining forces was substantially more than its effect on the surface flatness of the workpiece.

6. As a cutting fluid, the graphene-oxide nanofluid is a good replacement for the conventional water-oil base fluid thanks to its desirable thermal and antifriction properties.

References

- [1] R. Ranjbarzadeh, A.H. Meghdadi, M. Hojaji, "The Analysis of Experimental Process of Production, Stabilizing and Measurement of the Thermal Conductivity Coefficient of Water/Graphene Oxide as a Cooling Nanofluid in Machining", *Journal of Modern Processes in Manufacturing and Production*, Vol. 5, 2016, pp. 43-53.
- [2] S.K. Das, S.U. Choi, W. Yu, T. Pradeep, "Nanofluids: science and technology", John Wiley & Sons, 2007.
- [3] M. Shabgard, M. Seyedzavvar, M. Mohammadpourfard, "Experimental investigation into lubrication properties and mechanism of vegetable-based CuO nanofluid in MQL grinding", *The International Journal of*

- Advanced Manufacturing Technology, 2017, pp. 1-17.
- [4] X.J. Wang, X.F. Li, Y.H. Xu, D.S. Zhu, "Thermal energy storage characteristics of Cu–H₂O nanofluids", *Energy*, Vol. 78, 2014, pp. 212-217.
- [5] H.J. Jouybari, S. Saedodin, A. Zamzamian, M.E. Nimvari, S. Wongwises, "Effects of porous material and nanoparticles on the thermal performance of a flat plate solar collector: An experimental study", *Renewable Energy*, Vol. 114, 2017, pp. 1407-1418.
- [6] A. Nekoubin, H. Ghayour Najafabadi, M. Nasr Esfahani, "An illustration of photocatalytic properties of ZnO nanorods array films", *Journal of Advanced Materials and Processing*, Vol. 1, 2013, pp. 39-46.
- [7] B. Li, C. Li, Y. Zhang, Y. Wang, M. Yang, D. Jia, N. Zhang, Q. Wu, "Effect of the physical properties of different vegetable oil-based nanofluids on MQLC grinding temperature of Ni-based alloy", *The International Journal of Advanced Manufacturing Technology*, Vol. 89, 2017, pp. 3459-3474.
- [8] S. Chol, "Enhancing thermal conductivity of fluids with nanoparticles", *ASME-Publications-Fed*, Vol. 231, 1995, pp. 99-106.
- [9] S.L. Candelaria, Y. Shao, W. Zhou, X. Li, J. Xiao, J.-G. Zhang, Y. Wang, J. Liu, J. Li, G. Cao, "Nanostructured carbon for energy storage and conversion", *Nano Energy*, Vol. 1, 2012, pp. 195-220.
- [10] Z. González, C. Botas, C. Blanco, R. Santamaría, M. Granda, P. Álvarez, R. Menéndez, "Thermally reduced graphite and graphene oxides in VRFBs", *Nano Energy*, Vol. 2, 2013, pp. 1322-1328.
- [11] A. Rashidi, H. Ahmadi, S.S. Mohtasebi, M. Pourkhalil, "Thermal and rheological properties of oil-based nanofluids from different carbon nanostructures", *International Communications in Heat and Mass Transfer*, Vol. 48, 2013, pp. 178-182.
- [12] F. Izadi, R. Ranjbarzadeh, R. Kalbasi, M. Afrand, "A new experimental correlation for non-Newtonian behavior of COOH-DWCNTs/antifreeze nanofluid", *Physica E: Low-dimensional Systems and Nanostructures*, Vol. 98, 2018, pp. 83-89.
- [13] R. Ranjbarzadeh, A. Karimipour, M. Afrand, A.H.M. Isfahani, A. Shirneshan, "Empirical analysis of heat transfer and friction factor of water/graphene oxide nanofluid flow in turbulent regime through an isothermal pipe", *Applied Thermal Engineering*, Vol. 126, 2017, pp. 538-547.
- [14] Q. Wu, R. Xu, R. Wang, Y. Li, "Effect of C60 nanofluid on the thermal performance of a flat-plate pulsating heat pipe", *International Journal of Heat and Mass Transfer*, Vol. 100, 2016, pp. 892-898.
- [15] R.K. Layek, A.K. Nandi, "A review on synthesis and properties of polymer functionalized graphene", *Polymer*, Vol. 54, 2013, pp. 5087-5103.
- [16] T.T. Baby, R. Sundara, "Synthesis and transport properties of metal oxide decorated graphene dispersed nanofluids", *The Journal of Physical Chemistry C*, Vol. 115, 2011, pp. 8527-8533.
- [17] A.K. Sharma, A.K. Tiwari, A.R. Dixit, "Rheological behaviour of nanofluids: a review", *Renewable and Sustainable Energy Reviews*, Vol. 53, 2016, pp. 779-791.
- [18] M. Soltanimehr, M. Afrand, "Thermal conductivity enhancement of COOH-functionalized MWCNTs/ethylene glycol–water nanofluid for application in heating and cooling systems", *Applied Thermal Engineering*, Vol. 105, 2016, pp. 716-723.
- [19] M. Afrand, D. Toghraie, N. Sina, "Experimental study on thermal conductivity of water-based Fe₃O₄ nanofluid: Development of a new correlation and modeled by artificial neural network", *International Communications in Heat and Mass Transfer*, Vol. 75, 2016, pp. 262-269.
- [20] M. Hemmat Esfe, M. Afrand, W.-M. Yan, H. Yarmand, D. Toghraie, M. Dahari, "Effects of temperature and concentration on rheological behavior of MWCNTs/SiO₂(20–80)-SAE40 hybrid nano-lubricant", *International Communications in Heat and Mass Transfer*, Vol. 76, 2016, pp. 133-138.
- [21] M. Afrand, K. Nazari Najafabadi, M. Akbari, "Effects of temperature and solid volume fraction on viscosity of SiO₂-MWCNTs/SAE40 hybrid nanofluid as a coolant and lubricant in heat engines", *Applied Thermal Engineering*, Vol. 102, 2016, pp. 45-54.
- [22] V.K. Jain, "Advanced machining processes", Allied publishers, 2009.
- [23] H. Salimi-Yasar, S.Z. Heris, M. Shanbedi, A. Amiri, A. Kameli, "Experimental

investigation of thermal properties of cutting fluid using soluble oil-based TiO₂ nanofluid, *Powder Technology*, Vol. 310, 2017, pp 213-220.

[24] Y. Yildiz, M. Nalbant, "A review of cryogenic cooling in machining processes", *International Journal of Machine Tools and Manufacture*, Vol. 48, 2008, pp. 947-964.

[25] J.P. Davim, *Machining: fundamentals and recent advances*, Springer Science & Business Media, 2008.

[26] M. Najiha, M. Rahman, K. Kadirgama, "Machining performance of aluminum alloy 6061-T6 on surface finish using minimum quantity lubrication", *International Journal of Automotive and Mechanical Engineering*, Vol. 11, 2015, pp. 2699.

[27] A.A. Khan, M.I. Ahmed, "Improving tool life using cryogenic cooling", *Journal of Materials Processing Technology*, Vol. 196, 2008, pp. 149-154.

[28] N.A.C. Sidik, S. Samion, J. Ghaderian, M.N.A.W.M. Yazid, "Recent progress on the application of nanofluids in minimum quantity lubrication machining: A review", *International Journal of Heat and Mass Transfer*, Vol. 108, 2017, pp. 79-89.

[29] Q. Li, Y. Xuan, J. Wang, "Investigation on convective heat transfer and flow features of nanofluids", *Journal of Heat transfer*, Vol. 125, 2003, pp 151-155.

[30] V. Bianco, O. Manca, S. Nardini, K. Vafai, "Heat transfer enhancement with nanofluids", CRC Press, 2015.

[31] B. Shen, Minimum quantity lubrication grinding using nanofluids, in, University of Michigan, 2008.

[32] A. Verma, W. Jiang, H.H. Abu Safe, W.D. Brown, A.P. Malshe, Tribological behavior of deagglomerated active inorganic nanoparticles for advanced lubrication, *Tribology Transactions*, Vol. 51, 2008, pp 673-678.

[33] D. Setti, S. Ghosh, P.V. Rao, "Application of nano cutting fluid under minimum quantity lubrication (MQL) technique to improve grinding of Ti-6Al-4V alloy", in: *Proceedings of World Academy of Science, Engineering and Technology*, World Academy of Science, Engineering and Technology, 2012, pp. 512-516.

[34] S. Prabhu, B. Vinayagam, Nano surface generation of grinding process using carbon nano tubes, *Sadhana*, 35 (2010) 747-760.

[35] M. Najiha, M. Rahman, K. Kadirgama, "Performance of water-based TiO₂ nanofluid during the minimum quantity lubrication machining of aluminium alloy, AA6061-T6", *Journal of cleaner production*, Vol. 135, 2016, pp. 1623-1636.

[36] S. Chandrasekaran, S.H. Hur, E.J. Kim, B. Rajagopalan, K.F. Babu, V. Senthilkumar, J.S. Chung, W.M. Choi, Y.S. Kim, "Highly-ordered maghemite/reduced graphene oxide nanocomposites for high-performance photoelectrochemical water splitting", *RSC Advances*, Vol. 5, 2015, pp 29159-29166.

[37] J. Cheng, Y. Qiu, R. Huang, W. Yang, J. Zhou, K. Cen, "Biodiesel production from wet microalgae by using graphene oxide as solid acid catalyst", *Bioresource Technology*, Vol. 221, 2016, pp. 344-349.

[38] R. Ranjbarzadeh, A.M. Isfahani, M. Afrand, A. Karimipour, M. Hojaji, An experimental study on heat transfer and pressure drop of water/graphene oxide nanofluid in a copper tube under air cross-flow: Applicable as a heat exchanger, *Applied Thermal Engineering*, Vol. 125, 2017, pp. 69-79.

[39] S.H. Aboutalebi, M.M. Gudarzi, Q.B. Zheng, J.K. Kim, "Spontaneous formation of liquid crystals in ultralarge graphene oxide dispersions", *Advanced Functional Materials*, Vol. 21, 2011, pp. 2978-2988.

[40] T. Hatchard, J. Dahn, "In situ XRD and electrochemical study of the reaction of lithium with amorphous silicon", *Journal of The Electrochemical Society*, Vol. 151, 2004, pp. 838-842.

[41] C. Hontoria-Lucas, A. Lopez-Peinado, J.d.D. López-González, M. Rojas-Cervantes, R. Martin-Aranda, "Study of oxygen-containing groups in a series of graphite oxides: physical and chemical characterization", *Carbon*, Vol. 33, 1995, pp. 1585-1592.