

Synergistic effects of alloying elements and solid solution treatment on the impact energy, density and conductivity of Cu-3Si-3(Zn, Sn) alloys system

Agatha Ifeoma Ijomah¹, Kingsley Chidi Nnakwo², Nkem Emelike Nwankwo^{3*},
Ifeanacho Uchenna Okeke⁴

Department of Metallurgical and Materials Engineering, Nnamdi Azikiwe University, Awka, Nigeria

Corresponding author address: ne.nwankwo@unizik.edu.ng

DOI: <https://doi.org/10.5281/zenodo.8348613>

Published Date: 15-September-2023

Abstract: The present study explored the synergistic effects of alloying elements and solid solution treatment on the impact energy, density, and conductivity of Cu-3Si-(Zn, Sn) alloys system. Response surface optimal design (RSOD) was utilized to design the alloys compositions. The Cu-3Si-3(Zn, Sn) alloys samples were cast employing stir-casting technique and machined to the required dimensions for the properties tests. The cast samples underwent solid solution at temperature of 900°C for 5 h. The microstructures of the cast samples were analyzed using optical metallurgical microscope (OM). The OM results revealed increased solid solution of zinc in the copper matrix after solid solution heat treatment. Conversely, tin showed increased segregation (coarse grains) in the copper matrix after heat treatment. This led to increase in electrical conductivity of Cu-3Si-3(Sn) ternary alloy in heat treated condition, unlike in Cu-3Si-3(Zn) where a decrease in electrical conductivity is obtained. Both Cu-3Si-3(Zn) and Cu-3Si-3(Sn) ternary alloys recorded increase in impact energy compared with the parent alloy (Cu-3Si). The impact energy of Cu-3Si-3(Sn) ternary alloy recorded a slight increase from 25.2 J to 25.9 J after heat treatment. Cu-3Si-3(Sn) ternary alloy also recorded a slight decrease in density compared with the as-cast Cu-3Si-3(Sn) and parent alloys. Solid solution heat treatment had no positive effect of the impact energy and electrical conductivity of Cu-3Si-3(Zn) ternary alloy.

Keywords: Cu-3Si-3Zn; Cu-3Si-3Sn; grains morphology; strength; hardness.

1. INTRODUCTION

The combination of electrical conductivity, cost-effectiveness, and formability of copper-based alloy makes it a preferred material in a wide range of applications across industries, particularly in electronics and manufacturing. The use of alloying elements, like silicon, allows for tailoring its properties to suit specific needs, although this may involve trade-offs between different characteristics (Nnakwo, 2019; Nnakwo et al., 2017a,b; 2019a,b; 2020, 2021, 2022; Nnakwo and Nnuka, 2018; Garbacz-Klempka et al., 2018). Copper is renowned for its high electrical conductivity. This property allows it to efficiently transmit electrical signals, making it an ideal choice for electrical connectors, lead frames, and micro-electronic devices. Copper possesses excellent ductility and malleability, hence can be easily shaped, bent, or formed into various components such as bolts, nuts, valves, and fittings. Copper possesses excellent ductility and malleability, making it suitable for applications where it needs to be shaped, bent, or formed into various components such as bolts, nuts, valves, and fittings (Qing et al., 2011; Xie et al., 2003; Lei et al., 2017; Gholami et al., 2017; Qian et al., 2017; Suzuki et al., 2006). Copper is often alloyed with other elements like silicon, tungsten, zinc, tin, magnesium, manganese, and nickel to enhance its properties. Silicon improves the fluidity and hardness of copper. However, this enhancement comes at the expense of reduced

ductility and electrical conductivity. The addition of silicon can induce the precipitation of hard but brittle phases, such as Cu_3Si , $\text{Cu}_{15}\text{Si}_4$, and Cu_5Si , when the material cools slowly to ambient temperature (Wang et al., 2016; Li et al., 2017; Pan et al., 2007; Li et al., 2009; Lei et al., 2013a, 2013c; Eungyeong et al., 2011; Ho et al., 2000).

Copper-silicon alloys are used as electrodes in lithium-ion batteries due to their ability to enhance battery performance in terms of capacity and cycling stability (Ketut et al., 2011). It also serves as catalysts in various chemical processes, such as the production of nanosized and nanotube zinc oxide rods (Pak et al., 2016; Mattern et al., 2007). Copper-silicon alloys are employed in the fabrication of musical equipment owing to their excellent damping properties (Cai et al., 2011). Copper-silicon alloys are versatile materials with a range of applications, and their properties can be tailored by incorporating different alloying elements to meet specific requirements in various industries. Nickel is known to enhance the hardness and electrical conductivity of Cu-Si alloys (Qian et al., 2017; Suzuki et al., 2006; Wang et al., 2016; Pan et al., 2007; Li et al., 2009; Lei et al., 2013b; Eungyeong et al., 2011; Ho et al., 2000). Elements like aluminium, chromium, iron, magnesium, and tin have also been used to modify Cu-Si alloys. For example, iron enhances both hardness and electrical conductivity, while chromium and zirconium induce microstructural refinement and the precipitation of specific intermetallic phases, leading to improved strength. Combining chromium and zirconium in nickel-doped Cu-Si alloys has been shown to result in alloys with excellent hardness and electrical conductivity. Precipitation of various phases ($\beta_1\text{-Ni}_3\text{Si}$, $\alpha\text{-Cu}(\text{Ni}, \text{Si})$, $\gamma\text{-Ni}_3\text{Al}$, $\beta\text{-Ni}_3\text{Si}$, and $\delta\text{-Ni}_2\text{Si}$) occurs as a result of the alloying elements and subsequent aging processes, contributing to the strengthening of copper alloys. These phases form as a result of the alloying elements and subsequent aging process (Suzuki et al., 2006; Wang et al., 2016, 2018; Li et al., 2017; Wang et al., 2018).

This present study seeks to modify Cu-Si base alloys with zinc and tin additions and optimize their properties through solid solution heat treatment. This is to enhance the impact energy and electrical conductivity, hence making the alloys more attractive for a wide range of engineering applications, thus contributing to the advancement of materials science and technology.

2. EXPERIMENTAL PROCEDURE

The Cu-3Si-3Zn and Cu-3Si-3Sn ternary alloys were prepared using analytical grades copper rods (99.8% pure), silicon powder (99.7% pure), zinc powder (98.5% pure), and tin powder (98.7% pure). The weight in gram of each material was determined, measured using an electronic compact scale (Model: BL20001), and charged into the platinum crucible pot in an inert gas atmosphere. The melt was cast into a steel mold of dimensions 250 x 16 mm² and cooled inside the steel mold to ambient temperature. The developed alloys were subjected to solid solution heat treatment at 900°C for 5 h using a tube furnace (TSH12/25024166CG) equipped with an external thermocouple ($\pm 1^\circ\text{C}$ accuracy). The Impact energy testing is used to measure the toughness of materials. In this case, samples with dimensions 55 cm x 10 cm x 10 cm and notched at the center (2 mm deep at 45°) were tested according to the BS EN ISO 148-1:2016 standard. The bulk density of the materials was measured using Archimedes' principle. This method involves measuring the weight of the sample in air and then in a liquid (water) to determine its density. The electrical properties of the materials, such as resistivity and conductivity, were determined using Standard Ohm's experiment. This is a common method for characterizing the electrical behavior of materials. The surface morphology of the developed Cu-3Si, and Cu-3Si-3(Zn, Sn) alloys was examined using an optical metallurgical microscope (OM). Prior to analysis, the sample surfaces underwent several preparation steps: grinding with emery paper of different grit sizes to smoothen the surface, polishing with pure aluminium powder, to achieve a fine and reflective surface, and etching in a solution of iron III chloride (FeCl_3), HCl (hydrochloric acid), and water.

3. RESULTS AND DISCUSSION

Figs. 1-3 show the effects of zinc and tin additions, and solid solution heat treatment on the impact energy, density, and electrical properties of Cu-3Si-3(Zn, Sn) ternary alloys. It is shown in Fig. 1 that impact energy of Cu-3Si alloys was improved significantly on the additions of zinc and tin. Additions of zinc and tin increased the impact energy of the parent alloy (Cu-3Si) from 13.2 J to 24.4 J and from 13.2 J to 25.2 J, respectively. The impact energy of Cu-3Si-3(Sn) ternary alloy increased further to 25.9 J after solid solution heat treatment. However, the Cu-3Si-3(Zn) ternary alloy recorded a slight decrease in impact energy (from 24.4 J to 19.5 J) after undergoing solid solution treatment. Analysis of Fig. 2 shows a decline in the density of the parent alloy from 8.21 g/cm³ to 7.96 g/cm³, after being doped with tin and subjected to solid solution treatment. Fig. 4 showed that the electrical conductivity of Cu-3Si alloy decreased from 26.88 S/m to 22.02 S/m and 20.02 S/m with the additions of zinc and tin respectively. The Cu-3Si-3(Sn) ternary alloy recorded a slight increase in electrical conductivity after undergoing solid solution at 900°C for 5 h. This can be linked with the precipitation of plate-like coarse grains in the copper matrix.

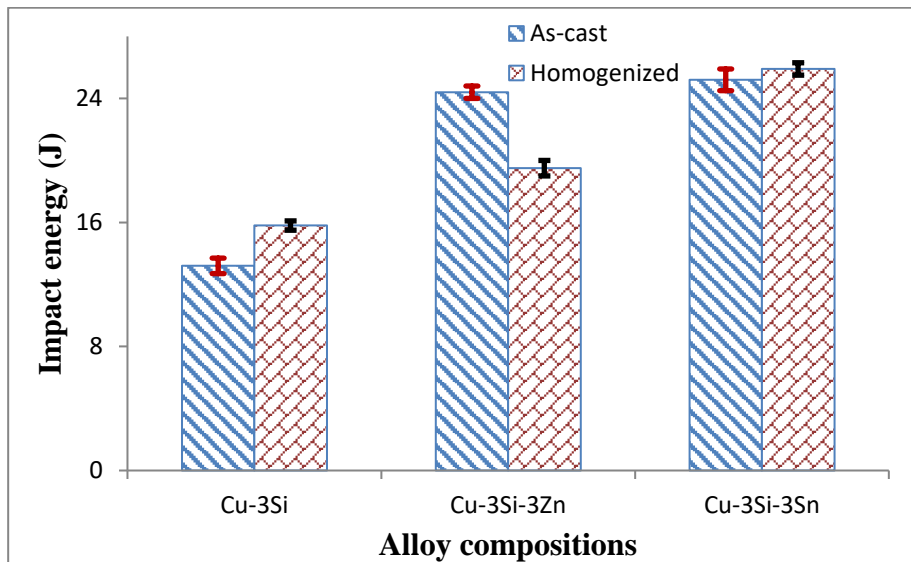


Fig. 1: Impact energy of Cu-3Si-3(Zn, Sn) ternary alloys subjected to solid solution treatment

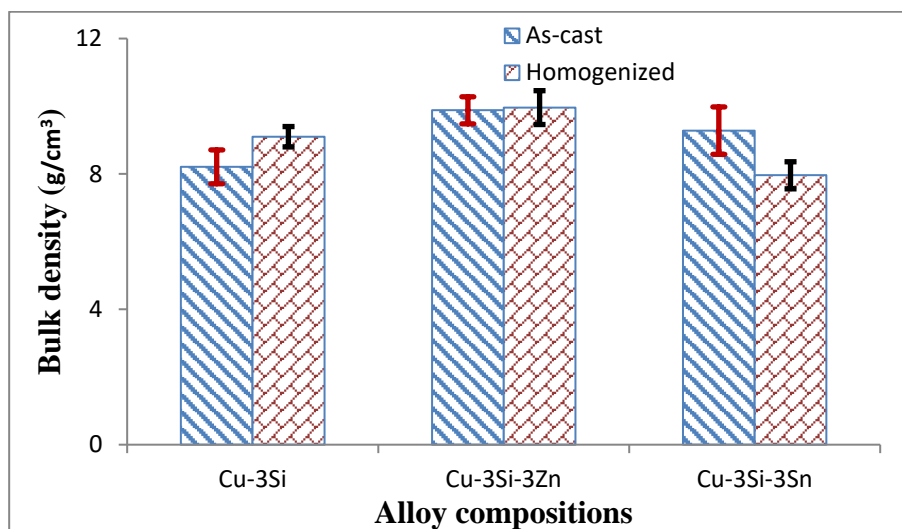


Fig. 2: Bulk density of Cu-3Si-3(Zn, Sn) ternary alloys subjected to solid solution treatment

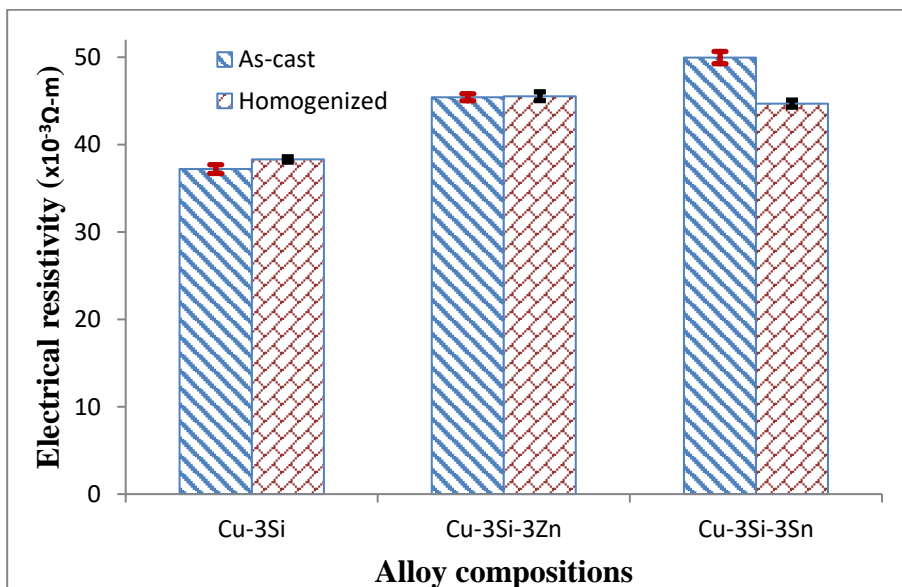


Fig. 3: Electrical resistivity of Cu-3Si-3(Zn, Sn) ternary alloys subjected to solid solution treatment

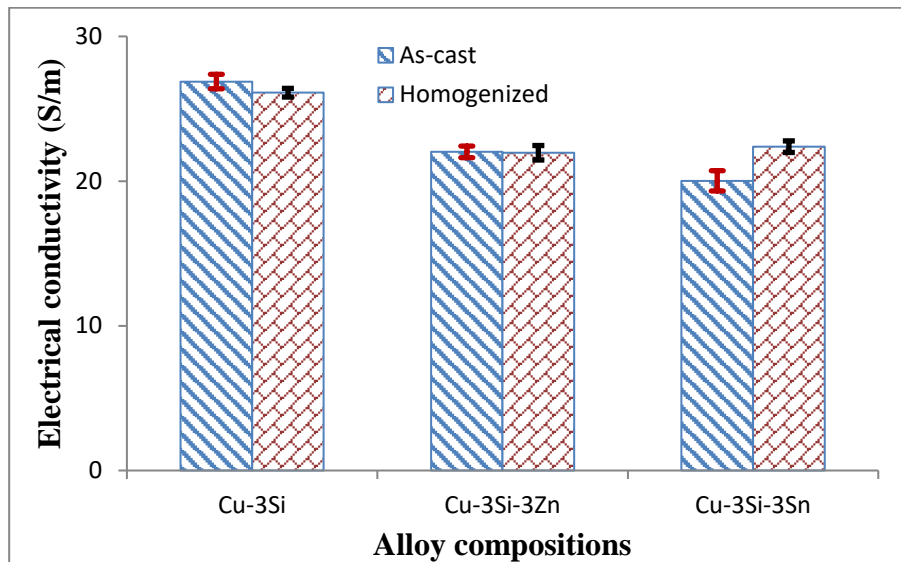


Fig. 4: Electrical conductivity of Cu-3Si-3(Zn, Sn) ternary alloys subjected to solid solution treatment

The surface morphologies of Cu-3Si-3(Zn, Sn) ternary alloys in as-cast and homogenized conditions are presented in Fig. 5. Fig. 5a reveals spherical grains separated by grain boundaries in the as-cast Cu-3Si-3Zn ternary alloy. After solid solution treatment, the zinc goes into solid solution as shown in Fig. 5b. This probably caused the decrease in the electrical conductivity of the alloy compared to the as-cast sample. The surface morphology of the as-cast Cu-3Si-3Sn ternary alloy reveals fine grain in the alloy structure with little solid solution regions. The OM analysis of solid solution heat treated Cu-3Si-3Sn ternary alloy shows coarse grains in the alloy structure with low dislocation density (Fig. 5b). This probably led to the increase in the electrical conductivity of the alloy compared to the as-cast sample.

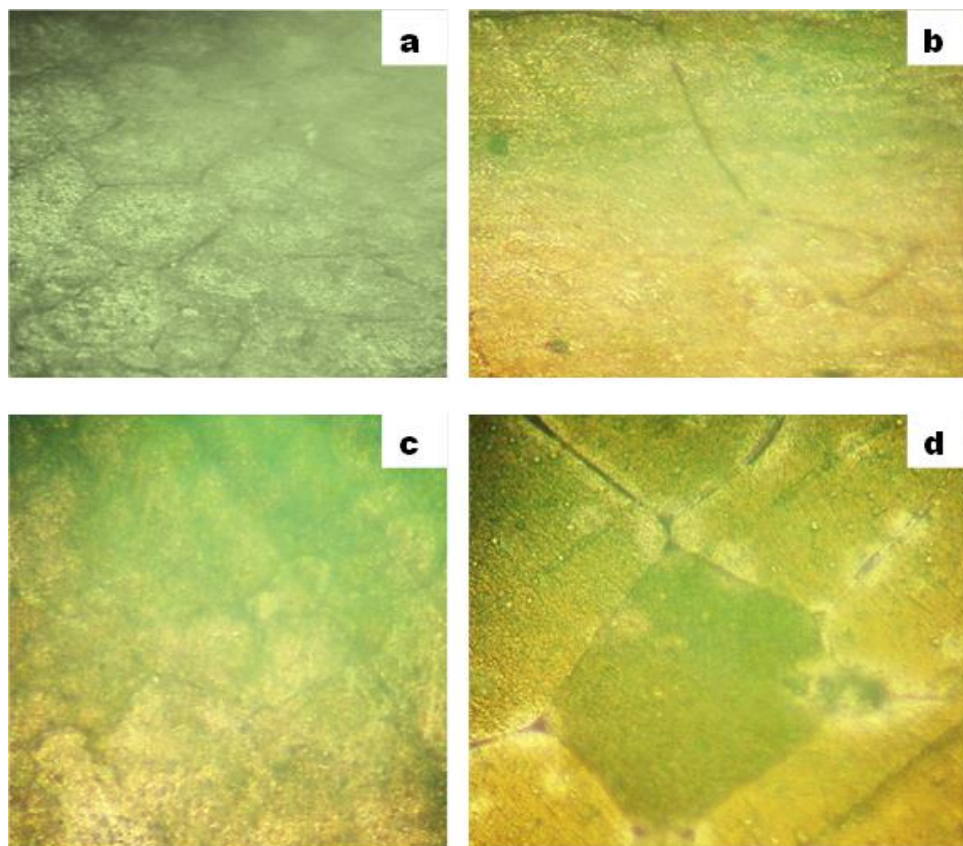


Fig. 5: Optical microstructure of (a) Cu-3Si-3Zn (as-cast)(b) Cu-3Si-3Zn (homogenized)(c) Cu-3Si-3Sn (as-cast)(D) Cu-3Si-3Sn (homogenized).

4. CONCLUSIONS

The synergistic effects of alloying elements and solid solution treatment on the impact energy, density, and conductivity of Cu-3Si-3(Zn, Sn) alloys system has been investigated. The results of the study showed that the Cu-3Si alloy demonstrated good impact energy. After doping with zinc and tin, the impact energy improved significantly. Specifically, the Cu-3Si-3Zn alloy exhibited impact energy of 24.4 J, while the Cu-3Si-3Sn alloy recorded higher impact energy of 25.2 J. After solid solution heat treatment, the Cu-3Si-3Sn recorded an increase in impact energy and electrical conductivity, with corresponding decrease in bulk density. The improvement of electrical conductivity is linked to the precipitation of large grains in the alloy structure. Cu-3Si-3Zn had no significant change in properties after solid solution treatment.

ACKNOWLEDGEMENT

The authors acknowledge the support of the management of Notex Electronics Nigeria Ltd and the management of Cutix Cable Plc, Nnewi Nigeria for providing equipment used for this research.

REFERENCES

- [1] Cai, H., Tong, D., Wang, Y., Song, X., Ding, B., 2011. Reactive synthesis of porous Cu₃Si compound. *J. Alloys Comp.* 509, 1672–1676. DOI: 10.1016/j.jallcom.2010.09.116.
- [2] Eungyeong, L., Seungzeon, H., Kwangjun, E., Sunghwan, L., Sangshik, K., 2011. Effect of Ti addition on tensile properties of Cu-Ni-Si alloys. *Met.Mater. Int.* 17 (4), 569–576. DOI: 10.1007/s12540-011-0807-7.
- [3] Garbacz-Klempka, A., Kozana, J., Piękoś, M., Papaj, M., Papaj, P., Perek-Nowak, M., 2018. Influence of modification in centrifugal casting on microstructure and mechanical properties of silicon bronzes. *Archives of Foundry Engineering.* 18, 11-18. DOI: 10.24425/123594.
- [4] Gholami, M., Vasely, J., Altenberger, I., Kuhn, H.A., Wollmann, M., Janecek, M., Wagner, L., 2017. Effect of microstructure on mechanical properties of CuNiSi alloys. *J. Alloy. Compd.* 696, 201–212. DOI: 10.1016/j.jallcom.2016.11.233.
- [5] Hines, W.W., Montgomery, D.C., Goldsman, D.M., Borrer, C.M., 2003. *Probability and Statistics in Engineering*, 4th Edition, John Wiley & Sons, 2003.
- [6] Ho, J.R., Hyung, K.B., Soon, H.H., 2000. Effect of thermo-mechanical treatments on microstructure and properties of Cu-base lead frame alloy. *J. Mater. Sci.* 35 (14), 3641–3646. DOI: 10.1023/A:1004830000742.
- [7] Jung, S.J., O’Kelly, C.J., Boland, J.J., 2015. Position controlled growth of single crystal Cu₃Si nanostructures. *Cryst.Growth Des.* 15, 5355-5359. DOI: 10.1021/acs.cgd.5b00947.
- [8] Ketut, G.S.I., Soekrisno, R., Suyitno, M.I. Made, 2011. Mechanical and damping properties of silicon bronze alloys for music applications. *Int. J. Eng. Tech. IJETIJENS.* 11 (06), 81–85.
- [9] Lei, Q., Li, Z., Dai, C., Wang, J., Chen, X., Xie, J.M., Yang, W.W., Chen, D.L., 2013a. Effect of aluminium on microstructure and property of Cu–Ni–Si alloys. *Mater. Sci. Eng., A* 572, 65–74. DOI: 10.1016/j.msea.2013.02.024.
- [10] Lei, Q., Li, Z., Xiao, T., Pang, Y., Xiang, Q.Z., Qiu, W.T., Xiao, Z., 2013b. A new ultrahigh strength Cu-Ni-Si alloy. *Intermetallics* 42, 77–84. DOI: 10.1016/j.intermet.2013.05.013.
- [11] Lei, Q., Xiao, Z., Hu, W., Derby, B., Li, Z., 2017. Phase transformation behaviors and properties of a high strength Cu-Ni-Si alloy. *Mater. Sci. Eng., A* 697, 37–47. DOI: 10.1016/j.msea.2017.05.001.
- [12] Li, Z., Pan, Z.Y., Zhao, Y.Y., Xiao, Z., Wang, M.P., 2009. Microstructure and properties of high-conductivity, super-high-strength Cu-8.0Ni-1.8Si-0.6Sn-0.15Mg alloy. *J. Mater. Res.* 24 (6), 2123–2129. DOI: 10.1557/jmr.2009.0251.
- [13] Li, D., Wang, Q., Jiang, B., Li, X., Zhou, W., Dong, C., Wang, H., Chen, Q., 2017. Minor-alloyed Cu-Ni-Si alloys with high hardness and electric conductivity designed by a cluster formula approach. *Progress in Nat. Sci.: Mater. Int.* 27 (4), 467–473. DOI: 10.1016/j.pnsc.2017.06.006.
- [14] Mattern, N., Seyrich, R., Wilde, L., Baehtz, C., Knapp, M., Acker, J., 2007. Phase formation of rapidly quenched Cu–Si alloys. *J. Alloy. Compd.* 429, 211–215. DOI: 10.1016/j.jallcom.2006.04.046.
- [15] Moon, T., Kim, Ch., Park, B., 2006. Electrochemical performance of amorphous-silicon thin films for lithium rechargeable batteries. *J. Power Sources.* 155, 391-394. DOI: 10.1016/j.jpowsour.2005.05.012.

- [16] Nnakwo, K. C., Okeke, I.U., Nnuka, E.E., 2017a. Structural modification and mechanical properties of Cu-3wt%Si-xwt%Sn alloy. *International Journal of Scientific Research in Science, Engineering and Technology*. 3, 184-187.
- [17] Nnakwo, K. C., Okeke, I.U., Nnuka, E.E., 2017b. Effect of zinc content on the structure and mechanical properties of silicon bronze. *International Journal of Scientific Research in Science, Engineering and Technology*. 3, 179-183.
- [18] Nnakwo, K. C., Nnuka, E. E., 2018. Correlation of the structure, mechanical and physical properties of Cu3wt%Si-xwt%Sn silicon bronze. *Journal of Engineering and Applied Sciences*. 13, 83-91.
- [19] **Nnakwo K. C.**, 2019. Effect of tungsten content on the structure, physical and mechanical properties of silicon bronze (Cu-3wt%Si), *Journal of King Saud University - Science*, 31(4), 844-848. doi: <https://doi.org/10.1016/j.jksus.2017.12.002>.
- [20] Nnakwo, K. C., Mbah, C. N., and Daniel-Mkpume, C. C., 2019a. Investigation of the structural sensitive behavior of Cu-3Si-xMn ternary Alloys. *Journal of King Saud University –Science*, 31(4), 1056-1063. <https://doi.org/10.1016/j.jksus.2019.01.001>.
- [21] Nnakwo, K. C., Mbah, C. N., and Nnuka, E. E., 2019b. Influence of trace additions of titanium on grain characteristics, conductivity and mechanical properties of copper-silicon-titanium alloys. *Heliyon*. 5(10), e02471. <https://doi.org/10.1016/j.heliyon.2019.e02471>.
- [22] Nnakwo, K. C., Mbah, C. N., and Ude, S. N., 2020. Influence of chemical composition on the conductivity and on some mechanical properties of Mg-doped Cu-Si alloy. *Journal of King Saud University–Engineering Science*. 32(5), 287-292 <https://doi.org/10.1016/j.jksues.2019.03.005>.
- [23] Nnakwo, K. C., Osakwe, F. O., Ugwuanyi, B. C., Oghenekowho, P. A., Okeke, I. U., & Maduka, E. A., 2021. Grain characteristics, electrical conductivity, and hardness of Zn-doped Cu–3Si alloys system. *SN Applied Sciences*, 3(11). <https://doi.org/10.1007/s42452-021-04784-1>.
- [24] Nnakwo, K. C., Odo, J. U., Eweka, K. O., Okafor, J. S., Ijomah, A. I., Maduka, E. A., and Ugwuanyi, B. C., 2022. Evaluation of the Electrical Conductivity and Mechanical Properties of Cu–3Ti–1.5Ni–0.5Si Quaternary Alloy, *JOM: the journal of the minerals, metals, and materials society*, Vol. 74, (Issue 5); 4174–4180.
- [25] Pak, A.Y., Shatrova, K.N., Aktaev, N.E., Ivashutenko, A.S., 2016. Preparation of ultrafine Cu₃Si in high-current pulsed arc discharge. *Nanotechnol. Russ.* 11 (9– 10), 548–552. DOI: 10.1134/S199507801605013X.
- [26] Pan, Z.Y., Wang, M.P., Li, Z., 2007. Effect of trace elements on properties of Cu-Ni-Si alloy. *Mater. Rev.* 21 (5), 86–89.
- [27] Polat, B.D., Eryilmaz, O.L., Keleş, O., Erdemir, A., Amine, K., 2015. Compositionally graded SiCu thin film anode by magnetron sputtering for lithium ion battery. *Thin Solid Films*. 596, 190–197. DOI: 10.1016/j.tsf.2015.09.085.
- [28] Qian, L., Zhou, L., Zhou, L., Yang, G., Xi, P., Benjamin, D., 2017. Microstructure and mechanical properties of a high strength Cu-Ni-Si alloy treated by combined aging processes. *J. Alloy. Compd.* 695, 2413–2423. DOI: 10.1016/j.jallcom.2016.11.137.
- [29] Qing, L., Li, Z., Wang, M.P., 2011. Phase transformation behavior in Cu–8.0Ni–1.8Si alloy. *J Alloy Compound*. 509 (8), 361-367. DOI: 10.1016/j.jallcom.2010.12.115.
- [30] Suzuki, S., Shibusani, N., Mimura, K., Isshiki, M., Waseda, Y., 2006. Improvement in strength and electrical conductivity of Cu–Ni–Si alloys by aging and cold rolling. *J. Alloy. Compd.* 417 (1–2), 116–120. DOI: 10.1016/j.jallcom.2005.09.037.
- [31] Wang, W., Kang, H., Chen, Z., Chen, Z., Li, R., Yin, G., Wang, Y., 2016. Effects of Cr and Zr addition on microstructure and properties of Cu-Ni-Si alloys. *Mater. Sci. Eng., A* 673, 378–390. DOI: 10.1016/j.msea.2016.07.021.
- [32] Wang, W., Guo, E., Chen, Z., Kang, H., Chen, Z., Zou, C., Lia, R., Yina, G., Wang, T., 2018. Correlation between microstructures and mechanical properties of cryorolled CuNiSi alloys with Cr and Zr alloying. *Materials Characterization*. 144, 532–546. DOI: 10.1016/j.matchar.2018.08.003.
- [33] Xie, S.S., Li, Y.L., Zhu, L., 2003. Progress of study on lead frame copper alloy and its implementation in electronic industry. *Rare Metals*. 27, 76-79.
- [34] Xu, K., He, Y., Ben, L., Li, H., Huang, H., 2015. Enhanced electrochemical performance of Si-Cu-Ti thin films by surface covered with Cu₃Si nanowires. *J. Power Sources*. 281, 455-460. DOI: 10.1016/j.jpowsour.2015.02.023.