Evaluation of solid solution strengthening of copper-silicon binary alloys by carbide forming elements

Agatha Ifeoma Ijomah[1], Kingsley Chidi Nnakwo[2], Nkem Emelike Nwankwo[3]*, Ifeanacho Uchenna Okeke[4]

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.8348120

Published Date: 15-September-2023

Abstract: **This study investigated the effects of carbide forming elements (manganese and tungsten) and solid solution heat treatment on the microstructure, tensile strength, hardness, and percentage elongation of copper-silicon binary alloys. The response of Cu-3Si-W and Cu-3Si-3Mn alloys on solid solution heat treatment was explored. The alloys compositions were designed and fabricated using stir-casting method. The cast samples were solution heat treated at 900ºC for 5 h and prepared for tensile strength and hardness tests. The microstructure of the as-cast and solution heat treated samples was analyzed and linked with the change in the mechanical properties, using an optical microscope (OM). The microstructure analysis revealed even distributions of fine grains in the copper matrix. The solution heat treated samples showed finer grains which led to improvements of both ultimate tensile strength and hardness of Cu-3Si-W and Cu-3Si-3Mn alloys. The Cu-3Si-W alloys recorded maximum ultimate tensile strength and hardness of 298 MPaand 364 BHN, respectively after solid solution treatment. The solution heat treated Cu-3Si-3Mn alloys recorded maximum ultimate tensile strength of 385 MPa and 390 BHN. The percentage elongation of each alloys decreased after undergoing solid solution treatment.**

Keywords: **Tungsten; manganese; carbide formers; microstructure; solid solution strengthening.**

1. INTRODUCTION

Copper is a widely used metal, particularly in various industrial and electronic applications, due to its unique combination of properties. Copper is renowned for its high electrical conductivity, which makes it an ideal choice for electrical connectors, lead frames, and micro-electronic devices(Nnakwo, 2019; Nnakwo et al., 2017a,b; 2019a,b; 2020, 2021, 2022;Nnakwo and Nnuka, 2018; Garbacz-Klempka et al., 2018). This property allows for efficient transmission of electrical signals. Copper is relatively low in cost compared to many other metals with similar electrical conductivity characteristics, making it a cost-effective choice for various applications.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. These alloying elements can increase strength and hardness while minimizing the reduction in electrical conductivity.Silicon, when added to copper, can improve its fluidity and hardness. However, it comes at the expense of reduced ductility and electrical conductivity. The addition of silicon induces the precipitation of hard but brittle phases, such as Cu_3Si, $Cu_{15}Si_4$, 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(Ketut et al., 2011). The addition of silicon can enhance the performance of these electrodes in terms of capacity and cycling stability. Copper-silicon alloys can also serve 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). They are also employed in the fabrication of musical equipment due to their excellent damping properties. These alloys help reduce vibrations and unwanted noise, making them suitable for musical instruments (Cai et al., 2011).Effects of various alloying elements on the enhancement of properties have been explored by various researchers. Nickel is one of the key alloying elements 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). Other elements like aluminium, chromium, iron, magnesium, and tin have also been used to modify Cu-Si alloys. For example, iron has been found to enhance both hardness and electrical conductivity, while chromium and zirconium induce microstructural refinement and the precipitation of specific intermetallic phases, leading to improved strength.Combined Addition of Chromium and Zirconium: Combining chromium and zirconium in nickel-doped Cu-Si alloys has been shown to result in alloys with excellent hardness and electrical conductivity.The strengthening of copper alloys is achieved through the precipitation of various phases, including β1-Ni_3Si, α-Cu(Ni, Si), γ′-Ni_3Al, β-Ni_3Si, and δ-Ni_2Si. 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).

The main objective of this research is to develop Cu-Si base alloys with improved tensile strength and hardness through additions of carbide former and appropriate solid solution treatment.

2. EXPERIMENTAL PROCEDURE

The Cu-3Si-3W and Cu-3Si-3Mn ternary alloys were prepared using analytical grades copper rods (99.8% pure), silicon powder (99.7% pure), manganese powder (99.8% pure), and tungsten powder (98.5% 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 mm^2 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 (±1°C accuracy). The tensile test samples were machined to the required dimensions with total length 120 mm, 50 mm gauge length, and 10 mm diameter. The samples surfaces were ground and polished adequately for hardness test using an electric grinder and aluminium oxide powder. The tensile strength test was determined using 100kN capacity automated tensile strength tester (Model: 130812) and the hardness measured using a Vickers hardness tester (Model: VM-50). The Vickers hardness was conducted at a load of 183.9kgf and dwelling time of 5s. The diagonals of indentations were measured using a 20X optical microscope (Olympus BH) and the mean diameter determined.

3. RESULTS AND DISCUSSION

Figs. 1-3 show the effects of solid solution heat treatment on the percentage elongation, ultimate tensile strength, and hardness of Cu-3Si-3W and Cu-3Si-3Mn ternary alloys. Fig. 1 showed that addition of manganese decreased the percentage elongation of Cu-3Si alloy. The percentage was decreased further after solid solution heat treatment. The Cu-3Si-3W alloy recorded a better percentage elongation than the parent alloy. Tungsten addition increased the percentage elongation from 9.4% to 20.8%. The percentage elongation decreased from 20.8% to 15.6% after solid solution heat treatment. Analysis of Fig. 2 shows that additions of manganese and tungsten increased the ultimate tensile strength and hardness of the parent alloy significantly. The hardness values were increased by 106.1% and 98.9% after incorporation of manganese and tungsten respectively. The Cu-3Si-3W and Cu-3Si-3Mn ternary alloys recorded further increase in ultimate tensile strength and hardness after undergoing solid solution heat treatment. The solid solution heat treatment further refined the grains, leading to increased dislocation density. This change in microstructure led to increase in ultimate tensile strength of Cu-3Si-3W and Cu-3Si-3Mn ternary alloys 286 MPa to 298 MPa, and from 378 MPa to 385 MPa, respectively. The hardness values of both alloys increased from 358 BHN to 364 BHN; and from 371 BHN to 390 BHN, respectively.

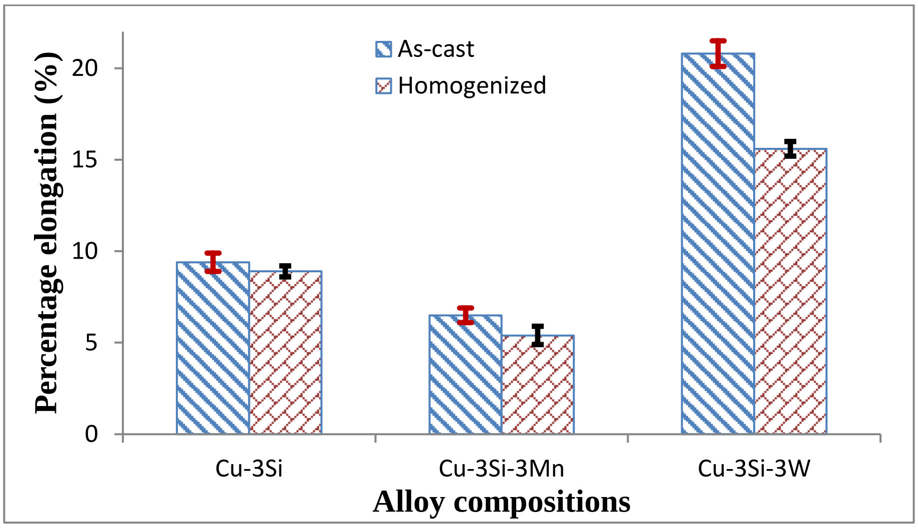

Fig. 1: Effect of solid solution treatment on the percentage elongation of Cu-3Si-3W and Cu-3Si-3Mn ternary alloys

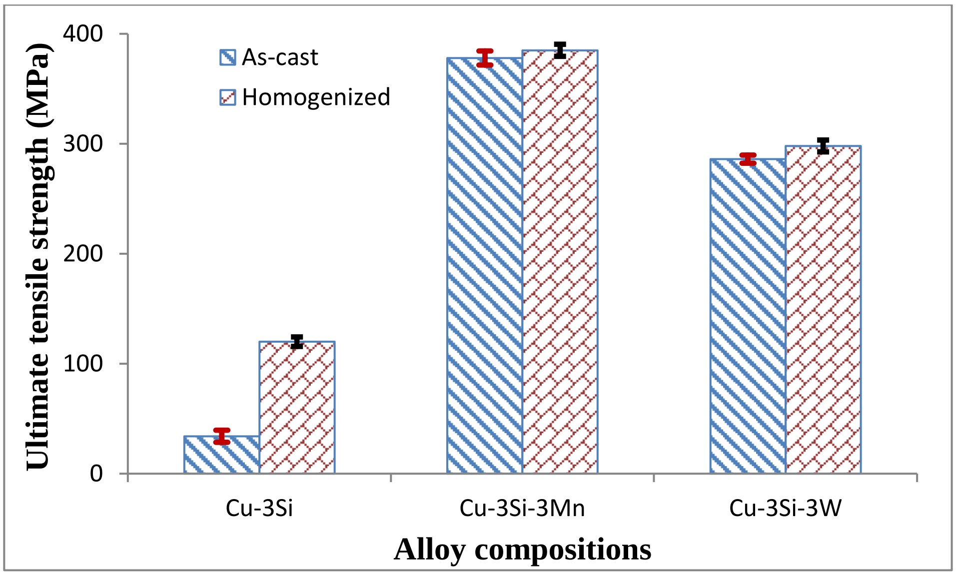

Fig. 2: Effect of solid solution treatment on the ultimate tensile strength of Cu-3Si-3W and Cu-3Si-3Mn ternary alloys

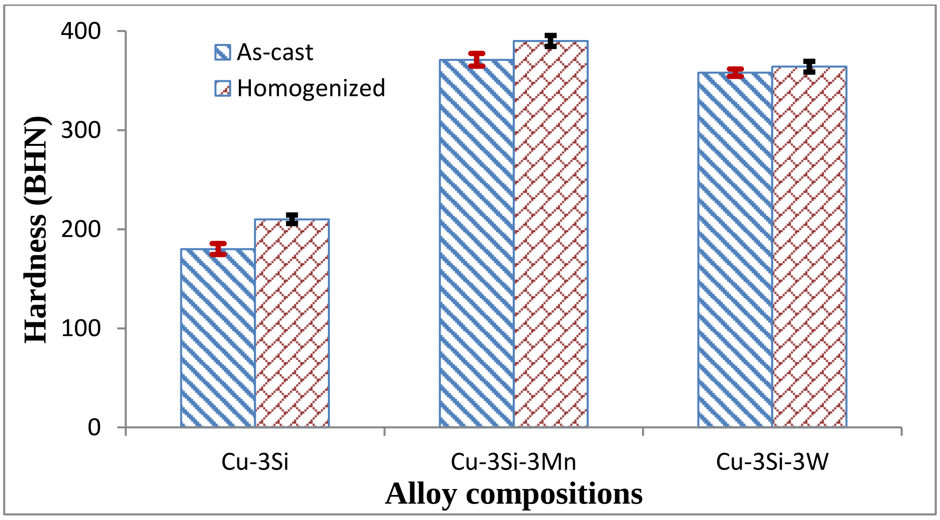

Fig. 3: Effect of solid solution treatment on the hardness of Cu-3Si-3W and Cu-3Si-3Mn ternary alloys

Fig. 4 shows the optical microstructures of Cu-3Si-3Mn and Cu-3Si-3W ternary alloys in as-cast and homogenized conditions. Analysis of Fig. 4a shows networks of spherical grains separated by grain boundaries. The surface morphology of both alloys revealed fine grains after solid solution heat treatment. The Cu-3Si-3W ternary alloy showed finer grains, evenly distributed in the copper matrix.A plate-like structure was observed in microstructure of as-cast Cu-3Si-3W ternary alloy. The grains were modified and refined into cored fine grains after undergoing solid solution heat treatment. This microstructural changes can be linked with increased ultimate tensile strength and hardness of the alloys as shown in Fig. 4.

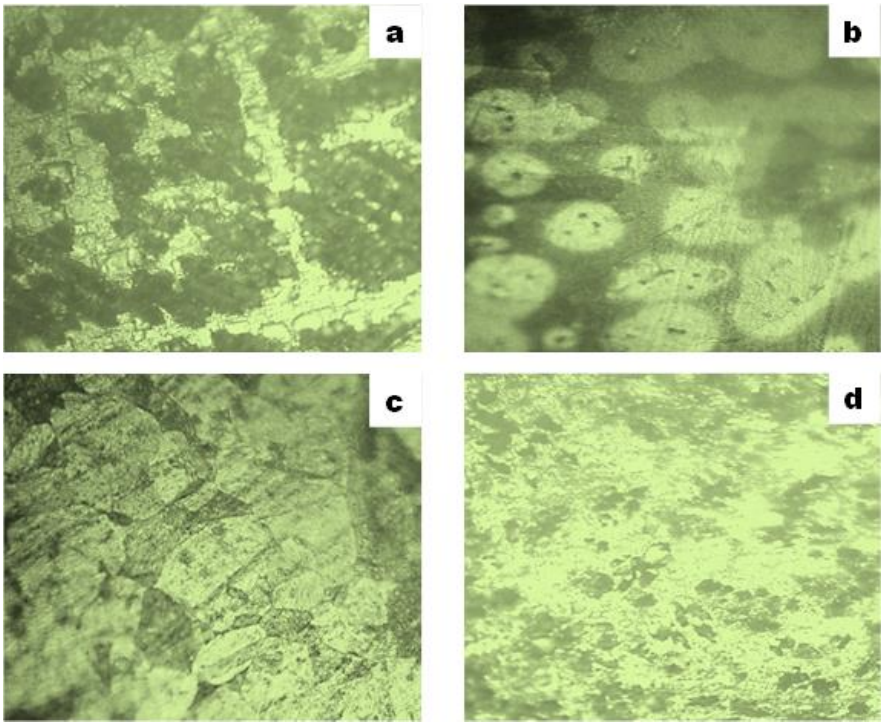

Fig. 4: Optical microstructure of (a) Cu-3Si-3Mn (as-cast) (b) Cu-3Si-3Mn (homogenized) (c) Cu-3Si-3W (as-cast) (D) Cu-3Si-3W (homogenized).

4. CONCLUSIONS

The study evaluated the solid solution strengthening of copper-silicon binary alloys by carbide forming elements. The response of Mn and W-doped Cu-3Si alloy to solid solution heat treatment was determined. Analysis of the results indicated that the addition of manganese and tungsten improved the mechanical properties of the Cu-3Si alloy, and solid solution heat treatment further enhanced these properties by refining the microstructure. From the obtained results, the following conclusions were made:

1. The addition of manganese to the Cu-3Si alloy decreased the percentage elongation. After solid solution heat treatment, the percentage elongation decreased further.

2. Tungsten addition increased the percentage elongation of the Cu-3Si alloy from 9.4% to 20.8%.After solid solution heat treatment, the percentage elongation decreased from 20.8% to 15.6%.

3. Additions of manganese and tungsten significantly increased the ultimate tensile strength and hardness of the parent alloy.

4. Both Cu-3Si-3W and Cu-3Si-3Mn ternary alloys experienced a further increase in ultimate tensile strength after solid solution heat treatment.

5. The ultimate tensile strength of Cu-3Si-3W increased from 286 MPato 298 MPa after heat treatment, while Cu-3Si-3Mn exhibited an increase in UTS from 378 MPa to 385 MPa after heat treatment.The improvements of mechanical properties are attributed to an increase in dislocation density accompanying microstructural changes in the alloys.

6. The hardness values of both alloys increased after heat treatment, with Cu-3Si-3W recording an increase from 358 BHN to 364 BHN. The hardness of Cu-3Si-3Mn increased from 371 BHN to 390 BHN.

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. Effectof 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., Borror, C.M., 2003. Probability and Statistics in Engineering, 4^{th} 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 Cu_3Si 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., Shibutani, 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: 10.1015/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 cryorolledCuNiSi 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.