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# Investigation of the structural sensitive behavior of Cu-3Si-xMn ternary alloys



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### ABSTRACT

The structural sensitive properties of Cu-3Si-xMn ternary alloys with six different manganese contents were properly studied. The refining effect of manganese addition on the cored dendritic grains of air-cooled cast Cu-3Si alloy was investigated. The microstructure of the Cu-3Si-xMn alloys was also analyzed by using an Optical Microscope (OM) and Carl ZEISS Scanning Electron Microscope (SEM). The elemental composition analysis was properly performed using Energy Dispersive X-ray Spectroscopy (EDS). The results showed that manganese addition refined the cored dendritic grains of Cu-3Si alloy. The ductility, tensile strength and Brinell hardness of Cu-3Si alloy were increased by 78.7%, 1,011.8%, and 106.1% respectively. The fine grains induced the improvements of the mechanical properties. Cu-3Si-xMn alloy showed ductility of 16.8%, a tensile strength of 378 MPa and hardness of 371 BHN. Manganese addition reduced the electrical conductivity of Cu-3Si alloy from 46.3% International Annealed Copper Standard (IACS) to 38.6 %IACS.

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## 1. Introduction

The unique strength, hardness, thermal and electrical conductivities of copper-silicon based alloys increased their demand in electronics, electrical, automobile and building industry for fabrication of connectors, bolts, electrical conduits, screws and lead frames etc. Cu-Si alloys are also suitable materials for the fabrication of musical instruments owing to their excellent acoustical and mechanical properties (Ketut et al., 2011; Kulczyk et al., 2012). Alloying, thermomechanical, annealing, and/or aging treatments have been proven as a sure means of improving strength, hardness and electrical conductivity of Cu-Si based alloys (Cheng et al., 2014; Ryoichi and Chihiro, 2008; Gholami et al., 2017a; Jia et al., 2012). The  $\beta$ -Ni<sub>3</sub>Si and  $\delta$ -Ni<sub>2</sub>Si phases gave rise to improvements in alloy's properties (Gholami et al., 2017b; Qian et al., 2010, Qing et al., 2011). Studies by Xie et al. (2009) and Wang et al. (2014) have shown that most of those alloys are very brittle, hence

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will show a sudden failure when subjected under load. Studies by Mattern et al. (2007) and Nnakwo (2019) have shown that suppression of  $\varepsilon$ -phase (cored dendrites) through rapid cooling or addition of good refining element greatly improves the ductility of Cu-Si alloys.

The present study focused on the improvement of ductility and hardness of Cu-Si based alloys with good strength and electrical conductivity.

A study by Li et al. (2009) has shown that through aging treatment, Cu-1.8Si-8.0Ni-(0.6Sn + 0.15 Mg) alloys showed excellent strength (1180 MPa), hardness (345 HV), and electrical conductivity (26.5 %IACS) but with very low ductility (2.75%). A study by Huang et al. (2003) also revealed that via aging treatment, Cu-Ni-Si-Zn alloy showed electrical conductivity of 31 %IACS. Eungyeong et al. (2011) in their study of cast Cu-3Ni-0.7Si-xTi (x = 0.12, 0.24) alloys obtained UTS of 745–837 MPa, the ductility of 15.2% and electrical conductivity of 43 %IACS. Božića et al. (2008) found that dispersion of TiSi<sub>2</sub>-phase in copper matrix greatly improves the strength of Cu-Ni-Si-Ti alloys. Lei et al. (2013a) in their study of cast copper-nickel-silicon-aluminium alloy recorded high strength (1080 MPa) and hardness (343 HV) with low electrical conductivity (28.1 %IACS) and ductility (3.1%). A study by Ho et al. (2000) has shown that by addition of phosphorus and magnesium, cast Cu-1.5Ni-0.3Si alloy showed improved strength, ductility, and electrical conductivity. Puathawee et al.

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Fig. 1. Percentage elongation of Cu-3Si and Cu-3Si-xMn alloys.



Fig. 2. Ultimate tensile strength of Cu-3Si and Cu-3Si-xMn alloys.

(2013) fabricated Cu-2Si-39.5Zn alloy and recorded an average hardness of 123.4 HV. Xiao et al. (2013) via thermomechanical treatment obtained Cu-Ni-Si-Zr alloy of excellent UTS (665 MPa) and electrical conductivity (47 %IACS). The study by Qian et al. (2017) revealed that Cu-6.0Ni-1.0Si-(0.5Al + 0.15 Mg + 0.1Cr) alloy showed lower conductivity (25.2 %IACS) than Cu-Ni-Si-Zr alloy after undergoing thermomechanical and aging treatments.

Yi et al. (2012) in their study found that by addition of Ag, work hardening and aging treatment, Cu-2.0Ni-0.5Si alloy showed

average micro-hardness of 203 HV and electrical conductivity of 36.4 %IACS. A study by Nnakwo (2019) has shown that by addition of tungsten (W), Cu-3Si-W alloy showed average UTS of 286 MPa, hardness of 358 BHN, ductility of 25.8% and electrical conductivity of 61.25% IACS. Studies by Lei et al. (2013b, 2017) have shown that Cu-Ni-Si-(Al + Mg + Cr) alloy subjected to annealing and aging treatments showed excellent yield strength, UTS and very low ductility (3.5%). A study by Suzuki et al. (2006) revealed that via solutionizing, cold rolling and aging treatment, Cu-2.5Ni-



Fig. 3. Brinell hardness of Cu-3Si and Cu-3Si-xMn alloys.



Fig. 4. Electrical conductivity of Cu-3Si and Cu-3Si-xMn alloys.

(1.7Si + 0.3Fe) alloy showed an average hardness of 270 HV, UTS of 1000 MPa and conductivity of 40 %IACS. Wang et al. (2016) revealed that addition of Cr + Zr improved strength, ductility and electrical conductivity of copper-nickel-silicon alloy. Srivastava et al. (2004) found that through a combination of cold rolling and solution heat treatment, the hardness and electrical conductivity of Cu-2.4Ni-0.6Si alloy improved. Li et al. (2017) revealed that Cu-3.32Ni-(0.93Si + 0.37(Cr/Fe) + 0.30Zr) and Cu-3.2Ni-0.7Si-1.1Zn alloys showed the average hardness of 2.6 GPa and electrical conductivity of 35 %IACS. Pan et al. (2007) revealed that Cu-4.0Ni-1.0Si alloy showed improved UTS by magnesium addition but the electrical conductivity decreased correspondingly.

The structural sensitive properties of Cu-3Si-Mn ternary alloys with different manganese content had not been investigated. Hence this research aims at enhancing the structural sensitive properties of Cu-3Si-xMn alloys through structural refinement with manganese.

# 2. Materials and method

In this present paper, materials used were a copper wire (99.9% purity), silicon powder (98.5% purity) and manganese powder (99.5% purity). Cutix Plc, Nnewi, Nigeria supplied the copper wire



Fig. 5. Optical micrograph (OM) of Cu-3Si alloy.



Fig. 6. Optical micrograph (OM) of Cu-3Si-1Mn alloy.



Fig. 7. Optical micrograph (OM) of Cu-3Si-1.5Mn alloy.



Fig. 8. SEM of Cu-3Si alloy.



Fig. 9. EDS spectrum of Cu-3Si alloy.

while the silicon and magnesium metals powder were successfully supplied by the Kermel Chemical Reagent Co. Ltd. Hebei, Tianjin, China. Cu-3Si alloy and Cu-3Si-xMn alloys with six different manganese content were thoroughly melted in a crucible furnace and cast in a metal mold of internal length and diameter of 250 mm and 16 mm respectively. The tensile strength test samples were of the dimension 120 mm total length, 10 mm diameter, 50 mm gauge length, and 8 mm gauge diameter. The hardness test samples had dimension of 20 mm length and 16 mm diameter.

The tensile strength, hardness, and electrical conductivity of the samples were thoroughly measured at room temperature by using 100KN capacity automated tensometer (Model: 130812), Brinell hardness tester (Model: DHT-6) and Standard Ohm's experiment apparatus (Nnakwo, 2019). The samples for microstructure and elemental composition analyses were ground using silicon carbide papers of different grits size (400, 800, 1200  $\mu$ m), polished using an aluminium oxide powder and etched. The etching process entailed swabbing the sample in a mixture of iron III chloride powder and

aqueous hydrochloric acid for 30 s, rinsed and dried using hot air gun machine (Bosch PHG500-2-1600 W). With the aid of an optical microscope (Model: L2003A), Carl ZEISS Scanning Electron Microscope (SEM) (EVO/NA10) and EDS, the microstructure and the elemental composition of the samples were thoroughly analyzed.

# 3. Results and discussion

#### 3.1. Structural sensitive properties of Cu-3Si and Cu-3Si-xMn alloy

Figs. 1–4 show the effect of manganese contents on the ductility, tensile strength, hardness and electrical conductivity of Cu-3Si-xMn ternary alloys. Fig. 1 revealed improvement of percentage elongation (ductility) of Cu-3Si alloy by adding manganese. By adding 0.1 wt% manganese, the ductility increased from 9.4% to 16.8%, indicating about 78.7% increase. As shown in Fig. 1, the ductility decreased progressively with increasing manganese contents. Figs. 2 and 3 revealed substantial improvements



Fig. 10. SEM of Cu-3Si-1Mn alloy.



Fig. 11. EDS spectrum of Cu-3Si-1Mn alloy.

of both tensile strength and hardness of Cu-3Si alloy by adding 0.1 wt% manganese, indicating about 605.9% and 39.4% increase respectively. Figs. 2 and 3 showed that within 0.1–1 wt% manganese addition, both the tensile strength and hardness of Cu-3Si-xMn alloy increased. Both the tensile strength and hardness reached the maximum at 1 wt% manganese addition. The tensile strength increased by 1,011.8% while the hardness increased by 106.1%. This trend in mechanical behavior indicates clearly that the strength and hardness of Cu-3Si-xMn alloys correlate with the size, morphology, and dispersion of grains in the copper matrix, as evidence in the microstructural analysis. Figs. 6 and 10 showed that by adding manganese ranging from 0.1 to 1 wt%, the size and morphology of the cored dendritic grains of Cu-3Si alloy were

obviously refined and modified respectively. The fine grains evenly dispersed in the copper matrix led to increase in number of grain boundaries which systematically impede the dislocation movement, hence increasing both the strength and hardness of the alloys (Gholami et al., 2017a). As shown in Fig. 2, increasing manganese content to 1.5 wt% led to a slight reduction of both the tensile strength and hardness of Cu-3Si-xMn alloys. This mechanical behavior was as a result of the enlarged grains as evidence in Figs. 7 and 12. As shown in Figs. 7 and 12, the fine grains increased in size after increasing the manganese content to 1.5 wt%. This led to a drastic decrease in grain boundary area which caused a reduction of the dislocation motion impediment, hence decreasing both the strength and hardness of the Cu-3Si-xMn alloys. As shown in



Fig 12. SEM of Cu-3Si-1.5Mn alloy.



Fig 13. EDS spectrum of Cu-3Si-1.5Mn alloy.

Fig. 4, the electrical conductivity of Cu-3Si alloy was higher than the Cu-3Si-xMn alloys. Fig. 4 showed that by adding 0.1 wt% manganese, the electrical conductivity of Cu-3Si alloy reduced from 46.3% International Annealed Copper Standard (IACS) to 38.6 % IACS, indicating about 16.6% decrease. By increasing manganese content, the electrical conductivity decreased progressively. This electrical behavior indicates that reduction of copper content from 97 wt% to 95.5 wt% as the manganese content increased to 1.5 wt% had a negative effect on the electrical conductivity of the Cu-3SixMn alloys. Reduction of electrical conductivity of the alloys could also be caused by the reduction of the number of free copper atoms resulting from the solid solution of manganese and silicon metals in the copper matrix (Suzuki et al., 2006; Jia et al., 2012).

#### 3.2. Structural analysis of Cu-3Si and Cu-3Si-xMn alloys

Fig. 5-13 show the optical microscope (OM), SEM and elemental composition analyses of the Cu-3Si binary alloy and Cu-3SixMn ternary alloys with different manganese contents. As shown in Figs. 5 and 8, both OM and SEM micrographs of Cu-3Si alloy revealed patches of cored dendritic grains in the copper matrix. These dendrites could be linked to the low mechanical properties of the alloy. At room temperature, silicon forms dendrites of primary silicon and  $\eta''$ -Cu<sub>3</sub>Si-phase in the copper matrix when cooled slowly (Li et al., 2009; Lei et al., 2017; Pak et al., 2016; Chromic et al., 1999). As shown in Fig. 9, the EDS spectrum of Cu-3Si alloy indicated the two based elements (Cu and Si) with minor impurities such as Al, Fe, K, Ca, C and O. Figs. 6 and 10 show OM and SEM micrographs of the Cu-3Si-1Mn alloy. Figs. 6 and 10 revealed fine grains which are evenly dispersed in the copper matrix. This showed clearly that manganese can effectively refine the cored dendritic grains of Cu-3Si alloy. These fine grains led to improvements of both tensile strength and hardness of Cu-3Si alloy. As shown in Figs. 7 and 12, both the OM and SEM micrographs of Cu-3Si-1.5Mn alloy revealed largely rounded and angular grains scarcely dispersed in the copper matrix. This caused a slight decrease in strength and hardness of the Cu-Si-1.5Mn alloy, resulting from the reduction of the number of grain boundaries in the alloy structure. As shown in Figs. 11 and 13, the EDS spectrum of Cu-3Si-1Mn and Cu-3Si-1.5Mn alloys respectively revealed the three major elements (Cu, Si, Mn) with traces of Fe, Ca, Al, O, Cl and C elements.

#### 4. Conclusions

The structural sensitive properties of Cu-3Si-xMn ternary alloys with six different manganese contents were properly investigated. The refining effect of manganese addition on the cored dendritic grains of Cu-3Si alloy was thoroughly examined using OM and SEM. The results showed clearly that by adding manganese to Cu-3Si alloy, the cored dendritic grains (primary silicon or Cu<sub>3</sub>Si phase) were efficiently refined and modified; thereby improving the ductility, tensile strength, and hardness of the alloy. Both UTS and the Brinell hardness of Cu-3Si alloy were increased by 1011.8% and 106.1% respectively.

Increasing manganese content to 1.5 wt% led to the formation of large rounded and angular grains which caused a slight decrease in both the strength and hardness of the Cu-3Si-xMn alloys. The ductility of Cu-3Si alloy increased by 78.7% while the electrical conductivity decreased from 46.3 %IACS to 38.6 %IACS. Dispersion of fine grains in the copper matrix induced reduction of electrical conductivity by increasing the electron scattering points. The decrease in the number of free copper atoms in the copper matrix also influenced the reduction of electrical conductivity.

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