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Synthesis and Characterization of Heat Treated Cu-Al alloys for Energy Applications

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Abstract

Three alloys with different atomic percent (at. %) Cu-Al were designed and synthetized, using an electromagnetic induction furnace system. Alloys were designed in a substitutional way, varying the Al content respect to Cu, from 10 to 50 at. %. Microstructure changes from dendritic structure to equiaxed grains depending the heat treatment. Hardness test evaluation has shown values in the order of 700 kg/mm^2 which represents an increment of 600 percent, while compression tests have shown an important strengthening increment. Besides, electrical resistivity test was carried out, in order to analyze a future application in an electrochemical system, obtaining an improvement three times more in comparison with the unalloyed sample. Strengthening results were interpreted in terms of defects generation, caused by the thermal treatments.

Keywords

Solid Solution, Mechanical Properties, Heat Treatments, Electrical Properties

1. Introduction

The importance of the materials design of metallic alloys lies in that it can provide some physical, chemical or electrical features, different from pure metals [1]. The microstructure plays an important role when some mechanic characteristics are persecuted, even the original microstructure can be modified when alloys are exposed to thermal treatments [2] [3] [4]. As it is known, copper and aluminum are metals widely used in many industrial applications. Aluminum is probably the most alloyed element with Cu [5]. Among the applications of this alloy, the electronic one is possibly the most important, for example in conductor wires, conduction bands and transition pieces in high direct-current systems

[6] [7] [8]. Recently, several researches are focused on explosive welding [9] [10] [11]. The characteristic microstructures of this binary system, are similar to stainless steels, e.g. martensitic, perlite and austenite [12]. Specifically, in Cu-Al alloys, the first element provides strength, resistance to deformation and malleability [1] [2] [5], as well as improved resistance to the aging processes and corrosive environments [2] [3] [13]. One similar compound to Cu-Al system and quiet researched is the Zn/Cu system. When Al atoms replace zinc atoms in Zn-Cu lattice, can result in improvement in the mechanical properties, such as hardness, elongation and yield strength [14]. Nevertheless, Zn/Cu alloys are expensive to fabricate and more brittle alloys. In this way, the present work pretends to provide an alternative when Cu-Zn system is not reliable as well as to add information relative to mechanical and electrical behavior of Al-Cu system, principally after thermal treatment.

2. Materials and Methods

Cu and Al ingots (99.99% purity) were used for the alloys fabrication. Three different Cu-Al alloys were synthetized, containing 10, 25 and 50 of at.% Al (Al10-Cu, Al25-Cu and Al50-Cu respectively). An extra 0.5 at.% Al was added to compensate the evaporation and Inductively couple plasma analyses were performed to corroborate the composition. According to E800b ASTM, metals were cut in small pieces and cleaned up using ethanol (99% purity) in an ultrasonic bath, then were melted in an induction furnace system, at atmospheric conditions, by using a stainless steel crucible. The electromagnetic induction power ranged from 2 to 3 kW for a lap of 4 to 5 minutes until the metals were melted. Annealing temperatures varied from 500˚C, 600˚C and 700˚C during 1 h, in a furnace previously heated under a controlled atmosphere (Ar) and then cooled slowly inside the furnace. The alloys were polished (ASTM E9-89a) using up to 0.3 μm alumina powder. To reveal the microstructure, 3% hydrofluoric acid (HF) diluted in ethanol was used during 2 to 5 s. The metallographic images were taken with a Zeiss (LEO) 1450VP Scanning Electron Microscope (SEM). The hardness tests were carried out using a Vickers micro-hardness testing machine, with pyramidal point and indentations were performed in accordance with ASTM E384-17. For compression tests, specimens were machined with final dimensions of 4 × 4 × 8 mm, and was used a 10 tons universal testing machine, at 0.5 mm/min rate (ASTM E8). The chemical compounds were identified by an X-ray diffractometer (XRD Bruker) using Cu-Kα (λ = 1.541 Å) radiation. The electrical resistivity was measured with an AEMC micro-ohmmeter, by applying a current up to 10 A, at room temperature, using specimens of 1 cm^2 cross-sectional area.

3. Results and Discussion

3.1. Microstructural Characterization

3.1.1. X-Ray Diffraction Analyses

X-ray diffraction patterns are shown in **Figure 1**. Al50-Cu alloy (**Figure 1(a)**) is mainly composed of stable CuAl phase and oxide phases like Cu_2O; after annealing for 500˚C, no significant change in crystallographic phases can easily be observed, however above the 700˚C, the most crystalline compound is Cu_2Al_3. Figure 1(b) corresponds to Al25-Cu, also exhibits the predominance of CuAl phase and the same phases of previous alloy, but at high annealing appears the formation $CuAlO_2$ phase. In Al10-Cu alloy (Figure 1(c)), it is clear to observe that monoatomic metallic Cu phase is the most crystalline specie even at 600˚C annealing, whose structure becomes amorphous at a higher annealing, where Cu_2O and CuAl transitions phases appear, with a clear decrease in crystallinity. The high temperature of the thermal treatment tends to form complex and non-crystalline compounds. Oxides formation can be attributed to the cooling samples after the heat treatment.

3.1.2. SEM Analyses

The SEM images of the microstructure of the alloys are shown in Figure 2. The Al50-Cu (Figure 2(a)) image reveals a highly porous non-equiaxial grain structure, in which an austenite structure is located. Grains size oscillates from 50 μm to 500 μm, and the Electron Dispersion Spectroscopy (EDS) analysis indicates that are composed principally of Cu. However, inside the grains, lamellar structures can be observed (inset 2a'). A significant change in metallographic structure is noticed when a less quantity of Al at % is employed (Figure 2(c)); it can be observed the appearance of an eutectoid $\alpha + \delta$ phase, which consists of lamellar eutectic formations in the manner of perlite structure, where alternative zone of Cu coexist whit Al-Cu phase, according to EDS analysis shown in Figure 3. In Al25-Cu alloy (Figure 2(b)), zones with Cu non-equiaxial big grains coexists in similar proportions to that of Al-Cu lamellar structures. The effect of the thermal treatment is the coarsening of the lamellar structures [15], while the decrease

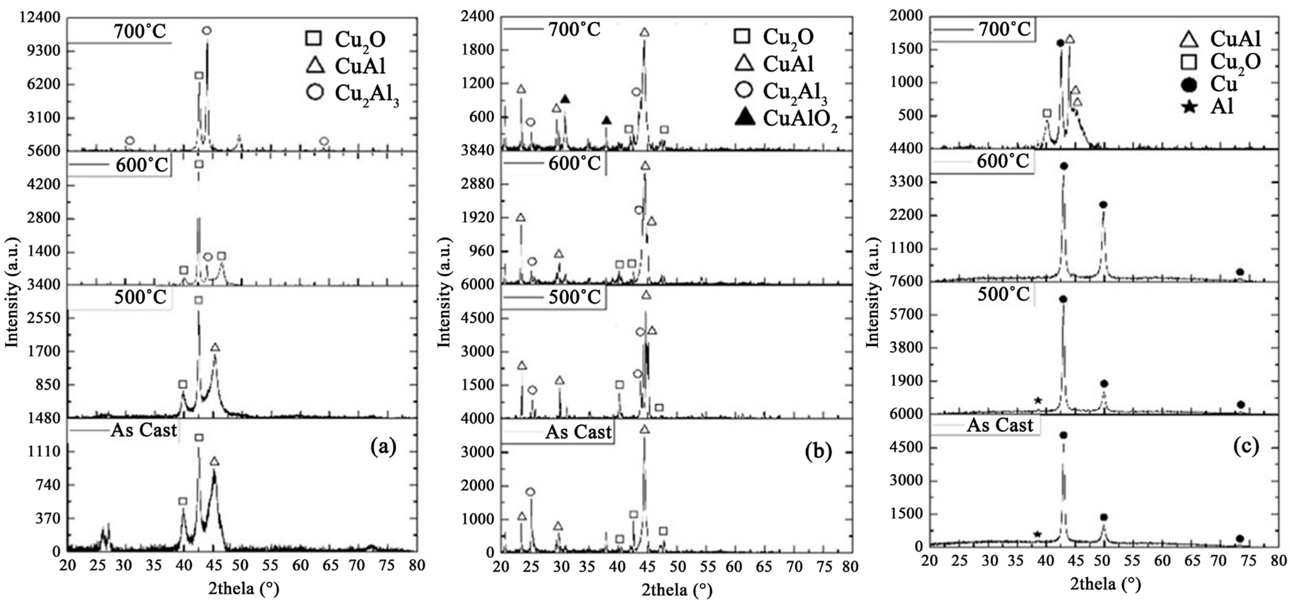


Figure 1. X-ray diffraction patterns of Cu Alloys, (a) Al-50 at% Cu alloy, (b) Al-25 at% Cu, and (c) Al-10 at% Cu alloy.

of Al% leads to well defined coarse grained lamellar structures, due to slow cooling process [16]. This microstructure is shown in Figure 2(d), where the grain limits were edited to show grain limits.

Corresponding to as cast samples, change in the microstructure alloys is evident as the Al content decreases, from bigger grains upper than 10 µm to lamellar eutectic forms when the Al content does not exceed 10%wt. Inset in Figure 2(a) shows the lamellar structure of Al10-Cu alloy, the grain limits where edited in white lines, inside of them, the $\alpha + \delta$ lamellar eutectic phase is observed.

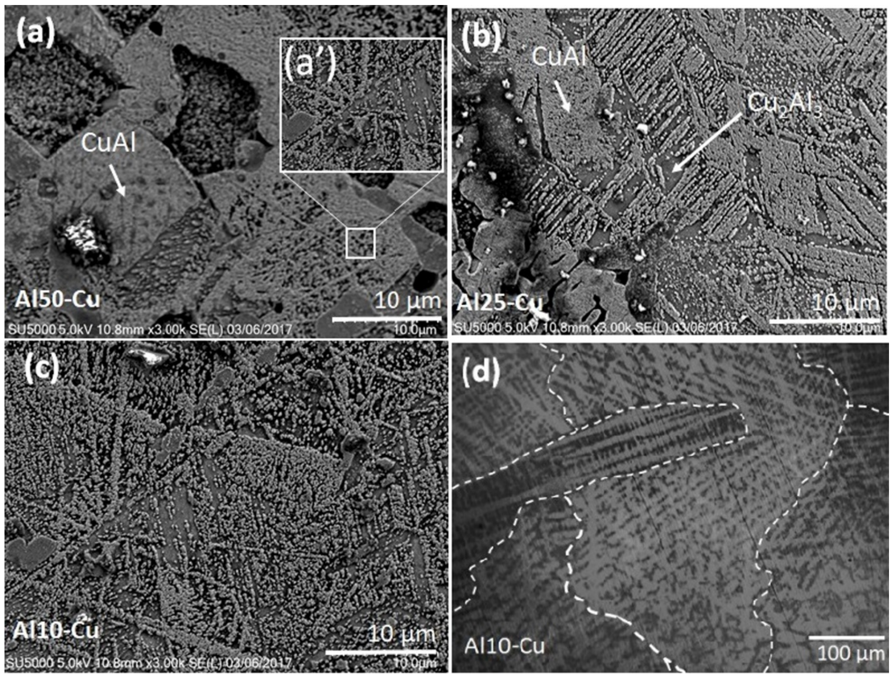
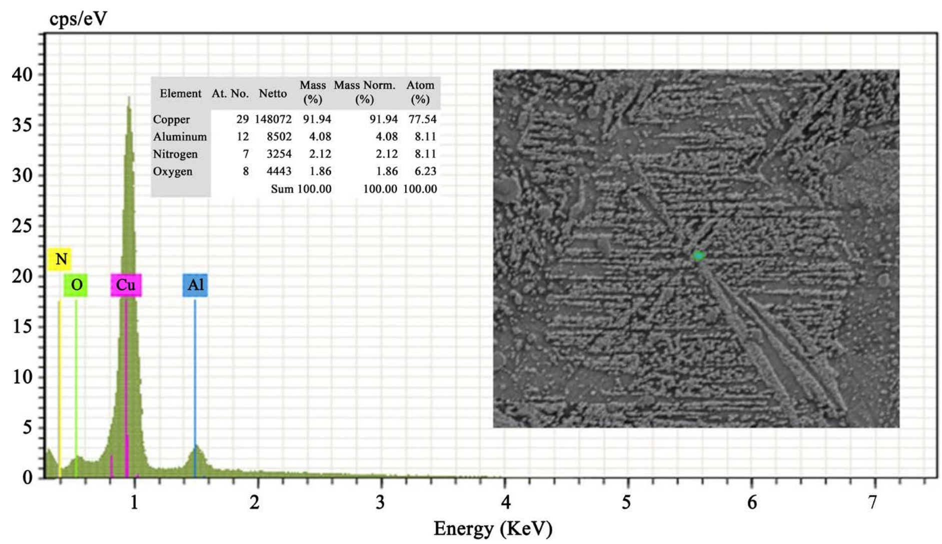


Figure 2. SEM micrographs of Cu alloys. (a) Al50-Cu, (b) Al25-Cu and (c) Al10-Cu. (d) Optical image of sample Al10-Cu indicating the grain arrangement with dashed lines.



Element	At. No.	Netto	Mass (%)	Mass Norm. (%)	Atom (%)
Copper	29	148072	91.94	91.94	77.54
Aluminum	12	8502	4.08	4.08	8.11
Nitrogen	7	3254	2.12	2.12	8.11
Oxygen	8	4443	1.86	1.86	6.23
		Sum	100.00	100.00	100.00

Figure 3. EDS spectral analysis of Al50-Cu alloy. Copper is the main constituent of the lamellar eutectic structures and Al is located principally in the matrix region.

3.2. Mechanical Properties

3.2.1. Hardness Tests

Plots of Vickers hardness versus annealing time is showed in **Figure 4**. It can be observed that sample with Al50-Cu present the higher hardness value for all the different annealing temperatures, these values represent an increment of hardness of approximately two times in comparison with samples with lower aluminum content, a reason for this increment is explained taking in consideration the difference between atomic radii of aluminum and copper (1.3607 and 1.8648 Å) of 0.5 Å, fact that implies a contraction in the lattice when aluminum is incremented in the alloy which is traduced in a lower possibility of dislocation movement. Therefore this composition results in more brittle alloys. Al10-Cu sample is the softest alloys, maybe due to its dominant eutectic structure, which opposes less resistance to compression stresses [17].

3.2.2. Compression Test

Figure 5 shows the stress-strain curves of alloys. For the analysis, 0.2% offset of the strain was calculated, which is the maximum stress than the material can undertake and return to its original form, when the compression force is removed. It was not possible to determine the value of the yield strength for Al50-Cu alloy due to its brittleness and porosity (**Figure 5(a)**). The Al25-Cu solid solution (**Figure 5(b)**) does not present substantial change both in yield strength and in ultimate strength below the 500˚C annealing, this probably because of the irregular eutectic structures even remain. As temperature increases, the morphology changes to regular eutectic dendritic formations, resulting in a harder but brittle alloy. The small crystals, of the Al10-Cu alloy, tend to promote plastic behavior under compression stress (**Figure 5(c)**), since it is capable to

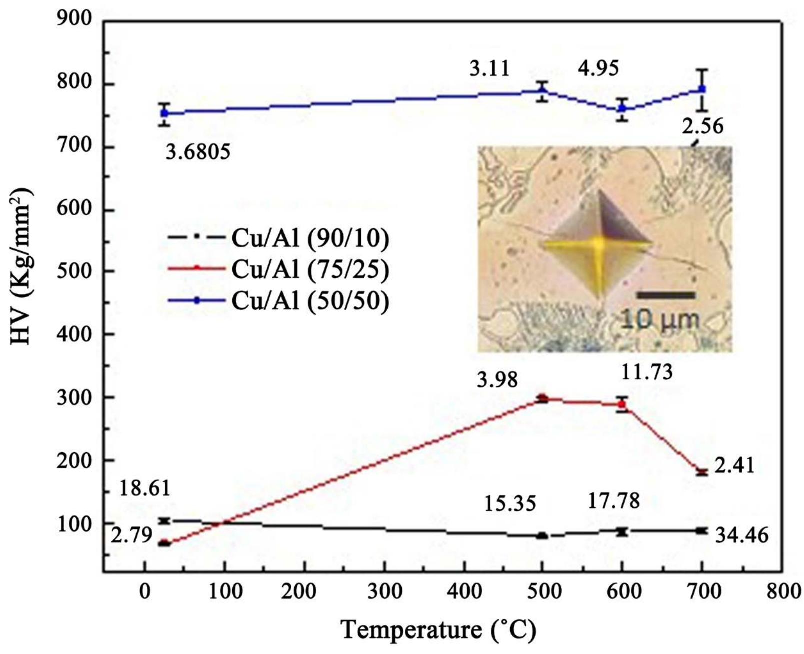


Figure 4. Vickers Hardness curves of all alloys versus annealing temperature.

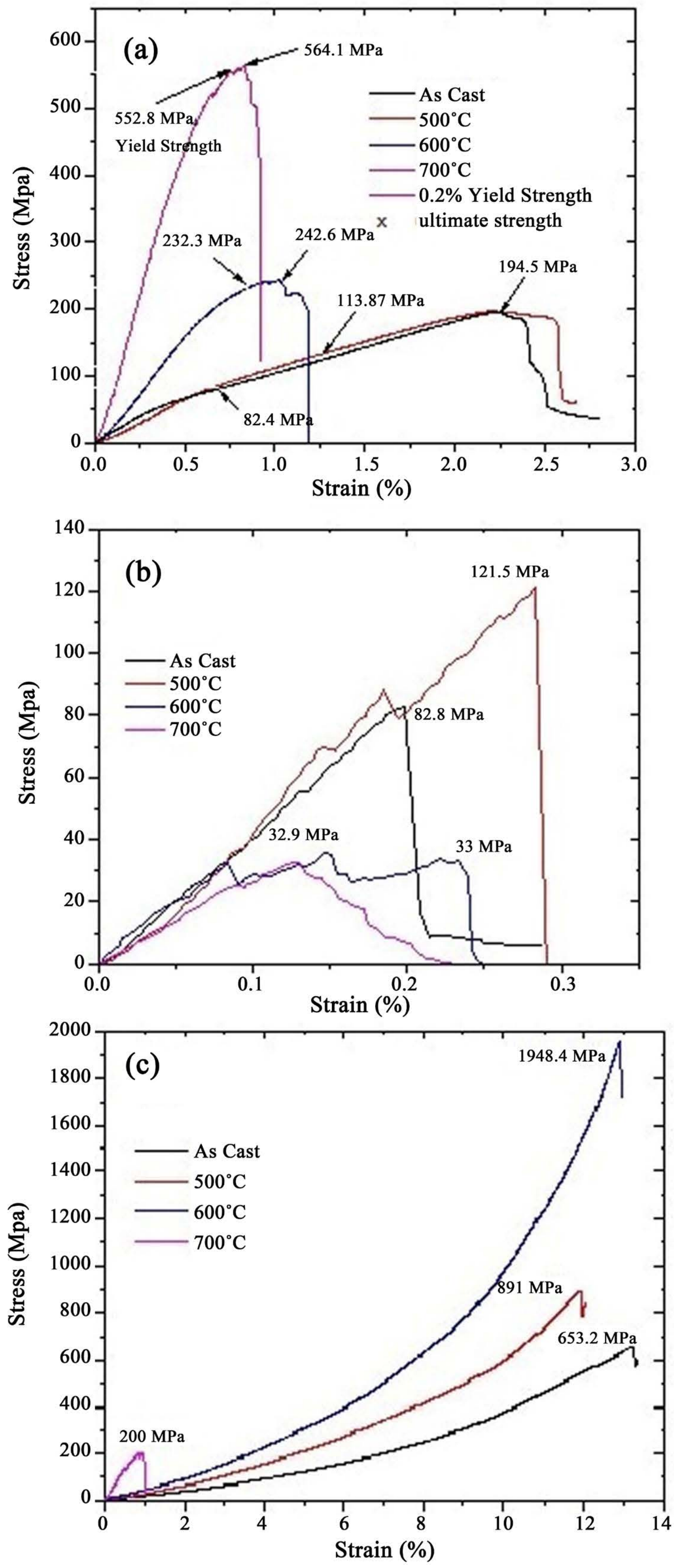


Figure 5. Strain-Stress curves of Al50-Cu (a), Al25-Cu (b) and Al10-Cu (c) samples.

support more stress at the highest loads, until it fails. So, two main mechanisms are proposed as hardening mechanisms of precipitation and solid solution hardening. Precipitates tend to located throughout the entire matrix according the annealing temperature and the Al quantity increase in the alloys. Also, an increase of hardness and strength is observed as aluminum content increases in the alloys.

3.3. Electrical Characterization

Resistance characterization behavior is shown in **Figure 5**. Electrical resistance of a material is proportional to electrical resistivity and this inversely proportional to electrical conductivity. According to the International Annealed Copper Standard, the value of the electrical resistivity of annealed pure Cu is around 1.724 $\mu\Omega^{-cm}$ at 20˚C. Annealed Al-Cu alloys display higher resistivity than pure Cu, this is related to impurities in accordance with Matthiessen's rule [5]. Inset in **Figure 5**, appears the typical microstructure of studied alloys, where the biggest grains corresponding to more conductivity samples in comparison with dendritic structures, limits of grains play an important role in this issue. Thermal treatments generally lead to an overall decrease in electrical conductivity, which is associated to growth of eutectic structures in the general microstructure, since more limits of grains are present. According to **Figure 6** the resistivity decrease when a mayor Al at. % is present in the solid solutions. It can be observed also that the resistivity increase when the annealing is applied to alloys. However, Al50-Cu alloy is the most stable, below 500˚C annealing. Al25-Cu alloy shows the best mechanical properties and a resistivity about 5 $\mu\Omega^{-cm}$ higher than Al50-Cu alloys. **Table 1** summarizes the data of both mechanical and electrical characterization. These results are interesting from the point of view for many industrial applications due to the high resistivity ranges obtained after heat treatment, mainly because the cost reductions for components with better mechanical properties and good electrical responses.

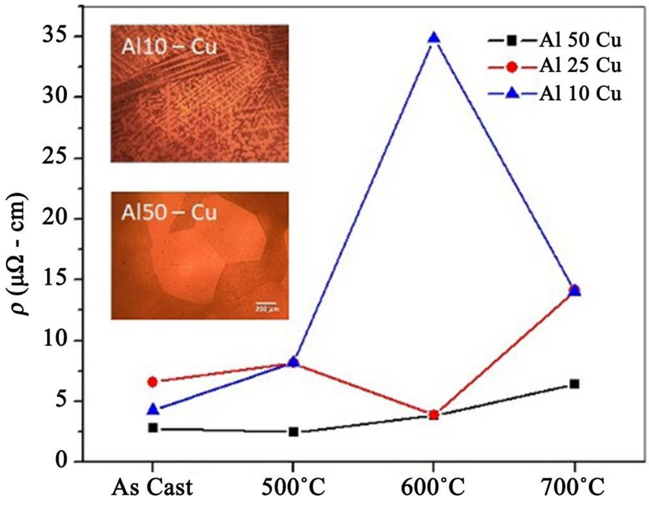


Figure 6. Resistivity versus thermal treatment of Al-Cu Alloys.

Table 1. Summary of mechanical and electrical data of Cu-Al alloys.

Annealing	Al50-Cu	Al25-Cu	Al10-Cu	Al50-Cu	Al25-Cu	Al10-Cu	Al50-Cu	Al25-Cu	Al10-Cu	Al50-Cu	Al25-Cu	Al10-Cu
	Vicker Hardness (HV)			Yield Strength (MPa)			Ultimate Strength (MPa)			Resistivity (μΩ cm)		
As cast	750.91	67.52	103.51	---	82.4	653.2	82.8	194.5	653.2	2.792	6.601	4.278
500˚C	786.19	298.68	79.23	---	113.87	891	121.5	181.52	891	2.455	8.166	8.198
600˚C	757.41	288.41	88.05	---	232.3	1948.4	33	242.6	1948.4	3.834	3.886	34.874
700˚C	788.97	181.69	89.01	---	552.8	200	32.9	564.1	188.4	6.371	14.118	14.065
Pure Al		20			90						2.82	
Pure Cy		72			314						1.71	

4. Conclusion

Copper alloys were synthetized varying aluminum concentration, in air conditions, using an induction furnace. Composition and annealing treatment were studied as variables. As Al atomic percent decreases, the micro-structure is modified from geometric grains to dendritic structures, parallel to reduction in crystal size. Conversely as Al atomic percent increases, harder and but brittle structures tend to develop. At the same time, the increase of crystal size (approximately 1 mm) produces alloys with high brittleness and smaller plastic zones. While the presence of Cu increases, it induces a ductile behavior under stress testing. The annealing treatment enhances some initial mechanical properties, specifically the yield strength and does not seem to affect the Vickers hardness. Samples with 25% of Al and 700˚C annealed, can endure considerable stress (up to 500 MPa) until failure. While samples with Al 10 at% and 500˚C annealed, exhibit a ductile behavior under tension forces, remaining stable its mechanical properties below 700˚C annealed. Al25-Cu alloy was found to exhibits the best combination of electrical and mechanical properties when annealed. Vacuum atmosphere is now used to analyze the effect on the material performance.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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