# FEASIBILITY OF REPLACING HIGH CONDUCTIVITY Be-BRONZE ALLOYS BY Cu-Ni-Al ALLOYS

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## الملخص

من الاستخدامات الشائعة للبرونز البريليومي (نحاس- 1.9% بريليوم) هو إنتاج الأجزاء التي تتطلب موصلية عالية للتيار الكهربائي بالإضافة إلى خواص ميكانيكية جيدة. ولكن نتيجة لسمية البريليوم وما يحدثه من مشاكل تخص تلوث البيئة اتجهت الأنظار إلى إيجاد البديل لهذه السبيكة من سبائك النحاس. تركزت الأبحاث في هذا المجال على سبائك النحاس مع الالومينيوم والنيكل.

تم تحضير أربعة عينات من هذه السبيكة تختلف في نسبة الالومينيوم وتتراوح ما بين 1 % إلى 4 % في حين كانت نسبة النيكل ثابتة عند 14 %. تمت معالجة هذه العينات عند درجة حرارة 900 م° لمدة ساعة للحصول على تركيب أحادي الطور، ومن تم أجريت لها عملية تخمير لمدة ساعتين عند درجات حرارة تتراوح ما بين 300 م° إلى 460 م° بزيادة قدرها 40 م°.

بعد عملية التخمير تم اختبار الصلادة ومقاومة الشد والموصلية الكهربائية لهذه العينات ومن خلال نتائج هذه الاختبارات لوحظ أن العينة التي تحتوي على 3 ٪ الومينيوم المخمرة لمدة ساعتين عند درجة حرارة 380 م° لها أعلى رقم صلادة وهو 220 وهذا الرقم يمثل 60% مما هو مسجل لسبائك البرونز البريليومي. القيمة القصوى لإجهاد الشد لنفس العينة كانت 798 ميجابسكال وهي تعادل 0.73 من القيمة المسجلة لسبائك البرونز البريليومي. أما فيما يخص الموصلية الكهربائية فكانت القيمة المسجلة والمناظرة للقيمة القصوى لإجهاد الشد تعادل ما هو مسجل لسبائك البرونز البريليومي. هذه القيمة العسبائك البرونز البريليومي. أما فيما يخص الموصلية الكهربائية فكانت القيمة المسجلة والمناظرة للقيمة القصوى لإجهاد الشد تعادل ما هو مسجل لسبائك البرونز البريليومي. هذه القيم العالية نسبياً هي نتيجة للتكون المرط للمركب مسجل لسبائك البرونز البريليومي. هذه القيم العالية نسبياً مي نتيجة للتكون المرط للمركب

## ABSTRACT

Beryllium bronze (Cu-1.9 wt.% Be) commonly used for the manufacture of articles that required high electrical conductivity in addition to good mechanical properties. However, the toxicity and environmental problems connected with beryllium has given attention to replace Be-bronze by other Cu-base alloys. The aim of this work is to find such an alternative alloy, which could fairly compare with the properties offered by Be-bronze. The search has been directed towards Cu-Ni-Al alloys, known as cunial. The idea was to systemize both the chemical composition of cunials and their subsequent heat treatment regimes, which guaranty the precipitation of proper amount of nickel-aluminum intermetallic dispersiod particles. Thus providing optimum electrical conductivity and mechanical properties.

Four alloy compositions with different aluminum content have been prepared. These were all based on Cu-14 wt.% Ni with aluminum content varying from 1-4 wt.%. All specimens have been given a solution treatment at 900°C for one hour. Age hardening was carried for two hours at temperatures varying between 300°C and 460°C with an increment of 40°C. The hardness, strength and electrical conductivity of aged specimens have been measured.

Among the investigated alloys the alloy containing 3 wt.% Al aged at 380°C for two hours has the highest maximum hardness value of 220 Hv<sub>1</sub> which is 0.6 of that reported for Be-bronze [1]. The measured maximum value of  $\sigma_{uts}$  for the same alloy was 798 MPa which is 0.73 of that of Be-bronze [1]. The value of the electrical conductivity corresponding to the maximum strength is the same as that of Be-bronze. Such findings were attributed to the more intensive formation of Ni<sub>3</sub>Al under this heat treatment conditions.

**KEYWARDS:** Beryllium bronze; Cunial; Hardness measurement; Tensile testing; Electrical conductivity;

### **INTRODUCTION**

High electrical conductivity and good mechanical properties are required for an alloy used to fabricate high power contactors as well as other electrical applications. The principle alloy which compromises these requirements is Cu-1.9 wt.% Be-bronze. This alloy is a precipitation hardenable one. In aged condition this alloy has a high strength value reaching 600 MPa for yield strength and 1200 MPa for ultimate tensile strength [1]. On the other hand, during aging, the alloying element leaves the matrix lattice to produce a coherent precipitates. These precipitates does not interfere with conductivity as much as the solid solution atoms. Hence, aging process may simultaneously improve both strength and electrical conductivity at least within certain rang of temperature and time [2]. Moreover, the precipitation of Be-intermetallic compound particles strongly limits electron scattering and thus increasing electrical conductivity. The problems connected with the toxicity of beryllium encourage the search for new alloy which may replace Be-bronze. One of the promising directions is the development of Cu-Ni-Al alloys (known as cunial). In these alloys the precipitation of Ni<sub>3</sub>Al dispersoids may increase both strength and elastic properties from one side and electrical conductivity form the other side.

There are a lot of similarities between Be-bronze and cunail alloys. In cunail  $Ni_3Al$  dispersoids [3] may play the same role as Be-intermetallic phase in Be-bronze. Moreover, the precipitation of  $Ni_3Al$  leaves the matrix with high electrical conductivity in similar manner as in the case of Be-bronze. However, some points remain unclear; the most important of which is the hardening capacity given by  $Ni_3Al$  to the copper matrix in comparison with Be-intermetallic phase. Further more, it is not well established what is the weight ratio of Ni to Al which should affect the maximum precipitation of  $Ni_3Al$  as a precipitate phase [4].

The aim of this research work is to study the effect of aluminum content in Cu-Ni-Al alloys on the hardness under various heat treatment regimes.

#### EXPERIMENTAL PROCEDURE

In order to achieve the aim of the present research work four Cu-Ni-Al alloys with nominal composition given in Table (1) were prepared. The ingots were homogenized at 900°C for two hours. Five specimens were prepared from each ingot for hardness, tensile and electrical measurements. The prepared specimens were then heat treated at 900°C for one hour followed by water quench to produce supper-saturated solid solution (single phase structure). Aging treatment was performed at five different

temperatures (300°C, 340°C, 380°C, 420°C and 460°C) for constant time of two hours followed by air cooling.

Tuble It chemieur composition of the unogs used in the present research work								
Element	Wt.% Al	Wt.% Ni	Wt.% Cu					
Alloy number								
Alloy 1	1	14	Balance					
Alloy 2	2	14	Balance					
Alloy 3	3	14	Balance					
Alloy 4	4	14	Balance					

Table 1: Chemical composition of the alloys used in the present research work

## Hardness test

For hardness measurement, five specimens of 20 mm in height and 12 mm in diameter were cut from the homogenized rods of each alloy composition. After heat treatment these specimens were prepared by conventional way. The hardness values were obtained by means of Zwick hardness tester using Vickers principles. At least averages of five readings were taken.

## Tensile test

Five flat tensile specimens were machined from the homogenized rods of each alloy composition according to British standard [5]. The gauge length of the specimen was taken to be more than 5.65 of the square root of the cross section area. The surfaces of the machined specimens were smoothly finished by grinding to remove the highly deformed surface layer caused by machining. The test was carried out using Universal Testing Machine of type Instron. Constant strain rate of  $3.3 \times 10^{-3} \text{ sec}^{-1}$  was used.

## **Electrical conductivity measurement**

Cylindrical specimens, 12 mm in diameter (d) and 200 mm long (L), were used for measuring the electrical conductivity. They were cut and machined to the required dimensions from the homogenized rods after performing heat treatment. The surfaces of specimens were smoothed by grinding. The electrical resistance ( $\rho$ ) of the specimens was measured by simple determination of the voltage applied to the specimen (V) and the current passing through them (I). The resistance of the specimens (R) was calculated using Ohm's law. The electrical conductivity ( $\delta_a$ ) was then calculated using the relationship [ $\delta_a=1/\rho=4L/(\pi Rd^2)$ ]. The relative conductivity (in IACS- International Annealed Copper Standard- percent) was calculated according to the relationship [% IACS= ( $\delta_a/\delta_{Cu}$ )x100] where  $\delta_{Cu}$  is the electrical conductivity of pure annealed copper (58.9x10<sup>6</sup>  $\Omega^{-1}m^{-1}$ ) and  $\delta_a$  is the electrical conductivity of the alloy in  $\Omega^{-1}m^{-1}$ .

## **RESULTS AND DISCUSION** Hardness

Table (2) shows a summary of Vickers hardness measurements of investigated alloys in as-cast, solution treated and aged conditions. In Table (2) hardness values for solution treated samples show a slight softening compared to the as-cast values.

The softening effect is due to the dissolution of intermetallic precipitate particles into the solution and the homogenization effect on the cored denderitc structure. The average hardness values for aged samples for alloy containing 1 wt.% Al (Table (2) and Figure (1)) shows a monotonous increase with increasing aging temperatures for isochronal annealing between  $\sim 300^{\circ}$ C and  $400^{\circ}$ C.

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Alloy number	Alloy 1	Alloy 2	Alloy 3	Alloy 4		
Aging temperature (°C)	Hardness values					
As-casted	54± 3	62±5	69±4	75±6		
Solution treated	49± 3	51±4	53±4	54± 3		
300	86±3	124± 3	138±4	$133 \pm 7$		
340	101±9	130± 5	171±9	149± 5		
380	114± 5	145±6	218±7	160±10		
420	117±8	183±8	184± 9	203±7		
460	145±7	192±7	156±5	$181 \pm 6$		

Table 2: Summary of Vickers hardness measurements ( $Hv_1 \pm \sigma$ )

Where  $\sigma$ : standard deviation



Figure 1: Change in hardness values of the investigated alloys with increasing the aging temperatures

The hardness values then level down between ~ 400°C and ~ 450°C and then start a new more pronounced phase of increase. Such behavior is typical for age-hardenable alloys aged at lower temperatures. For Al-Cu alloys the first phase of hardness increase is due to the formation of GP (Guinier-Preston) zones. The second intensive hardness increase is due to the formation of a matrix of coherent and semi-coherent ( $\theta' + \theta''$ ) metastable phases [6]. In the present case, the hardening effect is due to similar effect.

The alloy containing 2 wt.% Al shows similar behavior but with higher hardness values achieving a steady state maximum hardness of 190 Hv<sub>1</sub>. Such behavior indicates more intensive formation of zones and metastable phases during aging. This effect is due to the more intensive formation of Ni<sub>3</sub>Al zones and metastable phases caused by incraseing the Al/Ni ratio in the alloy composition.

Isochronal aging of the alloy containing 3 wt.% Al shows an intensive hardness increase reaching a maximum value of 218 Hv<sub>1</sub> on aging at 380°C. However, the hardness drops rapidly on aging at higher temperatures. Such behavior may be attributed to the more intensive formation of Ni<sub>3</sub>Al and more rapid coarsening of metastable versions of this phase and their transformation into the stable incoherent Ni<sub>3</sub>Al (i.e. averaging ). Moreover, some of Ni may form NiAl rather than Ni<sub>3</sub>Al due to the abundance of aluminum [7,8].

The aging behavior of the alloy containing 4 wt.% Al is almost similar to the one containing 3 wt.% Al but with lower maximum hardness achieved on aging at  $\sim 420^{\circ}$ C.

In this case it seems that the Ni and Al atoms interact to form a combination of  $Ni_3Al$  and NiAl phases because of the higher Al/Ni ratio (0.296) which lies between 0.153 of the  $Ni_3Al$  and 0.460 of the NiAl [7,8].

Figure (2) shows the maximum hardness values achieved as a result of isochronal aging as a function of Al/Ni ratio. It is clear that the highest hardness value is achieved in alloys containing between 2.5 and 3.5 wt.% Al. This range of composition should be more rigorously investigated to obtain the alloy with Al/Ni ratio that gives the maximum hardness value.



Figure 2: The maximum hardness values achieved in the investigated alloys as a function of Al/Ni % ratio

#### Strength

In the most applications of Be-bronze, strength rather than hardness is the mechanical property of prime importance. Figure (3) and Figure (4) illustrates the effect of isochronal aging for two hours at given temperatures on the  $\sigma_{0.2}$  and  $\sigma_{uts}$  of the investigated alloys respectively.



Figure 3: The effect of aging temperature on the yield strength of the investigated alloys



Figure 4: The effect of aging temperature on the ultimate tensile strength of the investigated alloys

The measured values are given in Table (3). These curves show almost similar pattern effect as those for hardness. The alloy with the lowest aluminum content (1%) experience two stages of strengthening. Primary in the temperature range of  $300-360^{\circ}C$  and secondary from  $420^{\circ}C$  and above. The first stage is due to grouping of Ni and Al atoms in a certain crystallographic sites at a very high frequency by short distance diffusion. Such groups of atoms will cut through by dislocations creating slight resistance to their movement. However, due to their high frequency of occurrence, these groups cause a noticeable increase in the yield strength. Increasing the aging temperature between  $360-420^{\circ}C$  does not show any noticeable change in the yield strength, indicating that the grouping stage has reached saturation. The yield strength increases again due to the precipitation of some coherent and/or semi coherent metastable versions of Ni<sub>3</sub>Al.

Alloy number	Al	loy 1	All	oy 2	Alle	oy 3	Alle	oy 4
Aging temperature (°C)	$\sigma_{0.2}$	$\sigma_{uts}$	$\sigma_{0.2}$	$\sigma_{uts}$	$\sigma_{0.2}$	$\sigma_{uts}$	$\sigma_{0.2}$	$\sigma_{uts}$
	(MPa)							
300	218	290	266	516	306	561	287	531
340	263	340	284	534	410	668	338	598
380	317	383	328	586	543	798	371	634
420	324	392	434	745	402	745	498	779
460	369	484	437	743	299	678	534	702

Table 3: Summary of the tensile test results of heat treated alloys

The alloy containing 2% Al shows almost similar behavior but with higher values of yield strength, indicating more volumetric fraction of Ni<sub>3</sub>Al precipitation. Such interpretation is supported by the fact that Al/Ni ratio of this alloy composition (0.17) is very close to that of Ni<sub>3</sub>Al (0.153).

The alloy contains 3% Al shows the maximum strengthening effect achieved in the investigated alloys. Although it is Al/Ni ratio exceeds that of  $Ni_3Al$ , such effect

indicates that the ability of Al to combine with Ni forming Ni<sub>3</sub>Al requires some over saturation. Moreover, the rapid decrease of the yield strength with increasing the aging temperature above 380 °C indicates an intensive coarsening of precipitates and loss of coherency in the temperature 380-460 °C.

The alloy with 4% Al shows again a double stage strengthening during isochronal aging. However, in this case the maximum value of yield strength is achieved at higher aging temperature and its value is lower in comparison with that of 3% Al alloy. The Al/Ni ratio of this alloy (0.3) is midway between Ni<sub>3</sub>Al (0.153) and NiAl (0.46). Such decrease in yield strength with increasing Al content from 3% to 4% is due to the gradual and partial change of the precipitates from Ni<sub>3</sub>Al to NiAl which is softer. On the other hand the coarsening effect of temperature is slower in the alloy with higher Al content [7,8]. The effect of isochronal aging on the ultimate tensile strength of the investigated alloys is shown in Figure (4). These curves follow almost similar pattern to those shown in Figure (3) for hardness.

### **Electrical conductivity**

Figure (5) shows the measured electrical conductivity of the investigated alloys as a function of aging temperatures. The measured values of the electrical conductivity were recalculated into %IACS units. The measured electrical conductivity values are introduced in Table (4). All of the investigated alloys show the same pattern. The electrical conductivity increases as the aging temperature increases (300-400°C). At higher aging temperatures a gradual leveling of the conductivity was observed. The electrical conductivity of the investigated alloys has almost the same value on aging at 340 °C. Below this temperature the electrical conductivity is lower for high Al content alloys. At higher aging temperatures the electrical conductivity show different manner. The higher the Al content (up to 3% Al) the higher the electrical conductivity. Then it becomes lower with increasing Al content.



Figure 5: The effect of aging temperature on the electrical conductivity of the investigated alloys

						v		
Alloy number	Alloy 1		Alloy 2		Alloy 3		Alloy 4	
Aging	$\delta_a x 10^6$	%	$\delta_a x 10^6$	%	$\delta_a x 10^6$	%	$\delta_a x 10^6$	%
temperature (°C)	$(\Omega^{-1}m)$	IACS	$(\Omega^{-1}m^{-1})$	IACS	$(\Omega^{-1}m^{-1})$	IACS	$(\Omega^{-1}m^{-1})$	IACS
	1)							
300	8.9	15	8.4	14	6.7	11	5.4	9
340	12.1	20	11.9	20	12.1	20	11.5	19
380	13.1	22	13.8	23	15.8	26.5	14.4	24
420	13.9	23	15.1	25	17.5	29	16.3	27
460	13.8	23	15.6	26	17.7	29.5	16.8	28

Table 4: Electrical conductivity of heat treated alloys

These observations can be explained as follows. During aging at lower temperatures intensive decomposition of the solid solution takes place. The more supersaturated alloys being decompose at higher rates. Hence, the first part of these curves shows a rapid increase of electrical conductivity. At temperatures between 340-380 °C a maximum amount of alloying elements has been precipitated from the solid solution. Further increase in aging temperatures will accelerate the coarsening of precipitates. As a result the scattering effect of precipitates will be decreased giving raise to the mean free path of electrons. The alloy with 3% Al shows the maximum electrical conductivity, indicating maximum precipitation of alloying elements.

# CONCLUSIONS AND RECOMMENDATIONS

Based on the results obtained in this paper, it can be concluded that:

- The mechanical properties and electrical conductivity of the investigated alloys can simultaneously be improved by heat treatment.
- The maximum hardness values are expected to be obtained in alloys containing 2.5-3.5 wt.% aluminum. This alloy composition range should be precisely investigated.
- The measured hardness values encourage further investigations to adjust more precisely the chemical composition and heat treatment regime.
- The electrical conductivity of the investigated alloys in optimal heat treatment regime compares well with that of Be-bronze reaching 30% IACS.
- The alloy contains 3% Al (Al/Ni ratio of 0.25) showed the best combination of mechanical strength and electrical conductivity.
- Other alloy compositions with lower total alloy content should also be investigated.
- The partial replacement of Al by other elements such as Ti would be beneficial for improving mechanical and other properties.

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