Rapid Solidification of Cu-Al Alloys and its Effects on some of the Properties of these Alloys and their Corrosion Rates

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Abstract:

This paper presents the results of an experimental investigation of the effects of rapid solidification on the general properties of two types of copper aluminum, (Cu-Al), alloys during the process of their manufacture. The two alloys were prepared by melting their constituents, at the same proportions recommended by the international standards, in a graphitic furnace in an oil fired furnace. The rapid solidification unit and metal moulds were designed and fabricated in order to allow the castings in the mould to be cooled and solidified quickly. Strips of various thicknesses ranging from 3mm to 6mm have been subjected to different cooling media including air, ordinary water and iced water. Examinations of the fabricated castings included optical microstructure observations, Vickers hardness and tensile strength testing as well as their corrosion rates against sea water. The results showed an improvement in some of the mechanical properties such as hardness, tensile strength and corrosion resistance of the Cu-Al alloys.

Keywords: solidification; Cu-Al alloys; corrosion rate; tensile strength

Symbols and Abbreviations

Symbol	Description
A	Exposure area (cm^2)
Al	Aluminum
ASTM	American Standards for Tests and Measures
BS	British Standards
Cu	Copper
F.C.C.	Face Centered Cube
D_{av}	Average Diameter of indentation (mm)
Fe	Iron
HCl	Hydrochloric Acid
H_2SO_4	Sulfuric Acid
Icorr	Corrosion Current (nA)
K_2CO_7	Potassium Chromates
Li	Lithium
mpy	Corrosion Rate (mils per year)
Ni	Nickel
P	Applied Load (kg)
RS	Rapid Solidification
w	Weight (gm)
We	Equivalent Weight (g/gmol)
ρ	Density (g/cm^3)

Introduction:

Rapid solidification is a means of developing new alloys that offer advantages not easily provided by conventional ingot casting practices or methods. Copper alloys have been widely used in a variety of environments, especially, in the marine applications due to their excellent corrosion resistance and good ductility, [1].

Nucleation of structures depends on the cooling rate, for example at very fast cooling rates unstable amorphous or non-crystalline phases form. This technique has enabled the development of engineering materials with desirable properties. The increased cooling rates would; therefore, directly affect the castings microstructure with a large number of nuclei. This is due to the little time available for the grains to form at the sites, hence the very small grain size formed in these castings, which may reach ≈ 0.1 micron. Also, the small distance between the dedritic arms decides the differences between normal alloys and rapid solidification alloys, which is ≈ 0.25 micron, [2].

Higher temperatures than 1250 ^{o}C are required for thicker sections than (12.5 mm) or less. However, for casting sections of (38 mm) or greater, lower temperatures are recommended, [3, 4]. Rapid solidification processing rates of about 100 times more than those used in conventional casting have enabled the formation of very fine grain structures with small segregation regions. This is due to the solid solubility and the complete prevention of segregation in some alloys, [5, 6].

Cu-Al alloys are well known for their application in the marine service due to their high tensile strength, especially for the thin propeller blade sections, and their good castability, and good resistance to corrosion. For example, marine propellers castings for blades and bosses require to be free from any surface or internal defects, and these castings are to heat treatable, where necessary, [7]. Therefore, segregation in the microstructure may result due to the differences in thickness between various sections of the blades, which would lead to poor mechanical properties leading to rupture or failure of blade sections.

The Cu-Al phase diagram shows that solid solubility of Al in Cu exists up to (7.4 %) in the solidus and then increases to (9.4 %) at 565 ^{o}C. This means that high Al content alloys can be heat treated in a manner similar to steel. This can be quenched after holding at about 343 to 677 ^{o}C, in order to give optimum combination of strength, hardness and ductility. These aluminum bronzes are divided into cold and hot working alloys. Those alloys containing about (5 % Al) are ductile and malleable, they are completely solid solution in structure, and therefore, they have good capacity for cold-working processes. They also, have good corrosion resistance. But, the hot-working alloys contain about (10 % Al) and if allowed to cool slowly, the structure becomes brittle due to the precipitation of a hard compound of (Cu_9Al_4). If this structure is allowed to cool to about 800 ^{o}C, it transforms to a completely solid solution, and hence becomes malleable and can be successfully hot-worked, [8]. To prevent precipitation of the above mentioned brittle compound, castings are usually ejected from the moulds as quickly as possible so that they cool rapidly.

The two grades AB1 and AB2 both have the same specified range of aluminum content (8.5-10.5 %), but AB2 contains higher levels of iron and nickel. The properties of AB2 alloy can be further modified by suitable heat treatments.

Rapid Solidification (RS) has, for example, been employed for the trapping of impurities in the laser melting and re-solidification of semi-conductors, [9], and (RS) has resulted in the production of high conductivity copper alloys, [10]. Some rapidly solidified aluminum alloys were designed to compete with the (Al – Li) alloys in the structural aerospace applications which require light loads, [11]. Tests were also carried out in the air craft industry on rapidly solidified (Cu – Ni) alloys, [12], which have resulted in refined grain size, elimination of segregation and improvement in hardness and increase of strength. RS has enabled the development of high silicon content wear and high temperature resistant materials with low coefficient of thermal expansion which gave profitable applications in the aircraft and automobile industries, [13].

This shows that (RS) involves cooling the metallic melts at a high rate and results in significant microstructural modifications including grain refinement and formation of saturated solid solutions and amorphous phases, [14]. (RS) is, also, vital in order to achieve uniform distribution of the alloying elements in the copper metal.

Experimental Work:

The materials which compose each alloy, were prepared from a selection of available raw materials, and melted, poured and cast in four carbon steel moulds designed and made for this purpose. Rapid solidification was accomplished through the proper design and manufacture of the unit which allowed the castings in the moulds to be cooled and quenched very quickly. Strips of 3,4,5,6 mm thicknesses were then produced and made ready for further testing and inspection.

The tests covered: (1) hardness measurements, (2) tensile strength estimation, and (3) optical microscopic inspection, as well as, (4) corrosion resistance evaluation in seawater environment.

The equipment consists of a melting unit situated in one of the local workshops of the Basrah industrial district. The melting unit is in the form of a crucible furnace, and alloying elements including copper, aluminum, iron and nickel were exactly weighed to the correct percentages, according to (BS 1400), [1].

Due to the differences in melting temperatures between the various constituent alloying elements, (1538 ^{o}C and 565 ^{o}C), iron was melted first and after its complete melting, copper was added and finally aluminum while waiting for a few minutes.

These elements were chopped into small pieces before melting. Carbon steel moulds of a trapezoidal shape and dimensions of {155 × 48 × 13 mm} have been used. These moulds were designed such that thin ribbons of different thicknesses could be produced. The ribbons have enabled the process of rapid solidification to be achieved by obtaining high cooling rates through the use of different cooling media, including natural air, ordinary water and iced water. A time-temperature measurement unit was employed to enable the recording of temperatures at various time periods during the melting and solidification stages. The samples, dog-bone shaped each of dimensions 12mm gauge length x (6 mm x 3 mm) cross section, were prepared and cast using the crucible oil-fired furnace of a local workshop in the industrial district of Basrah. These samples were cut into the proper dimensions, ground, polished, washed, dried, and etched with an etching solution of 39 mg (K_2CrO_7), 8 ml (H_2SO_4), 4 drops (HCl) and 100 ml (H_2O) for about (15 – 30 seconds).

The corrosion test samples were of round shapes, each with a diameter of 15 mm and thickness of not more than 3 mm.

The four tests carried out included the following:

(1) Metallographic Testing:

After the preparation of the samples, a microstructure examination was conducted for each sample, using an Opton type computerized microscope, and observations were recorded and saved on a computer disc. These tests were carried out at the inspection department of one of the local state companies. See Figures (1), (2) and (3) as typical examples for these tests

(2) Hardness Testing:

Many samples of Cu-Al alloys have been subjected to hardness tests using a Japanese made Vickers hardness tester, type VHK-1. Vickers hardness numbers (VH) were then calculated from the formula:

$HN = 1.85437\ P/ d_{av}^2$, [15], where

See Table (1) for the hardness numbers of both AB1 and AB2 alloys.

(3) Tensile Testing:

The tensile testing was carried out on an Instron (1195) Tester at the strength of materials laboratory, University of Technology, Baghdad. Rectangular and round section bars were dog-bone or dumb-bell shaped, according to BS 18, and ASTM-E8, [16]. See Table (2) for the tensile strengths of the two alloys AB1 and AB2.

(4) Corrosion Resistance Testing:

This test was performed at the College of Science, University of Basrah, using the corrosion measurement console mode 350A (USA), when the samples were placed in seawater environment. The corroded weight of each sample was calculated using the formula, [17]:

$$mpy = \frac{0.13\ Icorr\ We}{A\ \rho}$$

The corrosion rates for the 3 mm diameter samples using the three different cooling media are shown in Table (3) for both AB1 and AB2 alloys.

Results and Discussion:

Two types of aluminum bronze alloys (AB1 and AB2) have been produced employing the simple rapid solidification equipment available at a local workshop located in the Basrah industrial district. The components (by weight) of these two alloys are as listed in Table (4) below:The discussion covers the comments made on the results obtained from carrying out the manufacture of four different thickness Cu-Al castings and to reflect the following effects on the properties outlined earlier in this paper.

(1) Effect of cooling rates on the microstructure: Three different cooling media, i.e. air, water at room temperature or (ordinary water), and iced water were used. See Figures (1 – 3) for the effect of the three above mentioned cooling media on the microstructure of alloy AB1.

(2) Corrosion Effect: Samples, each of 3 mm thickness at different rates of cooling were tested against seawater. The results showed a decrease in corrosion rates due to the increase in the cooling rates, see Tables (5) and (6) for the effect of the three different cooling media on the corrosion rates of both AB1 and AB2 alloys.

(3) General properties effects: This included the results of cooling rates effect on tensile strength and alloying elements for both alloys, as shown in Tables (3) and (4).

These effects can be justified by the causes of the microstructure which consists of a uniform dispersion of intermetallic particles in both **α**-phase and **β**-phase. The **α**-phase represents a face centered cube (F.C.C.) copper-rich solid solution with Al and Fe while the **β**-phase consists of a martensitic crystal structure with a proportion of Al more than in the α-phase. The intermetallic precipitations were identified as the compound Fe_3Al, [8]. This structure compares well with the previous research results by [18] and [19].

The fast cooling rates have effects on the grain refinement compared with air cooling rates. This is because the increasing cooling rates cause a decrease in the nucleation barrier and the required free energy for nucleation increases, [20]. The reason for this is due to the microstructure consisting of only the **β**-phase at temperatures exceeding (1000 ^oC). This is similar to the formation of austenite (or **γ**-phase) in steel, and this **β**-phase transforms to martensite when quenched. Then, the (Fe_3Al) particles nucleate, both inside the **β**-grains and at the grain boundaries, as temperature falls to around (900 ^oC).

Precipitation of **α**-phase starts forming when quenching from (860 ^oC). Nucleation of **α**-phase takes place at **β**-phase grain boundaries or at the (Fe_3Al) particles located in the **β**-phase. From (560 ^oC) and below, the microstructure is similar to the as cast case, which implies that the alloy does not undergo any appreciable change below this temperature.

Low cooling rates lead to the formation of coarse grains due to the decrease in the nucleation free energy. Dendritic arms have a chance to extend and give enough time for grains to grow. On the other hand, as cooling rates increase, free energy and more nucleation sites exist, allowing more grains to nucleate. Moreover, these rates allow the dedritic arms to interact quickly leading to the suppression of grains growth, hence resulting in grain refinement, [2]. This is justified by the increase in Vickers hardness numbers as proportionate with the increase of cooling rates, i.e. there is an improvement in hardness. It shows that hardness has increased from a minimum value of (133 HV) in the air cooled specimen to a maximum value of (192 HV) for the iced water quenched specimen of the alloy (AB1); see Figure (4). Also, Vickers hardness has changed from 179.5 in the 3mm thick specimen which was rapidly quenched in ordinary water, reaching a value of 202 in the same thickness specimen that was rapidly quenched in iced water. This improvement was due to the grain refinement that took place and because of increasing the solubility of Al in Cu during the rapid quenching operation.

Table (1) Hardness values (VH) for four thicknesses of the AB1 and AB2 alloys

Casting	AB1				AB2			
ST / CM	3	4	5	6	3	4	5	6
Air	-----	133	-----	-----	-----	138		
Ordinary Water	170	143	142	173	179.5	-----	179	173
Iced Water	192	199	176	175	202	199	157	175

Note: ST = Sample Thickness in (mm)
CM = Cooling Medium

Table (2) Tensile strength of the AB1 and AB2 alloys (in N/mm^2)

Casting	AB1				AB2			
ST / CM	3	4	5	6	3	4	5	6
Air	----	491	----	----	----	225	----	----
Ordinary Water	----	551.9	313	400	234	----	171	----
Iced Water	436	----	548	492	129.8	217	----	300

Note: ST = Sample Thickness in (mm)
CM = Cooling Medium

Table (3) Corrosion rates for the 15 mm diameter, 3mm thickness samples using different cooling media

Casting	AB1		AB2	
Cooling Medium ↓	Corrosion Current (x10^4 nA)	Corrosion Rate (mpy)	Corrosion Current (x10^4 nA)	Corrosion Rate (mpy)
Air	1.916	10.26	0.470	2.639
Ordinary Water	1.07	6.003	0.427	2.396
Iced Water	0.5005	5.052	0.452	2.538

Table 4 Chemical Compositions (%) of the two Cu-Al alloys

Casting	Chemical Composition (%)			
	Al	Fe	Ni	Cu
AB1	10	2.5	---	Balance Remaining
AB2	10	5.0	5	Balance Remaining

The seawater analysis, Table (5), has shown that the presence of chlorine ions has strongly affected the corrosion mechanism of the Al-bronze alloys. The chemical activities of metals in collaboration with these ions destroy the strong protection layer forming on the surfaces of the corrosion resistant metals. The corrosion results show a maximum corrosion rate of (10.25 mils/year) for the air cooled specimens and 6.003 and 5.052 mils/year for those specimens rapidly cooled in ordinary water and iced water, respectively. This indicates that the increase in cooling rates has affected a decrease in corrosion rate.

The classifications of corrosion rate are good when the alloy corrodes by less than (5 mils/year) and satisfactory when the rates are less than (50 mils/year), [17]. These alloys contain about (5% by weight) of aluminum.

The Figures (5 – 8) show the stress-strain curves for the tensile test of various alloys at different cooling rates and different structure compositions. They all show an improvement in tensile strength as cooling rates increased. These improvements were due to the forming of a fine microstructure with small grain sizes and more grain boundaries which make the slips and dislocation movements more difficult for those cases tested.

Table (5) Sea Water Chemical Analysis

Type of analysis	Result	Unit
Acidity index	7.1	---
Chlorine	42850	Mg/L
Magnesium	972	Mg/L
Calcium	4800	Mg/L
Phosphoric acid	52.3	Mg/L
Sulphate	1212.9	Mg/L

Iron Additions:

Iron acted as a grain refiner and prevented self-annealing when added at a percentage of (2.5%). This condition resulted in the dissolution of **β**-phase into the α-δ eutectoid. By suppression, the iron has improved the mechanical properties of Al-Cu alloys, when more than (0.75% of iron) is present. In such cases, the liquid temperature is raised and freezing begins with the solidification of δ-iron which serves as a nucleation point for the fine grain sizes and thus preventing the grain growth, [20].

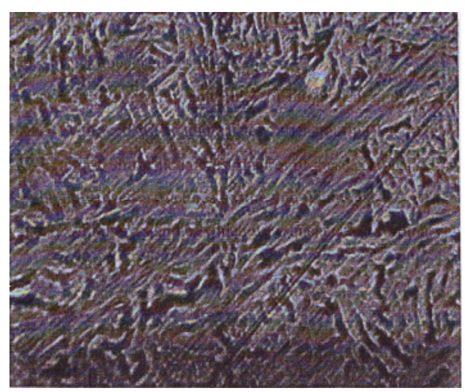

Figure (1) Microstructure of 4 mm thick casting from AB1 alloy, cooled in air (x 150)

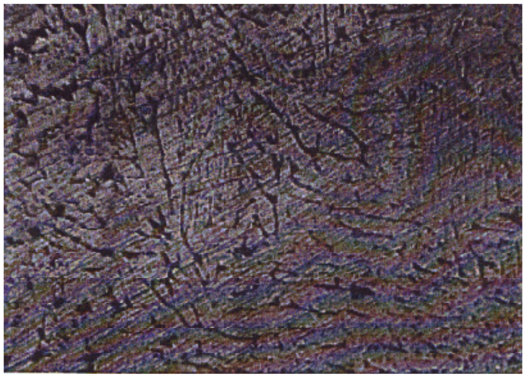

Figure (2) Microstructure of 5 mm thick casting from AB1 alloy, cooled in ordinary water (x 150)

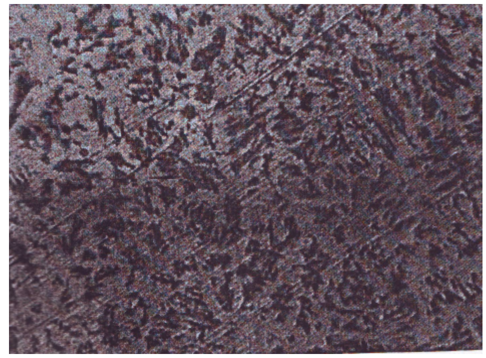

Figure (3) Microstructure of 6 mm thick casting from AB2 alloy, cooled in iced water (x 150)

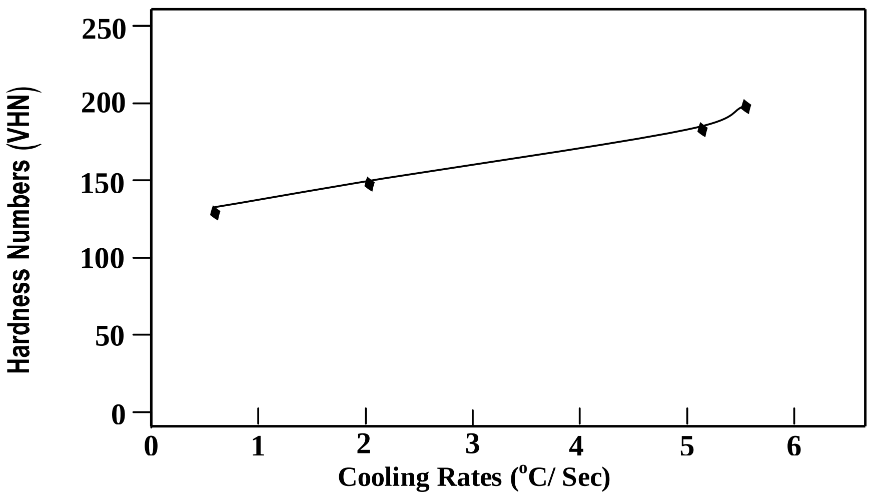

Fig. 4 Relationship between Hardness Numbers and Cooling Rates

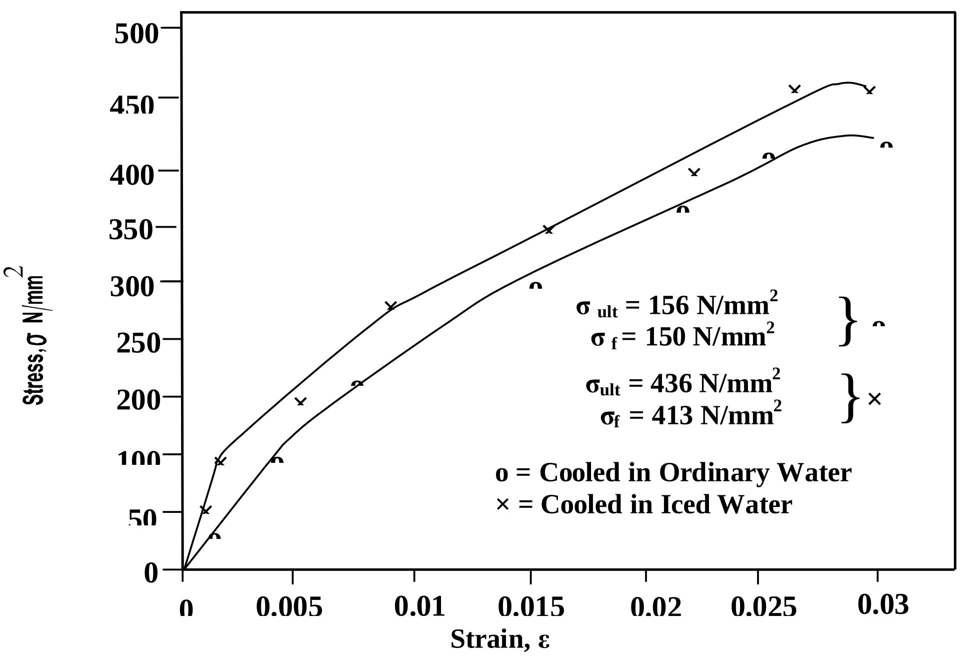

Fig. 5 Stress-Strain Curves for the 3mm Thick Castings of Cu-Al Alloy Cooled in Ordinary water and Iced Water

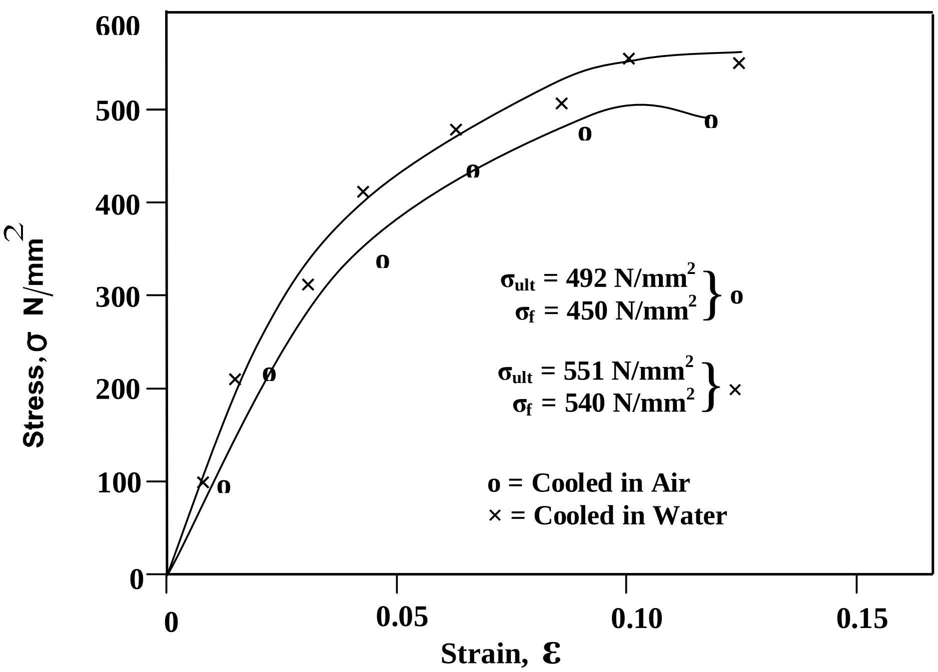

Fig. 6 Stress-Strain Curves for the 4mm Thick Castings of Cu-Al Alloy Cooled in both Air and Water

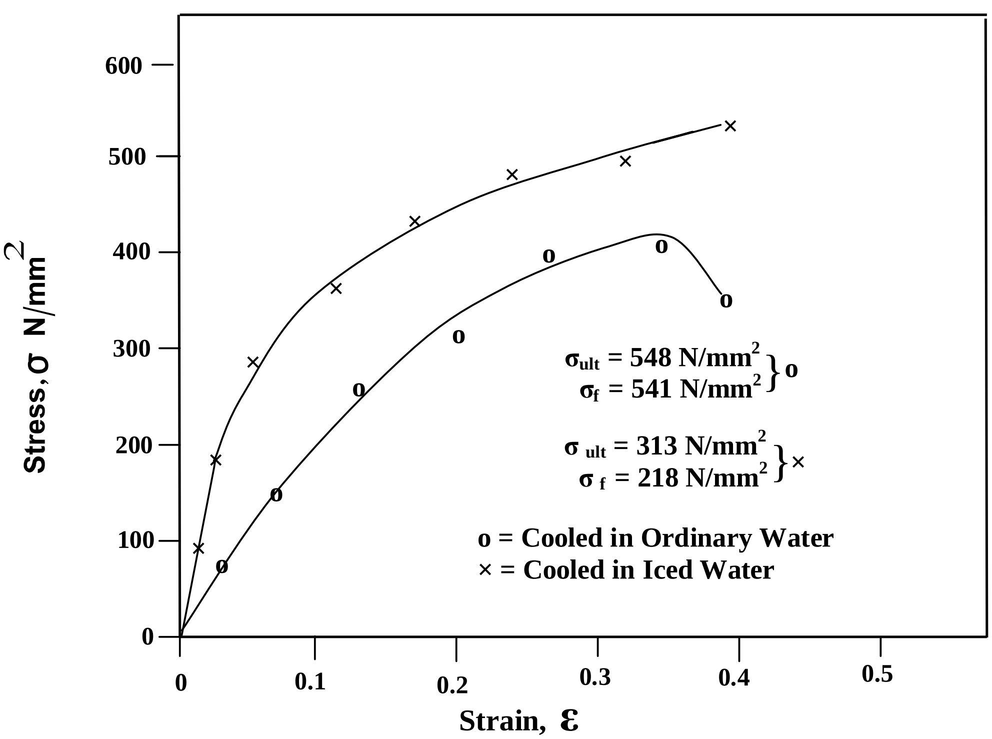

Fig. 7 Stress-Strain Curves for the 5mm Thick Casting of Cu-Al Alloy Cooled in Ordinary water and Iced Water.

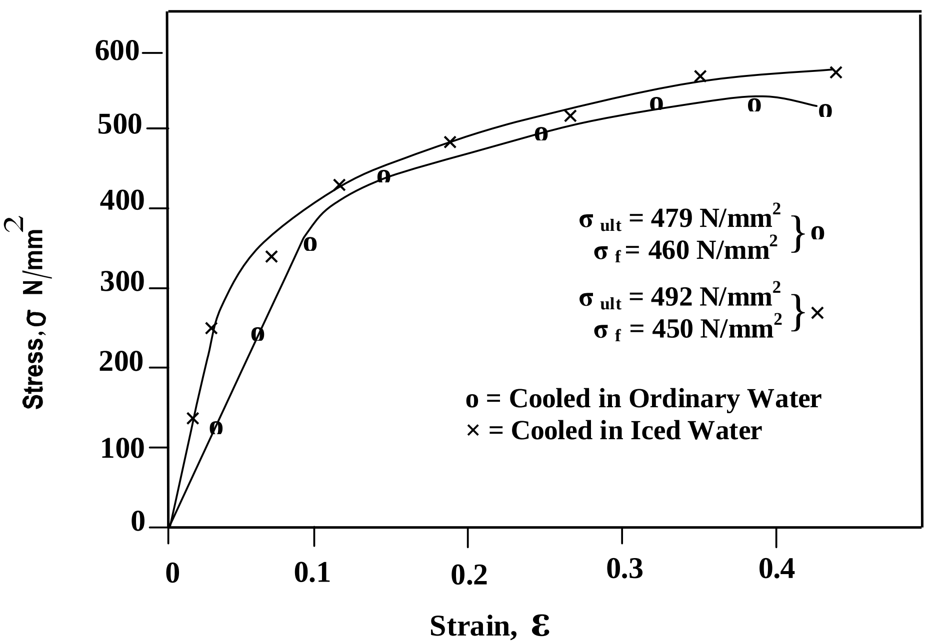

Fig. 8 Stress-Strain Curves for the 6mm Thick Castings of Cu-Al Alloy Cooled in Ordinary Water and Iced Water

Conclusion:

Rapid quenching of alloy (or solidification) both in ordinary water and iced water lead to a grain refinement effect in Cu–Al alloys. This in turn, lead to increases in the hardness and tensile strength of the alloys as well as an improvement in the corrosion resistance of these materials, as the cooling rates have increased during the rapid solidification processes.

References:

[1] M. Lai, O.P. Khanna, "Foundry Technology", 2nd Edition, Dhanpat Rai and Sons, Delhi, India, 1979.

[2] Ali H. M. Al-Hilfi, "Study the Effect of Rapid Solidification on Some Copper Aluminum Alloys and Asses their General Properties for Marine Applications", M.Sc. Thesis, College of Engineering, Basrah University, Basrah, Iraq, 2004.

[3] K. Strass, "Applied Science in the Casting of Materials", 1st Edition, Pergeman Press Ltd., Oxford, UK, 1970.

[4] P. Sommer, K. Eschert, "Information Technology for Materials Heat Treatment", The Heat Treatment Market, No. 3, pp 5 – 9, 2000.

[5] G.H. Gilmer, "Models of Impurity Trapping during Rapid Solidification", Materials Science and Engineering Journal, 65, 1984.

[6] Sommer, P., "Study of grain Growth in Hot – Worked Metal from Various Steel Manufacturers", The Heat Treatment Market, No. 2, pp 5 – 10, 2004.

[7] Aziz, H. Al-Hilfi, "Applications in Marine Engineering", Basrah University Press, Basrah, Iraq, 1995, (in Arabic).

[8] F.H. Fores, "Examination of Rapid Solidification Materials", Journal of Materials, August, 1986.
[9] Gilmer, G.H., "Models of Impurity Trapping During Rapid Solidification", Materials Science and Engineering Journal", 65, 1984.
[10] R.A. Higgins, “Materials for the Engineering Technology”, 1st Edition, Hooder and Stoughton Ltd., London, England, 1972.
[11] A. Lawly, "Modern Power Metallurgy Science and Technology", Journal of Metals, August 1986.
[12] F.H. Fores, R. Carbonora, "Applications of Rapid Solidification", Journal of Metals, February 1988.
[13] R. Tongstri, J. Minay, R. Thakray, R. Dashwood, H. Mcshane, "Microstructure-Processing- Property-Relationship of Rapidly Solidified (Al-Fe) v. (Si) Alloys", Science Asia, Vol. 30, 2004.
[14] F. Hassan, J. Iqbal, N. Bidley, “Microstructure of as Cast Aluminum Bronze Containing Iron”, Journal of Material Science and Technology”, Vol. 1, April, 1985.
[15] Akashi, “Table for Vickers Hardness Numbers”, Akashi Company, Japan, 1980.
[16] Smithells, “Metal reference Book”, Butterworth, Hellman, 1976.
[17] H.H. Uhliq, R., W. Revie, “Corrosion and Corrosion Control”, 3rd Edition, Wiley Interscience Publication, USA, 1985.
[18] D.R. Askeland, “The Science and Engineering of Materials”, 2nd Edition, Pews-Kent Publishing Company, Boston, USA, 1989.
[19] W.R. Heine, R.C. Loper, C.P. Rosenthal, “Principles of Metal Casting”, 2nd Edition, McGraw- Hill Book Company, New York, USA, 1976.
[20] F.H. Fores, Y.M. Kim, F. Henmann, "Rapid Solidification of Al, Mg and Ti", Journal of Metals", August, 1987.

الإصلاد السريع لسبائك النحاس والالمنيوم وتأثيراته على بعض الخواص الميكانيكية ومعدلات التآكل لهذه السبائك

عزيز حافظ زاجي الحلفي

قسم هندسة المواد – كلية الهندسة – جامعة البصرة

<u>المستخلص:</u>

يتناول البحث نتائج العمل على نوعين من سبائك نحاس– الالمنيوم كمحصلة لعملية التبريد السريع أو الإصلاد السريع أثناء مرحلة التصنيع. حيث تم اختيار سبيكتين من عدة مواد من البراص المستخدمة في بيئات مختلفة كالمجال البحري الذي يستخدم فيه هذا النوع من السبائك بصورة واسعة. فبينت النتائج تحسناً ملحوظاً في بعض الخواص الميكانيكية بالإضافة إلى مقاومة التآكل الكيمياوي لسبائك نحاس الألمنيوم.