

## Retarding of Precipitation Hardening of Al-Cu Alloy by Cadmium Addition

**Dr. Amin D. Thamir**

Production and Metallurgy Engineering Department, University of Technology/ Baghdad

**Dr. Alaa A. Atiyah**

Materials Engineering Department, University of Technology / Baghdad

Email: Dr.alaaatiyah@uotechnology.edu.iq

**Sabreen Ali**

Materials Engineering Department, University of Technology / Baghdad

Received on: 20/3/2013 & Accepted on: 4/7/2013

### ABSTRACT

The aim of the present work is to prepare a set of Al-Cu alloys with slow precipitation hardening by aging. Present work results can be utilized during the importing or exporting of such alloys at solution treatment conditions. In order to establish this aim, a set of Al-4%Cu alloys have been prepared in the laboratory to investigate the effect of Cd-addition with the percentage varied from (0.1, 0.3 and 0.5) weight percentage. The prepared alloys with different Cd additions were subjected to a natural aging up to 60 days after solution treatment. As a result, the alloys showed an obvious retarding in the aging kinetics as the percentage of Cd-additions increasing. This retarding was found to be due to the trapping of the vacancies that resulted during the quenching step that resulted in delays of Guinier-Preston zones precipitation. SEM has been used in monitoring of microstructure as well as optical microscopy.

**Keywords:** Precipitation Hardening Retarding, Al-Cu-Cd Alloy, Vacancies Trapping.

### تأخير عملية التصليد بالترسيب لسبيكة (المنيوم – نحاس) بواسطة إضافة الكاديوم

#### الخلاصة

ان الهدف من هذا البحث هو تحضير مجموعه من سبائك (Al-Cu) تستجيب بصوره بطيئه للتصليد بالترسيب بواسطة التقادم الطبيعي. ويمكن الاستفادة من نتائج البحث الحالي بإمكانية إستيراد هذه السبائك بظروف مابعد المعالجة المحلوليه. ولتحقيق هذا الهدف فقد تم في هذا البحث إضافة عنصر الكاديوم النقي بنسب قليله تتراوح بين (0.1, 0.3 و 0.5) نسبة وزنيه لسبيكة الألمنيوم-4% نحاس التي تم تحضيرها مختبريا لهذا الهدف ثم إجراء التقادم الطبيعي لهذه السبائك بعد المعالجة المحلوليه لفترة أقصاها شهران. وقد أثبتت النتائج إن تأثير إضافة الكاديوم يكون واضحا في تأخير حركية التقادم اعتمادا على نسبة الكاديوم المضاف وذلك لأن الأخير يعمل على غلق الثغرات الناتجة خلال مرحلة التبريد السريع للسبيكة ضمن المعالجة المحلوليه للسبائك وبذلك سوف يتم تأخير ترسيب مناطق (جون يور- بري ستون) المسبب الرئيسي لعملية التصليد بالتقادم. وقد تم استخدام المجهر الالكتروني الماسح وكذلك المجهر الضوئي في مراقبة البنية المجهرية.

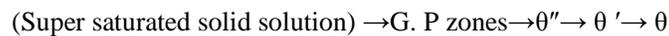
**الكلمات المرشده:** تأخير عملية التصليد بالترسيب, سبيكة ألمنيوم – نحاس – كاديوم, أنغلاق الثغرات.

## INTRODUCTION

The aim of the work at hand was to investigate experimentally the effect of Cd addition to the retarding of precipitation hardening in Al-4%Cu alloy. The efforts of researchers are always directed into the improvement of the response of aluminum alloys to the natural and artificial aging. It has rarely considered to find literatures talking about how could retarding of the aging response be done by alloying addition. Knowing that, the retarding of the aging process is very important in many engineering applications and during the storing of components for exporting. The traditional method of retarding the aging process was by refrigeration of the Al-Cu quenched alloys to keep them soft [1 to 4].

Therefore, the aging processes, variation in the chemical composition of the alloys which could be retarding the aging, and then controlling the rate of hardening and their effects on the overall mechanical properties in Al-Cu alloys required more investigation.

Cadmium element is a relatively low melting element that finds limited use in aluminum. Up to 0.5% cadmium may be added to aluminum-copper alloys to control the rate of age hardening, also increases strength, and increases corrosion resistance [5]. It is known that, the Al-Cu alloys are heat treatable alloys by a precipitation hardening method, with the following sequence [6]:



( $\theta$ ) precipitate is the equilibrium ( $\text{CuAl}_2$ ) intermetallic compound. The intermediate precipitates ( $\theta''$ ) and ( $\theta'$ ) have been identified as distinct crystal structures from their diffraction patterns [6].

Most of the industrial men have a little capability to control the natural aging interval between quenching and the artificial aging step. So that, it is very important to develop a full understanding of this problem in order to produce a metal having less sensitivity to these processing variables. The Al-Cu alloys are very sensitive to most aging variables such as (temperature, time), but the one that has received the greatest attention is the natural aging interval. Some of these alloys exhibit a deleterious effect of natural aging like 6061 aluminum alloys. This is due to the decomposition that occurs at room temperature that depending on the solute super saturation and the number of excess vacancies [7].

It is hoped in this work to investigate experimentally the effect of cadmium addition on the Al-4%Cu alloy age retarding. The work will focus on the hardness and tensile properties of set of prepared alloys containing (0.1, 0.3 and 0.5wt%) of cadmium and comparing the behavior with cadmium free alloy.

## EXPERIMENTAL PROCEDURE

### Melting and alloying practices

The Al-Cu alloys with composition presented in Table (1) were prepared and melted in the electrical resistance furnace from aluminum (99.99 %) and refined copper (99.99 %). Cadmium element (with 99.99% purity) has been added as flakes at required percentages. Many corrections have been made to correct the weight percentage of each constituent (i.e. Cu and Cd) of prepared alloys after checking with XRF technique. The alloys are cast in a gray cast iron mold of a cylindrical shape of internal diameter 20 mm and length 125 mm as shown in Figure (1). Furthermore, the

as cast specimens were homogenized at temperature 520°C for 8 hrs and cooled to room temperature.

The specimens for natural aging analysis are machined to disks of 10 mm diameter and 5 mm high. Knowing that A<sub>0</sub> was used as a reference alloy.



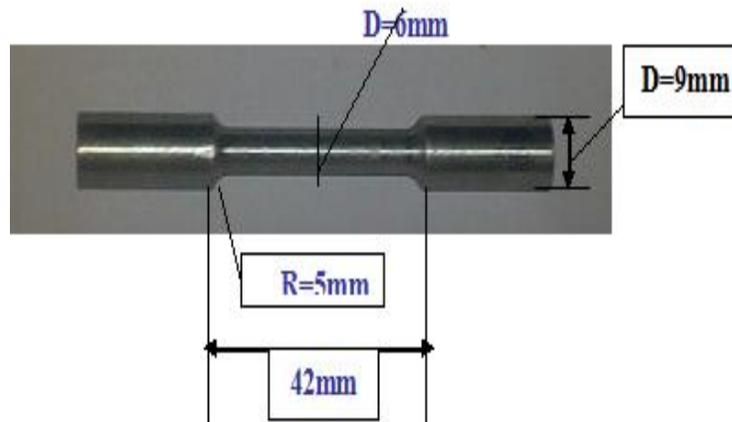
Figure (1) Samples of prepared alloys in as cast conditions.

Table (1) Average chemical composition of prepared alloys.

Alloy No.	Cu%	Cd%	Al%
A <sub>0</sub>	4.0	-	Balance
A <sub>1</sub>	4.0	0.1	Balance
A <sub>2</sub>	4.0	0.3	Balance
A <sub>3</sub>	4.0	0.5	Balance

#### Aging practices and characterizations

All prepared samples were solution treated at 540°C for 50 minutes and given a water quench [5]. The samples were then aged at room temperature for varying times up to 60 days. Microhardness measurements of prepared samples in as cast conditions and after each 24 hrs were conducting systematically. Yield and ultimate tensile strength were also examined according to ASTM E-8 for aged samples at maximum hardness conditions. Figure (2), shows the shape and dimensions of tensile test samples.



Figure(2) Shape and dimensions of tensile test sample [ASTM E-8].

#### Optical & Scanning microscopy

Optical microscopy observations have accompanied hardness testing in every 10 days to observe any possibility of microstructural changes with the time. X-ray diffraction examinations and scanning microscopy of naturally aged samples that shows maximum retarding of aging (i.e. A<sub>3</sub>) are conducting. All samples of microstructural observations have been ground, polished and etched according to the ASTM E3 – 11. The etching solution was (95% HF+5% H<sub>2</sub>O).

#### RESULTS AND DISCUSSION

The detrimental effect of natural aging on precipitation hardening have been generally reported generally in, and is thought due to the fact that the clusters formed during natural aging consume the vacancies and solute atoms. These facts were in aluminum-copper alloys which are free of any Cadmium [7]. The effect of Cd is to be expected very mysterious about how long the alloy (Al-4%Cu) has taken to develop its hardness at natural aging conditions. Figure (3) shows the response of alloys A<sub>0</sub>, A<sub>1</sub>, A<sub>2</sub> and A<sub>3</sub> alloys to the natural aging. It is clear from the figure that initial solid solution microhardness found to be almost constant at all investigated alloys. This behavior characterized by hardness readings of cadmium free alloy or the so-called reference alloy in this work in comparison with A<sub>1</sub>, A<sub>2</sub> and A<sub>3</sub> alloys. The hardening kinetics were developing differently according to the percentage of cadmium that added. The hardness response as shown above is in agreement with the tensile properties as shown in Figure (4).

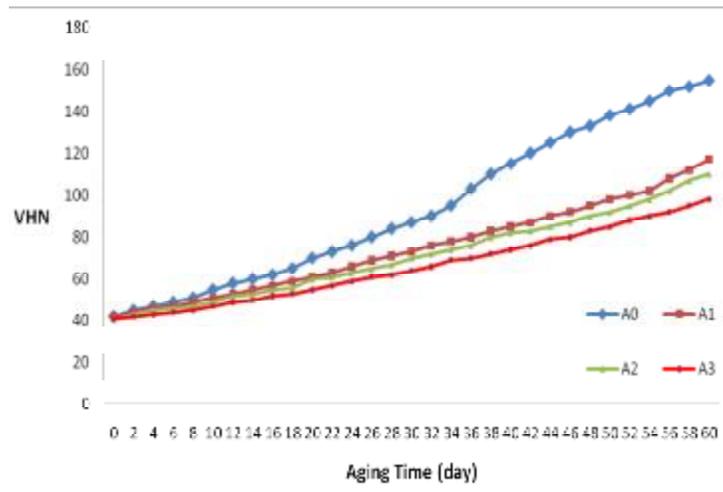


Figure (3) Response of prepared alloys to the natural aging up to 60 days.

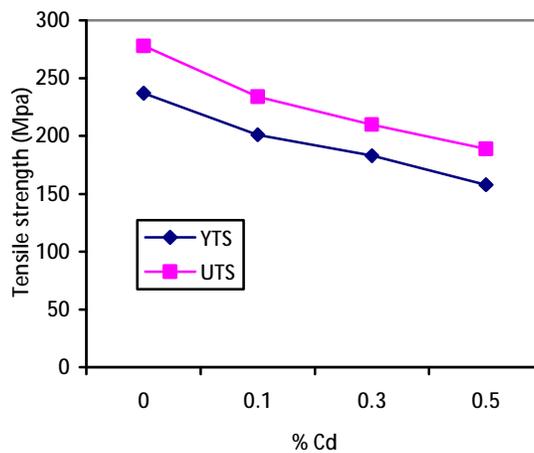


Figure (4) Effect of Cd addition on the yield and ultimate tensile strength properties of alloys subjected to the natural aging.

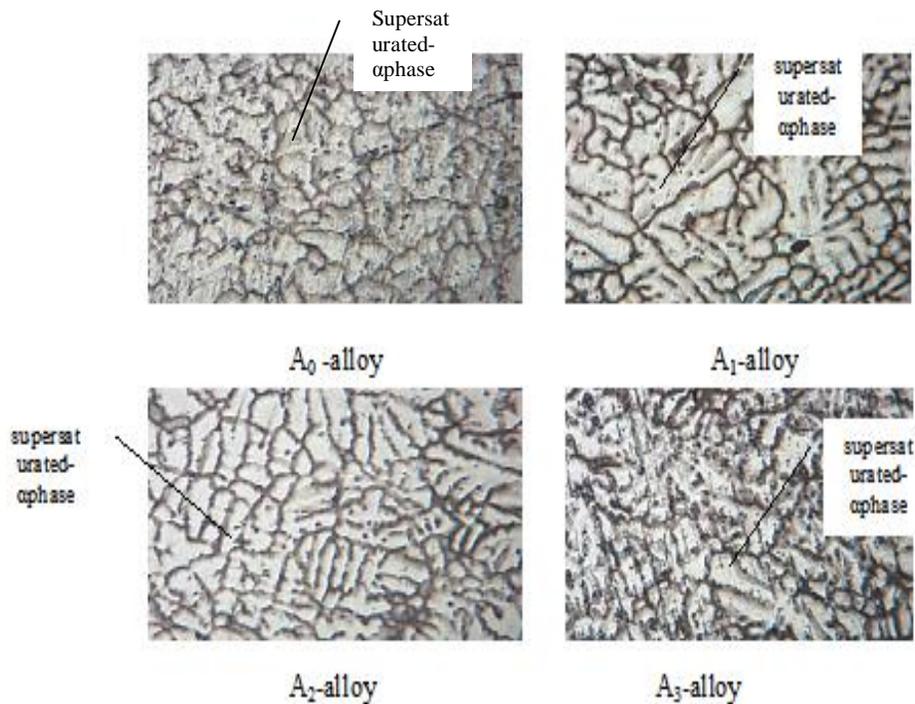
In the case of cadmium free alloy, the behavior is normal and in agreement with the literature [8], where the hardness developed uniformly with the time. Now, as the percentage of cadmium increasing, a clear retarding in the kinetics of hardening has achieved. The cadmium free alloys show a higher tensile strength among all the prepared alloys. Ultimate and yield strength values are dropping down as %Cd is increased.

The microstructure examinations as shown in Figures (5 & 6) for the samples of alloys in as quenched conditions consist mainly of grains of supersaturated aluminum with the copper atoms. Vacancies are expecting to be less stable at the conditions of as quenched conditions due to the instability of the supersaturated solid solution. The resulted microstructure is now waiting a dramatic transformation due to many factors such as natural time and aging temperatures. The increasing in Cd-addition has

clearly affecting the number and size of vacancies that developed as a result of quenching as shown in SEM photographs in Figures (7).

SEM observations of A<sub>3</sub> alloy that shows maximum retarding in aging response; it contains  $\alpha$  and CuAl<sub>2</sub> phases Figure (7-a). Based upon the Al-Cu phase diagram [8], it is primary CuAl<sub>2</sub> compound because the content of Cadmium is less than 0.5wt% and the Copper to Cd is greater than 0.5. The micrograph of the alloy A<sub>3</sub> as shown in Figure (7-b & c) shows many double layers of CuAl<sub>2</sub> phase with little coherency to the matrix and no obvious vacancies appears.

X-ray diffraction of A<sub>3</sub> sample did not show any development of new peaks that may result of cadmium additions. However, the X-ray diffraction peaks as shown in Figure (8) was identical to the standard data of the alloy (Al-4%Cu). The addition of cadmium can affect the process of clustering which is normally occurs during the natural aging. Therefore, the interaction between the vacancies and the solute of cadmium leads to sinking of vacancies.



**Figure (5) The optical microstructure of the alloys at the conditions of supersaturated solid solution (after quenching), (250 X magnifications for all alloys above).**

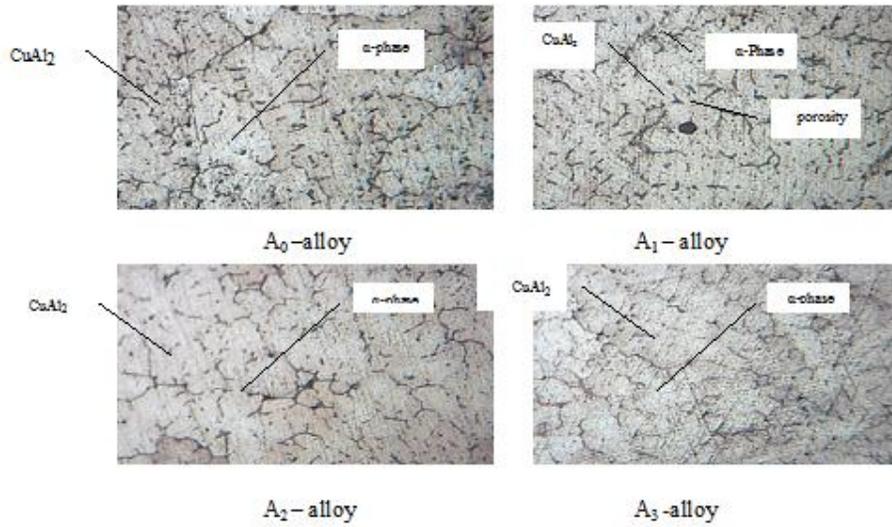


Figure (6) Optical microscopy of tested alloys at the peak hardness conditions. (250 X magnification) for all above alloys.

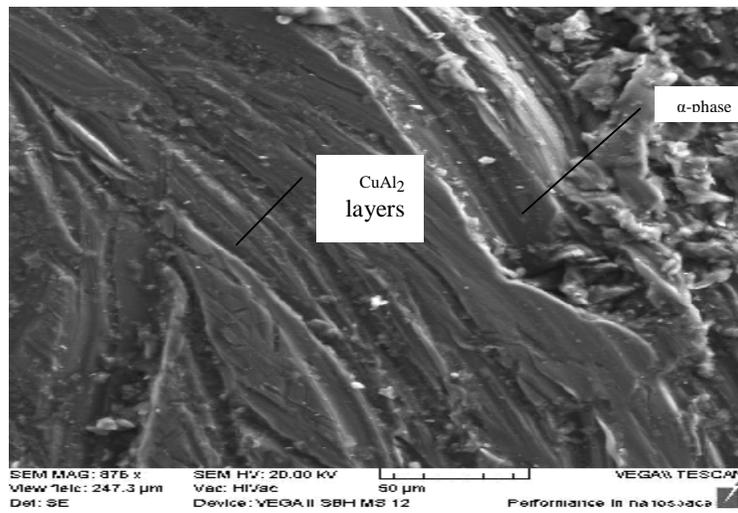


Figure (7-a) SEM observation of alloy (A<sub>3</sub>) at the peak hardness conditions.

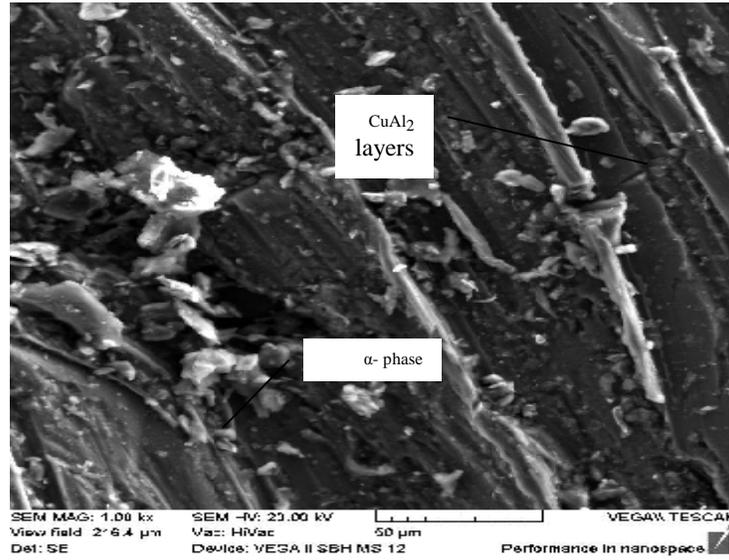


Figure (7-b) SEM observation of alloy (A<sub>3</sub>) at the peak hardness conditions.

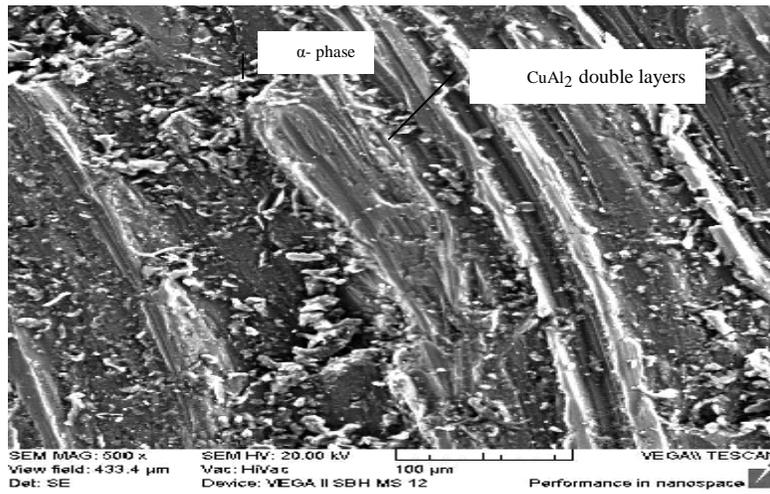
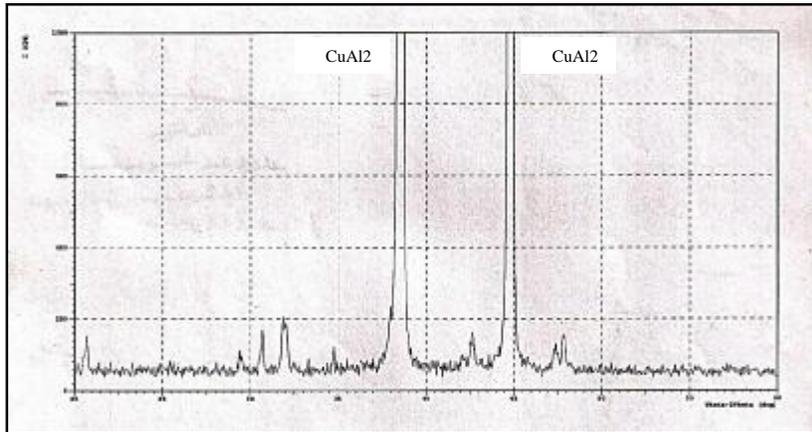


Figure (7-c) SEM observation of alloy (A<sub>3</sub>) at the peak hardness conditions.



**Figure (8) XRD observation of alloy A<sub>3</sub> at the peak hardness conditions.**

As a result from the above analysis, It is thought that, the cadmium atoms trap the excess vacancies that retained during the process of quench and reducing the rate of G.P. Zone formation. In this way Cd atoms can help the formation of  $\theta''$ - particles by segregating to  $\theta'$ -matrix interfaces and reducing the interfacial energy as shown in SEM observations of A<sub>3</sub> sample at peak hardness conditions.

### CONCLUSIONS

It can be conclude the following:

1. All the alloys with cadmium does display age hardening behavior up to the extent where it can even compete with cadmium free alloy.
2. The strengthening precipitates are confirmed to be of the same type (CuAl<sub>2</sub>) as was suggested by previous workers in the age hardening abilities of 2000 series aluminum alloys containing Cu.
3. The high Cu content was responsible for the good response in aging kinetics.
4. Although the actual precipitation sequences are the same as mentioned for Al-Cu-Cd alloys. The percentage of Cd has a little or no effect on the initial hardness of naturally aged alloys and clear retarding of the aging process that achieved in the alloy containing cadmium element and the rate of hardening have delayed.
5. As the natural aging time was increased, the cadmium alloys samples shows a little but obvious development in the rate of hardening.
6. It is thought that the trapping of vacancies that developed during the quenching process help to retard the formation of G.P zones that plays a great role in hardening of this alloy.

**REFERENCES**

- [1]. Hassan and V. S. Aigbodion, S. B. “The study of the Microstructure and Interfacial Reaction of Al-Cu-Mg/Bagasse Ash Particulate Composite”, *Journal of Alloy & Compounds*, 491, pp. 571–574, (2010).
- [2]. Ahmet Meyveci<sup>1</sup>, İsmail Karacan<sup>1</sup>, Hülya Durmuş<sup>2</sup>, Uğur Çalığülü<sup>3</sup>,” using of artificial neural networks for modeling wear behavior of aged 2024 and 6063 aluminum alloy” *Journal of Yasar University*, 4 (13), pp. 2063-2077, 2009.
- [3]. Maja Vončina<sup>1</sup>, Anton Smolej<sup>1</sup>, Jožef Medved<sup>1</sup>, Primož Mrvar<sup>1</sup> & Rok Barbič<sup>2</sup>, "Determination of precipitation sequence in Al-alloys using DSC method", *RMZ – Materials and Geoenvironment*, Vol. 57, No. 3, pp. 295–304, 2010.
- [4]. Melikhova, O. J. Cizek, I. Pprochazka, Kuripiach, I. Stulikova and J. Faltus, "Positron-Lifetime investigation of precipitation effects in Al-Cu alloy", *Materials Structure Journal*, Vol. 8, no. 2 (2001).
- [5]. Askeland, D.R., “The Science and Engineering of Materials”, Third SI Edition, Chapman and Hall, London, 1996.
- [6]. Kang, S.B. L. Zhen, H.W. Kim, and S.T. Lee;” Solidification and precipitation behavior of Al-Si-Mg casting alloys”, *Mater. Sci. Forum* 217-222, 827 (1996).
- [7]. Alaa A. Ateia, " Effect of Thermomechanical treatments on aging behavior and fracture toughness of Al-Cu-Mg alloy plates used in aircraft structure ", *Iraqian Journal of Mechanical and Materials Engineering*, Volume no. 8, Issue 1, 2008.
- [8]. Norbert Ponweiser, Klaus W. Richter, "New investigation of phase equilibria in the system Al–Cu–Si" *Journal of Alloys and Compounds*, Volume 512, Issue 1, Pages 1-366 (25 January 2012).