

FABRICATION POROUS COPPER BY SINTERING'S TECHNIQUE UNDER VACUUM CONDITIONS

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ABSTRACT :

In this study, porous copper was produced using powder metallurgical techniques. Zinc element (21%wt) was used as a transitional element to be pulled during sintering process under vacuum environment. A set of samples was produced with different sintering's conditions to investigate the optimal parameters for production of porous copper. SEM test was used to measure the resulted porosity for the prepared samples. It was found that 3 hours is a sufficient duration for the first stage of sintering at (350°C) and for the second stages at (850°C) to pull all of the zinc vapors and thus get the highest percentage of porosity for the remaining copper which was found to be (19%).

Key words: Metal foam, porous copper, membrane, fuel cell, powder metallurgy, sintering.

انتاج نحاس مسامي باستخدام تقنية التلييد في أجواء مفرغة

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الخلاصة :

في هذه الدراسة، تم إنتاج النحاس المسامي باستخدام تكنولوجيا المساحيق. وقد استخدم عنصر الزنك بنسبة وزنية (21%wt) كعنصر انتقالي ليتم سحبه بعد ذلك خلال عملية التلييد في ظل أجواء مفرغة. تم انتاج مجموعة من العينات تحت ظروف تلييد مختلفة لغرض استقصاء تلك الظروف التي تحقق أفضل المعايير في انتاج النحاس المسامي. تم استخدام المجهر الألكتروني لغرض قياس المسامية للعينات المعدة. وقد وجد أن التلييد لمدة ثلاث ساعات خلال المرحلة الأولى بدرجة حرارة (350°C) و للمرحلة الثانية بدرجة حرارة (850°C) للتلييد ينتج عنه تبخر محتوى الزنك بشكل شبه كامل وبالتالي الحصول على أعلى نسبة من المسامية للنحاس المتبقي بلغت قيمتها (19%).

1- INTRODUCTION :

Renewable energy sources like fuel cells have increasingly been used during recent years because of some serious difficulties like shortcomings and also pollution nature of fossil fuels. The Polymer Electrolyte Membrane Fuel Cell (PEMFC) is one of the most important types of the fuel cells. It is mainly consists of fluid flow plates to be used as a membrane to separate the cathode and anode. Fluid flow plates are traditionally made from graphite based materials. Recently the use of low permeability open pore metallic foams has been attended to overcome the brittleness of graphite. Additionally, heat and electrical conductivity of metallic materials are several orders of magnitudes higher than graphite.

Stainless steel foam was used as fluid field plates (FFPs) by Kumar and Reddy (**Kumar and Reddy, 2003**). Parvanian and Panjepour enhanced stack power density by using porous copper foam as conventional BPs (**Parvanian and Panjepour, 2013**). The cost of production metallic foams with open interconnected pores added another restriction to using this kind of membranes in fuel cells.

There are several methods developed to produce metal foams. As a general, the use of melts of constitutional metals is the most popular conventional manufacturing process used in production of metallic foams. Such techniques have limitation in forming thin metallic foam because of difficulties in controlling the thickness and porosity of foam (**Jeong et al., 2008**). Shin et al. succeeded in manufacturing thin copper foam by a fast electrodeposition (**Shin et al., 2003**). They generated hydrogen bubbles at high cathodic current densities.

Lost carbonate sintering process (LCS) is another method used in production of copper foams (**Zhao et al., 2005; El-Hadek and Kaytbay, 2008**). Copper and K_2CO_3 powders are mixed together, according to this method, with presence of a certain volumetric rates of a binder such as ethanol (**Mahmoud, 2012**). The raw materials used in LCS for manufacturing metal foam are in powder form. Economically, it is an acceptable method but unfortunately, it is still difficult to control the resulted porosity.

Porous copper can be prepared also electrochemically in a dry nitrogen-filled glove box by using ionic liquids near or below ambient temperature such as 50–50 mol % $ZnCl_2$ -EMIC ionic liquid which is prepared by the reacting between Zinc chloride and 1-ethyl-3-methylimidazolium chloride (**Lin et al., 2007**).

The aim of this study is the development of porous copper produced by powder metallurgy (PM) method with minimum cost to be used as a membrane in fuel cells because of its high heat and electrical conductivity.

2- MATERIALS AND EXPERIMENTAL PROCEDURES :

The elemental powders used in this study were provided by the Sky Spring nanomaterial's Inc. with purity and mesh of (99.9%) and (-325) respectively. All powders used were prepared by the electrolytic technique. Aluminum powder was added (6%wt) to improve the machinability of the Copper foam while the Zinc content was (21%wt). The Zinc content will be the main parameter that controls the final porosity of the cu-foam. After mixing the elemental powders on a roll mixer, green compacts were prepared inside a single action cylindrical steel die under a compacting stress of 800MPa. Five samples were sintered by solid phase sintering technique (**Fig.1**) using a vacuum tube furnace shown in (**Fig.2**) at materials laboratory of engineering's

college-University of Kerbala. The vacuum environment was achieved using a two stages vacuum pump which is very suitable to achieve (6.7 E -02 Pa). Each sample was sintered with a different time for each stage of sintering as illustrated in (Fig.3) and table-1.

3 - CHARACTERIZATION TESTS :

A tabletop scanning electron microscope of Hitachi TM3000 model, which is shown in (Fig.4), was used to measure the porosity of the sintered samples. All images which are took for the tested samples illustrated in Table-1 were evaluated using (Imagej) image processing's package. At the beginning, all images were converted to binary system of colors and then porosity was measured by calculating the area fraction of the black color to the overall area of the image. Three images were taken for each sample and three corresponding values of porosity were calculated to evaluate the average porosity for each sample. On the other side, EDS was used to evaluate the evaporation of the Zinc content after sintering.

In order to evaluate the evaporation of the zinc content, Inel Equinox 3000 X-Ray Diffractometer was used in this study (Fig.5). Firstly, a green compact was tested with Cu K α radiation at 60 Kv and 60 mA. The specimen was held at a fixed angle of 6 degrees relative to the incident X-ray while the detector is moved through an angle of $2\theta = 10^\circ$ to 120 degrees at a scanning speed of $12^\circ(2\theta)$ per minute.

All characterization tests were conducted at Net Shape laboratory at the University of Birmingham-UK.

4 - RESULTS AND DISCUSSION :

The SEM results can be observed through (Fig.6) which represents a selective image for each sample. It is clear that the sample No.3 has the highest porosity among all other corresponding samples. This sample was sintered with three hours soaking time for the first and second stages of sintering. The comparison between porosities of all solid phase sintering samples can be seen in (Fig.7). The final porosity of sample No.3 was 19%. By comparing this result of porosity with the original weight percentage content of zinc element which was (21%wt.), it can be concluded that it is possible to control the final porosity of any sample by controlling the content of the zinc element which can be used to prepare green compacts.

By observing the results of porosities of the prepared samples, it can be noted that there is a direct relationship between the soaking time of the first stage of sintering and the resulting porosity. Most zinc content was evaporated when sintering with three hours soaking time. The boiling temperature of the zinc element at atmospheric pressure is 907 °C. This value is reduced dramatically under vacuum environment and hence, boiling was takes place for the zinc during the first stage of sintering. In addition to that important factor, there is another but less influential factor which is the duration of the second stage of the sintering process.

The results of the EDS test supported this conclusion as can be noted through (Fig.8) and (Fig.9). Aluminum and Copper elements could be diffused and surround the areas of the presence of zinc and closed it. The diffusion process could be very helpful in stopping loosing of the Zinc vapors and hence, there was still zinc content when minimizing the soaking time of the first stage of sintering.

Sample No. 3, which recorded the highest percentage of porosity through the approximately full evaporation of zinc, was selected for the purpose of the XRD test. At the beginning, a green compact was tested and (Fig.10) represents the XRD test for the green compact. The standard peaks of x-ray diffraction pattern for copper, Aluminum and Zinc are obtained. The peaks of Aluminum and zinc were disappearing when testing sample No.3 as shown in (Fig.11).

5- CONCLUSIONS :

The preparation of porous copper by powder metallurgy using sintering of green compacts inside a vacuum tube furnace was studied. The following conclusions can be remarked:

1. The final porosity of the products can be controlled through the controlling of the zinc powders quantity which added to the copper powder.
2. The duration of the soaking time plays a main role in producing porous copper. Three hours is a sufficient duration for the first stage at 350°C and for the second stages of sintering at 850°C. All of the zinc vapors can be pulled, under these conditions, and thus get the highest percentage of porosity for the remaining copper which was 19%.

Table-1 : solid phase sintering attempts

No. of sample	T ₁ (°C)	t ₁ (hrs)	T ₂ (°C)	t ₂ (hrs)
1	350	1	850	1
2	350	2	850	2
3	350	3	850	3
4	350	2	850	4
5	350	1	850	5



Fig.1 : Solid phase sintered samples



Fig.2 : The tubular furnace of 1200 °C maximum temperature used in this study

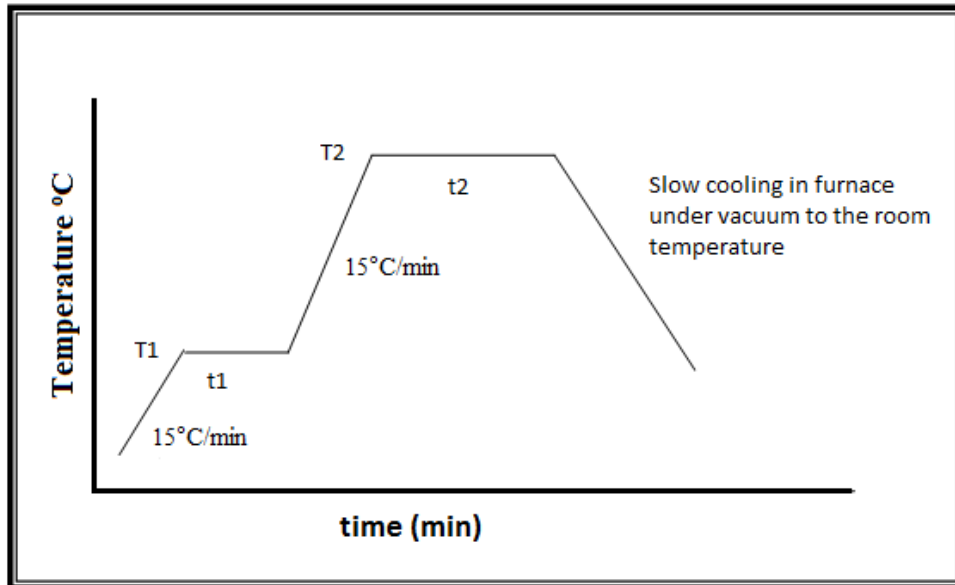


Fig.3 : heating cycles during sintering processes

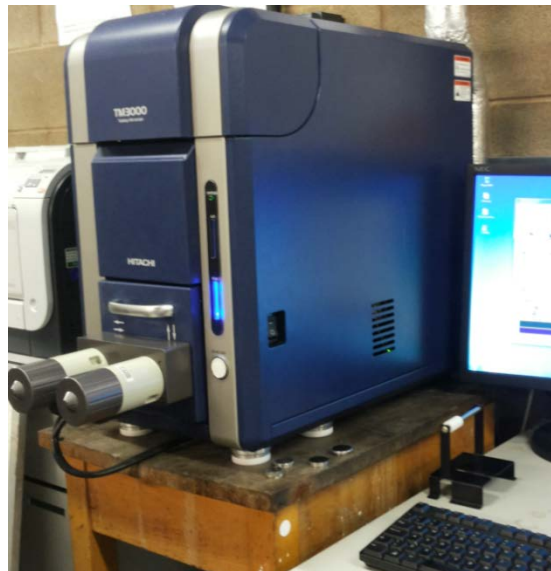


Fig.4 : Hitachi TM3000 SEM



Fig.5 : Inel Equinox 3000 X-Ray Diffractometer used in this study.

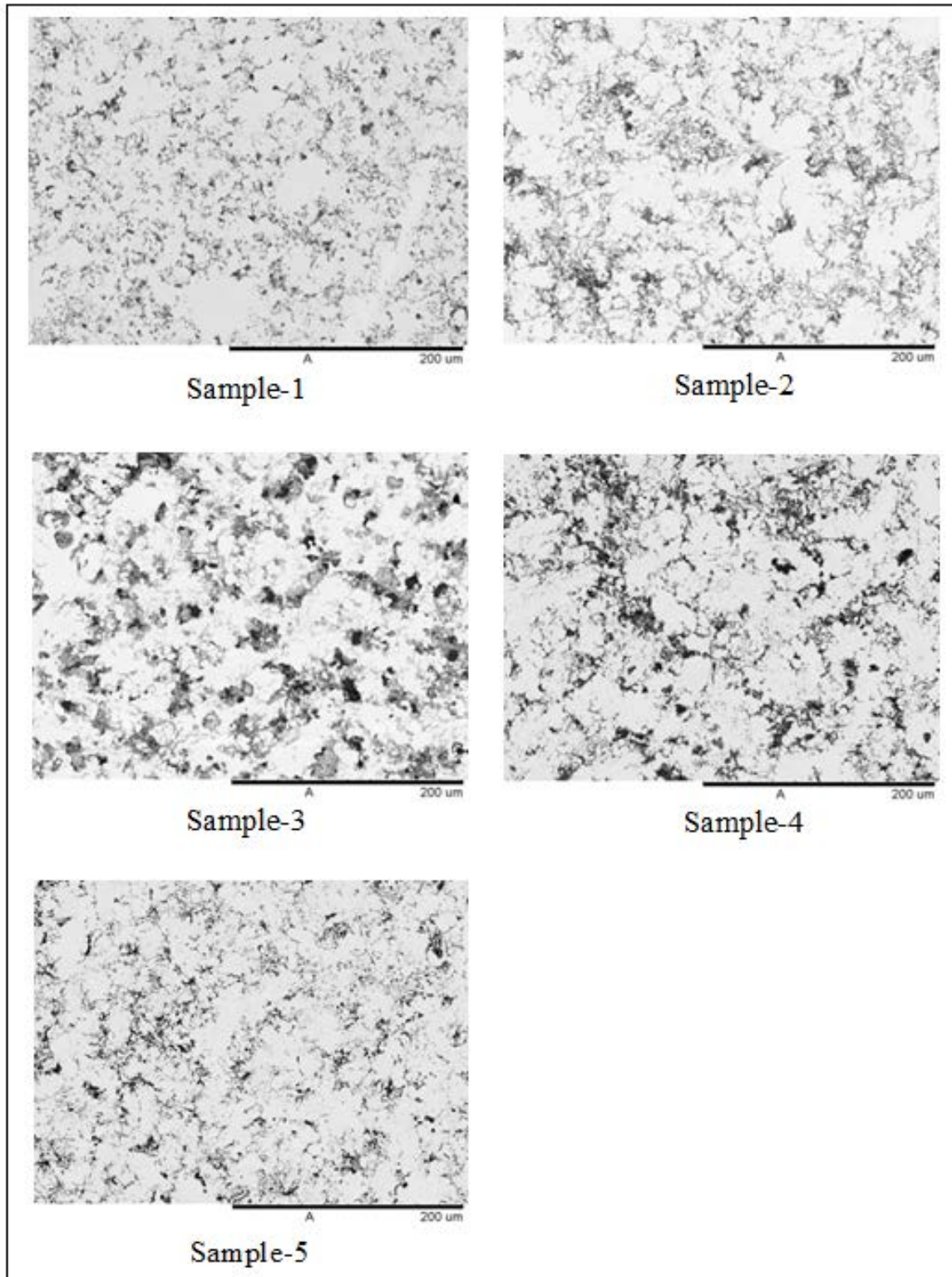


Fig.(6) : Selective SEM images for the five samples prepared.

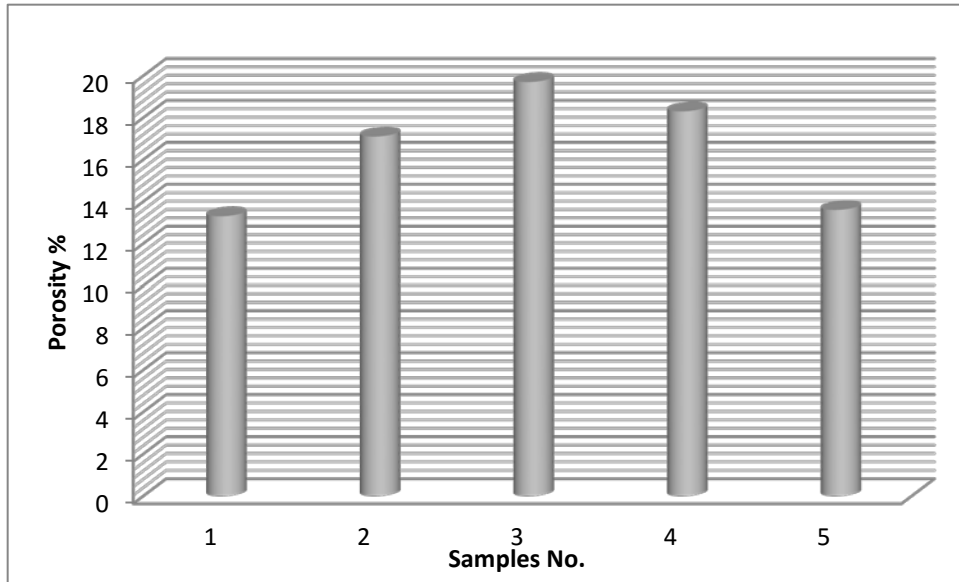


Fig.(7) : A comparison between porosities of solid phase sintering samples

Spectrum: Map/ Sample No.1					Spectrum: Map/ Sample No.2						
El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
Cu	29	K-series	69.32	82.86	75.79	Cu	29	K-series	72.94	88.15	79.87
Zn	30	K-series	8.41	10.05	8.94	Al	13	K-series	6.40	7.74	16.51
Al	13	K-series	5.93	7.09	15.27	Zn	30	K-series	3.40	4.11	3.62
Total:			83.67	100.00	100.00	Total:			82.74	100.00	100.00
Spectrum: Map/ Sample No.3					Spectrum: Map/ Sample No.4						
El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
Cu	29	K-series	77.13	91.11	81.99	Cu	29	K-series	74.37	89.63	81.58
Al	13	K-series	6.96	8.22	17.42	Al	13	K-series	6.10	7.35	15.75
Zn	30	K-series	0.57	0.67	0.59	Zn	30	K-series	2.51	3.02	2.67
Total:			84.66	100.00	100.00	Total:			82.97	100.00	100.00
Spectrum: Map/ Sample No.5											
El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]						
Cu	29	K-series	66.78	85.93	78.16						
Al	13	K-series	5.81	7.47	16.01						
Zn	30	K-series	5.13	6.60	5.83						
Total:			77.72	100.00	100.00						

Fig.(8) : spectrum map EDS result for the main elements.

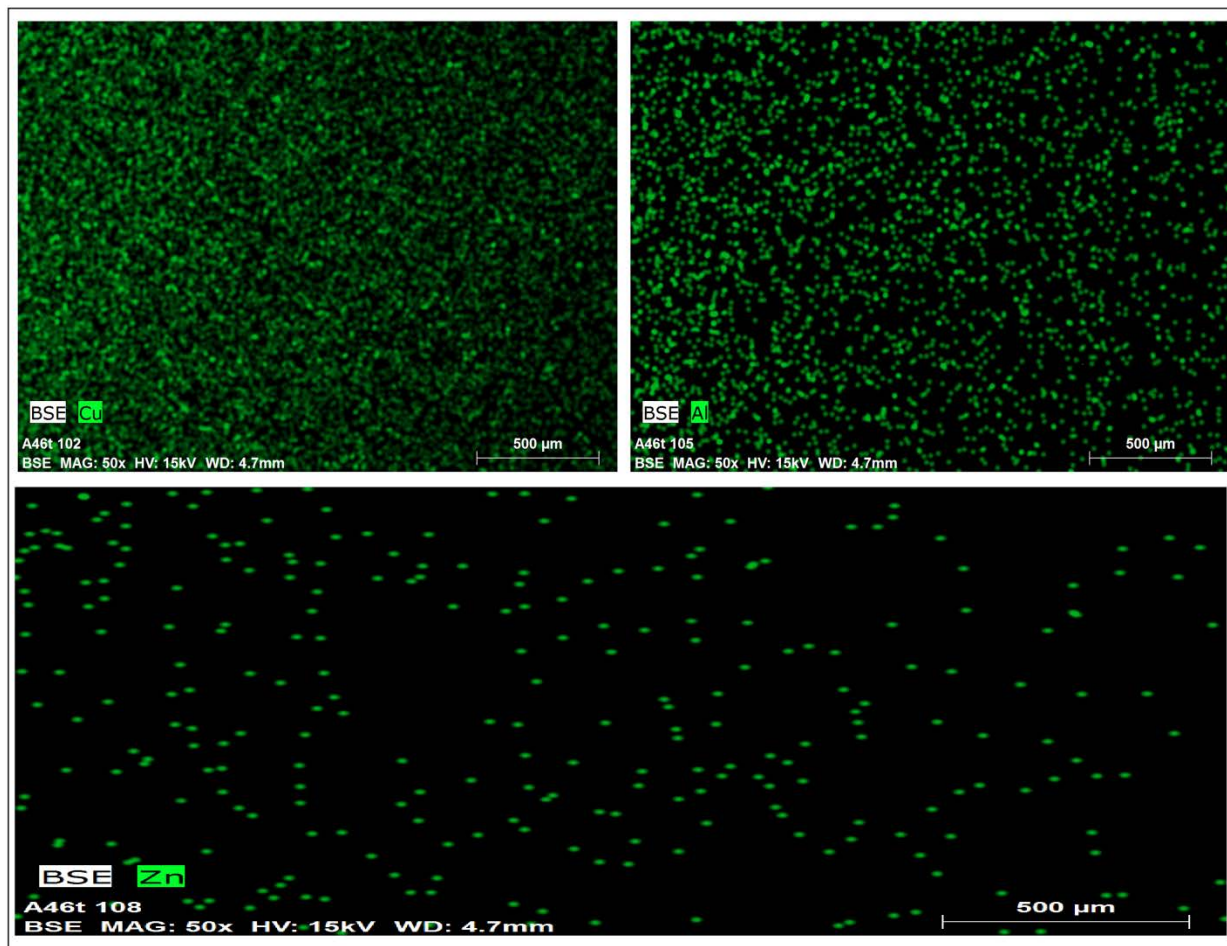


Fig.(9) : spectrum map EDS image for sample No.3

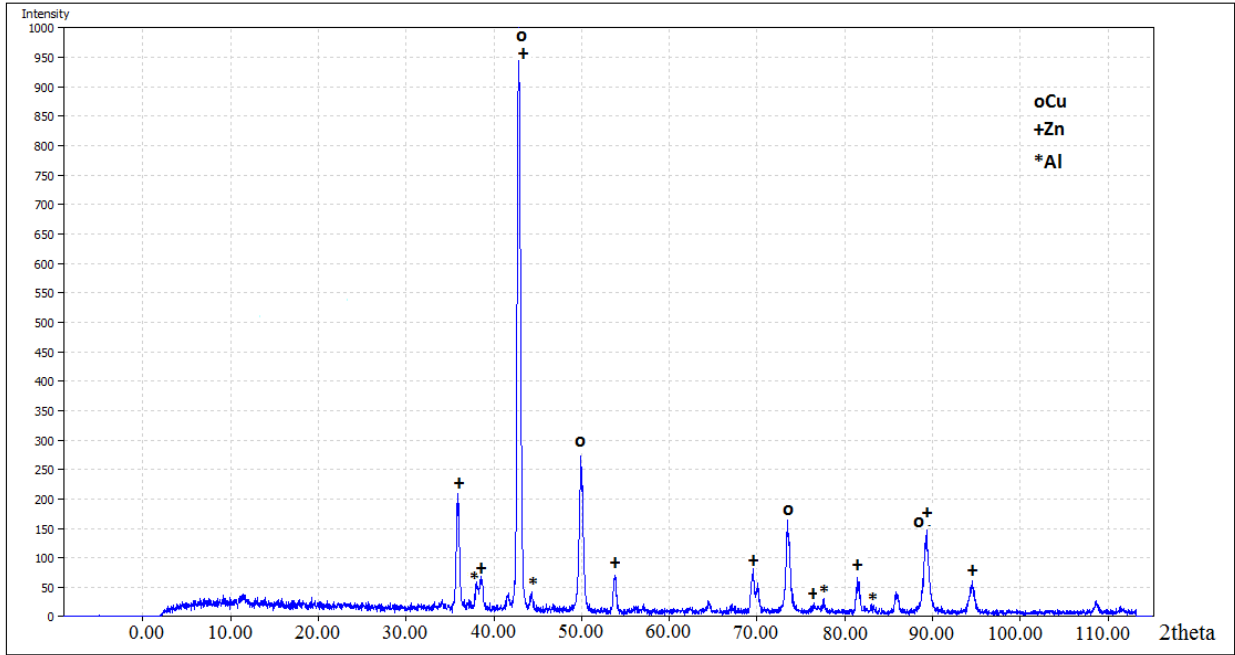


Fig.(10) : XRD test for the green compact

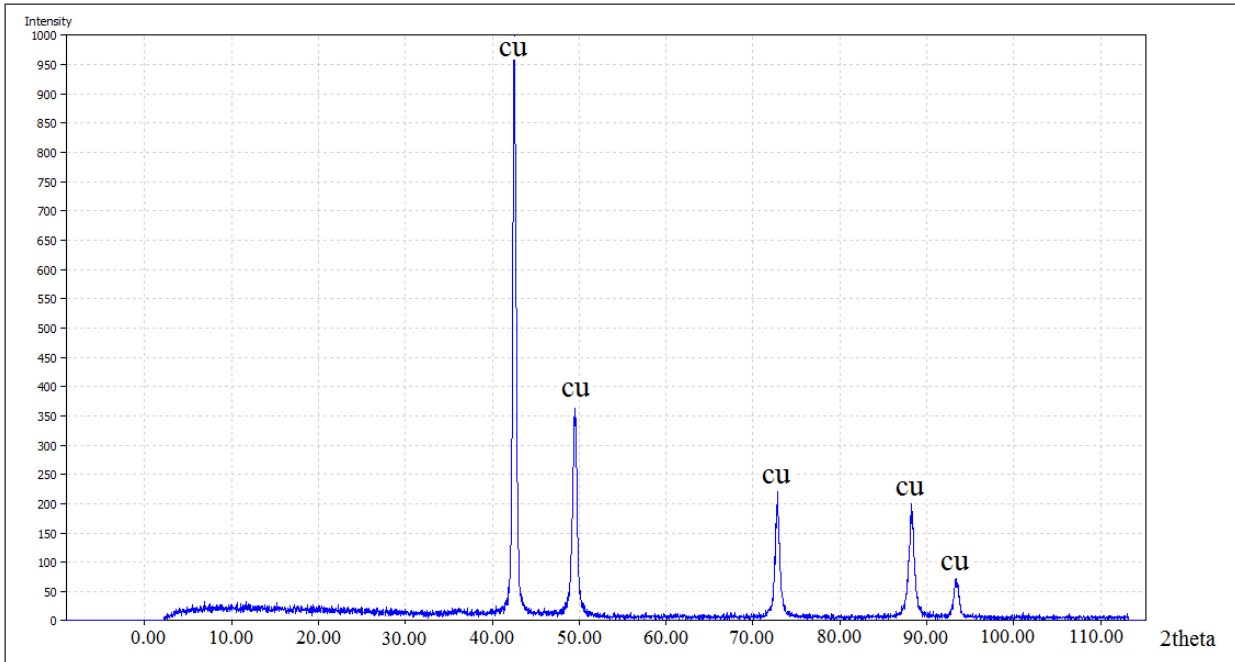


Fig.(11) : XRD test for sample No.3

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