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Research Article

Fabrication of Copper Open Cell Foam by Electrochemical Deposition Method and Investigation on the Effect of Current Intensity and Plating Solution on the Created Microstructure

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ABSTRACT

Copper foams with open cells are suitable for use in battery electrodes, catalysts, filters, sound insulation, heat and catalytic exchangers due to the unique combination of properties such as high thermal and electrical conductivity and very low density. In the current research, copper foam containing open cells are produced using polyurethane polymer substrate with the help of electroless-electrochemical deposition, combined methods. The effect of various parameters, including the current intensity of the electro-deposition process, the presence of sulfuric acid and various additives in the electrochemical plating solution, on the microstructure of produced open-cell copper foam is investigated. The purity and microstructure of the fabricated foam are analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM). Mechanical strength of the foams are evealuted with a compression test. The results show that the current intensity in the range of 0.1-0.2 A is suitable for creating a uniform deposit. Moreover, it has been shown that, copper open cell foam with a uniform microstructure can be created by applying 0.1 A current, plating duration of 48 h and with plating solution including; aqueous copper sulfate 65 g/L, sulfuric acid 30 ml/L, phosphoric acid 2 ml/L, dextrin 20 mg/L, thiourea 20 mg/L, potassium chloride 2 g/L and sodium sulfate 25 g/L. Compression test results show that the compressive strength of the foam is about 0.82 MPa, the plateau stress is 0.52 MPa, and the absorption energy is about 0.5 MJ/m^3.

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1. Introduction

Metal foams are a group of solid materials with a unique combination of properties such as stiffness with low density or high gas permeability as well as high thermal conductivity. Metal foams are made of different materials such as aluminum, nickel, copper, zinc, and stainless steel. Copper foams are suitable for use in battery electrodes, catalysts, filters, sound insulation, heat exchangers, and catalytic converters because of their high thermal and electrical conductivity and very low density [1, 2].

Metal foams are divided into two groups of open and

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closed cells. Open cell metal foams have interconnected pores, which fluid can pass through, but for closed cell foams, pores are not interconnected and therefore it can not be used as a filter. Closed cell metal foams are usually denser and require more materials to be produced, so they are more expensive to produce. Compared to open cell foams, closed cell foams have higher dimensional stability, energy absorption ability, and mechanical resistance [3].

The production process of closed cell metal foams is divided into two main groups: melting and powder metallurgy. The production process of open cell metal foams also includes: physical vapor deposition method and non-electrical and electrochemical deposition [3].

Open cell metal foams can be produced by depositing the desired metal on a polymer substrate such as polyurethane foam. Since polyurethane foam has a regular and interconnected network of pores, it can be expected that the metal foam produced by this method also has a regular network with the same size of holes. Open cell copper foams are usually produced by a combination of electroless and electrochemical deposition methods [4]. As polyurethane foam is a non-conductive material, it is necessary to make it conductive before the electrochemical deposition process. The electroless plating method is a common process to form a thin and uniform layer of conductive metal on nonconductive substrates, typically polymers. In this method, desired materials are deposited on the surface of the substrate without having to apply an electric current and by performing an oxidation-reduction chemical reaction instead. After ensuring that the substrate is conductive, the electrochemical deposition process can be used to increase the thickness of the metal deposit created in the electroless stage, to produce open cell foam with the required characteristics [5].

Open cell metal foams of nickel and copper by deposition method on the activated surface of polyurethane foam were introduced by NASA in 1974. This generation of open cell metal foams was more flexible and lighter than open-cell metal materials produced by other methods [6]. In a research, Tian and his colleagues produced copper-zinc composite open cell foam and investigated the effect of electroless deposition method parameters. In their research, a uniform layer of copper metal was formed on polyurethane polymer foam and then a zinc coating on the copper foam surface was created using electrochemical deposition method. This showed that the deposition rate in the electroless process increases with increasing temperature, pH, $CuSO_4$ concentration and formaldehyde concentration. The appropriate range of pH in electroless copper bath and the optimum temperature value was reported to be 12.5-13 and 40-50°C, respectively [5].

Shahsavan and her colleagues succeeded to produce copper open cell foam utilizing a combined electroless-electrochemical method and investigated the effect of time in the electroless and electrochemical process. Their results indicated that with the increase in the time of the electroless process, the weight of the samples increases with an almost constant slope, that becomes constant after a certain time. Additionally, it was shown that shortening the time of the electrochemical process results in the unsuficient thickness of the foam while prolonging the time causes irregular, coarse, and globular deposition of atoms on the surface [7].

Jafari Esfad and her colleagues produced nickel open cell foam using combined electroless-electrochemical methods and investigated the effect of the type of current on the mechanical properties of the fabricated foam. They showed that the nickel foam produced using direct flow has relatively high brittleness and does not have any strain until the failure stage. The results also showed that the strength of the foams produced using pulse and direct flow is almost equal [8].

However, the quality of open cell metal foams and creating a uniform coating on the surface of polymer foam depends on various parameters and has always been a challenge. In the current study, the researchers have attempted to produce copper open cell foam utilizing a combined electroless-electrochemical method. The effect of various factors on its microstructure have also been investigated. Mechanical strength of the fabricated foams are also evaluated with a compression test.

2. Experimental

2.1. Materials and methods

Polyurethane (PU) foams with an average of 10 pores per inch (PPI) and dimensions of 2×2×2 cm were used as substarte. The electroless copper plating bath contained 25 g/L $CuSO_4.5H_2O$, 30 g/L $NaKC_4H_4O_6$, 20 g/L Na_2EDTA, 25 mg/L $K_4Fe(CN)_6$, and 5 ml/L HCHO. The electrochemical bath solution composition used in this study is introduced in Table 1. In the electrodeposition process, copper coated PU foams by electroless method were used as cathode and four pure copper sheets located around the cathode were used as anodes (Fig. 1) to supply copper ions, uniformly. Futhermore, the electrolyte solution was stirred during the plating process and its temperature was kept constant at 30°C.

2.2. Procedure

The electroless plating was carried out by a multi-step process, which includes degreasing, rinsing, roughening, rinsing, sensitization, activation, and electroless copper plating. The specimens were cleaned, degreased and polished with ethanol for 5 min, and then scoured in solution (35 g/L NaOH, 25 g/L Na_2CO_3) at 50°C for 15 min to remove the dirt and release agent on the surface of polyurethane foam, firstly. The samples were then rinsed in distilled water and etched in a mixture of 1 g/L $KMnO_4$ and 0.5 ml/L H_2SO_4 solution at 40°C for 15 min to create surface anchors, for better metal atoms sticking to the polymer surface. The surface sensitization and activation was conducted by immersing the samples into an aqueous solution containing 20 g/L $SnCl_2$ and 40 ml/L HCl at 50°C for 60 min and in an activator aqueous solution containing 0.04 g/L $PdCl_2$ and 40 ml/L HCl at 50°C for 30 min, respectively. Electroless plating was carried out by immersing the activated PU foam in the electroless copper plating bath at 55°C with pH value ranges in a range of 12.5-13.0 (pH value was changed by the slow addition of concentrated NaOH solution to the electroless baths) for 7 min [5, 7].

Table 1. Chemical constituents of electrodeposition bath and their concentrations

Bath constituent	Concentration
$CuSO_4.5H_2O$	0.26 M
H_2SO_4	0.3 M
Na_2SO_4	0.17 M
Thiourea	0.00002 M
KCl	0.02 M
H_3PO_4	0.02 ml/L
Dextrin	0.02 g/L

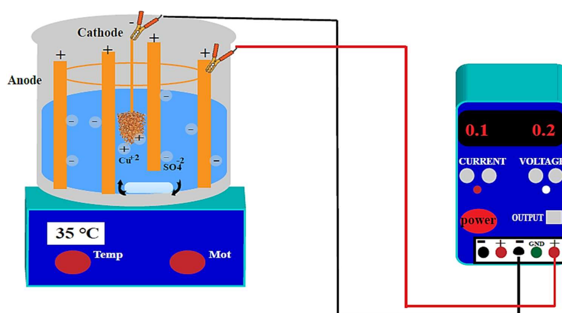

Fig. 1. Schematic of electrochemical deposition process.

In order to increase the thickness of the copper layer created by electroless process, the electrochemical deposition method was applied. In this process, the open cell foam obtained in the electroless stage is used as the cathode and four copper sheets are used as the anodes in the electrolyte. A schematic of the electrochemical deposition cell used in this research is presented in Fig. 1. When the electric current passes through the electrolyte solution, $CuSO_4$ is decomposed into Cu^{+2} and SO_4^{-2} ions, and the copper ions move towards the cathode and are reduced to copper atoms and deposited on the surface of the cathode.

The microstructure of the copper open cell foam is investigated by using scanning electron microscope (TESCAN -Vega 3 device and with a voltage of 20 kV). In order to ensure the formation of pure copper on the surface of the PU foam and the absence of copper oxide, X-ray analysis was performed (by Panalytical X'Pert Pro diffractometer and a Cu-K_α radiation source with 2θ in the range of 10° to 80°). The compression strength of the fabricated foams were evaluated by using SANTAM (model STM-150) tension-compression test machine and with a compression rate of 5 mm/min at ambient temperature.

3. Results and Discussion

The appearance of the used open cell polyurethane foam, before and after copper coating by electroless and electrodeposition processes, is shown in Fig. 2. As can be seen, no visible defects such as separation of copper deposition layer, non-uniform distribution of deposition layer, and dark color, can be seen, which is an indication of the favorable conditions of the bath and the combined process of electroless and electrochemical deposition. The favorable conditions are made possible by trial and error and by using previous research findings [5, 7, 10, 12, 14]. In this regard, at first, current intensity of 40 to 300 mA, plating time of 4 h and common plating solution introduced in previous studies [7, 14] were used to fabricate copper open cell foam, which resulted in a copper foam that lacked enough weight and strength. Therefore, for the next test, the samples were made by applying 200 mA current intensity, in 6 to 24 h time, and the same electroplating solution. The results show that the foam produced after 24 h has a weight of 5.56 g, but despite its appropriate weight, the appearance of the foam is cloudy and uneven distribution of sediment is observed in its corners. Hence, it is concluded that the applied conditions are not suitable for fabrication of suitable open cell copper foam. Appropratie conditions for producing optimal copper open cell foam and the mechanical properties of the fabricated foams are discussed in the following section.

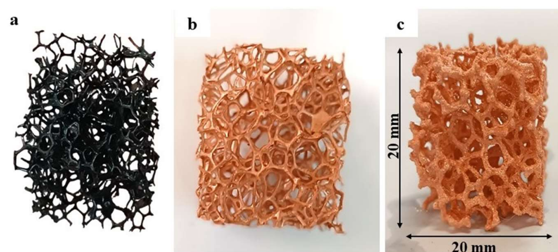

Fig. 2. The appearance of the polyurethane polymer foam, (a) before copper coating, (b) after electroless copper coating, (c) at the end of electrochemical copper deposition process.

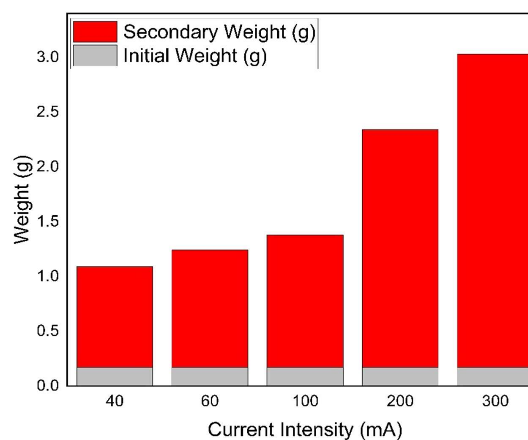

Fig. 3. The results of weight changes with current intensity during plating time of 8 h.

3.1. Morphological characterization

3.1.1. Effect of current intensity on the microstructure

The electroless open cell foams are subjected to the electrochemical deposition process by applying 40, 60, 100, 200, and 300 mA currents for 8 h. The weight changes of copper open cell foams are made by applying the above conditions presented in Fig. 3. SEM micrographs from the microstructure of copper open cell foams that are electrodeposited by applying currents of 200 and 300 mA are shown in Fig. 4. As can be seen, because of the high current value in both samples, the deposition layer is thick and globular at the edges and

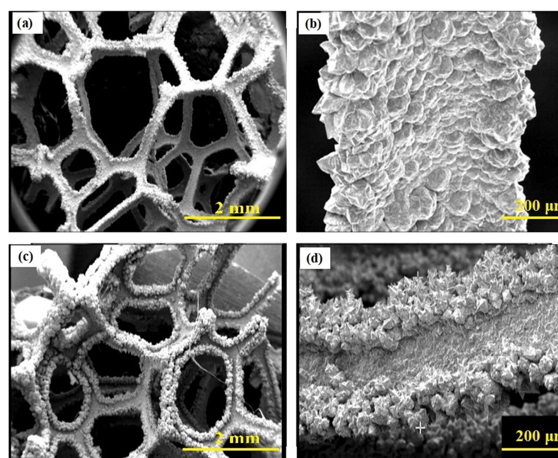

Fig. 4. SEM images of the fabricated copper open cell foam by applying different current intensities: (a) and (b) 200 mA, (c) and (d) 300 mA.

corners of the holes, but thin in other areas. This phenomenon is well known and is caused due to the increase in the growth rate of deposite by increasing current intensity and not enough time for uniformly depositing atoms on the surface of the foam.

3.1.2. Effect of sulfuric acid on microstructure

The ability of the electroplating solution in creating uniform coating on the surface of the cathode is called throwing power. The presence of sulfuric acid in the solution increases throwing power and also causes the formation of hydrogen bubbles on the surface of the cathode [11]. Therefore, sulfuric acid cannot be used in large amounts with the aim of increasing throwing power. Fig. 5 presents the SEM images of the microstructure of copper open cell foam fabricated in the absence or presence of sulfuric acid in the plating solution. As can be seen in Figs. 5(a) and 5(b), when there was no sulfuric acid in the solution, non-uniform deposit with globular morphology was formed on the surface of the foam. SEM image of the foam produced by using a plating solution containing 5 ml/L sulfuric acid is shown in Figs. 5(c) and 5(d). As it can be seen, in the presence of sulfuric acid, the shape of the deposit changed from globular to dendritic morphology. It can be concluded that sulfuric acid has an important influence on the throwing power and to some extent it can change the morphology of the deposit. To evaluate the effect of sulfuric acid on the morphology of the fabricated foam more clearly, the amount of sulfuric acid in the electrolyte solution was increased from 5 ml/L to 50 ml/L. The appearance of the foams shows that in the presence of low amounts of sulfuric acid, the shape of the deposit became dendritic and its color slightly lightened. By increasing the amount of sulfuric acid in the electrolyte solution and also by applying a constant current intensity, the voltage of the electrolyte solution (according to the ohmic relationship V=IR) decreased, due to the increase in the amount of acid causes more free H^+ ions. By increasing the amount of sulfuric acid up to 50 ml/L, the amount of created hydrogen bubbles increase, which is also evident in the microstructure of the foam (Figs. 5(e) and 5(f)) [12]. Regarding these results, the amount of sulfuric acid was chosen to be 30 ml/L to have enough high throwing power and not high hydrogen bubles evolution. Moreover, phosphoric acid in the amount of 2.5 ml/L is added to the plating solution to further increase the throwing power [12, 14].

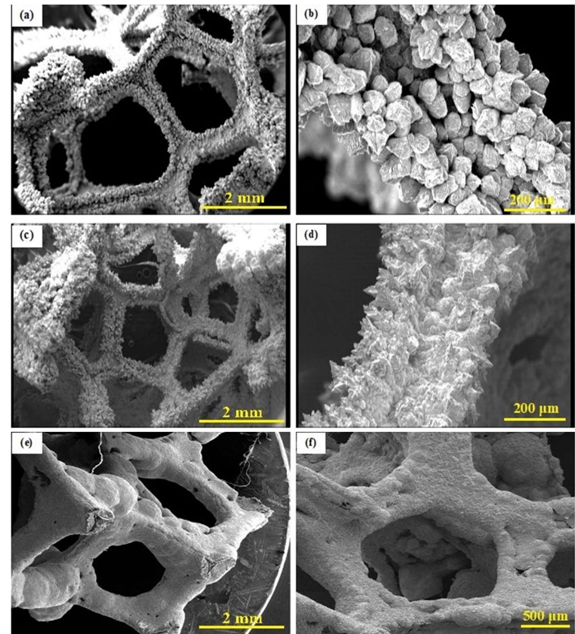

Fig. 5. SEM images of open cell copper foam in conditions of (a) and (b) absence of sulfuric acid in plating solution, (c) and (d) presence of 5 ml/L sulfuric acid, and (e) and (f) presence of 50 ml/L sulfuric acid in plating solution.

3.1.3. Effect of adding different additives in plating solution on the microstructure

The current distribution and throwing power of the plating solution are important factors for creating deposits with uniform thickness. The distance between anode and cathode affects the current distribution [13]; therefore, in this study, four pure copper sheets were used as anodes in the electrolyte so that all four faces of the foam are at the same distance from the anode so that the current distribution for the foam is uniform (Fig. 1). The results of this research, similar to the results presented by other researchers, showed that the common plating solution compounds are not completely effective in forming a uniform and clear deposit [7, 9]. Therefore, the reserarchers attempted to use additives to improve the uniformity of the deposit. These additives are introduced in Table 1. In this regard, thiourea, as a brightening agent, sodium sulfate, as a wetting agent, sulfuric and phosphoric acids, for increasing the throwing power of solution, dextrin, with the aim of increasing the current density, and potassium chloride, as a gap filler, are used [14]. Fig. 6 depicts the SEM images of the microstructure of the copper foam

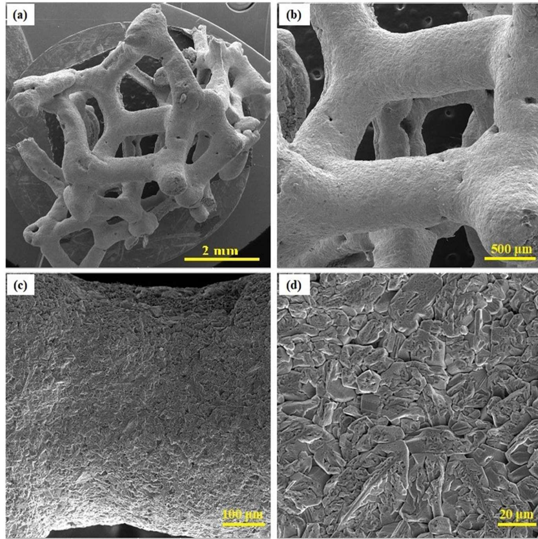

Fig. 6. SEM images of the copper open cell foam produced under the conditions introduced in Table 1.

fabricated by using the plating solution introduced in Table 1 and the applied current intensity of 100 mA, the deposition time of 48 h, and pH in the range of 0.5-0.6. The weight of the open cell foam produced under these conditions was measured as 6.33 g. As can be seen, the deposit has a favorable uniformity although containing limited holes that are caused by the formation of hydrogen bubbles.

The XRD analysis of the fabricated copper foam, by applying 100 mA current at 30°C for 48 h in the solution introduced in Table 1 is presented in Fig. 7. The peaks related to (111), (200) and (220) planes correspond to the 2θ angles of 43.6°, 50.8° and 74.4°, respectively, which confirm formation of pure copper. Additionally, as it is clear, no peaks for the copper oxide or other second phases are presence in the XRD pattern.

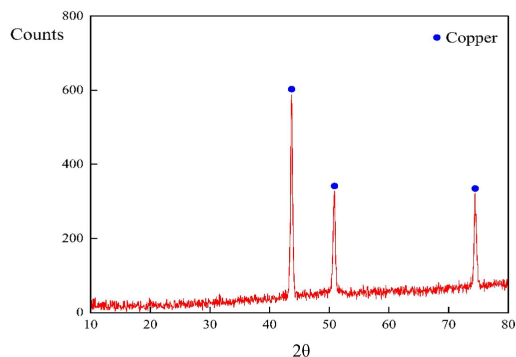

Fig. 7. X-ray diffraction pattern of the fabricated copper open cell foam.

3.2. Compression strength of the fabricated copper open cell foam

The compression test was performed on the copper open cell foam fabricated under optimum condition according to ISO 13314. Fig. 8 shows the copper foam fabricated by the electrochemical deposition method before and during the compression test. The SEM images of the copper foam after compression test is shown in Fig. 9. According to Fig. 9, the junctions between struts and nodes are the primary locations where failures occur. The nodes have a robust, geometric structure that enables them to withstand external stresses effectively, resulting in high structural strength and

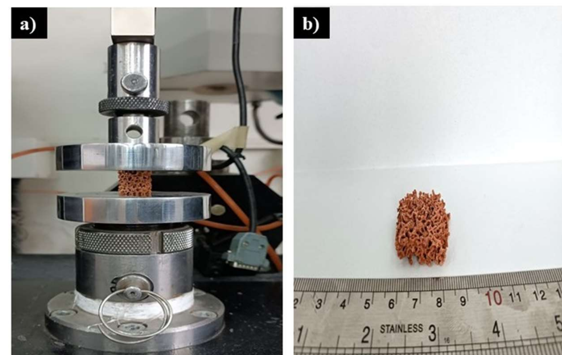

Fig. 8. Copper foam (a) before compression test and (b) after compression test.

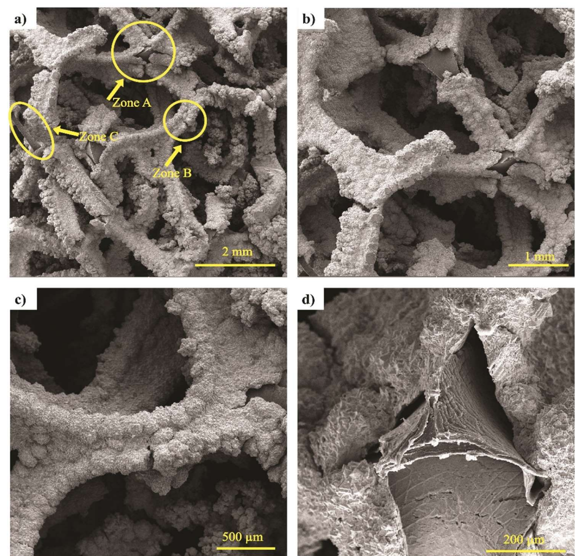

Fig. 9. SEM images of copper foam microstructure after compression test: (a) critical zones following compression test, (b) and (c) higher magnification fractured struts and nodes, (d) fracture behavior of both polymer and copper coating.

geometric stiffness. These attributes help maintain their structure until the point of collapse, which prevents them from experiencing the same failures observed in other areas [15].

Fig. 10 depicts the stress-strain graph for compression test of the copper open cell foam. According to the literature, the following three areas can be easily detected: an initial elastic zone, plastic deformation and energy absorption zone, and an ending region, where foam failure occurs. At low strains, the foam behaves almost linearly, so that as the strain increases, the stress also increases. The compressive strength of the copper foam is 0.82 MPa. In the second zone, the strain increases around an almost constant stress, which is called the plateau stress. the plateau stress is calculated as 0.52 MPa. Finally, with the crushing of the cell walls, the stress increases greatly, and in this case the foam is completely destroyed.

The capability of metal foams to absorb energy is a crucial application in various fields. To evaluate the characteristics of metal foams, the two aspects are their capacity to absorb energy (U) and their energy absorption efficiency (E). The amount of absorbed energy is actually the level under the stress-strain diagram until the end of the plateau strain, which is calculated by using the following equation [15]:

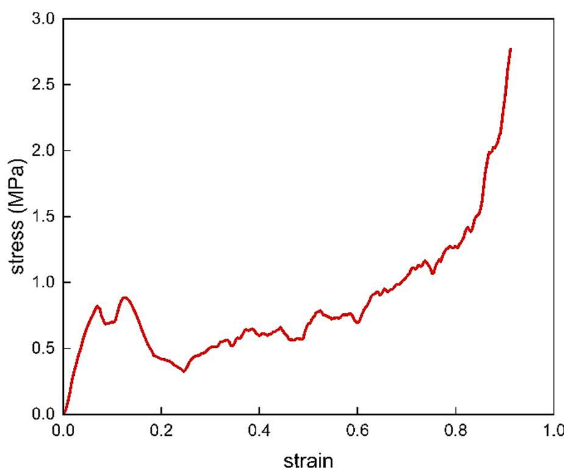

Fig. 10. The compressive stress-strain curve of the fabricated copper foam.

$$U = \int_0^{\varepsilon} \sigma \, d\varepsilon \quad (1)$$

where ε and σ denote strain and stress, respectively. For the fabricated copper foam, the amount of absorbed energy is estimated around 0.50318 MJ/m^3. The absorption energy at different strain and stress is presented in Fig. 11. It is clear that by increasing the strain, the energy absorbed also increases (Fig. 11(a)). According to Fig. 11(b), the copper foam exhibits minimal energy absorption at stress levels below 0.5 MPa. This can be attributed to the stress-strain curve's linear deformation stage. However, the copper foam exhibits higher energy absorption in the stress levels ranging from 0.5-1 MPa, which can be explained by the stress-strain second region [17].

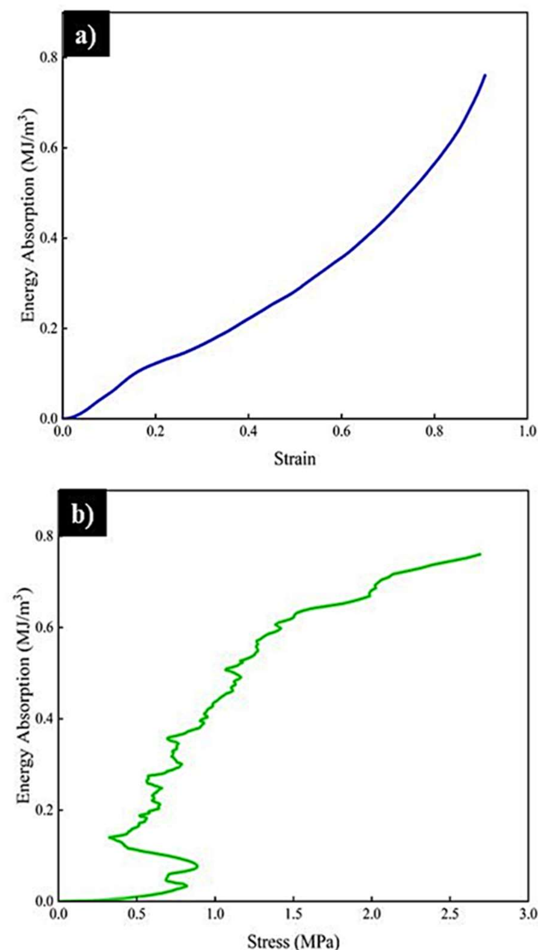

Fig. 11. Energy absorption of copper foam at (a) different strain and (b) different stress.

4. Conclusion

In this study; copper open-cell foam was produced by using the electroless-electrochemical combination method and the effect of various parameters such as current intensity, presence of additives such as thiourea, sodium sulfate, phosphoric acid and dextrin in plating solution on its microstructure quality was investigated. Moreover, the mechanical properties of the copper open cell foam fabricted under favorable conditions was investigated through a compression test. The results of this research can be summarized as follows:

- In the fabriacted copper open cell foam, there are no visible defects such as separation of copper deposition layer, non-uniform distribution of deposition layer and dark color, which is an indication of the favorable conditions of the bath and the combined process of electroless and electrochemical deposition.
- The geometry of the foam is such that the high current intensity cannot be used for creating the uniform deposition layer. The high current causes thick and globular deposits on the edges and corners of the holes. Current intensity in the range of 100-200 mA, is suitable for creating a uniform deposit.
- The presence of sulfuric acid in the solution increases the throwing power and also causes the formation of hydrogen bubbles on the surface of the cathode. Therefore, sulfuric acid cannot be used in large amounts with the aim of increasing the throwing power. The presence of phosphoric acid along with the sulfuric acid in the solution helps to increase the throwing power without unacceptable amounts of hydrogen evolution.
- Copper open cell foam with a uniform microstructure fabricated by applying current intensity of 100 mA, a plating time of 48 h by using plating solution including compounds: aqueous copper sulfate 65 g/L, sulfuric acid 30 ml/L, phosphoric acid 2 ml/L, dextrin 20 mg/L, thiourea 20 mg/L, potassium chloride 2 g/L, sodium sulfate 25 g/L.
- The compressive strength of the fabricated copper open cell foam in this research is evaluated at about 0.82 MPa, plateau stress at 0.52 MPa, and absorption energy of about 0.5 MJ/m^3.

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Conflict of Interests

The authors declare no conflict of interest.

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