SINTERING OF COPPER LAYERS WITH A CONTROLLED POROUS STRUCTURE

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Abstract

The aim of the experiment was to study the technique of production of porous metal foams by reduction of metal oxides during sintering. The foams were produced by powder metallurgy. This technique allows us to combine irregular cellular structures with open or closed pores. The porosity range is largely dependent on the component materials, i.e., the type and size of particles. The porosity is also affected by the ratio of metal oxide to matrix metal. To obtain a porous structure, it is necessary to apply a metal oxide that is easy to reduce by the protective atmosphere during the sintering process. The porous metal foam technology is suitable to produce components similar to those obtained by powder metallurgy. The process was slightly modified to produce porous layers on elements used in heat transfer exchangers. The study concerned layers with the pre-determined porosity, layer thickness and open pores on heat exchangers made of electrolytic copper which operate at boiling heat transfer. The porous layers were produced by sintering and reduction of a mixture of copper and copper oxide powders varying in grain size.

Keywords: Powder metallurgy, metallic foams, sintering

1. INDRODUCTION

1.1 Production and properties of metal foams

Metal foams are a new type of material with a wide range of applications because of their excellent properties including light weight, impact energy absorption capacity, specific thermal acoustic properties and low thermal conductivity [1, 2, 3]. Open porous metallic foams have been used in heat and mass transfer applications, for instance in heat pipes, vapor chambers, and loop heat pipe elements. In the past few years, there has been a growing interest in metal foams. Both the foam structure and the pore morphology depend on the fabrication method. M.F. Ashby et al. [1] classify the metal foam production methods according to the process and the state of matter. Nine process-routes have been developed and five of them have already been established commercially. They fall into four broad classes: those in which the foam is formed from the vapor phase; those in which the foam is electrodeposited from an aqueous solution; those which depend on liquid-state processing; and those in which the foam is created in the solid state. Each method can be used with a small subset of metals to create a porous material with a limited range of relative densities and cell sizes. Some produce open-cell foams, others produce foams in which the majority of the cells are closed. Similar classification was presented in the paper by G.J. Davis et al. [2]. The superior thermal conductivity of copper foams is particularly important. Porous sintered structures can also be produced by sintering small diameter wires. [4]

The powder metallurgy process appears particularly well-suited for the production of open cell structures intended for use in heat transfer processes. A common technique is the space holder technique. Parvanian A.M. et al. [5,6] used potassium carbonate to produce open cell copper foams. K_2CO_3 plays the role of the void space holding agent, which can be removed either by thermal decomposition or aqueous dissolution. Another type of space holder materials was investigated by Hangai Y. et al. [7]. They used a mixture of metal powder and soluble powder as a space holder (sodium chloride). The above works have greatly contributed to the development of the ideas presented by Y.Y. Zhao and D.X. Sun [8]. Another method providing good results is the production of pores through electrodeposition [9, 10] and sintering of materials with significantly different melting points, such as Cu and Al. The sintering process is carried out gradually, with a different temperature at each stage. In the case of Cu-Al nanofoam, the sequence 450, 700 and 900 degrees Celsius was necessary [11]. The infiltration technique proposed by Bednarova V. et al. [12] is still another method of production of Cu foams. Porous metallic material produced by shaping a melted metal do not require further forming, welding, machining or forging. The findings of the previous research on porous capillary copper fiber structures for heat transfer applications were used to develop a new technique of production of Cu foams.

2. EXPERIMENT

The investigations initiated at the Kielce University of Technology (Poland) focused on the use of porous metal foams as capillary films with predetermined structure parameters deposited on heating surfaces. It was assumed that the metal foams should be produced using a well-known and proven process, and cheap and easily accessible materials and technologies. Also, the number of operations should be reduced to a bare minimum. From the analysis it was evident that sintering of metal powders in a protective atmosphere was the best alternative. A powder mixture of copper and copper oxide was deposited on a copper substrate. The layers were sintered in an atmosphere of dissociated ammonia. The reduction of copper oxides resulted in the formation of diffusion-type pores. The sintering was carried out at a temperature of 950 °C for 45 minutes. During sintering, copper oxide reacted with hydrogen:

$$Cu_2O + 2H = 2Cu + H_2O.$$

Copper oxide was reduced to pure copper and hydrogen bonded with oxygen to form water vapor. As a result of this reaction, the mixture of copper powder and copper oxide powder was converted into a porous layer. The porous layer was sintered and simultaneously diffusion bonded with the copper substrate. The technology is protected by Polish patent No. 199720 [13]. The experiment was performed using electrolytic copper powder with a particle size of 45 - 63 microns. The copper oxide powder was produced by heating Cu powder in air at 850 °C. The particle size of copper oxide powder ranged from 80 to 200 microns. The particles of the copper and copper oxide powders are shown in **Fig. 1**.

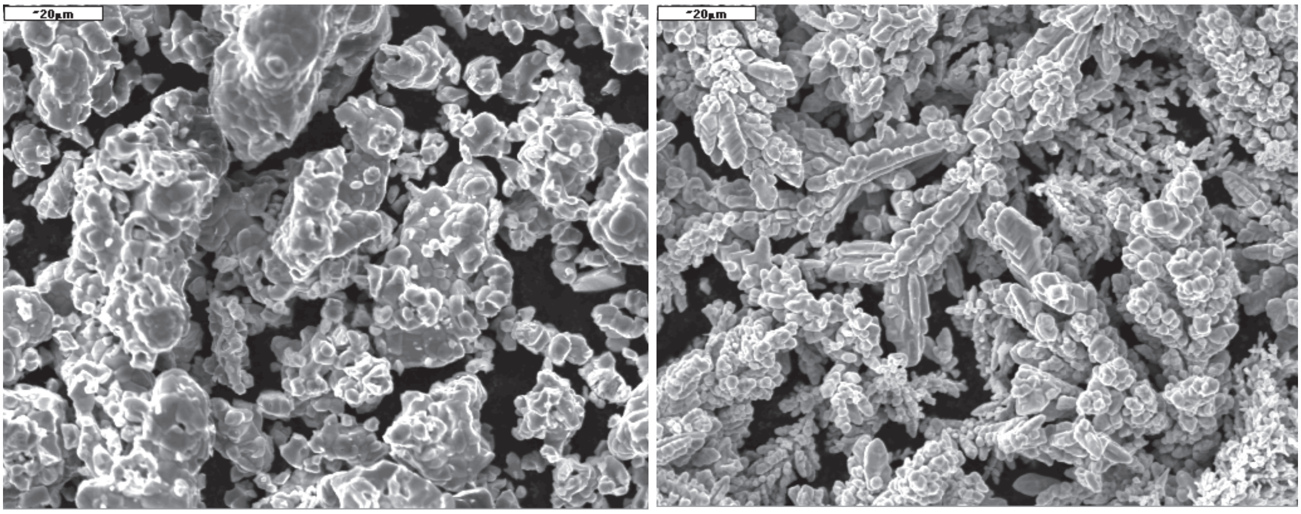
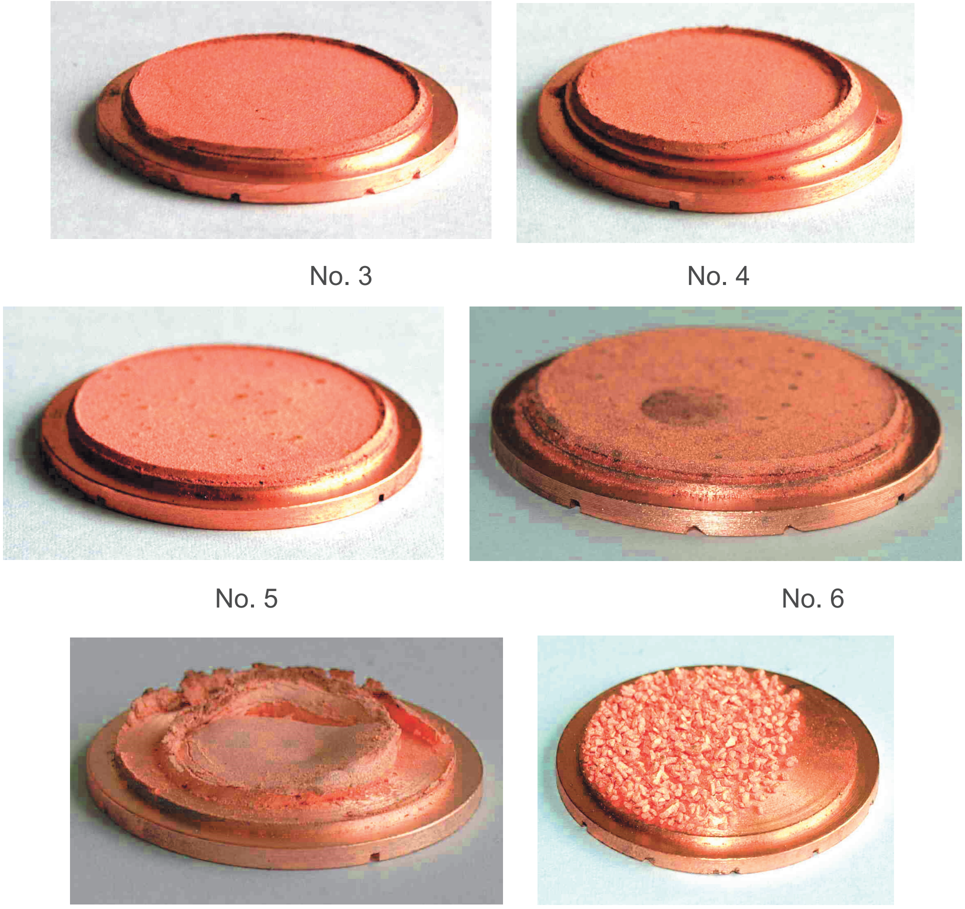


Fig. 1 Particles of the copper powder A (left) and particles of the copper oxide powder B (right) observed with a scanning microscope

Table 1 Parameters of making porous layers

Sample number	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Grain size Cu (μm)	45-63	45-63	45-63	45-63	-	-
Grain size Cu_2O (μm)	80<	80<	80-250	80-250	80<	>250
Proportions Cu / Cu_2O	3.5 g / 3.5 g	0.5 g / 1 g	0.8 g / 4 g	3.5 g / 3.5 g	Only Cu_2O	Only Cu_2O

A series of samples were produced. They differed in the ratio of copper to copper oxide and the size of particles of the copper oxide powder. The table above presents samples with predetermined geometric criteria. The distribution and size of pores were modified by changing the content and grain size of the copper oxide powder. Tests were conducted to study the application of the different porous layers to boiling heat transfer.


No. 3 No. 4

No. 5 No. 6

No. 7 No. 8

Fig. 2 Macrophotography of specimen with porous layers

3. RESULTS

3.1 Metallographic analysis

The samples were cut perpendicular to the plane of the substrate surface. The analysis shows the boundaries of copper grains and the structural effects of pore cavities. **Fig. 3** illustrate the structure of the samples observed with a Nikon MA 200 light microscope.

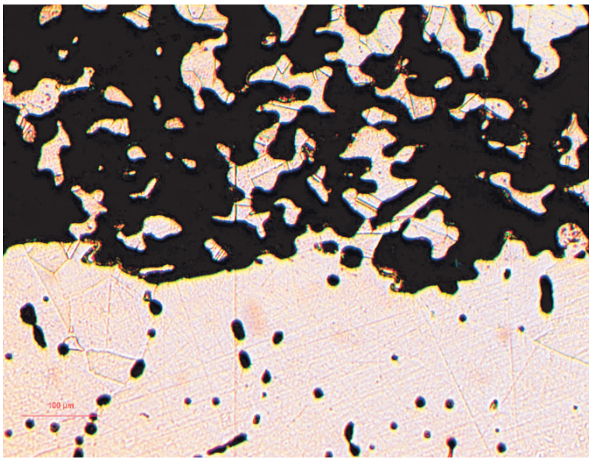


Fig. 3 Microstructure of the specimen No. 6

The porosity was studied using an NIS 4.20 image analyzer. **Fig. 3** shows an image of the porous structure of sample No. 6 formed on a flat copper substrate by diffusion bonding. Considerable expansion of the heat transfer surface inside the structure was achieved. It should be noted that the non-uniform distribution of pores was due to the diversity of the Cu_2O powder particle size. There are bridges connecting the porous layer with the copper substrate surface.

A quantitative analysis of the microstructure of sample No. 6 was conducted to determine its porosity. It was necessary to determine the number of pores per unit of the polished surface for different cross-sections. 37 areas of the structure were analyzed. The average porosity was 59.2 %.

3.2 Experimental results concerning boiling heat transfer

Two samples were produced made using the electrochemical method (Nos. 1 and 2) and six were made by sintering a powder mixture of copper and copper oxide. The samples were tested to determine the heat transfer coefficient. The study focused on the behavior of the porous layers at boiling heat transfer in a large volume of water, ethanol and fluorinert. **Fig. 4** shows the boiling curves obtained for samples 1 and 6 and a sample with a smooth surface [14].

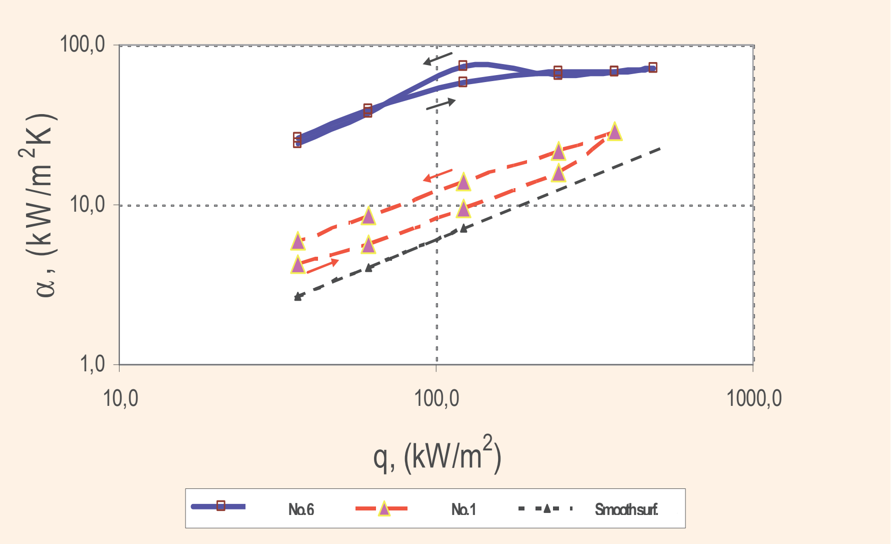


Fig. 4 Comparison of the heat transfer coefficients for samples 1, 6 and a smooth surface sample, with ethanol as a medium [14]

Offset curves to the left boiling, compared with a smooth surface boiling curve shows proves heat transfer intensification. For the sample No. 6 is considerable intensification. The strengthening of the heat exchange ratio provides heat transfer coefficients for the surface covered with a layer of porous α_p the residue to the coefficient for a smooth surface, i.e. α_g. It reached a maximum value of 11.5 for the sample No. 6 and ethanol as boiling. For boiling ethanol small hysteresis heat exchange is shown. This phenomenon hysteresis seen from properties of the liquid penetrating small wetting angles, resulting in the deactivation of potential nucleation centres.

4. DISCUSSION OF RESULTS

As a result of the planned experiments achieved the desired effect. The resulting layer of that meet the expected geometrical parameters. Thermal tests have shown great development potential of the presented technologies. T.M. Wojcik in his work [15] showed how they function layer formed during boiling volume related to the structure of the copper mesh and the technically smoothed surfaces. Performed results were in line with the assumptions. The scope of possibilities adjustment geometric of Cu metallic foam parameters produced by described method is less than methods of using space holder technique. [3 4, 5, 6]. However, it is competitive regarding the techniques based on the methods electrodeposition. [9, 10]. The range of possibilities to control the structure is even greater than the cited works. Using feedstock’s with the appropriate particle size can make possible with this technique to prepare materials with pores of nanometric size. This would be a competitive solution relatively to the reported [11] because it is pure copper resulting structure without the need for Al dealloying process. To study the structure appears necessary to employ methods of X-ray CT [16]. The current state of development of these methods allows their effective use in studies of geometric structure of metallic foams. Presented at work the results of porosity measurements are the result of the application of image analysis on cross sections. These values are consistent with the calculations carried out on the basis of the geometrical dimensions of the metallic foam and their mass.

CONCLUSIONS

The paper presents the method of production of porous structures deposited on a flat copper substrate to be used in pool boiling heat transfer applications. The layers contributed to a significant improvement in the heat transfer coefficient. The best results were obtained for a sample produced by sintering a powder mixture of copper and copper oxide in an atmosphere of hydrogen. A more than 11-fold increase in the heat transfer coefficient was reported. To obtain developed microstructures with increased amount of nucleating centres the research required cooperation of specialists from different disciplines including metal science and heat transfer. Also from the economic point of view, the method is advantageous because it can be commonly used in industry.

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