

ELECTRON PERCOLATION IN COPPER INFILTRATED CARBON

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The work describes the dependence of the electrical conductivity of carbon materials infiltrated with copper in a vacuum-pressure autoclave on copper concentration and on the effective pore radius of the carbon skeleton. In comparison with non-infiltrated material the electrical conductivity of copper infiltrated composite increased almost 500 times. If the composite contained less than 7.2 vol% of Cu, a linear dependence of the electrical conductivity upon copper content was observed. If infiltrated carbon contained more than 7.2 vol% of Cu, the dependence was nonlinear – the curve could be described by a power formula $(x - x_c)^t$. This is a typical formula describing the electron percolation process in regions containing higher Cu fraction than the critical one. The maximum measured electrical conductivity was $396 \times 10^4 \Omega^{-1} \text{m}^{-1}$ for copper concentration 27.6 vol%. Experiments and analysis of the electrical conductivity showed that electron percolation occurred in carbon materials infiltrated by copper when the copper volume exceeded the critical concentration. The analysis also showed a sharp increase of electrical conductivity in composites with copper concentration higher than the threshold, where the effective radius of carbon skeleton pores decreased to 350 nanometres.

Key words: skeleton composites, electron percolation, infiltrated carbon, porous structure

1 INTRODUCTION

Carbon materials feature a spectrum of physical and chemical properties which are unique and in many cases non-substitutable. In particular, the ability to conduct electric current and heat, elastic oscillations, sliding self-lubricating properties, porous skeleton, stability of both chemical and electric potential, dimensional stability and rigidity at high temperatures, and anti-corrosive properties at low temperatures. One of the most promising applications of the carbon material is its use as an electric conductor. This feature is used in current collectors in dynamic applications, in electrodes for electric current transmission in metallurgy, electrodes in accumulators and batteries, and resistant heating bodies for high temperatures.

In all these fields, new carbon materials with electrical properties suitable for current conduction are being developed. The electrical conductivity of carbon is on the level of semiconductors while the mechanism of electric charge transport is determined by excitations of electrons from the valence band to the conduction band. Electrical conductivity of the carbon material is defined by

$$G = \frac{\eta e^2 L}{m v_d} \quad (1)$$

where m is the effective electron mass, v_d is the drift velocity, η is the free electron content per unit volume, e is the electron charge and L is the mean free path of electrons.

Electrical conductivity of polycrystalline carbon material is on the level of $0.1 \times 10^4 \Omega^{-1} \text{m}^{-1}$ to $20 \times 10^4 \Omega^{-1} \text{m}^{-1}$ [1,2]. One way how to increase its electrical conductivity is its infiltration by electrically conductive metals such as copper and its alloys. This creates a composite in which the carbon porous material is the skeletal matrix and copper forms conductive clusters that copy the porous structure of the carbon matrix.

The carbon matrix contains a continuous system of pores. According to the technology of graphite material preparation many authors divide the pore structure into macropores (diameter larger than 50 nm), mesopores (between macro- and micropores) and micropores with diameter not exceeding 2 nm (average 1.5 nm) [3-5].

Macropores originate during the process of pressing the grains of the basic carbon powder and they are formed by interparticle porosity. Transition pores are pores inside individual grains of powder. Micropores mainly reflect the microstructure of pores between crystallites and cracks in the structure of the basic raw materials. Infiltration of metal into the porous structure results in a structure called "skeleton in skeleton".

The matrix skeleton consists of polycrystalline carbon material and the secondary skeleton consists of a metal phase. According to the linking of the secondary phase, there are three different types of skeleton composite structures [6].

The first type is characterized by perfect interconnection of a continuous cluster of secondary components resulting in the maximum mutual surface contact. The sec-

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ond type contains continuous and non-continuous interconnected clusters. The third type contains isolated locations which are not interconnected and have a minimal mutual surface contact.

Since there is no chemical reaction between the carbon matrix and the infiltrating metal and also due to the poor wetting angle between the matrix and the liquid copper only a mechanical bond is formed between the skeletons. There is an interface between skeletons which bears mechanical loading and dissipates the elastic energy. Mechanical stress is transferred by friction forces.

A physical bond is formed when the composite interface energy is created with a lower interface energy than the sum of the surface energies of individual components. The effect of the physical bond of individual components on the transport properties is stronger than in the case of the mechanical bond.

A chemical bond arises if a new phase of the composite is formed at the interface of individual components. This bond may create qualitative changes in the structure of the composite components. The technology of metal infiltration into a porous skeleton is similar to the method of mercury porosimetry.

Generally, the wetting properties of carbon and liquid metals are very poor. In this case $\sigma \cos \theta < 0$ for wetting angle $\theta > 90^\circ$, where σ is the surface tension of the liquid metal. Infiltration is based on injection of liquid metal into a porous substance by means of an external pressure P_{ext} . The Laplace equation shall apply to the capillary pressure P_c below the curved surface of the liquid as

$$P_c = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2)$$

where R_1 , R_2 are the radii of surface curvature in X and Y directions. The mean curvature R of the spherical meniscus surface is determined as

$$\frac{1}{2R} = \frac{1}{R_1} + \frac{1}{R_2} \quad (3)$$

Usually, the cylindrical pores in X and Y directions are the same and in order to simplify the problem an effective radius r_{eff} was introduced. It depends on the pressure to which the cylindrical pore with radius R is filled. The Washburn equation (4) for the effective radius r_{eff} was derived from it

$$r_{eff} = - \frac{2\sigma \cos \theta}{P_c} \quad (4)$$

This equation shows that the smaller the effective pore radius r_{eff} , the bigger the increase in capillary pressure P_c . For the wetting angle $\theta > 90^\circ$, which is usually measured for most of liquid metals on a graphite surface [7], the capillary pressure shall force out the liquid metal from the porous structure. Due to the external pressure $P_{ext} = -P_c$ rule, the gradual increase in the infiltration pressure on the liquid metal will fill in smaller pores. Filling the pores creates the conductive clusters which may be linked to each other at higher pressures. Increasing the

infiltration pressure will lead to an enlargement of the interface between components of the skeletal composite. The objective of this work is to identify the dependences of electrical conductivity of the carbon material on the infiltrated copper contents.

Infiltration of copper alloy to carbon and investigation of the composite structure are described in [8,9].

2 EXPERIMENTAL PROCEDURES

For the experiment it was important to prepare samples of carbon with various contents of copper. Their electrical conductivity was then measured and the results were analysed. The technological process of sample preparation consisted of two stages: preparation of carbon matrix skeleton samples, and infiltration of carbon samples with liquid copper.

The carbon skeletons were prepared by the typical technological process for preparing carbon materials using the powder metallurgical method. As a raw material, polycrystalline carbon -graphite - was used with a turbostratic structure (KU 111 L), commercially produced by KOMPOZITUM Ltd., pressed for the needs of experiments to 20 MPa. Samples with dimensions $12 \times 12 \times 42$ mm³ were subsequently infiltrated with copper by means of a laboratory vacuum-pressure autoclave. Liquid copper does not wet the carbon surface because the wetting angle θ is high ($\theta = 140^\circ$), [7]. A gradual increase in infiltration pressure resulted in obtaining samples with gradually higher copper content. The different batches of porous carbon samples were infiltrated by different external pressures that increased from 0.1 to 6 MPa, so that various concentrations of the metal in graphite were obtained. The metal concentration was measured by weighing the difference before and after infiltration using Sartorius Model MA45 scales. The maximum value of the copper content in the samples was 27.1 vol%. The infiltrated samples were subsequently machined to a diameter of 10 mm and length 30 mm. The structure of the samples was observed by an optical microscope.

Electrical characterization of the samples was performed using a four-point method on a test stand. The voltage on the test sample was measured at a distance of 20 mm by nanovoltmeter Agilent 34401A. The current through the sample was 1 A. The electrical conductivity G was then calculated according to formula

$$G = \frac{4l_x}{\pi d^2 R_N} \frac{U_N}{U_x} \quad (5)$$

where l_x is the voltage contact distance, d is the diameter of sample, R_N is the resistivity of a standard sample, U_N is the voltage measured on the resistivity standard and U_x is the voltage on the measured sample. The normal resistance R_N was 10 Ω . The temperature was 23 $^\circ\text{C}$ and the relative humidity 54%. The relative error of measurement was estimated as

$$\frac{\Delta G}{G} 100\% \leq 2.4\%. \quad (6)$$

3 RESULTS AND DISCUSSION

The measured values of electrical conductivity versus Cu concentration are shown in Fig. 1. At low metal concentrations, region I, the dependence of electrical conductivity is linear. At high metal contents, region II, above a critical copper concentration x_c , there is a clear deviation from the linear dependence.

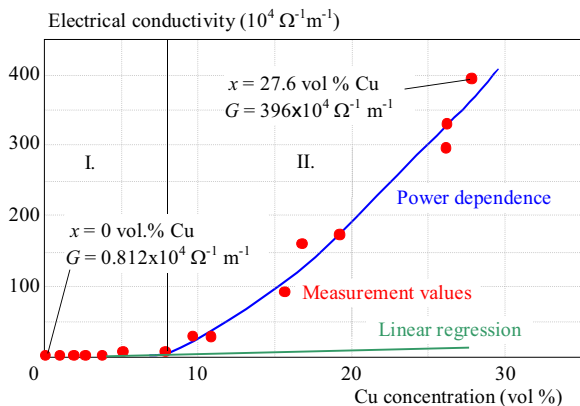


Fig. 1. Dependence of electrical conductivity G on Cu volume fraction, critical concentration is 7.2 vol% of Cu

This type of curve is typical for electron percolation. Bhlapibul and Pruksathorn described in [10] electron percolation where one component was graphite that formed more conductive clusters. Chen *et al* [11] described carbon binder additives in Li-ion battery cathodes. In [12] authors presented electrical conductivity measurements of the Cu matrix composites reinforced with carbon nanofibers. The existence of a percolation threshold was observed in [13] where the Cu-graphite composite was prepared by hot isostatic pressure from powder raw materials.

The principle of electron percolation is explained by means of a bond theory called the bond problem, first introduced in mathematics by Broadbent and Hammersley [14].

Electrical conductivity G_c above the non-conductor – conductor transition is given by the power law

$$G_c \propto (x - x_c)^t \quad \text{for } x \geq x_c \quad (7)$$

where x is the volume concentration of the conducting phase, x_c is the critical concentration, and t is an exponent. The quotation with power exponent t is valid in the region conductivity near the percolation threshold.

In the subcritical region, thus for $x < x_c$, the composite contains no infinite clusters. In this range the conductivity can be approximated by a linear dependence

$$G_{lin} = a_0 + a_1x. \quad (8)$$

A critical phenomenon may occur in the binary system where components of the binary system are in conductivity contrast (conductor – insulator). This condition where

the electrical conductivity of copper and carbon is only partly met since copper conductivity is 100 – 1,000 times bigger than carbon conductivity. The percolation condition, thus the contrast between electrical conductivities of individual components, is not met as the conductivity is influenced by the lower conductivity second component so called background.

Coexistence of the critical cluster and of the linear background could be represented by two electrical resistors connected in parallel according to Matthiessen’s rule. Then the resulting electrical conductivity G is given by the sum the electrical conductivity of the background, G_{lin} , and of the conductivity due to electron percolation, G_c

$$G = \begin{cases} a_0 + a_1x, & \text{for } x < x_c \\ a_0 + a_1x + a_2(x + x_c)^t, & \text{for } x \geq x_c \end{cases} \quad (9)$$

where a_0, a_1, a_2 are constant factors.

The critical concentration of copper $x_c = 0.072$ (7.2 vol%) and exponent $t = 1.39$ were determined by curve fitting of experimental data while maximizing the correlation coefficient. For metal concentrations $x \geq 7.2$ % the linear component is negligible and the electrical conductivity is described by a power type of function typical for electron percolation.

To achieve high metal concentrations, high external pressures P_{ext} had to be applied. The higher the external pressure, the smaller pores were filled with metal. The pore structure in the case of infiltration can be characterized by an effective pore radius which indicates which pore dimension in the graphite sample was filled-in with metal. According to the Washburn equation (4) the effective pore radius depends on the infiltration pressure. The effect of pore filling on electrical conductivity is demonstrated in Fig. 2. One axis of dependence is electrical conductivity G , the other axis is the effective pore radius r_{eff} . The values of both the surface tension and the liquid wetting angle of copper on graphite were obtained from the literature. According to [15] the surface tension of copper is $\sigma_{Cu} = 1.285 \text{ Nm}^{-1}$ and according to [7] the wetting angle of copper is $\theta_{Cu} = 140^\circ$.

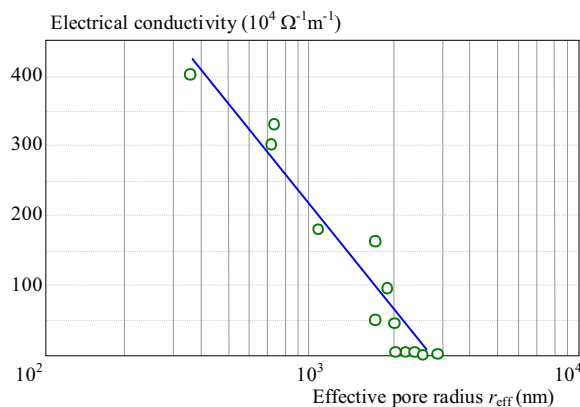


Fig. 2. Electrical conductivity G in dependence on the effective pore radius r_{eff}

By substituting the infiltration pressure P_{ext} in (4), the effective pore radius r_{eff} in the given sample was determined. Figure 2 shows the non-linear dependence of the electrical conductivity on the effective pore radius. The electrical conductivity increases sharply with a decrease in the effective radius of the filled pores. Infiltration of copper into smaller pores increased the probability of expanding the infinite cluster by interconnection in smaller pores.

The representative structure of composite sample in the subcritical region I is shown in Fig. 3 (5.6 vol% Cu). Dark areas represent the carbon matrix while the bright areas belong to the copper cluster. The black areas are the residual pores which are not filled with copper the structure of copper areas consists of isolated regions without forming the infinite cluster.

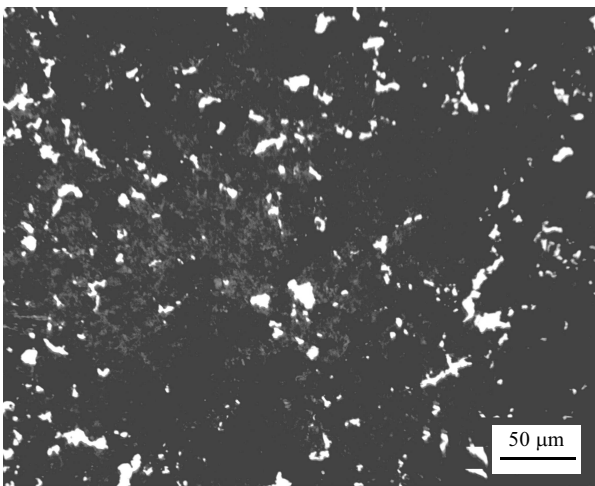


Fig. 3. Structure of Cu clusters – material containing 5.6 vol% of Cu — subcritical region

The overcritical region of the composite with maximum copper fraction of 27.6 vol% is shown in Fig. 4. Copper forms conductive clusters responsible for the power dependence of electrical conductivity. Dark grey areas represent the carbon matrix, the bright areas are copper clusters.

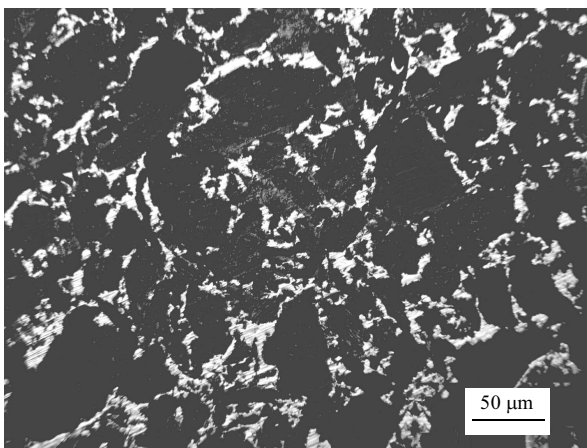


Fig. 4. Structure of Cu clusters — material containing 27.6 vol% of Cu — overcritical region

The increase of interconnections influences the rise of electrical conductivity on a non-linear basis and is consistent with the theory of electron percolation. The electrical conductivity of non-infiltrated samples was $0.812 \times 10^4 \Omega^{-1} \text{m}^{-1}$. On the other hand, samples with the best electrical conductivity (containing 27.6 vol% of Cu) exhibited a value of $396 \times 10^4 \Omega^{-1} \text{m}^{-1}$. It means that the conductivity increased by almost 500 times. The graphs presented in Figs. 1 and 2 show the trend of a non-linear increase of electrical conductivity, which is consistent with the assumptions of the percolation mechanism of electron transport.

4 CONCLUSION

The vacuum-pressure infiltration method was used to prepare carbon samples infiltrated with different copper contents. The analysis of the dependence of electrical conductivity of carbon skeletal composite on copper content showed that 7.2 vol% of Cu was a critical value. Below this content the electrical conductivity obeyed the linear dependence on copper content, while above it a power function curve. The dependence of the electrical conductivity on the effective radius of infiltrated pores showed a non-linear dependence. In this case the electrical conductivity increased sharply with decreasing effective radius of infiltrated pores, up to the value of 350 nm. The shape of the curves showed that electron percolation occurred in graphite samples infiltrated with copper with volume concentration $x \geq 7.2$ vol%.

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