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T. KNYCH*, G. KIESIEWICZ*, P. KWAŚNIEWSKI*, A. MAMALA*, A. KAWECKI*, B. SMYRAK*

FABRICATION AND COLD DRAWING OF COPPER COVETIC NANOSTRUCTURED CARBON COMPOSITES

OTRZYMYWANIE ORAZ CIĄGNIENIA KOMPOZYTÓW MIEDZIANYCH TYPU COVETIC O STRUKTURZE NANOMETRYCZNEJ

This paper presents the research results of copper Covetic metallurgical synthesis along with the characterization of cast material and the processing of casts into wires. The Cu-C composite production method was based on patent applications of Third Millennium Metals. Obtained materials were tested for their chemical composition (including Secondary Ion Mass Spectrometry (SIMS) analysis for carbon presence), mechanical properties and electrical conductivity. Measurements were also performed for wires which were first cut from obtained casts and next cold drawn into final wire form. Produced wires were tested for their mechanical and electrical properties. Electrical conductivity of wires was measured with the use of high precision Thompson's- Kelvin's bridge type device. A key objective of the research was to determine if Covetic copper has higher electrical conductivity than pure oxygen free copper.

Keywords: Covetic, copper, carbon, graphene, Cu-C

W ramach artykułu przedstawione zostały wyniki badań metalurgicznej syntezy miedzianego stopu typu Covetic, analizy uzyskanych odlewów oraz badań drutów uzyskanych w procesie ciągnienia. Metoda syntezy stopu Cu-C oparta została na patencie firmy Third Millennium Metals. Uzyskane odlewy przebadane zostały pod kątem ich składu chemicznego (wraz z analizą obecności węgla metodą SIMS), podstawowych własności materiałowych oraz przewodności elektrycznej. Ponadto badaniom własności wytrzymałościowych i elektrycznych poddane zostały druty, które otrzymane zostały poprzez ciągnienie z uzyskanych odlewów. Przewodność elektryczna drutów mierzona była na z wykorzystaniem mostka Thompsona – Kelvina. Celem przeprowadzonych badań było ustalenie czy miedziany kompozyt typu Covetic posiada, w formie odlewów bądź drutów, wyższą niż czysta miedź przewodność elektryczną.

1. Introduction

Solubility of carbon in copper is not higher than 8 ppm. Solubility depends on the temperature [1]. However there are many different methods for obtaining metal – carbon composites, with much higher carbon content, including powder metallurgy, electrochemical composition or melting and solidification processes [2-7]. Covetic materials are those produced by melting and solidification process with the use of stirring and electrical current flow during the addition of activated carbon to the molten metal – according to the Third Millennium Metals patent applications [8,9]. Intense stirring allows an even distribution of carbon particles in the metal melt. The role of electrical current flow is not yet known. Current might be enable the transformation of larger particles of activated carbon, added to the metal melt, into graphene layers.

An idea of the structure of Covetic materials shows that graphene layers could be arranged alternately with the (111) metal surface [10]. Fig. 1 presents possible graphene and copper arrangement with the assumption that the distance between gaps in (111) copper surface equals the distance between graphene atoms. Of course this is not a natural state of the FCC copper lattice because the presence of graphene atoms forces a change in the distance between copper atoms and changes the copper structure layer sequence (stacking fault). To deform and orient structure in this way, one must provide additional energy. This might be a role of the applied electrical current.

According to [11-13], the addition of nanoscale carbon particles to the aluminum and copper permitted a significant increase in their electrical conductivity and in other important operational properties like thermal conductivity or corrosion resistance. The metallurgical synthesis method was shown to increase aluminum electrical conductivity even up to 67% of IACS [14]. However there are still no research results of improved electrical conductivity in metallurgically bonded copper-carbon composites. The above-mentioned scientists from Non Ferrous Faculty at AGH – University of Science and Technology in Krakow produced samples of copper – carbon composite casting technology in cooperation with the inventors of Covetic materials based on the basic principles contained in Third Millennium Metals' patent application [9]. The key goal was to obtain an improvement in the fundamental material properties of copper – carbon composites in as-cast

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

temper and cold drawn wire form. Research was carried out for electrical and mechanical properties to investigate if the properties of this new kind of material are there are better than the standard properties of copper.

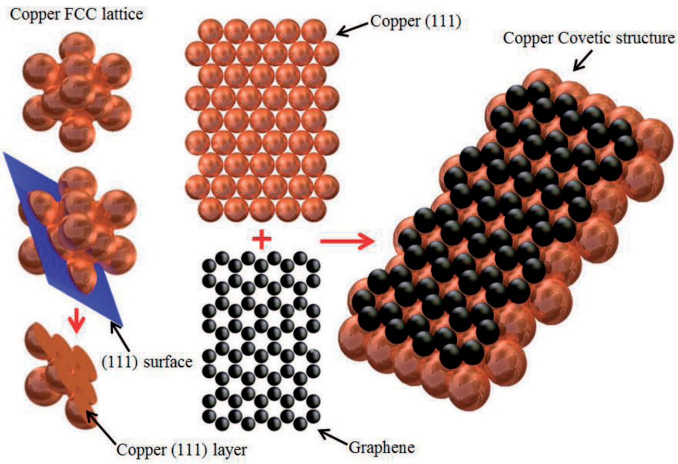

Fig. 1. Idea of copper Covetic material nanoscale structure

2. Copper carbon synthesis and processing method

Copper carbon synthesis was conducted with the use of special laboratory induction furnace equipped with the graphite crucible, mixing device and current electrodes. Addition of carbon was realized with the use of a feeding device that allowed carbon to be added slowly and directly into the molten metal surface, close to the electrical current flow zone. The process was carried out under argon gas protection to prevent copper from oxidizing and to ensure that the carbon would not be combusted in the air.

Cu-C metallurgical synthesis was carried out with the use of Cu-OFC base material and three different types of carbon powder as shown in the Table 1. Table 2 shows basic process conditions for produced casts W10, W15 and W16.

TABLE 1

Properties of carbon used in Cu-C metallurgical synthesis

	CWZ-14 Activated carbon	CWZ-22 Activated carbon	N330 Carbon black
Graining [mm]	0 – 0,12	0 – 0,12	0,00033
Iodine number [mg/g]	750	850	82
Bulk density [g/dm^3]	290 – 380	290 - 320	380
Carbon content [wt.%]	92	92	no data

TABLE 2

W10, W15 and W16 casts synthesis parameters

	Cast W10	Cast W15	Cast W16
Type and mass of Cu	5000g Cu-OFC	6000g Cu-OFC	6000g Cu-OFC
Type and mass of C	100g CWZ-14	170g CWZ-22	130g N330, 50g CWZ22
Temperature of liquid metal at the instant of rotor switching on [°C]	1376	1265	1170
Rotor Speed [RPS]	20	30	40
Duration of stirring [min]	5	15	18
Temperature of metal at the instant of current switching on [°C]	1379	1289	1200
Current [A]	150	150	150
Duration of current flow [min]	3	14	8
Residual mass of C after process [g]	0	20	150

After solidification copper-carbon composites were extracted from crucibles and tested for chemical composition and basic mechanical and electrical properties. In the next stage, 20 mm diameter rods were machined out of the casts and drawn into wires. While drawing, all samples were tested for their general formability and surface quality. Obtained wires were next tested for their electrical and basic mechanical properties in two different tempers – hard temper and annealed temper.

3. Chemical composition of casts

Chemical composition, tested for all obtained casts, is shown in the Table 3. Measurements were carried out using Solid-State Infrared (IR) Leco TC500 analyzer for oxygen content and Optical Emission Spectroscopy (OES) for remaining elements content.

The analysis shown that all casts have iron and sulfur impurities at the level of 10 – 40 ppm of Fe and 1 – 15 ppm of S. These impurities comes directly from the carbon powders. Oxygen content is in all cases lower than 3 ppm. Most popular analytical methods does not allow the measurement of carbon presence or content. For carbon presence Secondary Ion Mass Spectrometry (SIMS) method was used – Fig. 2. This method reveals the presence and distribution of carbon in analyzed cube samples. The lighter color in the cube, the higher level

TABLE 3

Chemical composition of produced casts

Cast id	Ag	As	Bi	Pb	Se	Sb	Te	Sn	Zn	Fe	Ni	S	P	O_2	Cu
	ppm														%
W10	8,59	<0,3	<0,3	<0,8	<0,3	<1	<0,4	<0,5	1,14	10,15	1,51	6,71	–	1,8	rem
W15	7,33	0,33	<0,3	<0,8	<0,3	<1	<0,4	<0,5	0,912	39,83	1,04	1,32	-	2,5	rem
W16	8,7	<0,3	<0,3	<0,8	<0,3	<1	<0,4	<0,5	0,847	22,75	0,933	15,16	–	1,4	rem

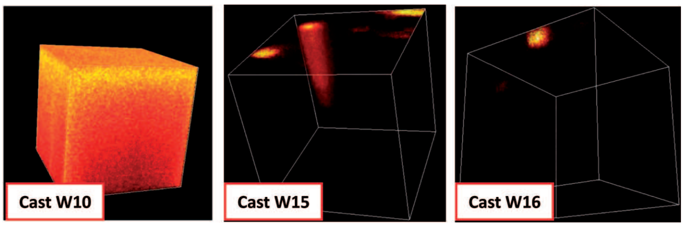

Fig. 2. Secondary Ion Mass Spectrometry (SIMS) carbon presence analysis for obtained casts

of carbon presence in the sample. Analysis shown that a sample cut from cast W10 has a large amount of carbon which is evenly distributed in the sample volume. In the samples W15 and W16, the presence of carbon is much lower and localized close to the surface area.

4. Basic mechanical and electrical properties of casts

Table 4 shows density, hardness and basic electrical properties of produced casts. All samples have density at the level of 8,91 – 8,92g/cm^3 which is slightly lower than pure copper density. Hardness for the sample W10 which is 58HV5 is about 20% lower than for casts W15 and W16. Electrical conductivity is between 98,28 – 100,17%IACS which is surprisingly high taking into account that those samples have significant amount of impurities like iron and sulfur. Electrical conductivity of standard copper cast with the same level of impurities is usually from 1 to 2MS/m lower.

TABLE 4

Basic properties of casts W10, W15 and W16

	Cast W10	Cast W15	Cast W16
Density [g/cm3]	8,914	8,916	8,925
Hardness [HV5]	58,1	72,4	75,6
Resistivity [nΩm]	17,212	17,544	17,241
Conductivity [MS/m]	58,10	57,0	58,0
IACS [%]	100,17	98,28	100,0

5. Basic mechanical and electrical properties of wires

Cold drawing of Covetic wires shown that produced composites have good formability and do not delaminate during drawing process. Obtained wires were tested in hard temper (λ =15,2 and λ =60,7) and in annealed (550°C/1h) temper. Tensile strength, yield strength and elongation of samples were measured along with electrical conductivity and shown in the Table 5. Electrical conductivity measurements were performed using Buster High-Precision Automatic Inspection and Test Unit for Electrical Resistance Testing RESISTOMAT®. All samples have electrical conductivity within the range of 96,07 to 98,66%IACS in hard temper and 98,02 to 100,68%IACS in annealed temper.

6. Conclusions

In this paper research results concerning production, characterization and processing of copper Covetic materials are presented. Measurements of mechanical properties shows that the obtained wires have tensile strength, yield strength and elongation in tested tempers that is not higher than pure copper material. Formability of synthesized composites is very good. Excellent material draw ability with level about four true total strain without breaks during laboratory rod cold rolling and cold drawing tests were reported.

The research conducted shows that the produced materials in as-cast and wire form do not have electrical conductivity at more than standard level. However, the obtained electrical conductivity parameters are relatively high and are therefore unusual and interesting taking into account that samples have significant amounts of impurities (mainly sulfur and iron) which came directly from used activated carbon. This suggests that it may be possible to obtain copper carbon composites with higher than pure copper electrical conductivity if Fe and S impurities are eliminated during the synthesis process. To test this hypothesis, authors are planning a next set of experiments with the higher purity activated carbon materials and possibly in a vacuum furnace.

TABLE 5

Mechanical and electrical properties of wires obtained from casts W10, W15 and W16

Cast id	Temper	Tensile strength [MPa]	Yield strength [MPa]	Elongation A100 [%]	Electrical Conductivity [MS/m]	IACS [%]
W10	**hard** (λ =15,2)	339	332	0,9	57,22	98,66
	annealed (T=550°C, 1h)	233	60,6	37,1	58,37	100,64
W15	**hard** (λ =60,7)	415	403	0,9	55,72	96,07
	annealed (T=550°C, 1h)	234	53,8	35,8	56,85	98,02
W16	**hard** (λ =60,7)	430	422	0,7	56,51	97,43
	annealed (T=550°C, 1h)	231	53,1	36,3	58,39	100,68

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