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Fabrication and Characteristics of Copper-Intermetallics Composites

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Abstract

The paper presents the results of research on the production and application of sintered copper matrix composite reinforced with titanium-copper intermetallic phases. Cu- Ti composites were fabricated by powder metallurgy. The starting materials for obtaining the sintered composites were commercial powders of copper and titanium. Experiments were carried out on specimens containing 2.5, 5, 7.5 and 10 % of titanium by weight. Finished powders mixtures containing appropriate quantities of titanium were subjected to single pressing with a hydraulic press at a compaction pressure of 620 MPa. Obtained samples were subjected to sintering process at 880 °C in an atmosphere of dissociated ammonia. The sintering time was 6 hours. The introduction of titanium into copper resulted in the formation of many particles containing intermetallic phases. The obtained sinters were subjected to hardness, density and electrical conductivity measurements. Observations of the microstructure on metallographic specimens made from the sintered compacts were also performed using a optical microscope. An analysis of the chemical composition (EDS) of the obtained composites was also performed using a scanning electron microscope. Microstructural investigations by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) showed that after 6 hours of sintering at 880°C intermetallic compounds: $TiCu$, $TiCu_2$, $TiCu_4$, Ti_2Cu_3, Ti_3Cu_4 were formed. The hardness increased in comparison with a sample made of pure copper whereas density and electrical conductivity decreased. The aim of this work was to fabricate copper matrix composites reinforced with titanium particles containing copper- titanium intermetallic phases using powder metallurgy technology and determine the influence of the titanium particles on the properties of the sintered compacts and, finally, analyse the potentials application for friction materials or electric motors brushes.

Keywords: Composites, Powder metallurgy, Sintering, Copper, Titanium

1. Introduction

Copper is widely used for the production of electrical and electronic devices due to its high electrical conductivity, corrosion resistance, low cost and easy production. Due to the high electrical conductivity of copper, electrical components such as relays, switches, electric motor components and electrode tips for resistance welding are produced using powder metallurgy [1-3]. Pure copper has low hardness, mechanical strength and abrasion resistance, which limits its use in a pure form. For this reason, pure copper is strengthened by introducing alloying additions. However, the introduction of any additions to copper significantly reduces the electrical conductivity [4-6]. For example, tin bronze, silicon bronze and manganese bronze have an electrical conductivity lover than 10 MS/m while pure copper has around 58 MS/m [7]. Copper strength and abrasion resistance can be increased in two ways. The first method is age hardening but it cannot be used for all copper alloys. In the case of age hardening, the addition of a small amount of chromium or zirconium will produce hard phases insoluble in copper at low temperatures [8-9]. The second method involves the addition of hard particles such as metal oxides, borides and nitrides. Characteristics of the copper could be improved by producing particles reinforced copper matrix composite materials. To improve the strength properties of copper particles such as metal oxides (Al_2O_3, SiO_2, ZrO_2, Cr_2O_3, BeO, MgO), carbides (SiC, TiC, Cr_7C_3, Cr_3C_2), nitrides and borides (TiB_2, ZrB_2, CrB_2, BN) are used like a reinforcement phases [10-12]. The addition of the above-mentioned particles will increase the strength of copper without significantly decreases the electrical conductivity. Improving the strength properties of copper can be obtained by adding alloying elements that will create intermetallic phases. Composites containing intermetallic phases have properties similar to those reinforced with ceramic particles. Copper-titanium, aluminum-iron and nickel-aluminum intermetallic phases are most often used as strengthening phases [13-15]. Copper and titanium alloys with high copper content are most frequently tested [16-17]. Copper and titanium alloys are considered the ideal replacement for the copper-beryllium alloy used in the electronics industry. Beryllium is an expensive and toxic element, therefore research is underway to replace beryllium with another element. The copper-titanium alloy has properties similar to the copper-beryllium alloy, therefore it can be a very good alternative to toxic beryllium [18]. Metal matrix composites reinforced with strengthening particles are usually fabricated using powder metallurgy. The main advantage of powder metallurgy is very good control over the distribution of strengthening particles in the matrix. An important role in powder metallurgy is the diffusion of solid state dependent on sintering time and temperature, which is involved in the formation of intermolecular bonds. In this work, an attempt was made to produce a sintered copper matrix composites reinforced with particles containing copper-titanium intermetallic phases. The fabricated sinters were subjected to microstructural investigations, chemical components analysis (EDS) and the measurements of density, hardness and electrical conductivity were performed. However, additional copper-titanium composite tests such as abrasion resistance tests are needed. An abrasion resistance test is required to check that the copper-titanium composite has the properties to apply it to the friction materials or electric motors brushes.

2. Materials and methods

Commercial copper and titanium powders were used for the production of composites. Electrolytic copper powder, with an average particle size of less than 63 μm and 99.5 % of purity was used as the matrix while mechanically fragmented titanium powder, with an average particle size of less than 1 mm and 99.1 % of purity was used as the reinforcement. The shapes and arrangements of the powder particles used in the experiments are shown in Figure 1 and 2.

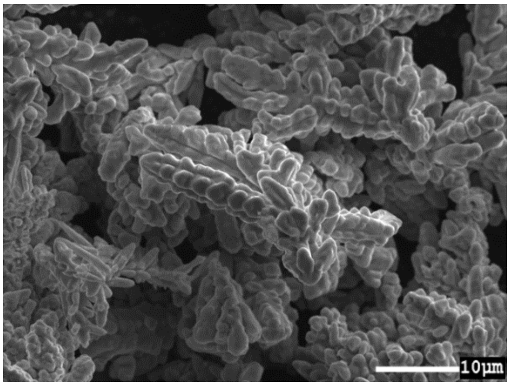

Fig.1. Electrolityc copper powder (SEM)

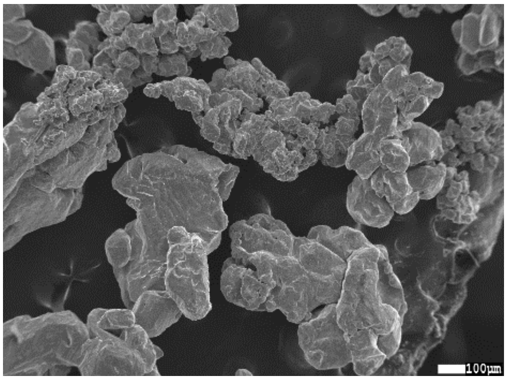

Fig.2. Titanium powder (SEM)

The powders of the materials used to fabricate the composites were observed using a JEOL JSM-7100F field emission scanning electron microscope. Powder mixtures with different titanium content (2.5, 5, 7.5 and 10 % by weight) were prepared for the tests. Cylindrical samples with a dimension of Φ20x10 mm were made of prepared powder mixtures on a hydraulic press at a compaction pressure of 620MPa. The specimens were sintered in a sillit tubular furnace at 880°C in the dissociated ammonia atmosphere. The sintering time was 6 hours. After the sintering process, the samples were subjected to cooling with cooling speed of 100°C/min. The fabricated composites were subjected to hardness, density and electrical conductivity tests. The micro-hardness of intermetallic phases occurring in the composite was measured using the Vickers method (with a diamond pyramid at a load of 0.1962 N) in accordance with the PN-EN ISO 6507-1:2007 standard. The hardness of the sintered compacts was measured using the Brinell method (with a steel ball of 5 mm in diameter at a load of 2452.5 N) in accordance with the PN EN ISO 6506-1:2014 standard. Tests of electrical conductivity were carried out using the eddy current method using a GE Phasec 3D device. The density was determined by weighing the specimens in air and water using WPA120 hydrostatic scales in line with the PN EN ISO 2738:2001 standard. Microstructure analysis on the previously prepared metallographic specimens were conducted using the JEOL JSM-7100F field emission scanning electron microscope fitted with OXFORD INSTRUMENTS EDS X-Max Aztec software for elemental analysis.

3. Results and discussion

3.1. Microstructural investigations

The addition of titanium particles into the copper matrix caused significant changes in the microstructure of fabricated composites. Titanium particles of various sizes (in a range of 0.01 to 1 mm) and shapes are very visible in a copper matrix. The visible differences in the particle size are due to the size range of the titanium powder used. Thorough mixing of copper and titanium powders led to even distribution of particles in the copper matrix. Exemplary microstructures of sintered copper-titanium composite obtained using an optical microscope are shown in Figures 3 and 4. Images of microstructures show titanium particles around which many layers of intermetallic phases formed during sintering. Titanium particles have been deformed with the pressing direction. During the microstructure observation, low porosity was found.

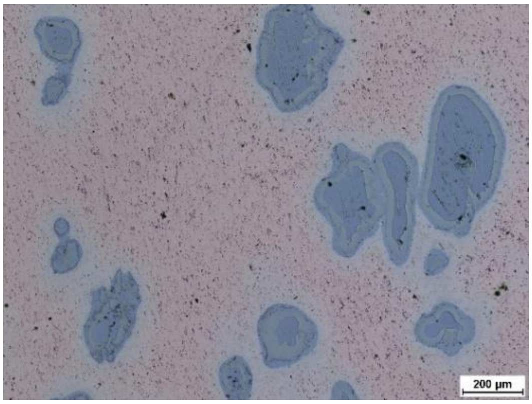

Fig.3. Microstructure of sintered compact obtained for Cu+ 5 % of Ti

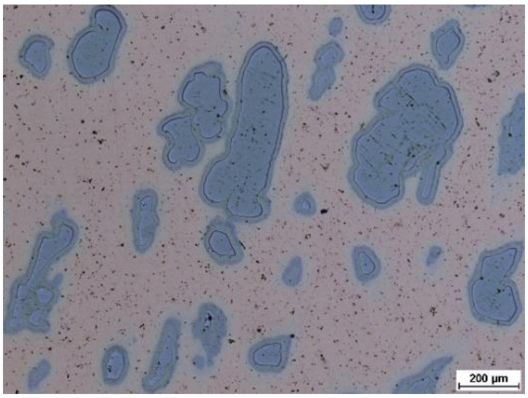

Fig.4. Microstructure of sintered compact obtained for Cu+ 10 % of Ti

Using a SEM with an attachment for chemical composition analysis (EDS), the intermetallic phases found in the composite were identified. The largest amount of titanium was recorded inside the particle, while the amount of titanium decreases towards the copper matrix, as shown in EDS line scan analysis in Figure 5.

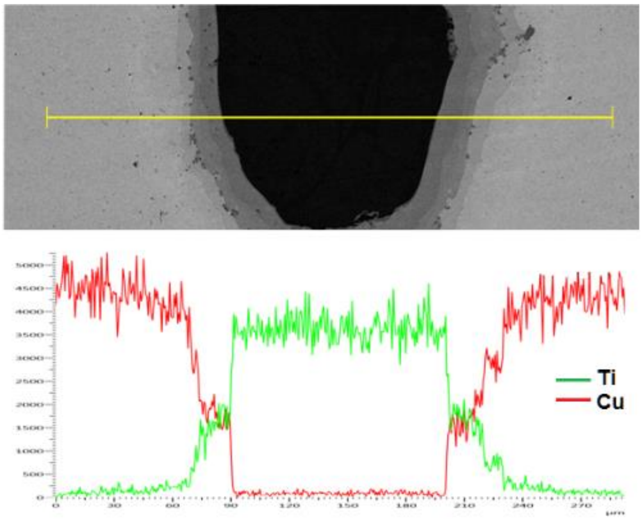

Fig.5. EDS line scan analysis of phases around a titanium particle

A bright titanium-rich diffusion layer is visible around the particle. The obtained layer is the result of the diffusion of titanium atoms into the copper matrix. The copper content is the highest in the matrix and it is stable over the entire tested surface, while it decreases dramatically from the particle boundary to its center. There is about 4 % of copper inside the particle. A structure similar to the martensite structure was observed inside the particle. It is probably a structure consisting of the α-β Ti phases and a small amount of copper. The occurrence of this structure may be due to rapid cooling after sintering. Similar phenomenon was also noticed by other researchers [15,21]. The microstructure of the center of particles are shown in Figure 6.

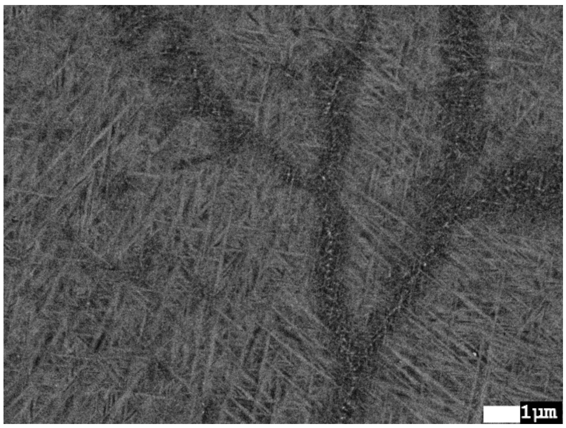

Fig.6. Microstructure of the titanium particle center (SEM)

Eight intermetallic compounds ($TiCu_4$, $TiCu_3$, $TiCu_2$, Ti_2Cu_3, Ti_3Cu_4, TiCu, Ti_2Cu and Ti_3Cu) were identified in the Ti-Cu system [19]. In this work only five intermetallic compounds were formed during the sintering process. A study of the above structures was based on the Ti-Cu binary phase diagram shown in Figure 7.

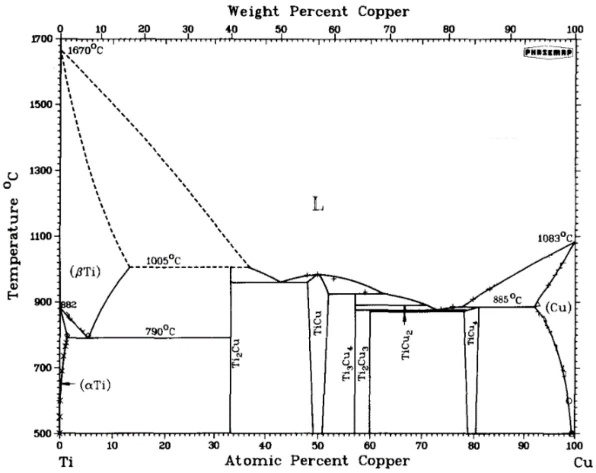

Fig.7. Ti- Cu binary phase diagram [20]

In order to identify intermetallic phases present in the composite, several point chemical composition analyzes were carried out. Figure 8 shows examples of places where the chemical composition was analyzed. The Table 1 presents the results of the analysis. The obtained results are similar for each analyzed particle.

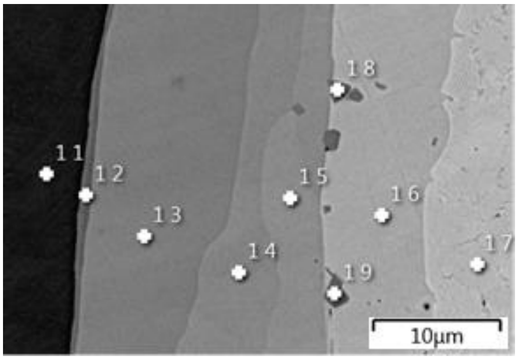

Fig.8. Examples of points where EDS analyses were taken

Table 1.
Chemical compositions and possible phases occurring in analyzed particle

Point in Figure 8	Titanium(%)	Copper(%)	Possible phase
11	95.9	4.1	Ti
12	51.7	48.3	TiCu
13	42.1	57.9	Ti_3Cu_4
14	39.5	60.5	Ti_2Cu_3
15	32.2	67.8	$TiCu_2$
16	19.2	80.8	$TiCu_4$
17	4.9	95.1	Cu
18	19.8	80.2	$TiCu_4$
19	19.8	80.2	$TiCu_4$

Analysis of the composite microstructure and the results of EDS point analysis showed that during the sintering process five intermetallic phases (TiCu, $TiCu_2$, $TiCu_4$, Ti_2Cu_3, Ti_3Cu_4) were formed. Similar results were received by other researchers [15-17].

3.2. Density and hardness mesaurements

Tests of sinter hardness and density were carried out to assess how the amount of titanium affects the above-mentioned properties. The hardness test was carried out both for the whole composite (by Brinell method) and for a single particle of strengthening phase (by Vickers method). The results of density and hardness measurements are presented in Table 2.

Table 2.
Results of a density and hardness (HB) measurements of Cu-Ti composites

Material	Density (g/cm^3)	Relative density (%)	Hardness HB
Cu	8.19± 0.02	92.01	36.65± 1.5
Cu + 2.5 % Ti	7.80± 0.04	89.23	67.19± 1.8
Cu + 5 % Ti	7.76± 0.05	92.90	78.33± 1.3
Cu + 7.5 % Ti	7.55± 0.03	88.28	87.29± 1.7
Cu + 10 % Ti	7.33± 0.07	89.97	93.28± 1.8

Analyzing the obtained results of hardness and density tests, it must be confirmed that the introduction of titanium particles into the copper matrix causes a significant increase in hardness and a decrease in the density of composites. This is due to the high hardness of the intermetallic phases formed during the sintering process and the relatively low density of titanium. The highest hardness was obtained for the sinter containing 10 % of Ti which reached 93 HB (250 % higher than pure copper sinter). The similar phenomenon was also noticed by other researchers [3,4,5,7,16]. The highest density was obtained for a sinter made from pure copper powder which amounted 8.19 g/cm^3. Addition 10 % of titanium powder caused decrease in density to 7.33 g/cm^3. The hardness of intermetallic phases decreases towards the copper matrix and ranges from 155 to 227 HV. In the middle of the particles the highest hardness was obtained, which was (depending on the measuring point) from 259 to 355 HV. Copper matrix hardness was from 60 to 82 HV. The highest hardness observed in the middle of the particles confirms the supposition of the presence of a martensitic or α-β Ti structure.

3.3. Electrical conductivity investigations

The examination showed that the introduction of even a small amount of titanium particles into copper matrix reduces the electrical conductivity. The obtained results confirm the rule that the introduction of even a small amount of alloying additives into copper reduces its electrical conductivity. The electrical conductivity of copper-titanium composites was compared with a sinter made of pure copper powder with a electrical conductivity of 50.39 MS/m (14 % less than pure copper in a solid state).

Similar results were received by other researchers [2-4]. The introduction of 2.5 % of titanium powder into copper matrix caused decrease in electrical conductivity to 41 MS/m but introduction of 10 % of titanium powder caused decrease in electrical conductivity to 24.9 MS/m. The relatively high conductivity of the composite was maintained due to the low diffusion of titanium atoms into the copper matrix. The results of electrical conductivity measurements are shown in Table 3.

Table 3.
The results of electrical conductivity measurements of copper-titanium composites depending on amount of titanium

Material	MS/m	% IACS
Cu	58	100
Cu- sinter	50.39± 0.32	86,71
Cu + 2.5 % Ti	41.05± 0.29	70,77
Cu + 5 % Ti	35.3± 0.36	60,86
Cu + 7.5 % Ti	34.1± 0.28	58,8
Cu + 10 % Ti	24.9± 0.31	42,93

4. Conclusions

The analysis of the microstructure of the fabricated composites showed that during the pressing process, the titanium powder particles combine into agglomerates. In order to obtain a homogeneous powders mixture, the powders should be thoroughly mixed in the mixers before the sintering process.

Appropriate parameters of pressing and sintering powders were selected on the basis of our own earlier research and on the basis of information available in the literature. The microstructural observations showed that there were no discontinuities at the interface between the copper matrix and the titanium particles. During the sintering process, a small porosity of the copper matrix was formed. In some places, on the border of the copper matrix with titanium particles, the Kirkendall effect appears associated with the formation of intermetallic phases. Titanium particles of different shape and size are clearly visible in the copper matrix. The introduction of titanium powder into the copper matrix caused the appearance of copper- titanium intermetallic phases. Due to the rapid cooling of the composites after sintering, a structure similar to martensitic structure was obtained inside the particles. The obtained structure is most likely a structure consisting α-β Ti with a small amount of copper. Spot analysis of the chemical composition (EDS) showed that the titanium particles during the sintering process transformed into intermetallic phases due to the diffusion of copper towards the center of the titanium particles. The introduction of titanium particles as a strengthening phase resulted in a significant increase in hardness and a decrease in density and electrical conductivity of composites. Conducted research showed that Cu-Ti composites produced by powder metallurgy can successfully replace other composites strengthened, for example with ceramic particles. One of the basic advantages of Cu-Ti composites is the small diffusion of titanium atoms inside the copper matrix. The low diffusion of titanium atoms maintains the sufficient electrical conductivity of the Cu-Ti composite. Cu-Ti composites produced by powder metallurgy has similar hardness and electrical conductivity like Cu- Be composites, therefore can successfully replace Cu-Be composites due to the high toxicity and beryllium price. The lower price and lack of titanium toxicity makes Cu-Ti composites more attractive than Cu-Be composites. The conducted tests allow the use of copper-titanium composite as a material for brushes of electric motors, however abrasion resistance tests are required to completely confirmed that.

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