J Therm Anal Calorim (2014) 117:1277–1283
DOI 10.1007/s10973-014-3900-6

Effect of the TiC content on microstructure and thermal properties of Cu–TiC composites prepared by powder metallurgy

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Received: 6 January 2014 / Accepted: 31 May 2014 / Published online: 10 July 2014

Abstract Copper matrix with an individual addition of TiC particles was prepared by means of powder metallurgy and hot pressing process, and the effect of TiC addition on microstructure, thermal properties, and electrical conductivity of Cu–TiC composites was investigated. The TiC quantity was changed as 1, 3, 5, 10, and 15 Cu (in mass%), and Cu–TiC powder mixtures were hot-pressed for 4 min at 700 °C under an applied pressure of 50 MPa. Microstructure studies revealed that TiC particles were distributed uniformly in the Cu matrix. Thermal Analysis result showed that there were two exothermic peaks and with rising TiC rate, oxidation amount of Cu composite decreased. With the increasing addition of TiC, hardness of composites changed between 58.6 $HV_{0.1}$ and 87.8 $HV_{0.1}$. The highest electrical conductivity for Cu–TiC composites was obtained in the Cu-1 mass% TiC composite, with approximately 81.2 % IACS.

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Keywords Hot pressing · Cu–TiC · Microstructure · Thermal properties · Electrical conductivity

Introduction

Copper has been remained the most important engineering material until today because of high corrosion strength, perfect electrical and thermal conductivity, attractive appearance, high ductility, and ease of forming [1, 2]. Pure copper is used extensively for cables and wires, electrical contacts, and a wide variety of other parts that are required to pass electrical current. Coppers and its alloys are used extensively for automobile radiators, heat exchangers, home heating systems, panels for absorbing solar energy, and various other applications requiring rapid conduction of heat across or along a metal section [3–6].

The application of copper is restricted in industry by its low hardness, low tensile yield strength, and poor creep resistance property, although it has high electrical and thermal conductivities, fabrication, and good corrosion resistance. Pure copper has 400 W m^{-1} K^{-1} thermal conductivity, 390 MPa tensile strength, and 490 MPa yield strength [7, 8]. Because, even if copper is cold hardened, it loses its strength quickly because of recrystallization at temperatures close to 500 °C. Copper having both perfect electrical conductivity and high strength can be manufactured by alloying. However, amount of the alloying element addition into the pure copper is about % 2 because decrease in the electrical conductivities is not desirable. Although these alloying (Cr or Zr) elements give the copper a high hardness by precipitation hardening, they lose their properties by dissolving in copper at high temperatures [9]. In order to overcome this problem, the copper matrix composites are manufactured by addition of

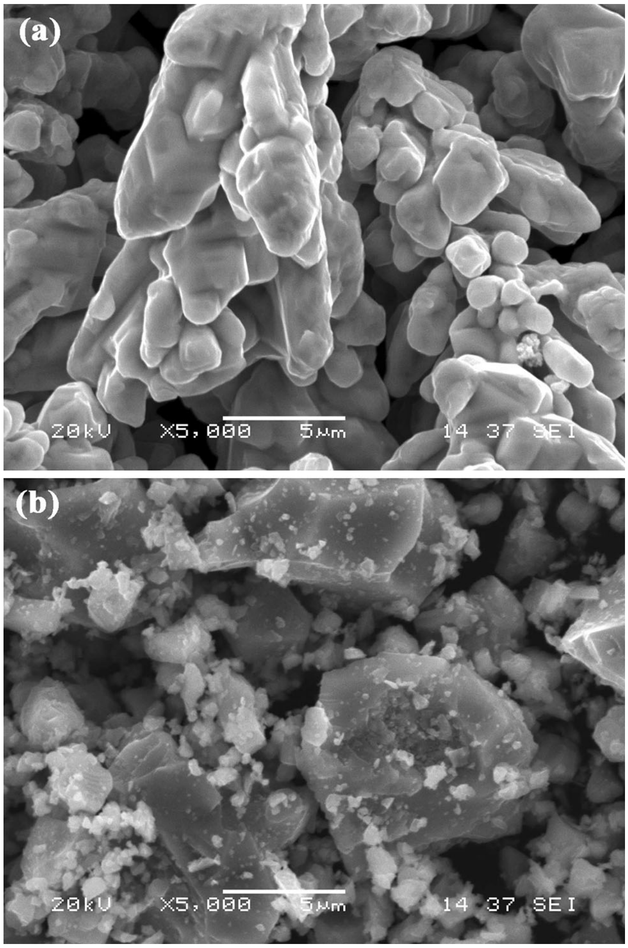

Fig. 1 SEM images of **a** copper and **b** titanium carbide powders

carbide, oxide, and ceramic particles into copper [10, 11]. The properties of perfect mechanical wear and erosive wear at high temperature of reinforced element together with the properties of electrical and thermal conductivities of copper determined characteristics of copper matrix composites. Particle-reinforced metal matrix composite materials are used for structural applications in wear industry due to super toughness and wear resistance. Especially, alumina- and silicon carbide-based composite materials do not lose their hardness and wear resistances during high temperature applications [12–14]. Cu matrix composite materials are alternative materials when high electrical/thermal conductivity and good wear resistance are required.

Therefore, in this study, the 1–15 mass% TiC/Cu composites were fabricated with hot press consolidation, and the effect of the TiC content on the microstructure, electrical features, thermal properties, and hardness behavior of the composites was investigated.

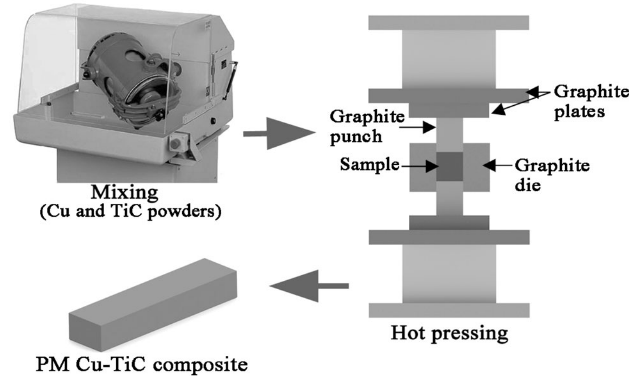

Fig. 2 Schematic presentation of PM Cu–TiC composites production

Experimental studies

Pure copper powder (in averagely 20 µm grain size) and titanium carbide powder (in averagely 10 µm grain size) were used in the experiments. TiC was added at 1, 3, 5, 10, and 15 mass% rate into Cu matrix. Figure 1 illustrates SEM images of copper and titanium carbide powders. While copper powder had a dendritic structure, titanium carbide powder had a sharp-edged structure.

Copper and titanium carbide powders were mixed using powder mixing machine at 20 rpm min^{-1} for 30 min in such a way that the mixture would become homogenous. The powder mixture was put into graphite molds and pressed using an automatic hot pressing machine for 4 min at 700 °C sintering temperature under pressure of 50 MPa as illustrated in Fig. 2. In order to avoid the negative effects of copper–ceramic reaction during sintering at high temperatures, the limit of sintering temperature of 750 °C is recommended in the literature [15]. Therefore, the appropriate sintering temperature was selected as 700 °C.

Relative densities of samples were measured according to Archimedes' principle. Micro-hardness measurements of pure copper and Cu–TiC composites were performed using a Vickers hardness instrument under a load of 100 gf. The electrical conductivity of Cu–TiC composites was evaluated with eddy current instruments in accordance with ASTM standard E1004-02 [16]. The electrical conductivity measured by this equipment is usually expressed as a percentage of the conductivity of the International Annealed Copper Standard (% IACS). Minimum five readings were taken for each sample. The average electrical conductivity value of % IACS was converted into SI unit ($S\ m^{-1}$) by multiply by 0.58×10^6, as the 100 % IACS equals to $0.58 \times 10^8\ S\ m^{-1}$. For metallographic study, the samples were prepared according to standard metallographic procedure. Scanning electron microscope and X-ray diffractometer were used to investigate

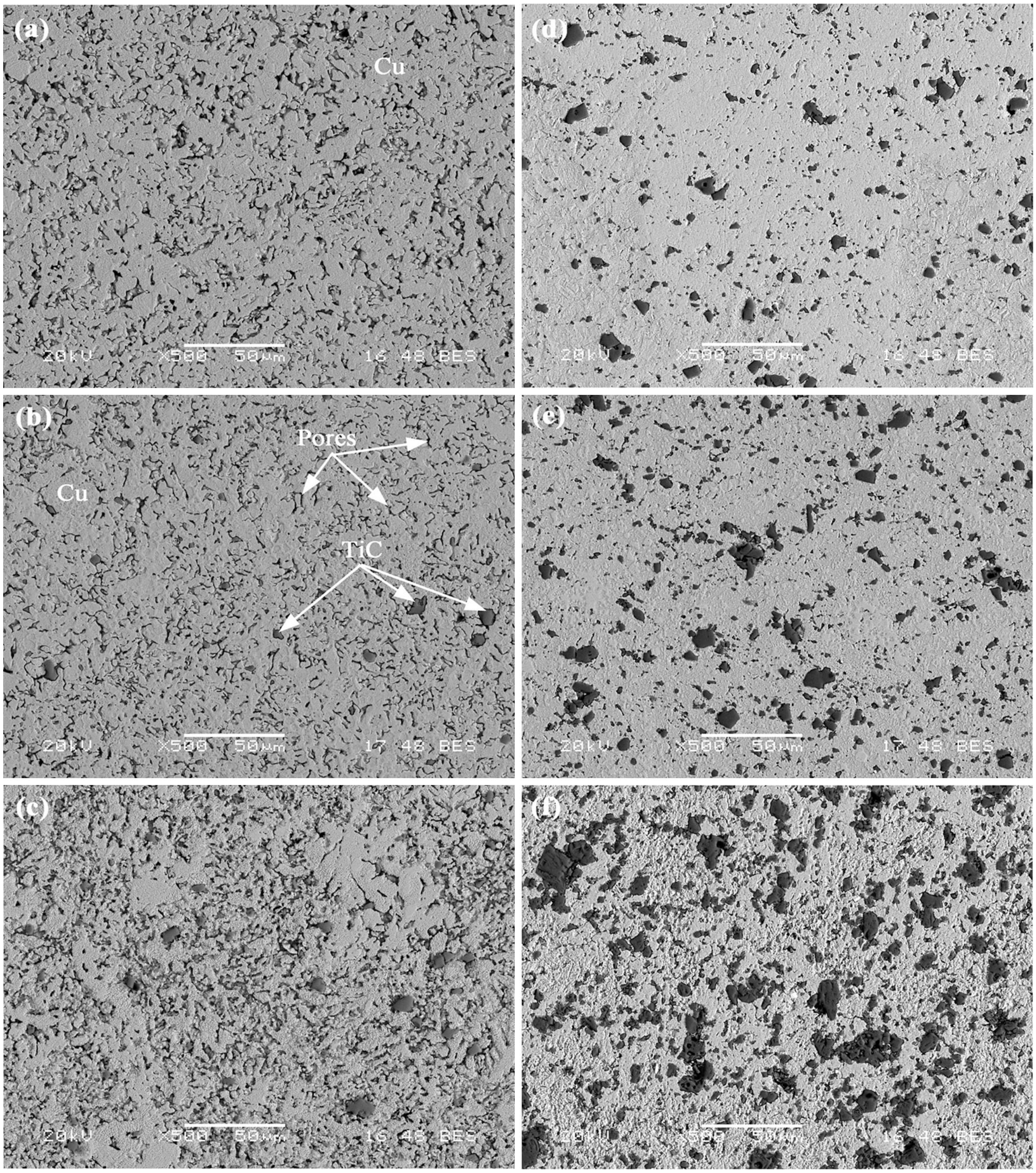

Fig. 3 SEM micrographs of Cu–TiC composites: **a** Cu un-reinforced, **b** Cu-1 mass% TiC, **c** Cu-3 mass% TiC, **d** Cu-5 mass% TiC, **e** Cu-10 mass% TiC, and **f** Cu-15 mass% TiC

microstructure and phase composition of composites. Thermal Analysis of Cu–TiC composites was carried out by Perkin Elmer Phyris TG/DTA thermal analysis system. All thermal measurements were made at the heating rate of 20 °C min^{-1} in air atmosphere between temperature range of 100 and 600 °C. For thermal measurement, platinum crucible was used.

Results and discussion

The Cu–TiC composites were successfully produced using the hot pressing method together with a sintering time of 4 min at 700 °C, under a pressure of 50 MPa. Figure 2 illustrates SEM images of Cu and Cu–TiC composites produced via hot pressing. When the microstructure is

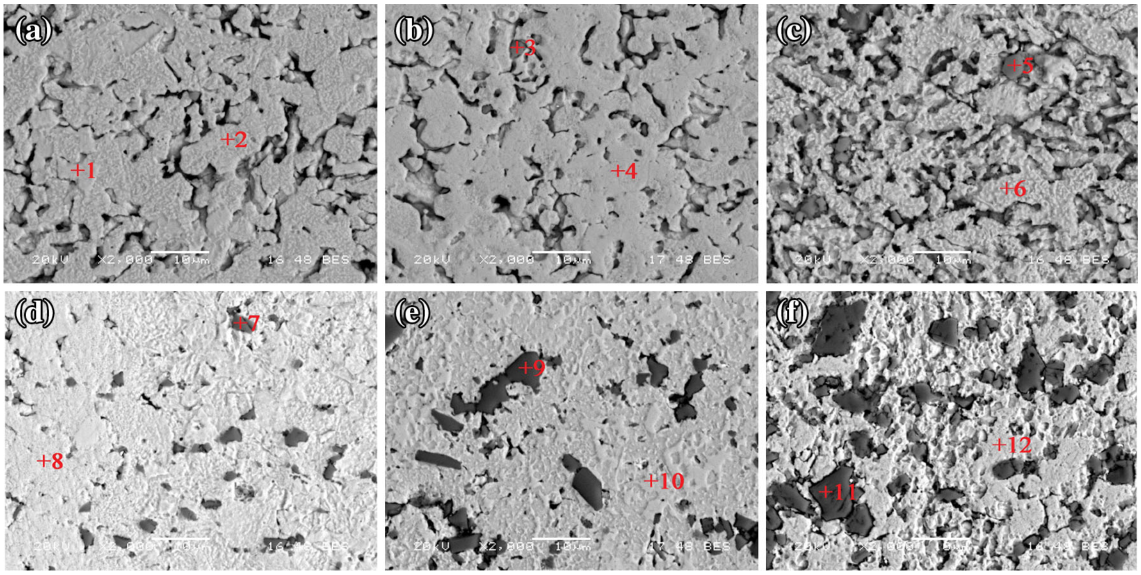

Fig. 4 EDXS marked in the SEM micrographs for Cu–TiC composites: **a** Cu un-reinforced, **b** Cu-1 mass% TiC, **c** Cu-3 mass% TiC, **d** Cu-5 mass% TiC, **e** Cu-10 mass% TiC, and **f** Cu-15 mass% TiC

Table 1 EDXS results for Cu–TiC composites

Elements	Marks											
	1	2	3	4	5	6	7	8	9	10	11	12
Cu	100.0	100.0	3.4	100.0	2.1	100.0	9.2	100.0	3.2	100.0	1.2	100.0
Ti			83.6		84.0		75.6		84.4		88.7	
C			13.0		13.9		15.2		12.4		10.1	

examined, three different structures draw the attention. Gray and sharp-edged grains represent TiC, dark gray areas represent porosities, and finally light gray areas represent Cu matrix. TiC particles distributed uniformly in the Cu matrix. Lee et al. [17] stated that if reinforced particles do not distribute homogeneously, this situation would affect mechanical and electrical features of the composite negatively. TiC particles were positioned as embedded since they were within grain borders of ductile Cu matrix. SEM images demonstrate that quantity of TiC in the microstructure increased depending on addition quantity of TiC (as seen Fig. 3a–f).

TiC particles homogeneously dispersed in Cu matrix (Fig. 3d–f). It is very important to obtain homogeneous distribution of reinforcement in the matrix in order to enhance mechanical, electrical, and thermal properties [6, 18]. As it can be seen from Fig. 3e, f, SEM studies showed that a homogenous and regular dispersion was seen in Cu-15 mass% TiC composite. Results of EDXS analyses corresponding to regions marked 1–12 in Fig. 4 are shown in Table 1. Figures 3a and 4 show microstructural features of the master Cu matrix without TiC that was produced (Fig. 4, regions marked by 1, 2, 4, 6, 8, 10, and 12). Using EDXS analysis, the phases present in the matrix were identified to be the primary α-Cu as the matrix constituent. The second phase clearly revealed in the matrix to also contain TiC particles (Fig. 4, regions marked by 3, 5, 7, 9, and 11, respectively).

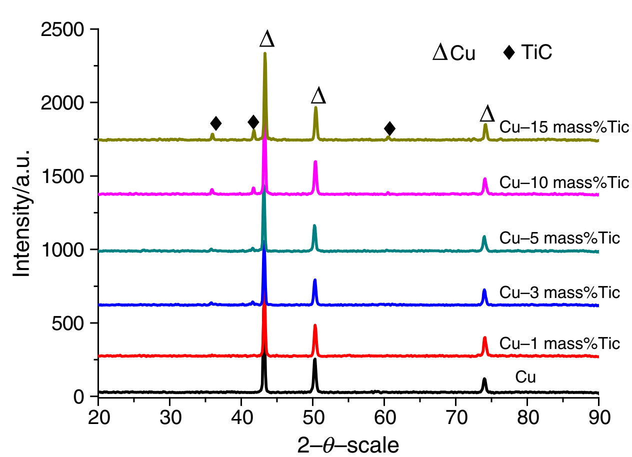

Fig. 5 XRD diffraction patterns of Cu–TiC composites

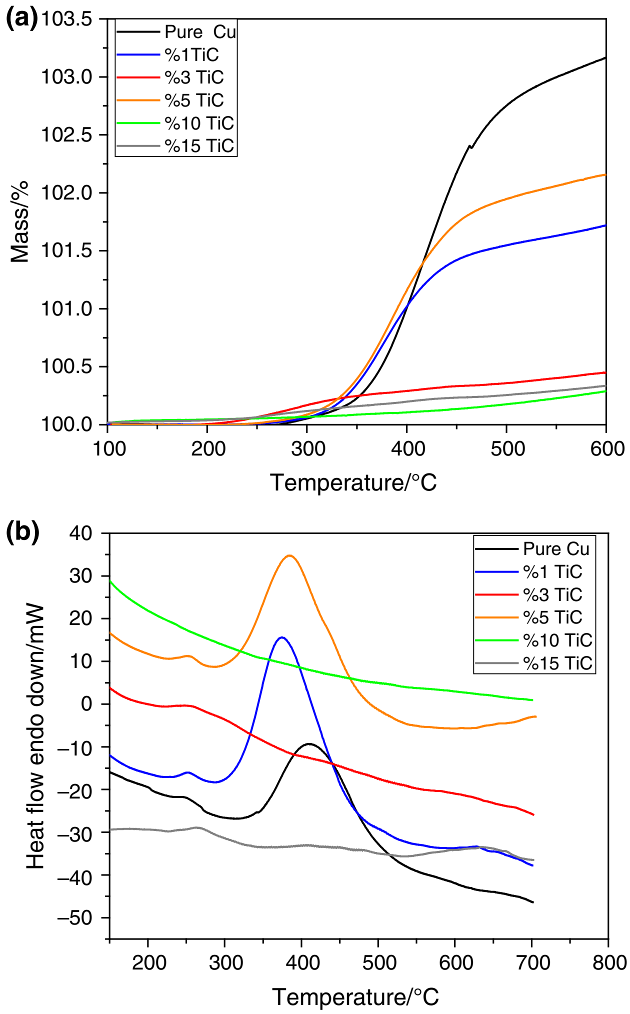

Fig. 6 **a** TG curves and **b** DTA curves of Cu–TiC composites

The XRD analysis was performed for each composite in order to determine whether a phase formed to provide bonding in the interface of copper (matrix) and titanium carbide (reinforcement) particles or not. Figure 5 illustrates XRD graphics of the composites. It is seen from graphics that Cu and TiC phases formed. There is not new phases by TiC addition on Cu composites. This situation demonstrated that there was no chemical reaction between Cu and TiC. It is evidently seen from graphics that there was an increase in peaks of TiC phase based on increasing titanium carbide rates [19]. Furthermore, XRD graphics obviously show that no oxide phase formed in Cu–TiC composites.

In order to understand thermal responses of Cu–TiC composites, TG/DTA measurements were done. All measurements were done at the heating rate of 20 °C min^{-1} in air atmosphere from 100 to 600 °C. TG and DTA curves of Cu and Cu–TiC composite prepared by pm were in Fig. 6a–b. As a result of this, mass gain is attributed to oxidation of copper. The highest mass gain was seen in pure copper; in other Cu composites, the mass gain was lesser than matrix copper. According to DTA, There were two exothermic peaks. The first peak at ~270 °C is referred to precipitation of $TiCu_4$ [20, 21], the second peak is indicator of oxidation (~370 °C). The second exothermic peaks (~370 °C) is very sharper for Pure Copper produced via hot pressing, and its composites 1 and %5 TiC addition. This result is compatible with TG. As seen TG curves, oxidation of pure Copper and its composites 1 and %5 TiC addition is higher than other. The mass gain of these samples is about 3, 2, and %1.5, respectively. By addition of TiC, oxidation of Copper was decreased. These results indicated that when second peak became shaper, the amount of oxide increased.

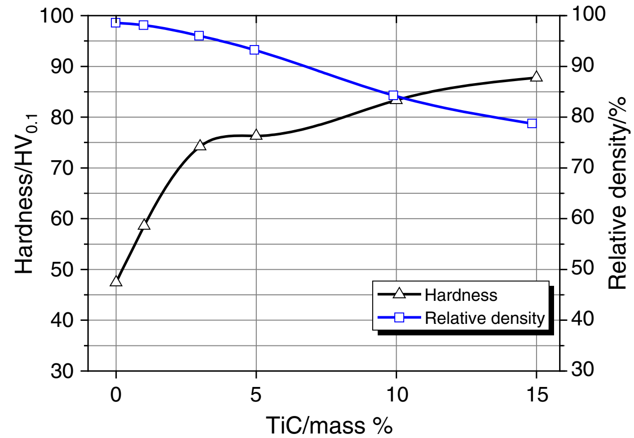

Fig. 7 Relative densities and hardness of Cu–TiC composites

Figure 7 illustrates effect of TiC addition on relative density and hardness of Cu–TiC composites produced via hot pressing. Relative densities of the composites were determined according to Archimedes' principle. With increasing TiC addition, relative densities decreased. In consideration of addition of TiC up to 15 mass%, relative densities decreased from 98.6 to 78.8 %. This decrease in the relative densities could be associated with the fact that increasing rate of TiC affected the sintering adversely [22]. Another reason is that huge difference between melting points of matrix and reinforcing member, namely Cu and TiC was an inhibiting factor in the rearrangement of particles during sintering. Moreover, the fact that density of TiC is lower than density of copper is another reason for the decrease in the relative densities.

Hardness of Cu–TiC composites produced with addition of TiC significantly increased. While hardness of pure copper produced via hot pressing method was 47.5 $HV_{0.1}$, hardness of composites with addition of TiC ranged from 58.6 $HV_{0.1}$ to 87.8 $HV_{0.1}$. This hardness increase was caused by dispersion strengthening effect of titanium carbide. Additionally, the increase in addition of TiC caused

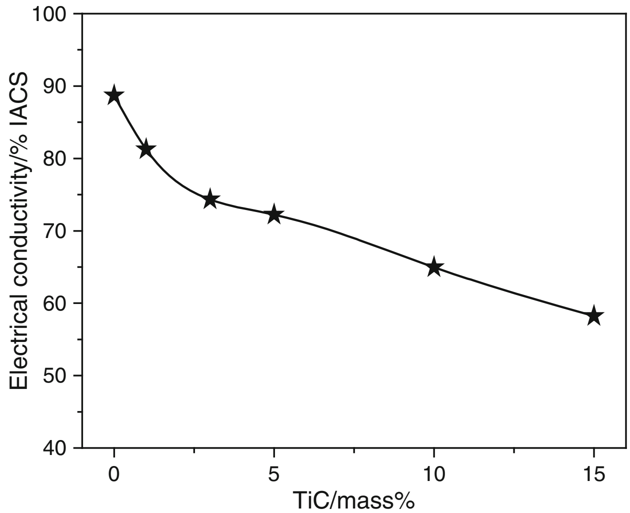

Fig. 8 Electrical conductivity of Cu–TiC composites

an increase in dislocation density in the Cu matrix, and consequently it is thought that hardness of composites increased.

Figure 8 illustrates results of electrical conductivity test of Cu–TiC composites, produced via hot pressing method, based on content of titanium carbide. With the increase in addition rates of titanium carbide, the electrical conductivity of composites decreased. While the electrical conductivity of Cu with no addition was measured as 88.7 % IACS, the electrical conductivity of composites with 1, 3, 5, 10, and 15 %TiC addition was measured as 81.3, 74.3, 72.2, 64.9, and 58.2 % IACS, respectively. Porosity and oxidation could be asserted as the reason for low electrical conductivity of pure copper [23]. Interaction between free electrons and nucleus is weak in the metals. Therefore, electrons easily move and accordingly electrical conductivity of metals is good. However, electrons are firmly bonding to the nucleus in the carbides and electrons do not move. For this reason, electrical conductivity of carbides is weak [24]. Since rate of Cu matrix in TiC addition in the Cu–TiC composite material decreased, it is an expected result that electrical conductivities of the composites would decrease with increasing addition of TiC. Reinforced TiC particles in the composite exhibited an effect inhibiting the movement of Cu electrons. The decrease of electrical conductivity with increasing the TiC content may be related to the following several aspects. Firstly, the increase of TiC content can certainly lead to the decrease of the electrical conductivity due to the intrinsic high electrical resistivity of TiC. Secondly, with increasing the TiC content, the density of dislocations induced by the difference of thermal expansion coefficients between TiC and Cu matrix increases. Increased dislocation density intensifies the electron scattering, resulting in decreased electrical conductivity. And finally, the presence of TiC can effectively refine the grains of Cu–TiC composite [25].

Conclusions

Cu–TiC composites were successfully produced using a hot pressing method together with 4 min sintering at 700 °C, under pressure of 50 MPa. Microstructure studies revealed that TiC particles were distributed uniformly in the Cu matrix. The presence of Cu and TiC was confirmed by X-ray diffraction analysis. XRD analysis showed that there was no formation of copper oxide which affected electrical properties of composites negatively. With the increasing addition of TiC, the hardness of composites increased while relative density decreased. High TiC contents decrease the electrical conductivity of Cu–TiC composites as expected. The highest electrical conductivity for Cu–TiC composites was obtained in the Cu-1 mass% TiC composite, with approximately 81.2 % IACS.

Acknowledgements This research was financially supported by Kastamonu University Scientific Research Projects Coordination Unit (Project No: KUBAP-01/2012-15) and Firat University Research-Project Unit (FUBAP) (Project No: FF. 12.05).

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