PROCESSING AND PROPERTIES OF Cu-5 WT% TiN COMPOSITES

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Abstract

In the present work, compact of Cu matrix composites reinforced with 5 wt% of TiN were prepared by mechanical alloying and spark plasma sintering method. Influence of sintering parameters on the electrical, mechanical, physical properties and microstructure of copper matrix composite material was investigated. From the results of the measurements, it follows that within the entire investigated temperature range, the density, hardness and electrical conductivity of copper-TiN composites change according to the temperature consolidation changes. It was determined that structure properties and density of sintered material have direct relations to electrical conductivity. Based on the study, it could be concluded that homogeneous distribution of reinforcement phase and maximize reduction of porosity in sintered material should have an impact for electrical conductivity of Cu matrix composites made by powder metallurgy route. A composite of copper and TiN particles reinforcement was prepared by mechanical alloying and consolidated by spark plasma sintering under different temperatures. Electrical conductivity and hardness of the composites change with the temperature of consolidation.

Keywords: Powder metallurgy, copper, titanium nitride, spark plasma sintering, mechanical alloying

1. INTRODUCTION

Copper and its alloys are widely used in the electronic and manufacturing industry which require for example high electrical conductivity, good mechanical properties and microstructural stability [1]. Pure copper is characterized by high ductility so it is necessary to increase its mechanical resistance being careful not to alter their electrical conductivity. There are two generally ways to improve the mechanical properties of copper: either by an age hardening mechanism or by incorporation of a hard second phase such as carbides, borides, oxides or nitrides into copper by developing copper base metal matrix composites (CMC). One of those reinforcing materials - TiN particles can be used to improve the property of material, as it has a high melting point and hardness, perfect ductility, wear resistance, and electric conductivity. Moreover, titanium nitride is susceptible to oxidation (whose products are TiO_xN_y and TiO_2 - potentially useful as protective coating materials) [1 - 4].

There are many methods of production of CMC. The most widely applied is based on powder metallurgy which seems to be better way to prepare composites [5]. In the present work, the effects of TiN particles on the electrical and mechanical a performance of Cu-5 wt% TiN composites were investigated.

2. METHODOLOGY

Electrolytic Copper (Cu) powder with purity of 99.7 % (Pometon) was used as a metal matrix. The particles size was less than 50 μm (dendritic shape). Titanium nitride powders (Sigma-Aldrich) were used as reinforcing material which particles size was less than 3 μm (irregular shape). Elemental powders of copper and titanium nitride particles were mechanically alloyed in a high-energy planetary ball mill for 25 h with a milling speed of 200 rpm and ball-to-powder weight ratio of 10:1 without a control agent. The container and balls were made from WC-Co material. The composite Cu-TiN powders were sintered by spark plasma sintering (SPS) under different temperatures: 680, 720, 760 and 800 °C and held for 5 min. The powder mixture was put into a cylindrical graphite die with a inner diameter of 20 mm. Samples were heated by passing alternating DC current through the die and punches from the room temperature to sintering temperatures. A pressure of 35 MPa was applied from the start to the end of the sintering. The SPS process was performed in a vacuum atmosphere. The microstructure (scanning electron microscope), hardness (Brinell test) and electrical conductivity (SIGMA TEST) were inspected. The density of the sintered composite powders was measured by Archimedes' principle.

3. RESULTS AND DISCUSSION

3.1. Composite powders after mechanical alloying

Mechanical alloying involves material transfer to obtain a homogeneous alloy by means of repeated deformation, joining and fracture mechanisms. Mechanical alloying is the process in which mixtures of different powders are milled together. Whereas, mechanical milling is the process in which material transfer is not required for homogenization. It consists of powders milling of uniform composition [6]. During high-energy ball milling the powder particles are repeatedly flattened, joined and fractured. Whenever steel balls collide, some amount of powder is trapped in between them. The force of the impact plastically deforms the powder particles leading to strengthening and fracture. The new surfaces created enable the particles to join together and this leads to an increase in particle size [6,7]. At the beginning of process, the ductile particles undergo deformation while brittle particles undergo fragmentation. The brittle particles come between two or more ductile particles at ball collision, whereas ductile particles start to joining. Finally, fragmented reinforcement particles are domicile in the interfacial boundaries of the joined metal particles. The composite particle is formed. [6,7]. In the **Figure 1** it is shown microstructure of Cu-TiN powders after 25 hours of mechanical alloying. It can be observed that composite powders are characterized by the presence of tungsten particles (white dots) inside the soft copper matrix (light grey area). The container and the balls in the planetary mill were made from WC-Co so tungsten carbide likely penetrated into copper matrix from one or all of these. Similar behavior noticed Kruger [8]. It can be also observed that titanium nitride particles (dark grey dots) are uniformly formed into matrix. The presence of Cu, TiN was confirmed by EDS analysis.

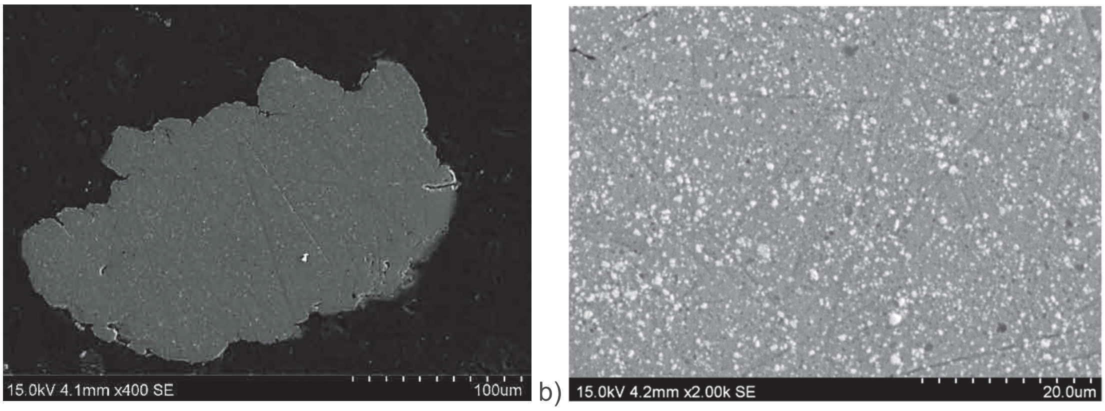
a) b)


Figure 1 Composite particle Cu-5 wt% TiN after 25 hours of mechanical alloying, SEM

The parameters of the milling process have a decisive influence on the speed and nature of changes in the powder structure. When using low energy mixing, the shape of the copper grains constituting the plastic matrix of the composite does not change, they remain close to the spherical shape. At the same time, it was observed that titanium nitride grains are arranged on the surface of copper grains, in extreme cases they are not related to the matrix and appear as loose individual grains of powder. Increasing energy causes plastic deformation of the grains, and as a result of interaction with the grinding elements they are broken. As a result of this process, sharp edges appear and the grains take the shape of petals. An extremely important aspect of this process is the mechanical bonding of the ceramic grains with copper, which results in its proper distribution in the entire volume. The elimination of agglomerations of ceramic powder should lead to the limitation of residual porosity in the material after sintering. This is particularly important when the sintered materials differ significantly in the melting point, which is directly related to the sintering temperature [9].

3.2. Composite powders after consolidation by spark plasma sintering under different temperatures

Composite powders after 25 h of mechanical alloying were consolidated by spark plasma sintering technology under (680, 720, 760, 800) °C and held for 5 min. A pressure of 35 MPa was applied for all of the samples. In the **Figure 2 (a-d)** shown the microstructure using scanning electron microscope.

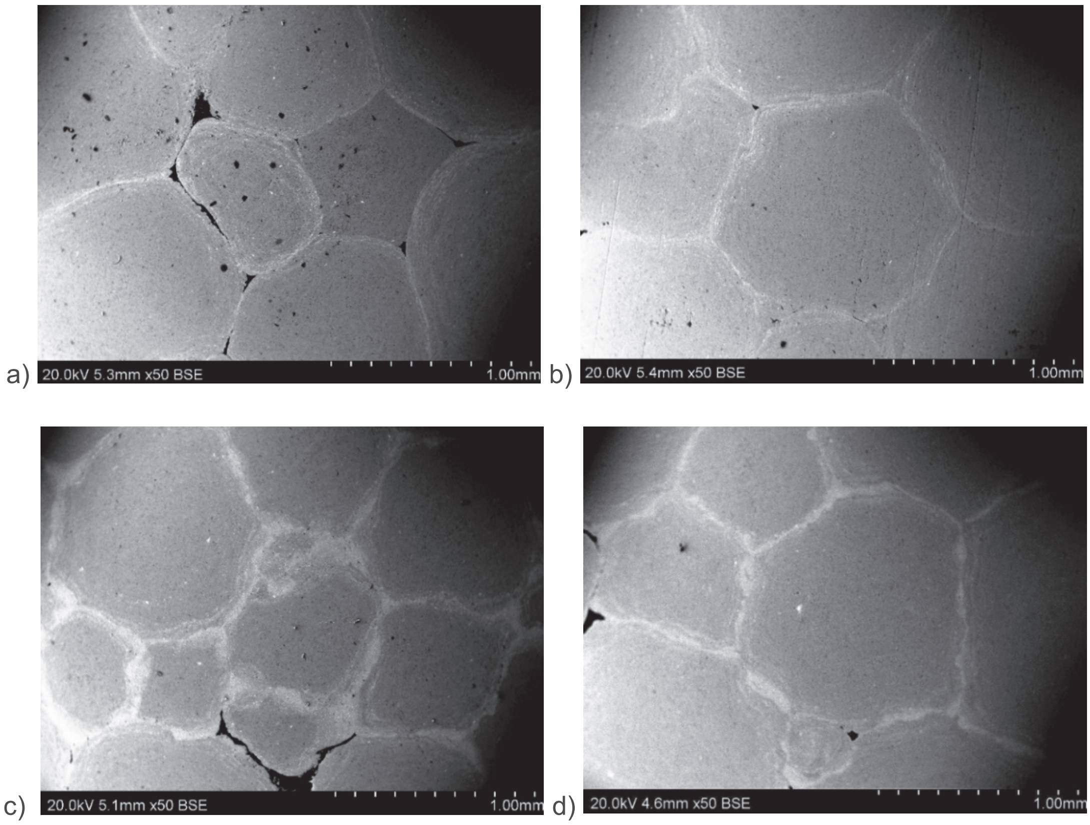


Figure 2 Composite powders after consolidation by spark plasma sintering under different temperatures: (a) 680 °C, (b) 720 °C, (c) 760 °C, (d) 800 °C, SEM

It can be observed that scanning electron microscope allows to observe the tungsten which is concentrated in grain boundary of matrix. The presence of tungsten particles coming from mechanical alloying process is visible on the point analysis of chemical composition performed by EDS analysis (**Figure 3**). In addition, discontinuities in the structure of the material in the form of porosity were found. It can be easily seen from the microstructure images that the material after sintering is not uniformly homogeneous, and the increase in temperature did not cause significant change in the size of particles and pores.

For composites consisting of metals and ceramics, generally differing in the sintering temperature, an increase in the proportion of pores in the structure is observed along with the increase in the proportion of the ceramic phase. In such cases, the ceramic phase forms clusters, and between the individual grains only limited diffusion changes may occur (the diffusion rate depends on the temperature). The effect of this is the observed discontinuity of the structure in these areas [10].

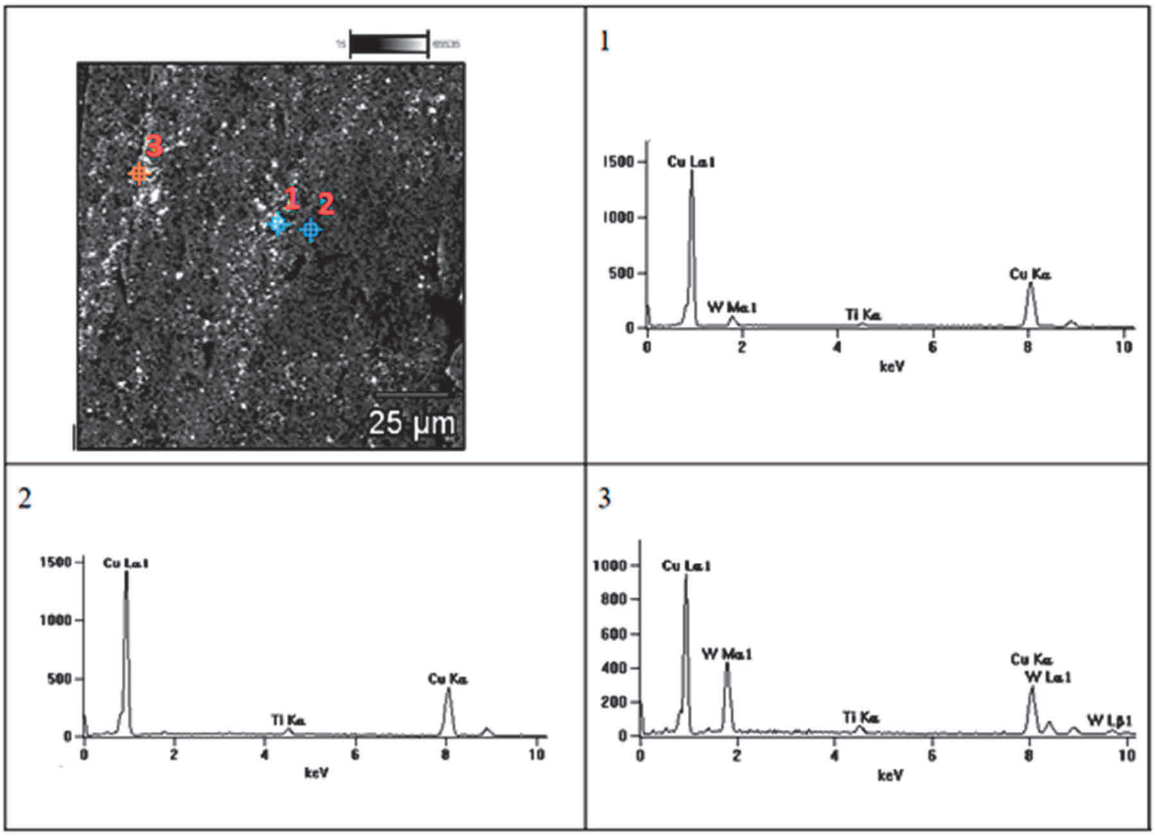


Figure 3 Microstructure and point EDS analysis of composite powders Cu-5 wt% TiN after consolidation by SPS at 800 °C

3.3. Density, hardness

The highest density was observed in the case of sintering under 680 and 720 °C (**Figure 4**). Increasing the sintering temperature does not cause significant differences in the density of the composites. In composites with low TiN volume fraction, less Cu-TiN interface means less copper atom diffusion barrier, copper atoms can diffuse easily and fill the interstices between the TiN particles, thus leading to a higher densification of the composite. However, there is the presence of tungsten carbide in material which may constitute an affective barrier to achieve a higher density value.

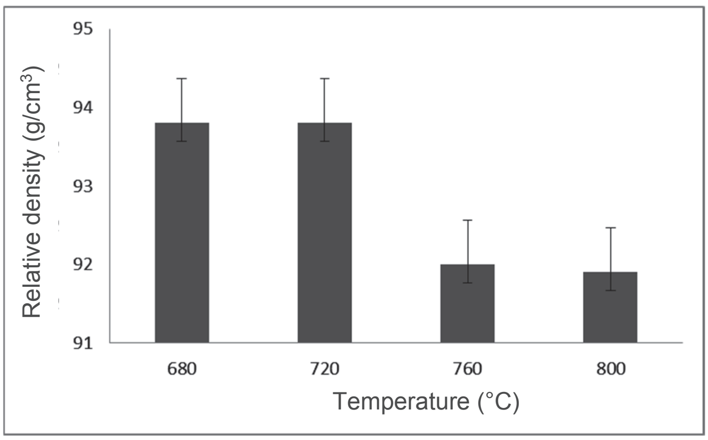


Figure 4 Relative density of composites

The hardness of sintered composite powders measured by Brinell hardness instrument ranged from 125 to 151 HBN (**Figure 5**). Hardness results refer to density results - hardness values are higher when the density is high. TiN with high hardness, which acts as reinforcing phases, is dispersed in copper matrix and become the obstacles to the movement of dislocation when plastic deformation occurs, and resulted in the distortion of lattice, which created much internal stress in composites. When the movement of dislocation was impeded by the dispersed phase and grain boundary, it would generate a strengthening effect [11,12].

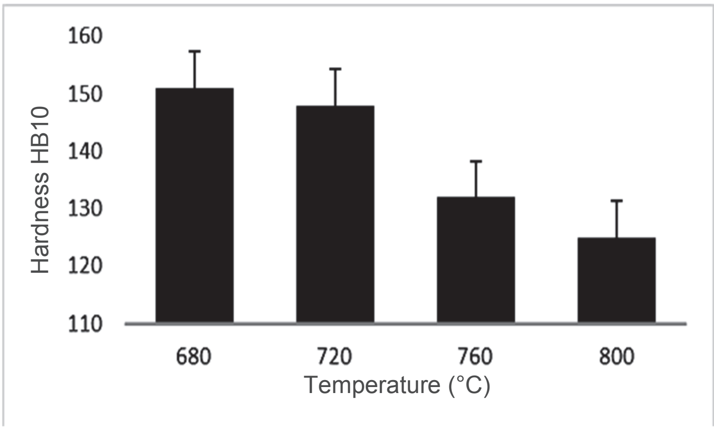


Figure 5 Brinell hardness of composites

3.4. Electrical conductivity

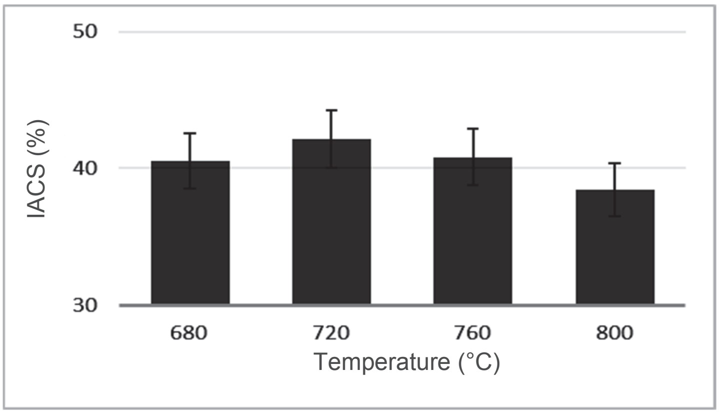


Figure 6 Electrical conductivity of Cu-5 wt% TiN composites, different temperatures of sintering

The similar tendency can be observed with electrical conductivity (**Figure 6**). Composites characterized by high value of density possess higher electrical conductivity. Composites with 5 wt% TiN addition to Cu matrix was measured as 38.4-42.1 % IACS. Porosity, oxidation and presence of tungsten carbide could be asserted as the reason for low electrical conductivity [13]. With the sintering temperature increased, the electrical conductivity of composites decreased which probably could be due to formation of oxide at high temperatures [13].

The electrical conduction of the metal is mainly dependent on the movement of the internal electrons. The electrical conductivity of the composites decreased because ceramic-based TiN forms a barrier to the motion of copper electrons, providing electrical conductivity [9]. The electrical properties of TiN are still not sufficiently known - researchers determined its electrical resistance in the temperature range 77 ≤ T ≤ 300 K, and in recent years have filled this gap by providing data in the range of 300-673 K [14]

4. CONCLUSION

In the presented work, copper matrix composites reinforced with titanium nitride was achieved by the mechanical alloying and Spark Plasma Sintering method. Composite powders were sintered by SPS under different temperatures (680, 720, 760 and 800 °C) which which did not show a significant difference in the density results. Hardness results and electrical conductivity refer to density results - these values are higher when the density is high.

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