Copper matrix composites reinforced with titanium nitride particles synthesized by mechanical alloying and spark plasma sintering

Kompozyty na osnowie miedzi umacniane cząstkami azotku tytanu wyтворzone w procesie mechanicznej syntezy i iskrowego spiekania plazmowego (SPS)

Abstract
Copper matrix composites containing ceramic particles such as carbides, borides, or nitrides have attracted much attention over the last few years. The increased interest in such materials has mainly been created by their high electrical and thermal conductivity, good mechanical and tribological properties, and microstructural stability. Among other nitrides, the titanium nitride seems to be considered as an attractive reinforcement due to its high hardness, excellent electrical conductivity, and stability at high temperatures. Moreover, its good corrosion resistance proves the uniqueness of the TiN particles above any other nitrides. In this work, Cu-10 wt.% TiN composite powders were produced by mechanical alloying and sintered by the spark plasma sintering (SPS) technique under different temperatures. The morphology and powder particle size after mechanical synthesis were inspected by a scanning electron microscopy (SEM) for all of the powder samples; chemical composition analyses (EDS) were also performed. The hydrostatic method was used to measure the density of the composite samples to analyze the influence of milling time on the process of consolidation in the composite powders.

Keywords: copper matrix composites, mechanical alloying, spark plasma sintering, titanium nitrides, powder metallurgy

Streszczenie
Kompozyty na osnowie miedzi zbrojone cząstkami ceramicznymi, m.in. węglikami, borkami i azotkami, w ostatnich latach wzbudziły spore zainteresowanie z uwagi na wysoką przewodność
cieplną i elektryczną oraz dobre właściwości mechaniczne i tribologiczne przy równoczesnym zachowaniu stabilnej mikrostruktury. Zastosowanie azotku tytanu jako zbrojenia kompozytu jest korzystne ze względu na: wysoką twardość, doskonałą przewodność elektryczną, odporność na korozję oraz stabilność w wysokich temperaturach. W pracy przedstawiono mieszankę kompozytową Cu-10% wag. TiN, wytworzoną w procesie mechanicznej syntety, którą następnie poddano spiekaniu za pomocą iskrowego spiekania plazmowego (SPS). Zbadano mikrostrukturę, wielkość cząstek, a także przeprowadzono analizę składu chemicznego (EDS, Energy Dispersive Spectroscopy) za pomocą skaningowego mikroskopu elektronowego (SEM). Metodą hydrostatyczną wykonano pomiar gęstości wytworzonych spieków w celu analizy wpływu czasu mielenia na proces konsolidacji proszku kompozytowego.

Słowa kluczowe: kompozyty na osnowie miedzi, mechaniczna syntety, iskrowe spiekanie plazmowe, azotek tytanu, metalurgia proszków

1. Introduction

Among any of the other commonly used metals, copper is the one characterized by the best thermal conductivity, which explains why it is commonly chosen in the first instance for a matrix material. On the other hand, having very low mechanical properties, it has to be strengthened by ceramic particles, for example, which is one of the most reliable methods of reinforcement [1].

Copper matrix composites are suitable for a variety of applications, such as heat sinks, connectors, high performance switches, electronic packaging, resistance welding electrodes, etc., due to the combination of both very good electrical/thermal conductivity and corrosion resistance [2, 3]. The most-widely-applied methods for producing copper matrix composites are based on the following: powder metallurgy methods, internal oxidation method, self-propagating high temperature synthesis process (SHS), accumulative roll bonding, mechanochemical route, and friction stir welding [4–16].

The carbides (e.g., SiC, TiC, NbC, WC, TaC, B₄C), oxides (e.g., Al₂O₃, Y₂O₃, SiO₂, Cr₂O₃, TiO₂), and borides (e.g., TiB₂, ZrB₂) are widely used as reinforcement additives; volcanic tuff, diamond particles, intermetallic phases, shavings of steel processing, and carbon tubes or fibers [4–16] are also starting to play a significant role in this domain. Among those modern reinforcing materials, TiN-based nitrides play a pronounced role, since they are characterized by high hardness, excellent electrical conductivity, good thermal and chemical stability, excellent stability at high temperatures, and good corrosion resistance [17, 18]. Moreover, titanium nitride is susceptible to oxidation (whose products are TiOₓNᵧ and TiO₂ – potentially useful as protective coating materials) [19].

The mechanical alloying (MA) process allows us to obtain a material with a variety of chemical, physical, and mechanical properties that combine the features of copper with those of titanium nitrides. Thus, this fabrication method seems to be a convenient one in order to produce materials with great electrical conductivity and durability at a relatively low cost of production [20].
2. Methodology

The presented investigations discuss observations pertaining to the synthesis of Cu-based composites reinforced with 10wt.% (15.47 vol.%) of titanium nitride particles. The average particle size of the electrolytic copper powder (purity 99.7%, Pometon Powder) and titanium nitride (Sigma-Aldrich) were less than 50 μm and 3 μm, respectively. Elemental powders of copper and titanium nitrides were mechanically alloyed in a high-energy planetary ball mill (Fritsch) for 5, 10, 15, 20, 25, and 30 hours with a milling speed of 200 RPM and a ball-to-weight ratio of 10:1 (without a control agent). The container and 15-mm balls were made from tungsten carbide. Mechanical alloying is an alternative method for producing ceramic and metallic powder particles in the solid state. A powder mixture placed in the ball mill is subjected to high-energy collision from the balls. This technique is based on the repeated welding, fracturing, and rewelding of the powder particles. The final stage of the process is characterized by a homogenous and micro-/nano-sized structure, which improves the properties and performance of the material. A variety of materials such as oxide dispersion strengthened materials, composites, and intermetallic compounds have been successfully synthesized – an achievement not possible by means of traditional methods [20, 21].

The copper powders were sintered by spark plasma sintering (SPS HP 5, FCT). The powder mixture was put into a cylindrical graphite die with an inner diameter of 15 mm. All of the samples were heated by passing alternating DC current through the die and punches from room temperature to 760°C and held for 5 min. 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 morphology, size of the milled powders, and chemical composition analyses were inspected by scanning electron microscopy (SEM, HITACHI) for all of the powder samples each time the mechanical-alloying process was completed. The density of the sintered composite powders was measured by Archimedes' principle.

3. Results and discussion

Figure 1 (a-f, magnification 2000×) shows the microstructures of the Cu-10 wt.% TiN powders after 5, 10, 15, 20, 25, and 30 hours of mechanical alloying, respectively. During the milling process, the powder particles were flattened, cold welded (Figs. 1a, 1b), fractured, and rewelded (Figs. 1c–1f). The impact force plastically deformed the powder particles, leading to work hardening and fracture. The newly created surfaces enabled particles to weld together, and this lead to an increase in particle size as a consequence (Figs. 1a, 1b). At the beginning of the milling process, the particles are soft, and their tendency to weld together and form large particles is high (Figs. 1a, 1b). The composite particles at this stage have a characteristic layered structure consisting of various combinations of the
starting constituents. With continued deformation, the particles get to work harder and fracture by a fatigue failure mechanism. Fragments generated by this mechanism may continue to reduce in size with the absence of strong agglomerating forces (Figs. 1c–1f). The tendency to fracture predominates over cold welding [20].

Fig. 1. SEM microstructures of Cu-10 wt.% TiN composite powders: a) 5 h mechanical alloying, magnification 2000×; b) 10 h mechanical alloying, magnification 2000×; c) 15 h mechanical alloying, magnification 2000×; d) 20 h mechanical alloying, magnification 2000×; e) 25 h mechanical alloying, magnification 2000×; f) 30 h mechanical alloying, magnification 2000×
In the early stage of milling, the particle sizes are enhanced and agglomerations of copper and titanium formed because of the plastic deformation and cold welding of the powders (Figs. 1a, 1b). At longer milling times, transferred energy to the powders increase due to ball-powder-ball and ball-powder-wall collisions (Figs. 1c–1f). This transferred energy causes more plastic deformation, increasing the dislocation density and work hardening of powders. Fracturing overcomes cold welding; therefore, particle size reduces. An average particle size of the Cu/TiN powders after 5 and 10 hours of milling is about 100 µm; after 15 hours of milling, it is about 50 µm. It can be observed that the particle size is decreased to 16 µm with increased milling time, and the titanium nitride particles are homogeneously distributed in the matrix (Figs. 1e–1f). It is suggested that 20 hours of milling is sufficient in the case of fabricating composite powder by mechanical alloying when the matrix is electrolytic copper. It is observed that the composite powder particles tend to agglomerate with an increase to 30 hours of milling time. Therefore, the highest relative density after pressing and sintering is obtained for Cu-TiN composite powders after 20 hours of milling (Fig. 2).

![Image](image_url)

**Fig. 2. EDS analysis after 20 h of mechanical alloying, magnification 3000×**

It can be observed that composite powders are characterized by the presence of tungsten particles inside the soft copper matrix after 5, 10, 15, 20, 25, and 30 hours of mechanical alloying. The container and balls in the high planetary mill were made
from WC, and tungsten likely penetrated into the copper from one or all of these. Figures 2–4 present an analysis of the chemical composition for the Cu-10 wt.% TiN composite powders performed by EDS analysis. Observations were made for specimens after different stages of mechanical alloying before the spark-plasma-sintering route. As shown, titanium nitride particles (dark grey dots) are uniformly formed in the copper matrix (grey area). It can be observed that the composite powders consist of white particles rich in tungsten, which can be related to the fact that the container and balls in the high planetary ball mill were made from WC.

Fig. 3. EDS analysis after 25 h of mechanical alloying, magnification 5000x
Figures 5 and 6 show the influence of milling time on the relative and apparent density of the Cu-10 wt.% TiN composite powder sintered at 760°C. As shown, with an increase in milling time, the relative density of the composites decreases from 77.46% for 20 hours to 74.79% for 30 hours of MA. The apparent density decreases from 6.94 g/cm³ after 20 hours of mechanical alloying to 6.07 g/cm³ after 30 hours of MA.

Fig. 4. EDS analysis after 30 h of mechanical alloying, magnification 5000×

Fig. 5. Influence of milling time on relative density of Cu-10 wt.% TiN
4. Conclusions

A copper matrix composite powder reinforced with titanium nitride was obtained by the mechanical alloying method at different times of milling (5, 10, 15, 20, 25, and 30 hours, respectively). Mechanical alloying of copper powder and the titanium nitride powder mixture leads to the following:
- cold welding of plastic Cu particles with brittle TiN and growth of powder particles in the initial stage of mechanical alloying (Figs. 1a, 1b),
- formation of composite powder with homogeneous distribution of TiN particle inside Cu matrix after 15 hours of MA,
- strong composite particle size reduction after 20 hours of MA (from 100 mm to 16 mm).

The prepared composite powders were sintered by the Spark Plasma Sintering method at 760°C with a holding pressure of 35 MPa and holding time 5 min in a vacuum atmosphere. Research proves that the best results by determinate by density measurements were obtained for composite powders milled for 20 hours. A longer mechanical alloying time results in a decrease in the relative and apparent density of the sintered composite (which is lower than 90% as a consequence).

Acknowledgements

Experiments were carried out under the statutory activity at AGH in Krakow No. 11.11.180.653

References

[1] Copper and Copper Alloys. ASM Specialty Handbook, USA (2001), 446–448
[2] You J.H.: Copper matrix composites as heat sink materials for water-cooled diverter target. Nuclear Materials and Energy, 5 (2015), 7–18
[3] Qu X., Zhang L., Wu M., Ren S.: Review of metal matrix composites with high thermal conductivity for thermal management applications. Progress in Natural Science: Materials International, 21, 3 (2011), 189–197

[4] Zou C., Kang H., Wang W., Chen Z., Li R., Gao X., Li T., Wang T.: Effect of La addition on the particle characteristics, mechanical and electrical properties of in situ Cu-TiB2 composites. Journal of Alloys and Compounds, 687 (2016), 312–319

[5] Rathod S., Modi O.P., Prasad B.K., Chrysanthou A., Vallauri D., Deshmukh V.P., Shah A.K.: Cast in situ Cu-TiC composites: Synthesis by SHS route and characterization. Materials Science and Engineering A: Structural Materials: Properties, Microstructure and Processing, 502, 1–2 (2009), 91–98

[6] Alaneme K.K., Odoni B.U.: Mechanical properties, wear and corrosion behavior of copper matrix composites reinforced with steel machining chips. Engineering Science and Technology, an International Journal, 19, 3 (2016), 1593–1599

[7] Mikuła J., Łach M.: Kompozyt miedź – tuf wulkaniczny. Wytwarzanie, własności i zastosowania. Czasopismo Techniczne. Mechanika, 108, 3-M (2011), 53–60

[8] Shojaeepour F., Abachi P., Purazrangi K., Moghanian A.H.: Production and properties of Cu/Cr2O3 nanocomposites. Powder Technology, 222 (2012), 80–84

[9] Shehata F., Fathy A., Abdelhameed M., Moustafa S.F.: Preparation and properties of Al2O3 nanoparticle reinforced copper matrix composites by in situ processing. Materials and Design, 30 (2009), 2756–2762

[10] Ying D.Y., Zhang D.L.: Processing of Cu-Al2O3 metal matrix nanocomposite materials by using high energy ball milling. Materials Science and Engineering A: Structural Materials: Properties, Microstructure and Processing, 286, 1 (2000), 152–156

[11] Sorkhe Y.A., Aghajani H., Taghizadeh Tabrizi A.: Mechanical alloying and sintering of nanostructured TiO2 reinforced copper composite and its characterization. Materials and Design, 58 (2014), 168–174

[12] Manotas-Albor M., Vargas-Uscategui A., Palma R., Mosquera E.: In situ production of tantalum carbide nanodispersoids in a copper matrix by reactive milling and hot extrusion. Journal of Alloys and Compounds, 598 (2014), 126–132

[13] Wang F., Li Y., Wang X., Koizumi Y., Kenta Y., Chiba A.: In-situ fabrication and characterization of ultrafine structured Cu-TiC composites with high strength and high conductivity by mechanical milling. Journal of Alloys and Compounds, 657 (2016), 122–132

[14] Kruszewski M., Rosiński M., Grzonka J., Ciupiński L., Michalski A., Kurzydlowski K. J.: Kompozyty Cu-diament o dużym przewodnictwie cieplnym wytwarzane metodą PPS. Materiały Ceramiczne, 64, 3 (2012), 333–337

[15] Sathiskumar R., Murugan N., Dinaharan I., Vijay S.J.: Characterization of boron carbide particulate reinforced in situ copper surface composites synthesized using friction stir processing. Materials Characterization, 84 (2013), 16–27

[16] Zhao N., Li J., Yang X.: Influence of the P/M process on the microstructure and properties of WC reinforced copper matrix composite. Journal of Materials Science, 39 (2004), 4829–4834

[17] Yinan L., Xianbao L., Zhikang Z., Zhang L., Peng Z.: The Microstructure and Wear Resistance of a Copper Matrix Composite Layer on Copper via Nitrogen-Shielded Arc Cladding. Coatings, 6, 4, 67

[18] Magdy A.M. Ibrahim, Kooli F., Alamri S.N.: Electrodeposition and Characterization of Nickel-TiN Microcomposite Coatings. International Journal of Electrochemical Science, 8, 11 (2013), 12308–12320

[19] Liu Y., Treadwell D.R., Kannisto M.R., Mueller B.L., Laine R.M.: Titanium Nitride/Carbon Coatings on Graphite Fibers. Journal of the American Ceramic Society, 80, 3 (1997), 705–716

[20] Suryanarayana C.: Mechanical alloying and milling. Progress in Materials Science, 46 (2001), 1–184

[21] Lü L., Lai M.O.: Introduction to Mechanical Alloying. Springer Science + Business Media, LLC, New York, 1998, 1–9