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Synthesis and Characterization of Cu-ZrB_2 Alloy Produced by PM Techniques

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Abstract:

The copper alloy with 7vol.% ZrB_2 examined in this study was consolidated via powder metallurgy processing (PM) by combining mechanical alloying and hot pressing process. Structural changes, morphological properties and elemental analysis of the hot-pressed samples were studied as a function of milling time with the use of X-ray diffraction, scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometry (EDS). Also, mechanical properties of the Cu-7vol.%ZrB_2 alloy was investigated. Distribution of ZrB_2 particles and presence of agglomerates in the Cu matrix directly depend on the milling time and show strong influence on hardness, compressive and electrical properties of Cu-ZrB_2 alloys.

Keywords: *Mechanical alloying, Hot pressing process, Cu-ZrB_2 Alloy, Mechanical properties, Electrical properties*

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1. Introduction

In past decades, improved copper-based alloys are being examined as potential candidate materials in aerospace, automotive, military and electrical industry [1-3]. The greatest challenge is to create a material with the best combination of excellent mechanical characteristics and conductivity. Low content of alloying elements in copper matrix enables the highest possible thermal or electrical conductivity and very good mechanical properties sufficient to withstand demanding operating conditions even in nuclear technology and rocket industry [4,5]. The three directions in research and development of new alloys and composites with copper matrix, in terms of reinforcement, have been dominated throughout last few years [5,6]: precipitates formed from solid solutions of copper, precipitates or dispersoids formed from the stable intermetallic compounds without copper and reinforced by metal borides.

In the present study, an attempt has been made to develop a Cu–ZrB_2 composite by using powder metallurgy (PM) technique. Addition of hard ceramic material such as ZrB_2 to

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[*)] **Corresponding author**: jruzic@vinca.rs, the Cu matrix can significantly improve mechanical properties, wear and spark resistance, as well as maintain high electrical and thermal conductivity of Cu based composites [7-12]. During mechanical alloying (MA) particles of Zr and B were mechanically activated which has enabled in situ forming of ZrB_2 in copper matrix in the course of hot pressing process [13]. The aim of this work was to investigate the influence of mechanical alloying parameters on microstructural, mechanical and electrical properties of Cu-7vol. % ZrB_2 alloy obtained by PM techniques.

2. Experimental

2.1. Synthesis of Cu-ZrB_2 alloy

Copper electrolytic powders with purity of 99.5% and average particles size around 14 μm, zirconium powders with 99.5% purity and average particles size around 1.16 μm and amorphous boron with 97% purity and average particles size around 0.08 μm were used as starting powders and weighed to give stoichiometric 7vol.% ZrB_2 in copper matrix. Mixture was homogenized for 1 hour and mechanically alloyed in Netzsch attritor mill with ball-to-powder weigh ratio of 5:1, by using stainless steel balls with 6 mm in diameter. Attrition milling atmosphere was protected by argon gas to prevent the oxidation of powder mixtures for different times from 5 up to 30 hours, with stirring speed of 330 rpm with. The particles sizes of starting and mechanically alloyed powders were measured in Mastersizer 2000. Hot pressing of mechanically alloyed mixtures was carried out in ASTRO furnace with the heating rate 15 ˚C/min, at temperature of 950 ˚C and under a pressure of 35 MPa, with retention time of 2.5 hours, with the use of graphite mold (10 mm diameter). Density of the compacts was determined by Archimedes method in water.

2.2. Characterization of powder mixtures and compacts

The powder mixtures and corresponding compacts were characterized by X-ray powder diffraction (XRD) analysis which was performed using a Ultima IV Rigaku, with CuKα Ni filtered radiation. Vickers micro and macrohardness was determined using Buehler Hardness Tester, under the load of 0.98N and 9.8 N, respectively, and presented values were obtained from an average of 12 indents. The morphological and microstructural properties of mechanically alloyed powders and compacts were observed with a JEOL-JSM 5800LV scanning electron microscope at an accelerating voltage of 20 kV equipped with an energy dispersive X-ray spectroscope (EDS). The compressive test was carried out at room-temperature using 1185 Instron-type testing machine on cylindrical samples with the length/diameter ratio of 2, at a strain rate of 1 mm per minute. Electrical conductivity was tested on device Forester Sigma Test 2069, at a frequency of 120 kHz.

3. Results and discussion

The changes in particle sizes and morphology during mechanical alloying treatment are shown in Figs. 1 and 2. At the beginning of mechanical alloying particles are soft and easily can be deformed due to high energy collisions of balls to particles, which leads to micro forging of particles powder. The collisions between balls and particles initiate cracks and propagate it more rapidly in Zr particles than in Cu (HCP Zr particles are more brittle than ductile FCC Cu particles) so Zr parts can propagate into Cu particles and fracture it. At this stage cold welding is dominant process and the initial particles shape is changed because of particles flattening. After 10 hours of milling particle sizes have decreased due to influence of work hardening on brittleness and fracturing of particles. Increasing in particles sizes has been noticed after 20 hours and up to 30 hours of milling, as a consequence of cold welding or forming relatively coarse agglomerated particles. Also, in this interval time more uniform and rounded shape of powder particles has been observed (Fig.2A-C). It can be concluded that influence of milling time and all mention processes of mechanical alloying on morphological and mechanical characteristics of particles significantly depend on amount of present alloying elements Zr and B [15, 16]. SEM analysis showed that at longer milling time characteristic layers are formed as a result of cold welding and deformation (Fig.2D).

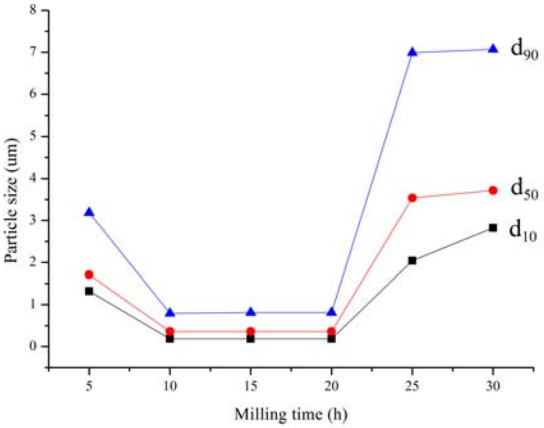

Fig. 1. The changes in particle sizes of mechanically alloyed powders for different milling times.

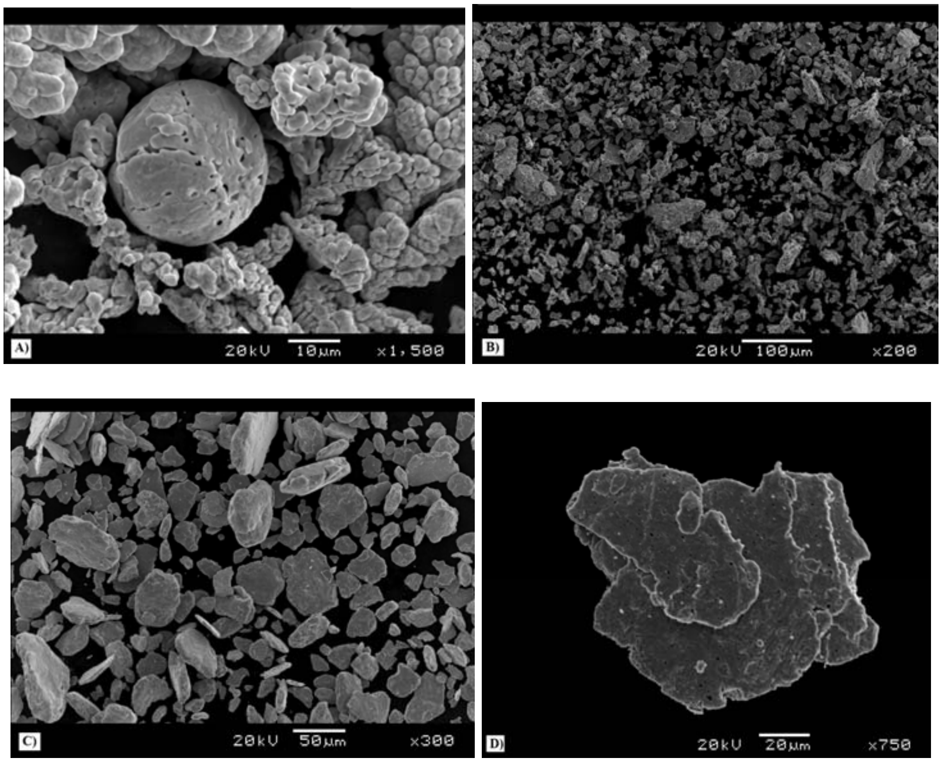

Fig. 2. Influence of milling time on mechanically alloyed powder particles shape and size, SEM photomicrographs: A) Copper, B) 5 h; C) 25 h; and SEM photomicrographs of formed characteristic layers D) 30 h.

The obtained values of microhardness show increasing at longer time of mechanical alloying (Fig. 3), and it's consequence of the fine-grained structure presence, which is characteristic for all mechanical alloying-treated powders, as well as effect of work hardening, deformation and cold welding of the particles. Compacts made of powders at shorter milling time shows larger deviation of microhardness values than compacts with longer milling time. A wider range of values up to 10 h of milling time indicates that mechanical alloying process is not finished, some of the particles are more brittle, or has various particle size or varying level of deformation and strengthening.

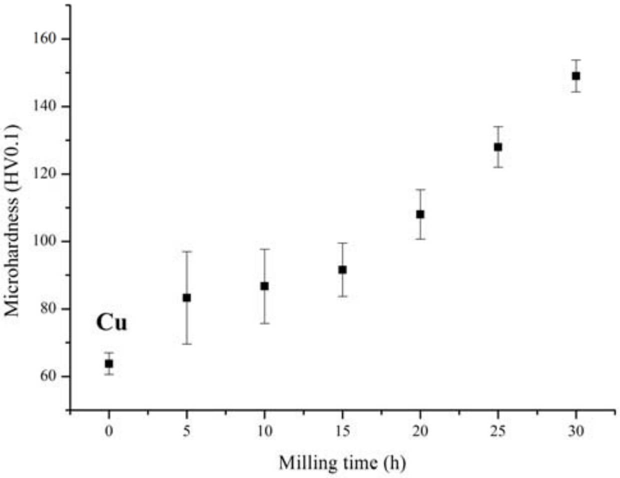

Fig. 3. Changing of microhardness values during milling time.

X ray analysis of mechanically alloyed powders showed that particles of ZrB_2 are not formed after mechanical alloying, so curves are consisted only of Cu and Zr lines, and low amount of B couldn't be detected. Analysing pattern of MA powders has been determined that extension of time MA leads to reduction in copper lattice parameter until it reach its minimum around 20 hours, followed by increases. The forming of ZrB_2 particles during hot pressing process was confirmed by XRD analysis (Fig.4.), and SEM-EDS analysis (Fig.5, for MA 30h).

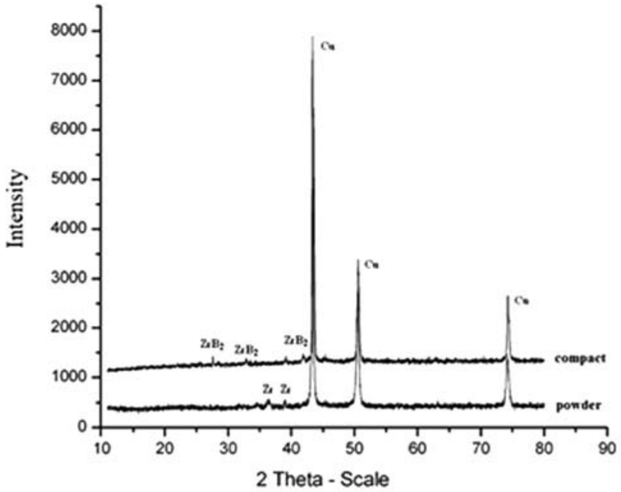

Fig. 4. XRD pattern of the mechanically alloyed powder and its corresponding compact.

The differences in the microstructure of the compacts are shown in Fig.5. Comparing microstructures of three samples (obtained from MA powders of 5, 20 and 30 hours) by using SEM analysis, has been shown that the size, shape and distribution of ZrB_2 particles in Cu matrix as also as presence of recrystallized areas and porosity are changing due to milling time duration. In the process of the MA dominant mechanism is particle fracture, which results in more homogenous distribution of reinforcement particles in the matrix, their smaller size and forming of smaller agglomerates. In situ forming of reinforcements ZrB_2, at an appropriate temperature and pressure during hot pressing, is result of Zr and B atoms diffusion in solid Cu matrix. The overall behaviour of materials under the influence of applied pressure and high temperature is very complex because of various densification mechanisms. Obtaining compacts by hot pressing process with present parameters enables high compact density but compared to pure copper compact, the full densification of Cu-7vol.% ZrB_2 alloy was not achieved because of hardening effects due to presence of ZrB_2 particles, hence the residual porosity is a result of the presence of ZrB_2 agglomerations with varying sizes. Maximum density values have compacts made of mechanically alloyed powders for more than 25 hours (above 95% of theoretical density) and minimum density values has compact for 5h MA (92% of theoretical density).

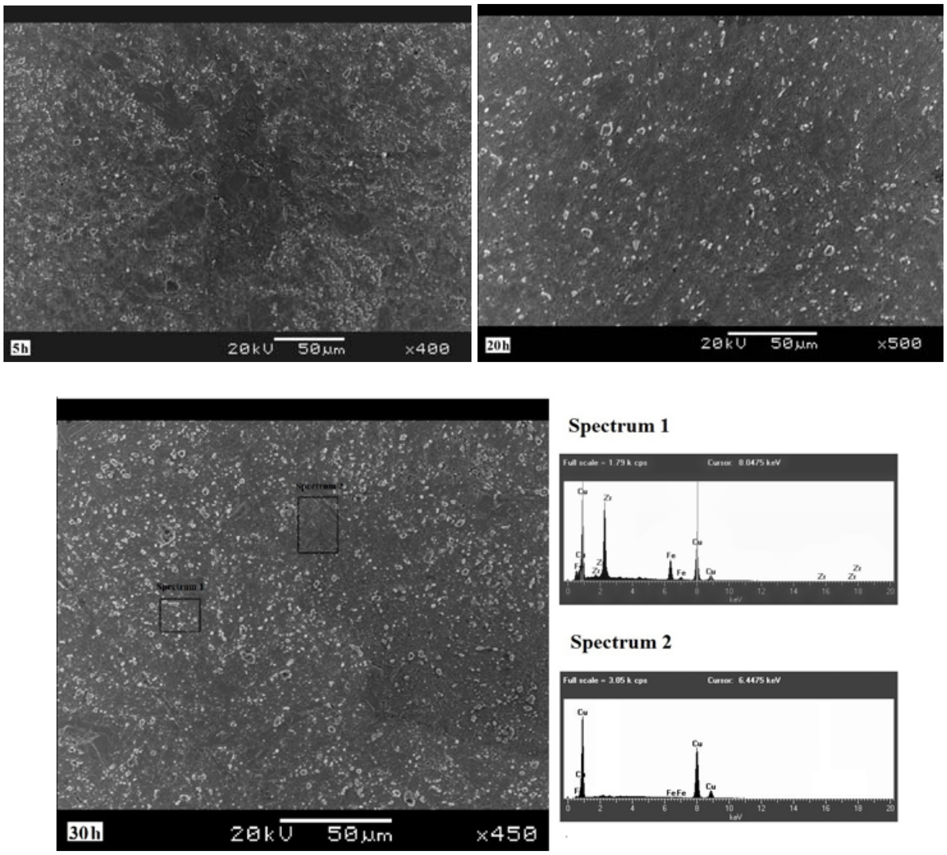

Fig. 5. Microstructure of compacts obtained from 5, 20 and 30 h milled powders. The EDS spectrums are marked in photomicrograph for MA 30h.

Effect of milling time duration of the starting powder mixtures on changes in the macrohardness and compressive strength of compacts are shown in Fig.6. The maximum value of the macrohardness is reached with powder compacts obtained from mechanically alloyed for 25 hours, which confirms the thesis that the particulate reinforcement of Cu matrix with increasing dislocation density leads to the increasing of hardness and strength of materials. The presence of reinforcements increases the density of dislocations and decreases the grain size, because ZrB_2 particles act as a place of nucleation during solidification. The grain size is reduced by the formation of subgrains when dislocations are rearranged into boundaries within the grain [16]. After 25h of milling time, mechanical properties slightly decrease due to appearance of coarse agglomerates. Compressive strength (σ_M – maximum and $\sigma_{0.2}$ – yield strength) of Cu-7vol. % ZrB_2 alloy at room temperature shows the same dependence of mechanical alloying time as a macrohardness, as can be seen in Fig.6.

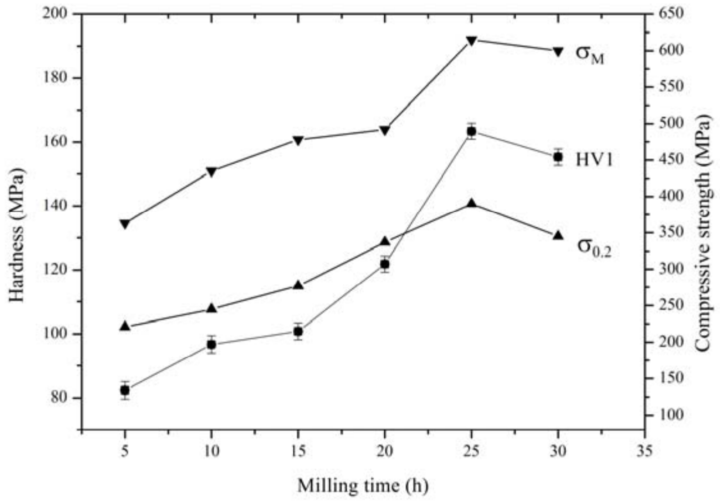

Fig. 6. The influence of milling time duration on macrohardness and compressive strength of Cu-7% vol.ZrB_2 alloy compacts at room temperature.

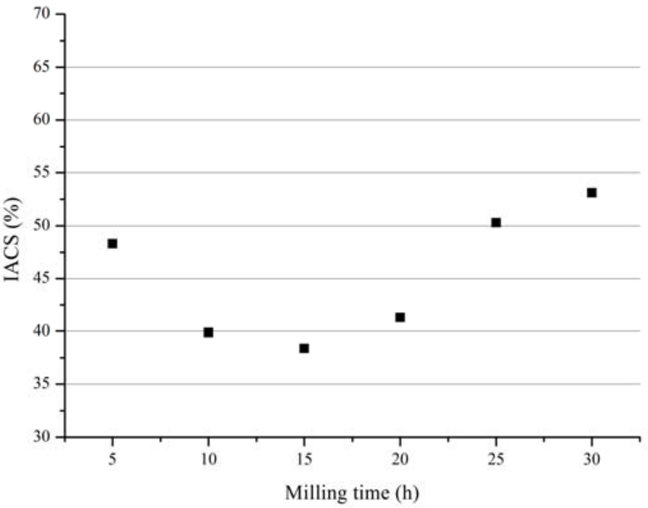

Fig.7. The influence of mechanical alloying time on electrical properties of Cu-7vol.% ZrB_2 alloy.

One of the most important characteristics of Cu alloys is their ability of electrical conductivity. Testing conductivity of Cu-7%vol.ZrB_2 alloy has shown that the electrical conductivity as well as strength and hardness are dependent on the particle size and distibution of reinforcements ZrB_2, the presence of the agglomerates, the pores and recrystallized grains. Thus, the electrical properties of the investigated alloy compacts depend on the length of mechanical alloying time (Fig.7). As dispersion of fine ZrB_2 particles in the metal matrix is higher (microstructure without recrystallized areas and coarse agglomerates) formation of metallic clouds are easier and the conduction of electricity is higher [17]. Regardless of the reduced electrical conductivity compared to pure copper, the Cu-7% vol.ZrB_2 alloy has excellent electric properties in comparison with other alloys, and belongs to a highly conductive alloy group – more than 50 IACS[1] (powders mechanically alloyed for a time longer than 25 hours). Electrical conductivity shows strong dependence on presence of pores, with increasing porosity the electrical conductivity decreases. Samples with lowest porosity (time of MA longer than 20 h) show the highest values of electrical conductivity.

4. Conclusions

1. Synthesis of Cu alloy reinforced with in situ formed ZrB_2 particles has been obtained via PM techniques up to near theoretical density.
2. Distribution and size of ZrB_2 particles and agglomerates in the copper matrix depends on the milling time and have strong influence on electrical and mechanical properties of Cu-7vol.%ZrB_2 alloy.
3. By increasing the time of mechanical alloying (until MA 25h) micro hardness of powders is increasing and accordingly macro hardness and strength of their corresponding compacts are also increased.
4. Present studies have shown that alloys with approximately 7 vol.% ZrB_2 has good performance and could be a candidate for obtaining materials which require high conductivity and good mechanical properties.

Acknowledgement

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Садржај: *Легура бакра са 7 вол. %* ZrB_2 *добијена је техником металургије праха (МП) тј. комбинацијом процеса механичког легирања и топлог пресовања. Структурне промене, састав и морфолошке карактеристике легуре испитиване су применом рендгенске дифракционе анализе, скенирајуће електронске микроскопије (СЕМ) са методом енергетски дисперзивне спектроскопије X – зрачења (ЕДС). Такође, испитиване су и механичке карактеристике легуре Cu-7вол.%* ZrB_2*. Расподела честица* ZrB_2 *и присуство агломерата у металној матрици бакра директно зависе од дужине времена механичког легирања и показују јак утицај на тврдоћу, притисну чврстоћу и електричне карактеристике испитиване легуре бакра.*

Кључне речи: *механичко легирање, топло пресовање, Cu-*ZrB_2 *легура, механичке карактеристике, електричне карактеристике*