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ISPLATIVA PROIZVODNJA LEGURE CuCrZr PRIMENOM METALURGIJE PRAHA

COST-EFFECTIVE PRODUCTION OF CuCrZr ALLOY USING POWDER METALLURGY

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Legura CuCrZr predstavlja aktuelan materijal sa potencijalnom primenom kao konstrukcioni materijal u budućim fuzionim reaktorima. Cilj ovog istraživanja je da se proizvede poboljšana CuCrZr legura primenom metalurgije praha (PM). Korišćene su PM tehnike mehaničko legiranje, hladno presovanje i sinterovanje. Komercijalno proizvedeni predlegirani CuCrZr prahovi su mehanički legirani 5 sati u inertnoj atmosferi argona korišćenjem visokoenergetskog mlina (Turbula mikser) sa kuglama različitih veličina. Mehaničkim legiranjem (ML) postignuto je povećanje gustine dislokacija matrice bakra, što dovodi do povećanja tvrdoće nakon densifikacije. Strukturni parametri (veličina kristalita, naprezanje i parametri rešetke) ML prahova i kompakta su ispitivani pomoću rendgenske difrakcije. Dobijeni rezultati pokazuju smanjenje veličine kristalita i parametra rešetke Cu matrice nakon ML. Dalje, XRD analiza je potvrdila prisustvo CuZr ojačavajućih čestica nakon sinterovanja. Mikrostrukturna analiza i distribucija ojačavajućih čestica Cu matrice izvršena je primenom SEM i XRD. Merenja tvrdoće su pokazala da in situ formiranje CuZr unutar Cu matrice povećava vrednosti tvrdoće za 45% u poređenju sa vrednostima tvrdoće čistog bakra.

Ključne reči: *CuCrZr; strukturni parametri; tvrdoća; metalurgija praha*

Promising copper-based material with potential application in future fusion reactors, as construction material, is CuCrZr alloy. The aim of this study was to produce improved CuCrZr alloy using powder metallurgy (PM). Applied PM techniques were mechanical alloying, cold pressing and sintering. The commercially produced prealloyed CuCrZr powders was mechanically alloyed (MA) for 5 hours in argon inert atmosphere using high-energy ball mill (Turbula mixer). Mechanical alloying was employed to increase dislocation density inside the Cu matrix which will contribute hardness enhancement after densification. Structural parameters (crystallite size, strain and lattice parameters) of MA powders and compacts were investigated using X-ray diffraction. Obtained results indicate that after mechanical alloying, crystallite size and lattice parameters of copper matrix decrease compared to starting material. Further, XRD analysis confirmed presence of CuZr reinforcing particles after sintering. Microstructural analysis and distribution of reinforcing particles inside the

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Cu matrix were performed using SEM and XRD. Measurements of hardness showed that in situ formation of CuZr inside the Cu matrix significantly raise hardness values 45% compared to hardness of pure copper compact.

Key words: *CuCrZr; structural parameters; hardness; powder metallurgy*

1. Introduction

Copper-based alloys have long been considered as viable candidate materials for first wall components in thermonuclear reactors [1]. Such application as a first wall material has been suggested in reactor designs with either substantial thermal loads on the initial barrier or the requirement for a surrounding shell of high electrical conductivity material to stabilize the plasma's position. One such alloy is a precipitation-strengthened CuCrZr alloy [2]. What makes this alloy a prime candidate for multiple uses in thermonuclear reactors is the fact that it offers a unique combination of desired mechanical properties and high thermal conductivity. Some of the key properties that put this alloy above almost all other Cu-based alloys include high strength even at elevated temperatures, excellent thermal and electrical conductivity, toughness, ductility, good fatigue resistance, high wear resistance, good tribological properties, low price and machinability [3-6]. As these properties are highly desirable for many applications, these alloys are also used in many different industries, including electronics, aerospace and military. As the CuCrZr alloy is classified as a structural material, two main properties of interest are mechanical properties and thermal conductivity [4].

The high strength of the CuCrZr alloy comes from the presence of nanoscale Cr-rich and Zr-rich phases, which precipitate from the matrix and contribute to particle-dispersion strengthening effects. Its high conductivity is a result of the limited solubility of Cr and Zr in the copper matrix [5, 7-10]. As the alloy undergoes aging, the supersaturated solid solution decomposes into fine and evenly distributed Cr-rich and Zr-rich phases. While the formation of these phases significantly enhances strength, they have minimal negative effects on the conductivity of the alloy [5, 11, 12]. Therefore, the presence of finely dispersed nano-precipitates within the copper matrix is crucial for achieving a CuCrZr alloy with both high strength and high conductivity. Based on this, it can be claimed that the alloy's high strength and high electrical conductivity are inversely related [12]. Many relevant studies in the literature focus on various aspects of Cu–Cr–(Zr) alloys, including their microstructure [6,11,13], aging kinetics [6,14], and mechanical properties [6, 15,16]. Furthermore, much research is dedicated to identifying the nature, composition, and distribution of the precipitates formed during the aging process of these alloys [6, 11,15].

Powder metallurgy represents an important method of obtaining CuCrZr alloys [17]. It offers a cost-effective and fast method for the fabrication of these alloys. It involves the production of alloy powders through mechanical alloying, followed by cold pressing and sintering in our case although various routes could be followed (e.g. hot isostatic pressing). The use of powder metallurgy eliminates many costly steps associated with traditional manufacturing techniques, such as ingot melting and casting [17]. Furthermore, the ability to control powder composition and particle size distribution provides an important advantage over traditional methods. Additionally, the rapid heating and cooling rates achievable during sintering enable the formation of fine microstructures with desired mechanical properties [18].

The aim of this study was to investigate possibilities of a cost-effective production of CuCrZr alloy with improved mechanical properties using powder metallurgy. The influence of mechanical alloying on structural parameters of Cu and CuCrZr powders was examined. Also, relationship between dislocation density of starting powders and hardness of material after sintering was discussed.

2. Experimental work

The commercially produced prealloyed CuCrZr, and pure copper powders were used as starting materials. Chemical composition of CuCrZr per suppliers' specifications: 0.96wt.% Cu-0.9 wt.% Cr – 0.07wt.% Zr - 0.011wt.% Fe – 0.005 wt.% Si). Mechanical alloying (MA) was carried out in the high-energy ball mill – shaker mill, for 5 hours, in argon inert atmosphere, with ball-to-powder ratio 1:15. Milling medium was stainless steel milling balls with different sizes (6 mm, 10 mm, 25 mm). Starting and MA powders were cold pressed under applied pressure of 350 MPa and for the holding time of 1 min. Sintering process was performed at 1030 °C, in argon atmosphere, with duration of 150 min.

Structural parameters were observed using X-ray powder diffraction (XRD). PDXL software was used to calculate structural parameters based on Williamson-Hall analysis: crystallite sizes (D, nm), lattice parameter (nm), lattice strain (ε, %). Dislocation density (ρ, m-2) was calculated according to relation $\rho=2\sqrt{3}\varepsilon/Db$, where ε is lattice strain, D is crystallite size, and b is the magnitude of the Burgers vector for copper. Morphological analysis was performed using scanning electron microscopy (SEM). Vickers macro hardness tests were done using 1 kg load, with 10 s holding. Presented results were obtained from an average of 7 indents.

3. Results and discussion

Morphological investigation of starting powders was performed using SEM. The presented micrographs in Figure 1. show that prealloyed CuCrZr powders have regular round shape, while particles of pure copper have irregular elongated shape.

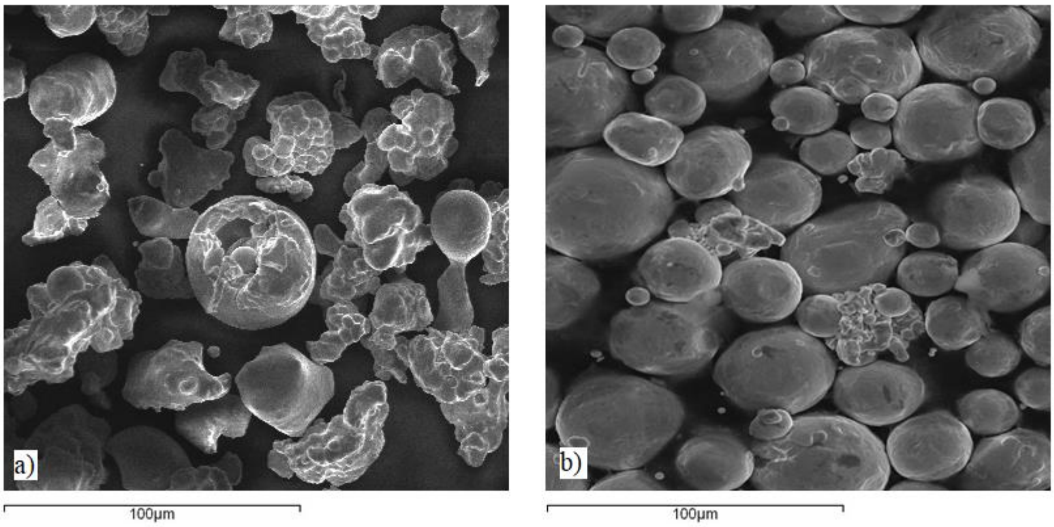

Figure 1. SEM micrographs of a) Cu, and b) CuCrZr powders.

Analysis of structural parameters, and chemical and phase composition was done using XRD. The obtained XRD patterns of starting and mechanically alloyed CuCrZr powders indicated peaks of only elemental copper (Figure 2.). Detection of Cr and Zr peaks was not achieved due to limitation of XRD device. The peaks were observed at 38.85°, 43.17°, 50.29°, 73.97° which corresponds to face-centered cubic (FCC) copper lattice. Accordingly, Burgers vector for FCC structure of Cu was calculated as b= a/2 <110>, and obtained value is 0.255 nm.

During 5 hours of MA numerous high-energy collisions happen between ball-powders-ball and ball-powders-mills' wall. Consequently, MA particles' structures undergo breakage and dissociation due to severe repetitive deformation induced during milling. Structural parameters of Cu and CuCrZr starting and MA particles are given in Table 1. Obtained results indicate that present deformation mechanisms, which occur during mechanical alloying process, lower lattice parameters and crystallite size, while lattice strain slightly increases. By observing values of dislocation density in Table 1, can be concluded that dislocation density in deformed MA particles increases during mechanical alloying process. It is well-known that copper-based material with increased dislocation density exhibits higher hardness after densification.

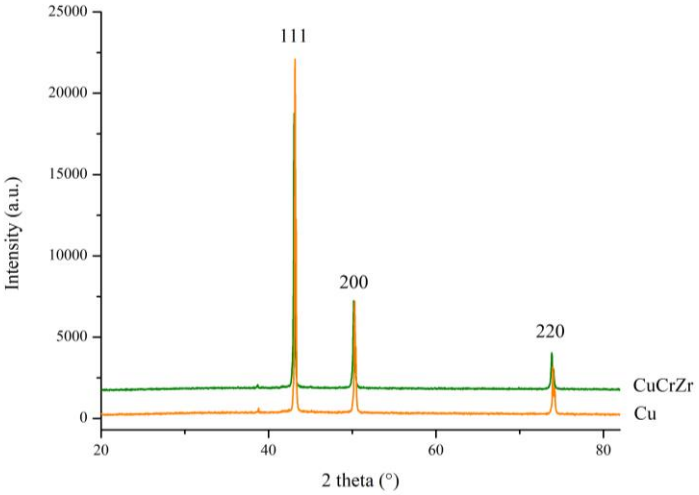

Figure 2. XRD patterns of Cu and CuCrZr powders.

Table 1. Structural parameters of Cu and CuCrZr starting and MA powders.

	Lattice parameter, a [A]	*Crystallite size, D* [nm]	*Lattice strain, ε* [%]	*Dislocation density, ρ* [10^{16} m^{-2}]
Cu	3.61878	67.9	0.06	4.90
Cu-MA	3.61781	51.3	0.07	7.01
CuCrZr	3.62766	66.7	0.1	6.44
CuCrZr-MA	3.62270	23.4	0.14	21.72

Microstructural parameters of CuCrZr sintered sample were investigated using XRD. In Figure 3, XRD pattern exhibits peaks with high intensity at 43.70°, 50.77°, 74.41°, which correlate with copper matrix, and peaks with very low intensity at 36.85°, and 39.38°, indicating presence of newly formed CuZr phase. It was found that the sintering temperature affects crystallographic parameters. Structural parameters of the CuCrZr sintered alloy revealed that after sintering, lattice parameter of copper matrix in CuCrZr alloy decreases to 3.59014 A, but crystallite size, and lattice strain increase to 317 nm and 0.34 %, respectively. During sintering, increased temperature promotes grain growth, as consequence of increased diffusion rate. Therefore, enlargement of the crystallite size occurs owing to the surface diffusion which endorsed coarsening mechanism.

Vickers hardness measurements exposed that CuCrZr alloy possess hardness values 45% higher compared to hardness of sintered pure copper (Figure 4.). Presence of CuZr phase significantly raises hardness values of the copper matrix. On the other hand, this finding also confirms hypothesis given above, that powders with higher dislocation density will exhibit higher hardness.

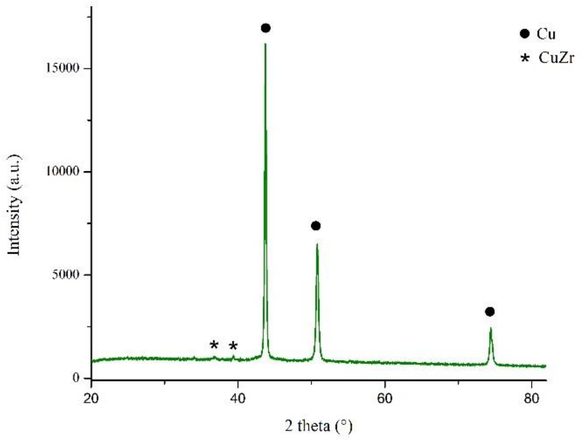

Figure 3. XRD pattern of sintered CuCrZr alloy

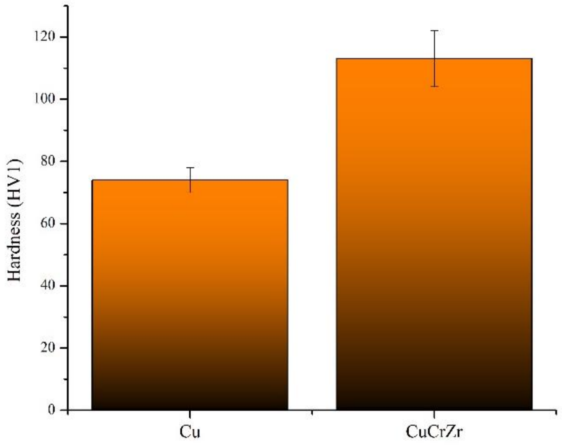

Figure 4. Hardness values of sintered Cu and CuCrZr alloy

4. Conclusions

PM techniques were applied for cost-effective production of CuCrZr alloy. XRD analysis revealed that mechanical alloying strongly affects structural parameters, and consequently increases dislocation density of MA powders. Also, presence of the CuZr phase in the copper matrix was detected after sintering. Using hardness test, relationship between dislocation density and hardness was analyzed. Obtained results showed that powders with higher dislocation density will increase hardness of the final product, i.e. material after sintering. It can be assumed that CuCrZr may be excellent substitution for pure copper as a matrix, which will contribute to improvement of mechanical properties of alloys and/or metal matrix composites. All these findings support ongoing and further research related to development of CuCrZr alloy as promising copper-based materials with various applications.

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