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Original Research Article

Effects of Sintering Temperature on the Densification, Microstructure, and Micro-hardness of Intermetallic Ti-Cu Alloy Prepared through Mechanical Alloying and Microwave-assisted Sintering Method

Mohammad Reza Akbarpour [a], *, Fatemeh Sadat Torknik [b], Touraj Ebadzadeh [c]

[a] *Professor, Department of Materials Engineering, University of Maragheh, P.O. Box: 83111-55181, Maragheh, Iran.*
[b] *PhD, Department of Semiconductors, Materials and Energy Research Center, Karaj, Iran.*
[c] *Professor, Department of Ceramic, Materials and Energy Research Center, Karaj, Iran.*

* Corresponding Author Email: akbarpour@maragheh.ac.ir (M.R. Akbarpour)

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ABSTRACT

Microwave sintering has emerged as a promising technique for the fabrication of Ti-based alloys, offering unique advantages over conventional sintering methods. The selective and volumetric heating capabilities of microwaves can result in rapid densification, microstructural refinement, and enhanced properties in Ti-Cu alloy systems. Therefore, this study aimed to synthesize an intermetallic alloy of Ti-50 at. % Cu through high-energy mechanical milling and a microwave-assisted sintering method. The objective was to expedite the sintering process of the Ti-Cu alloy using microwave assistance and analyze how this method influences the phases formed and the properties of the alloy. A Ti-50 at. % Cu powder mixture was milled for 30 hours under an argon atmosphere, then uniaxially compacted to form green samples, which were subsequently sintered by microwave heating. This method allowed for rapid consolidation without significant grain growth within a short sintering period. The effects of the sintering method and temperature on microstructure and mechanical properties were studied. The density of the sintered samples increased with rising temperatures, with the highest density of 6.54 g/cm³ obtained at 900°C. Microstructural examination revealed that the Ti3Cu4 and TiCu phases primarily formed, with an average grain size of approximately 28 nm. A high micro-hardness of ~880 HV was achieved for the dense alloy prepared using this method.

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1. INTRODUCTION

A number of outstanding characteristics, including light weight, high strength, low elastic moduli, biocompatibility, and corrosion resistance, have led titanium (Ti) and titanium-based alloys to find application in several biomedical fields (Mahmoudi et al., 2022; Moniri Javadhesari et al., 2019; Zhang et al., 2019). The Ti-Cu alloy is one of the fastest-growing alloys based on Ti. It has found application in dentistry and orthopedics as a promising material. The addition of Cu to Ti renders it harder, stronger, more wear-resistant, and enhances its bio-corrosion resistance, antibacterial activity, and biocompatibility (Akbarpour et al., 2022). Research has been conducted on binary Ti-Cu alloys with different Cu fractions over many years. Using various heat treatments, researchers have identified four intermetallic compounds in the Ti-Cu system: Ti_2Cu, TiCu, Ti_2Cu_3, and TiCu. The Ti_2Cu intermetallic compound is particularly important in Ti-rich alloys, on which numerous structural studies have been conducted (Alqattan et al., 2021; Kikuchi et al., 2003; Yuan et al., 2022). In recent years, it has been noted that the Ti-50

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at.% Cu alloy is being considered as a replacement for the conventional dental cast alloy Ti-Ag, which has a higher cost (Shon et al., 2010). Various methods such as casting, semi-solid processing, and powder metallurgy (PM) have been employed (Akbarpour et al., 2022). Despite casting being a common method of producing Ti-Cu alloys, it has some disadvantages, including undesirable segregation and challenges related to evaporation and oxidation (Liu et al., 2022; Moniri Javadhesari et al., 2020b). Powder metallurgy is a manufacturing technique used in many industries when lower processing temperatures are needed. By reducing both the processing temperature and time, this technique can effectively mitigate issues commonly encountered with casting. This technology involves blending, compacting, and sintering metal and ceramic powders. To fabricate dense components, conventional sintering of Ti-Cu alloys has been the focus of more research than other variations of PM. Zhang et al. investigated the eutectoid sintering of a blend of Ti and Cu powders (Zhang et al., 2019). During sintering, they observed flaky Ti2Cu precipitates forming at grain boundaries (β-sintering). As Cu content increases in Ti-Cu alloys, density increases accordingly due to the higher ductility and diffusion rates of the Cu powder (J. Liu et al., 2014). Shon et al. synthesized Ti-Cu alloy by high-frequency induction heating (HFIH) and investigated its mechanical and microstructural properties. They synthesized nanostructured TiCu powders through high-energy ball milling of micron-sized Ti and Cu powders. The consolidation of the milled powder was achieved using both induced and applied currents in their work. Several factors influence the structural properties, densification, and overall characteristics of Ti-Cu alloys prepared by the PM method, such as milling time (Akbarpour et al., 2016, 2020), Cu content (J. Liu et al., 2014) , and sintering method and temperature (Akbarpour et al., 2020, 2023; D. Zhang et al., 2019).

Akbarpour et al. prepared Ti-Cu alloy by conventional powder metallurgy and studied the effects of sintering temperature on the densification, hardness, and antibacterial activity of the alloy (Akbarpour et al., 2020). According to their results, the densest microstructure and highest densification of TiCu powders were achieved at a sintering temperature of 900 °C. A multi-phase structure consisting of TiCu and Ti2Cu3 phases with a high microhardness of 1000 HV was obtained for the Ti-50 at.% Cu alloy (Akbarpour et al., 2020). Studies on Ti-50 at.% Cu alloy have revealed an ultra-high hardness of 10 GPa, acceptable toughness, high antibacterial properties, excellent cell viability with MG-63 osteosarcoma cells, and a high osteoblast formation rate (Moniri Javadhesari et al., 2020a). Therefore, this alloy shows significant potential for use in biomedical applications due to its superior properties.

The sintering process plays a crucial role in determining the microstructural evolution, phase stability, and overall properties of the final Ti-Cu alloy product. Microwave sintering stands out as a particularly compelling method for the fabrication of Ti-based alloys, offering a unique set of advantages over traditional sintering techniques. The inherent ability of microwaves to selectively and volumetrically heat the material allows for rapid and uniform heating of alloys, overcoming the challenges posed by the low thermal conductivity of titanium. This selective heating mechanism leads to more efficient energy transfer and significantly reduced processing times compared to conventional methods. The rapid heating and cooling rates achievable with microwave sintering can also play a crucial role in the microstructural evolution of Ti-Cu alloys. The fast heating rates can suppress the formation of undesirable intermetallic phases, while the quick cooling minimizes the growth of detrimental microstructural features. This, in turn, results in a more homogeneous and stable microstructure, which directly translates to enhanced mechanical properties such as increased strength, hardness, and wear resistance. To date, microwave sintering of Ti-Cu alloys has not been extensively reported in the literature, presenting an opportunity for further research and development in this area. While the unique advantages of microwave-assisted processing have been well-documented for other metallic systems, the specific application of this technology to Ti-Cu alloys remains relatively unexplored.

In this research, the high-energy mechanical alloying and microwave-assisted sintering method are used to synthesize the Ti-50 at% Cu alloy. The effects of the microwave sintering method and the sintering temperature on the microstructure and mechanical properties of the alloy are investigated.

2. MATERIALS AND METHODS

This research used elemental copper powder with a particle size below 20 µm and a purity of 99.7%, as well as titanium powder with a particle size below 70 µm and a purity of 99.5%. A planetary ball mill (Retsch 400MA) was operated at 300 RPM for the milling of the Ti-50 at.% Cu powder mixture. The milling process was conducted in a high-chromium carbon steel vial with a ball-to-powder weight ratio (BPR) of 10:1 at room temperature for 30 hours. To accelerate the milling process, 0.5 wt.% stearic acid was added to the mixture. The processed powder was compacted at 1 GPa and then sintered by microwave heating at temperatures of 700 °C, 800 °C, and 900 °C under argon gas.

X-ray diffraction (XRD) was performed using a Philips diffractometer (CuKα radiation: $\lambda = 0.154$ nm) to determine the grain size. The average grain size and microstrain were calculated from the broadening of the XRD peaks using the Scherrer equation (Fernández et al., 2019). For analysis of powder morphology and the microstructure of sintered materials, scanning electron microscopes (SEMs, Philips XL30 and Mira3 XMU) equipped with energy-dispersive spectroscopy (EDS) were used. Additionally, for precise microstructural analysis of the samples, transmission electron microscopy (TEM, FEG Philips CM200) was employed. A Vickers indenter (QV-1000DAT) was used to measure the microhardness of the samples at a load of 30 kg with a dwell period of 15 seconds.

3. RESULTS AND DISCUSSION

3.1. Morphology and microstructure of the mechanically-milled powder

The Ti-50 at. % Cu powder mixture was mechanically milled for 30 hours until the synthesis of the TiCu intermetallic phase. Figure 1a shows SEM micrographs of the 30-hour milled powder, where a relatively equiaxed and spherical morphology of the powder can be observed. Figure 1b presents a bright-field TEM micrograph of the milled material, revealing a fine-grained structure after 30 hours of milling. The mean grain size, obtained by the intercept method from the TEM micrographs, was approximately 8 nm. The XRD pattern of the milled Ti-Cu alloy is also shown in Figure 1c. This pattern displays a broadened peak corresponding to the (111) planes of the TiCu phase, confirming the synthesis of the TiCu phase powder during 30 hours of milling, as noted in a previous study (Moniri Javadhesari et al., 2019).

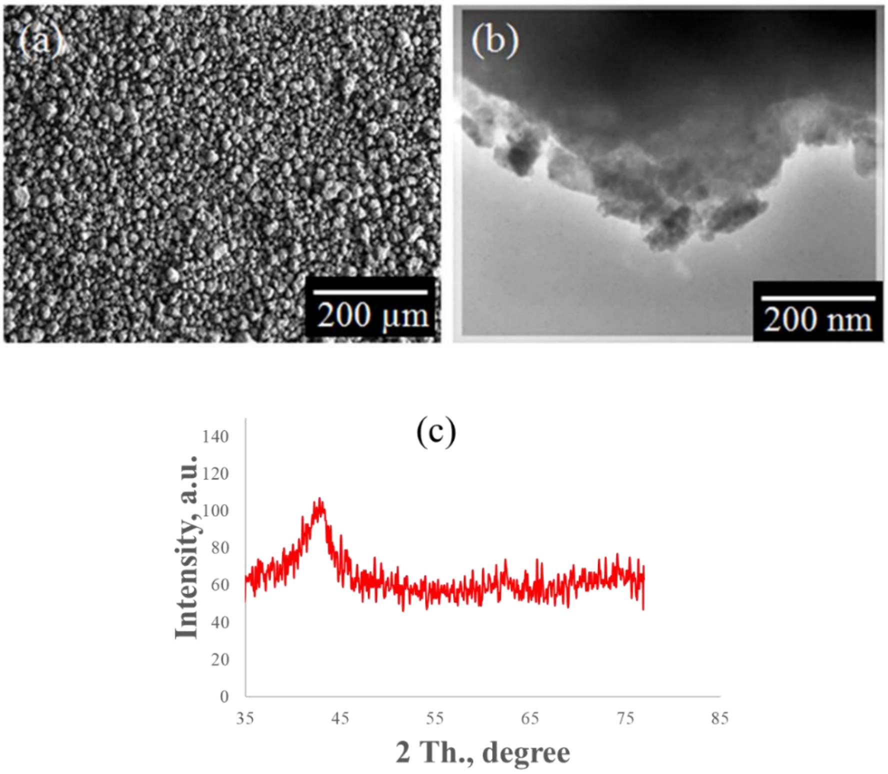

Figure 1. (a) SEM micrograph, (b) TEM micrograph, and (c) XRD pattern of 30h- mechanically alloyed Ti-Cu alloy.

3.2. Microstructure of bulk Ti-50 at.%Cu alloy

The TiCu powder was cold compacted and effectively sintered using a microwave-assisted heating method at processing temperatures ranging from 700 to 900 °C. Figure 2 shows SE and BSE SEM images of the samples sintered at different temperatures. As depicted in the figure, the porosity of the sintered sample decreases as the sintering temperature increases. At 900 °C, a nearly fully dense alloy was obtained. The BSE images also reveal microstructures consisting of two distinct phases and their distribution. Figure 3 displays a high-magnification BSE micrograph and chemical analysis of the alloy, showing the different phases of the sintered sample microstructure at 900 °C. This indicates the dual-phase structure developed during microwave-assisted sintering. XRD analysis supports the coexistence of the Ti3Cu4 and TiCu phases.

Figure 4 presents the XRD pattern of the sintered sample at various temperatures. The sample comprises the dominant phases of Ti_3Cu_4 and TiCu, which formed at high temperatures during sintering. The complex phase structure developed during microwave sintering of this alloy differs from the phases formed during vacuum sintering, as reported in previous studies (Akbarpour et al., 2016; Moniri Javadhesari et al., 2020a). In sintered TiCu powder processed by high-frequency induction heating, as conducted by In-Jin Shon et al. (Shon et al., 2010), the major phase of TiCu and various minor phases such as Cu2Ti, Cu_4Ti_3, and Cu_3Ti were reported. This difference in phase formation can be attributed to the different heating methods, which influence atomic diffusion behavior and the thermodynamics of phase formation. Table 1 summarizes the microstructural features of the microwave-sintered Ti-Cu alloy. The sample grain size remained within the nanoscale region, increasing from 23 nm to 28 nm with rising sintering temperatures. Microstrain also decreased during the sintering process, although a significant amount of strain remained in the sintered sample. This may be due to the complex phase structure and the varying thermal behaviors of the phases (Akbarpour et al., 2022).

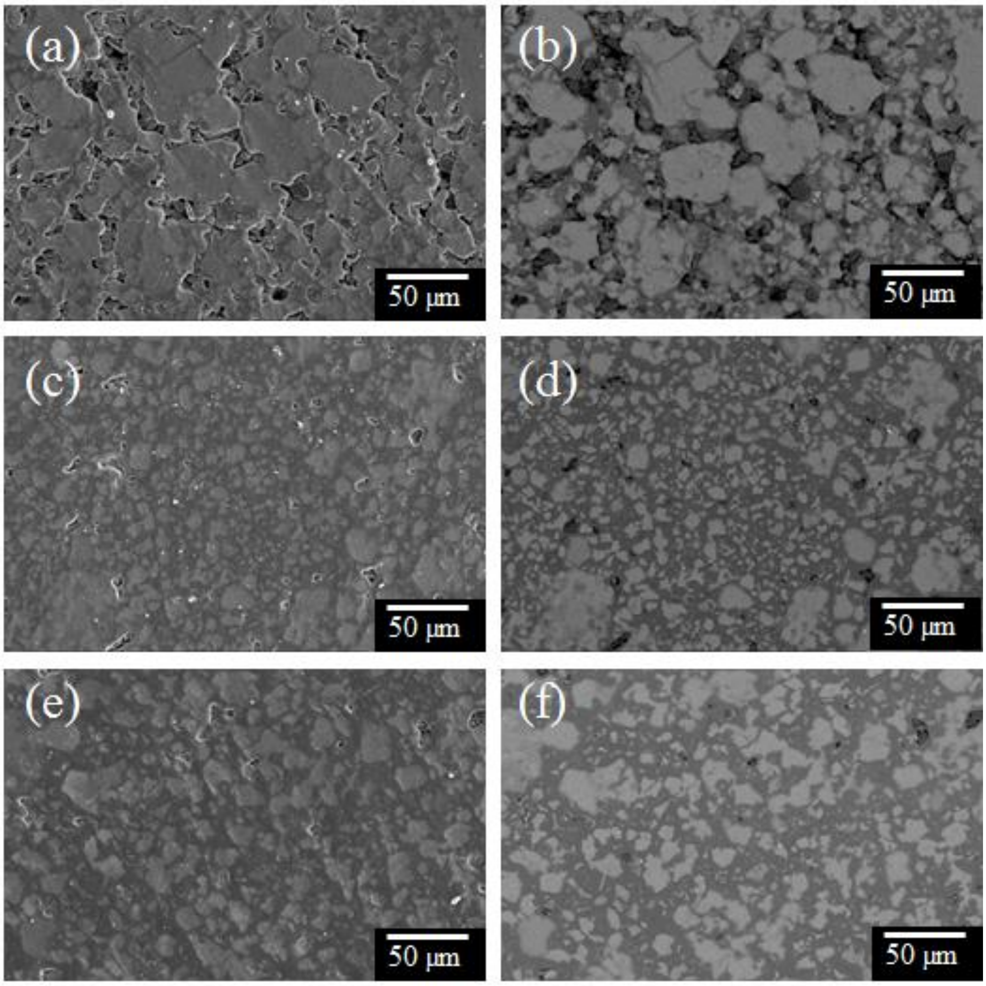

Figure 2. BSE and SE SEM micrographs of the Ti-Cu alloy sintered at different temperatures of (a, b) 700 °C, (c, d) 800 °C, and (e, f) 900 °C.

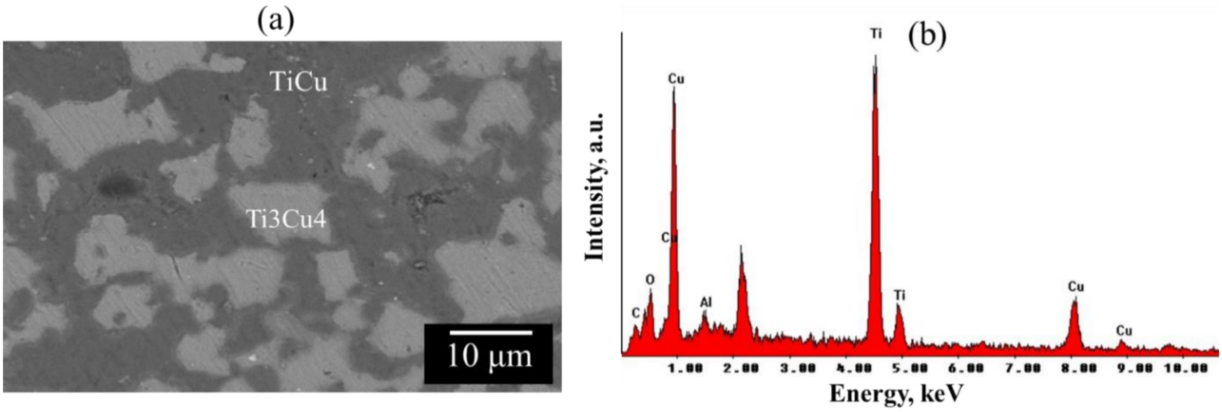

Figure 3. (a) High-magnification BSE micrograph and (b)EDS of the Ti-Cu alloy sintered at 900 °C.

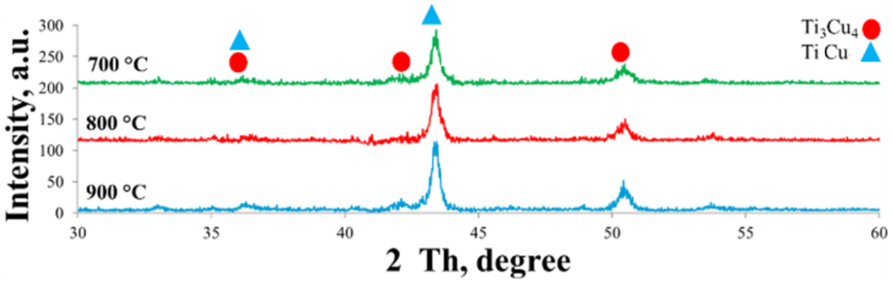

Figure 4. XRD patterns of the Ti-Cu alloy sintered at different temperatures.

Table 1. Density, grain size and microstrain of the Ti-Cu alloy sintered at different temperatures.

Temperature, °C	**700**	**800**	**900**
Density, g/cm^3	5.70	6.30	6.54
Grain size, nm	23	25	28
Microstrain, %	0.43	0.39	0.35

The transmission electron microscopy (TEM) image and selected area electron diffraction (SAED) pattern of the Ti-Cu alloy sintered at 900 °C are presented in Figure 5. The image confirms the nanocrystalline structure of the sintered TiCu alloy, with a grain size of 30 nm. The average grain size was obtained, which is slightly larger than the value obtained from X-ray diffraction (XRD). Additionally, the SAED pattern confirms the formation of the Ti_3Cu_4, TiCu, and Ti_2Cu phases.

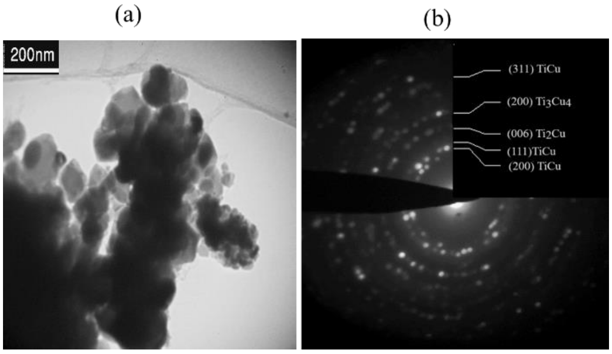

Figure 5. (a) TEM micrograph and (b) SAED pattern of the synthesized alloy.

3.3. Micro-hardness

Vickers micro-hardness measurements were performed on the polished surface of the TiCu. Figure 6 shows the microhardness as a function of sintering temperature. As shown, the microhardness increases with increasing temperature, which is related to the decreasing porosity with temperature, as shown in Table 1. The measured microhardness value of the sintered TiCu powder at 900 °C was approximately 880 HV, which is a very high value for a Ti-Cu alloy. The hardness value obtained for the TiCu vacuum-sintered alloy in this research is approximately 26 percent higher than the value reported by Shon et al. for TiCu produced by high-energy milling and high-frequency induction heating (Shon et al., 2010). The hardness achieved through microwave-assisted sintering in this study was lower than that of the conventionally sintered alloy (10 GPa) (Moniri Javadhesari et al., 2020a). The variation in the hardness of the Ti-Cu alloy prepared by different methods is attributed to the phases formed, their inherent hardness values, and the volume fraction of these phases in the microstructure of the sample. The hardness of the various phases in this system has been reported in the literature (Akbarpour et al., 2022; Moniri Javadhesari et al., 2020a).

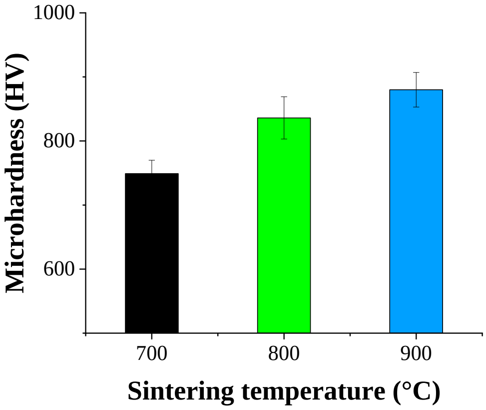

Figure 6. Microhardness as a function of sintering temperature.

4. CONCLUSION(S)

In this research, a Ti-50 at% Cu alloy was produced by high-energy mechanical alloying of elemental micron-sized Ti and Cu powders, followed by a microwave-assisted sintering process at different temperatures. The densification, microstructure, and mechanical properties of the synthesized alloy were characterized. In this method, rapid consolidation of the Ti-Cu alloy was achieved without significant grain growth, and it occurred in a short sintering time. The effects of the sintering method and temperature on the microstructure and mechanical properties were studied. The sintering density increased with temperature, and the highest density of 6.54 g/cm³ was obtained at 900°C. Microstructural studies showed a nanocrystalline structure for the alloy, consisting mainly of Ti_3Cu_4 and TiCu phases as the major phases, with Ti_2Cu as a minor phase and a grain size of approximately 28 nm. Mechanical tests revealed a high microhardness of 880 HV for the dense Ti-Cu alloy.

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