Characterization of Cu-Ti powder metallurgical materials

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Abstract:

Powder metallurgical Cu-Ti alloys with different titanium additions produced by hot pressing were characterizied by optical microscopy, scanning electron microscopy, X-ray diffraction analysis, and hardness, wear and bending tests. The addition of titanium to copper caused the formation of different intermetallic layers around the titanium particles. The titanium content of the intermetallics decreased from the center of the particle to the copper matrix. The hardness, wear resistance and bending strength of the materials increased with increasing Ti content, whereas strain in bending test decreased. Worn surface analyses showed that different wear mechanisms were active during the wear tests of specimens with different chemical compositions. Changes in properties of materials with titanium addition were explained by high hardness of different Cu-Ti intermetallic phases.

Keywords: copper titanium alloys; powder metallurgy; sintering; mechanical properties; wear

1. Introduction

Copper and its alloys are widely used in numereous industrial applications because of their advantageous properties such as high electrical and heat conductivity and ease of casting and deforming [1-5]. Pure copper has low hardness and strength; however, certain copper alloys have relatively higher mechanical properties that are required for some applications; for example, age hardenable copper-based alloys are widely used in different industrial applications. However, the mechanical properties of these alloys may vary depending on the applied heat treatment [6]. Cu-Be alloys are usually selected for applications where high hardness, wear resistance, and strength are required [7-9]. However, although these alloys have superior properties, beryllium is an expensive and toxic element [10-13], which both increases the cost of these age hardenable alloys and makes them dangerous to human health. Cu-Ti alloys are age hardenable materials in which precipitation occurs with the spinodal decomposition of a single phase into two phases: one Ti enriched and the other Ti depleted [14-17]. These alloys have been developed mainly to replace Cu-Be alloys as both alloy groups are age hardenable, and it has been reported that Cu-Ti alloys show mechanical properties similar to those of Cu-Be alloys [18-20].

Compared to studies relating to other copper alloys, relatively few number of studies have been reported in literature on Cu-Ti alloys; most existing studies relate to cast materials and report the aging behaviour, mechanical properties like tensile strength, hardness and fatigue strength, electrical and thermal conductivities, and microstructures of cast binary Cu-Ti alloys and some ternary alloys like Cu-Ti-Co, Cu-Ti-Cd, Cu-Ti-Cr and Cu-Ti-Al [21-26].

Powder metallurgy is usually employed to produce small sized copper-based parts that are used in electrical switches, contacter components, connectors, heatsinks, and brushes and is widely used in electronic packaging industry [15, 27-31]. It is highly possible to produce components from Cu-Ti alloys through a powder metallurgical route. However, there is limited literature pertaining to powder metallurgical Cu-Ti alloys, although Wang et al. [32] showed the effect of C addition on electrical conductivity of spark plasma sintered Cu-Ti alloys. Moreover, Ruzic et al. [33] showed the effect of precipitation and dispersion hardening on pre-alloyed Cu-Ti alloys. This study therefore aims to understand the effect of titanium addition on the mechanical properties of hot pressed Cu-Ti alloys starting with pure metal powders. For this purpose, samples of Cu-Ti alloys with different titanium contents were produced using a hot-press under vacuum atmosphere, and microstructure, mechanical properties and wear resistance of the alloys were investigated in detail. However, similar investigations are needed to understand suitibility of Cu-Ti powder metallurgical materials in different industrial applications. The production of components from sintered Cu-Ti materials can cause an increase in hardness and wear resistance resulting in the extended life time of the component.

2. Experimental

Pure copper and pure titanium powders were selected as starting materials. Powder mixtures with different Ti contents (0 wt.-% - 5wt.-% Ti) were ball milled for 4 hours in an alumina container with alumina balls (6 mm in diameter) to obtain a homogenaous distribution of titanium powders. Scanning electron microscope (SEM) images of the starting powders and the powder mixture of Cu-2Ti after ball milling are given in Fig. 1. The ball milled mixtures obtained were then sintered in a Diex vacuum assisted hot pres at 900 °C for 15 minutes under a pressure of 45 MPa using a graphite die set. The densities of sintered samples were measured according to the Achimedes' principle with an AND GR200 microbalance. Samples were ground and polished in the usual manner, with a final polishing conducted using 1 μm diamond. Polished samples were etched with Keller's reagent and microstructural investigations were then conducted with an Olympus BX41M-LED light microscope and a Jeol JSM 6060 SEM with an energy dispersive X-Ray spectrometer (EDS). Phases in the sintered samples were identified using X-Ray Diffractometer (Rigaku SA-HF3; Rigaku Corp. Tokyo, Japan) with Cu Kα radiation at 40kV. Hardness tests were performed according to ASTM E384-11 using a Future-Tech Vickers hardness tester under 3 kg load and with 10 s loading duration. All reported hardness values are the average of 10 measurements. Polished samples were then prepared for wear tests. Dry sliding wear tests were realized at room temperature according to ASTM G99-05, and a Nanovea MT/60/NI ball-on-disc type tribometer was used in wear tests, which were conducte under 20 N load using AISI 52100 steel balls (5 mm in diameter and approximately 800 HV hardness) as counterfaces. The sliding speed and distance were kept constant at 0.1 ms^{-1} and 300 m, respectively, during wear tests. All specimens were cleaned with alcohol and dried before and after wear tests. The weight loss of samples during wear tests were measured using the same microbalance used in density measurements. Three-point bending tests were applied to the prepared samples where an Instron universal tester was used with a three-point bending attachment.

3. Results

3.1. Density measurements

After the sintering process, the densities of specimens were measured to evaluate the sintering process, and the Archimedes' principle was used to measure the densities of sintered specimens. As expected, the densities of specimens were decreased with the addition of titanium. A comparison of experimental and theoretical densities showed that all sintered samples contained 95 % of their theoretical densities (the relative densities and the amounts of porosity in sintered samples with different titanium additions can be seen in Fig. 2). Measured densities were also used to calculate the wear rate values of specimens.

3.2. Microstructural investigations

Some of the representative microstuructures of sintered Cu-Ti alloys obtained using an optical microscope are shown in Fig. 3, where multiple layers of different intermetallic phases can be seen around the titanium particles inside sintered specimens. In some of the micrographs, the Ti particles are seen to be deformed in the pressing direction. No visible porosity was reported during the investigations on the microstructures of specimens, which is consisted with results of density measurements.

SEM with an EDS attachment was used to understand the chemical compositions of different phases in the microstructures of the specimens. As expected, the amount of Ti was found to be higher at the center of the particle and decreased dramatically at the interface between the particle and matrix, as shown in EDS line scan analysis in Fig. 4. A wide diffusion layer which was rich with titanium atoms was also seen around the particle; this wide layer is a result of the diffusion of titanium atoms towards the copper matrix. The copper content was higher in the matrix, and this value remained almost stable until the particle matrix interface and dropped dramatically inside the particle.

Several point analyses were conducted to obtain quantitive results of the chemical compositions of the different phases in the interface. Fig. 5 shows an example of the points where these analyses were taken. As can be seen in the figure, different phases can be indentified according to the their contrasts, including the titanium particle and copper matrix. The avareges from numerous point analyses taken from smilar regions around different particles are shown in Table 1. The result of EDS analyses shows that the particle at the center of the Fig. 5 contains Ti and nearly 32 wt.-% Cu. X-ray diffraction tests were performed on samples to identify phases in specimens, and corresponding XRD patterns are given in Fig. 6. The chemical formulation of possible phases according to the chemical compositions and the XRD patterns are also given in Table 1.

3.3. Hardness tests

Hardness tests were conducted to understand the effect of titanium addition on the hardness of sintered Cu-Ti samples, and the results are given in Fig. 7. As shown from the graph, the hardness of materials increases almost linearly with an increasing addition of Ti; with a 5 wt.-% addition, the hardness of the sintered samples increased from 35 to 101 HV_3. The increase in hardness is a result of an increase in the number and amount of intermetallic phases.

3.4. Mechanical tests

The three-point bending test is one of the most common methods to understand the mechanical properties of powder metallurgical materials [34, 35]; thus, these test were conducted to understand the effect of titanium on the mechanical properties, namely, the bending strength and strain of the materials. The test results can be seen on Fig. 8, where it can be seen from the graph that the addition of titanium to copper causes an increase in the strength with a decrease in the strain of the materials. Mechanical test results showed the same trend as that of hardness tests. There was an increase in the volume fraction of hard intermetallic phases with an increase in the amount of titanium in the alloy. An increased amount of intermetallic phases creates a higher number of obstacles for moving dislocations, which results in an increase in the strength of materials. However, the low deformability of these hard intermetallic phases causes a dramatic drop in the strain of specimens with increasing titanium content.

Fracture surfaces obtained after bending tests were investigated using SEM to understand effect of different titanium additions on the fracture mechanisms of specimens; moreover, examples of fracture surface images for different alloys can be seen on Fig. 9. For the sample without titanium addition, the fracture surface consists of dimples as a result of the high ductility of pure copper. In addition, there was no change reported on the behaviour of copper phase when titanium was added. However, the fracture behaviour of titanium and the intermatalic phases around titanium particles were totally different and because of the high hardness of the intemetallics these phases showed brittle fracture with highly faceted fracture surfaces. The titanium phase also showed brittle fracture with a smoother fracture surface and wider facets that were smaller in number compared to the intermetallic phases. Furthermore, some cracks were reported on the fracture surfaces of both titanium particles and in the intermetallic phases.

3.5. Wear Tests

The weight loss of specimens during wear tests was measured by weighing the specimens before and after the wear tests. The wear loss values obtained were used to calculate wear rate according to the following equation: $W = M/\rho D$, where W is wear rate (cm^3m^{-1}), M denotes mass loss (g) and ρ (gcm^{-3}) and D (m) are the density and sliding distance respectively [36]. The effect of titanium addition on the wear rate of the materials can be seen in Fig. 10; it can be seen from the image that with increasing titanium content in the alloy there is a dramatic decrease in the wear rate as a result of an increase in the hardness of the materials.

3.6. Worn surface analyses

SEM images of the worn surfaces of the specimens after wear tests are given in Fig. 11. The addition of titanium changes hardness and surface properties of the materials and also changes the wear mechanism that operates during wear tests. In the sample without titanium addition, deformation is the main mechanism and the movement of the deformed materials from the center of the wear track to the edges is obvious. This behavior is a result of soft and malleable character of copper. However, with increasing Ti content the deformation on the worn surface decreases and the dominant wear mechanism changes to that of abrassive wear. Grooves caused by the movement of hard steel ball on the specimen surface can be seen on worn surfaces of specimens with 1 wt.-% - 3wt.-% Ti additions. Furthermore, increasing the titanium content over 3 wt.-% causes an increase in the amount of hard intermetallic phases and increases the general hardness and wear resistance of the materials.

However, the high number of fragile intermetallic phases results in the formation of microscracks and cracks. Particulates formed by breaking of fragile phases are reported on the worn surfaces of high titanium containing specimens.

4. Discussion

The addition of pure titanium powders to the copper matrix causes the formation of different intermetallic layers around these particles. EDS analyses showed that titanium particles were converted to intermetallic phases because of copper diffusion towards the center of the particle. It is known that copper diffuses faster in titanium matrix than titanium diffuses in copper matrix [22]. It is also well known that most intermetallic phases have a loosely packed atomic structure compared to their pure elements, due to the size mismatch of different atoms in the intermetallic phases; therefore, the diffusivity of atoms in intermetallic phases is higher than the diffusivity in pure metals [28]. The formation of intermetallic layers facilitates diffusion and causes the transformation of all titanium particles into intermetallics, and the formation of these hard intermetallic phases cause an increase in the hardness and strength of the materials. Increasing titanium content causes an increase in the volume fraction of hard intermetallic phases, and the strentgh of material increases but the ductility decreases.

The increase in the hardness caused by intermetallic phases also results with a higher wear resistance. The morphology of formed intermetallic phases can affect the wear properties of the materials. In particula, coarse intermetallic phases with a high length-to-width ratio can cause a decrease in the wear resistance of the materials. These types of intermetallics begin to break during the wear tests and increase weight loss. In this study there were no reported negative effects associated with the intermetallics. With an addition of 5 wt.-% titanium to pure copper, a 76 % reduction in the wear rate was obtained. Although there are currently no reported data on the effect of Ti addition on the mechanical and wear properties of powder metallurgical copper-based materials, the results of this current study are compatible with published data on similar materials. For example, Sang et al. [37] reported the increasing wear resistance and bending strentgh of copper-alumina composites with increasing alumina ratio, and Bagheri [38] showed and increases in hardness and wear resistance with increased TiC formed inside the material during processing in a powder metallurgical copper-based material.

5. Conclusion

- It is possible to use hot pressing to produce sintered parts from Cu-Ti alloys with 95 % of theoretical density.

- During the sintering of Cu-Ti powder mixtures, different intermetallic phases form as layers in the Cu-Ti interface.
- An increasing amount of titanium in the alloy increases hardness as a result of an increase in the volume fraction of hard intermetallic phases.
- In addition, with increasing Ti content strength of the specimens increases, whereas the strain at break values decreases.
- The addition of titanium to copper changes wear mechanism and increases wear resistance of the materials.

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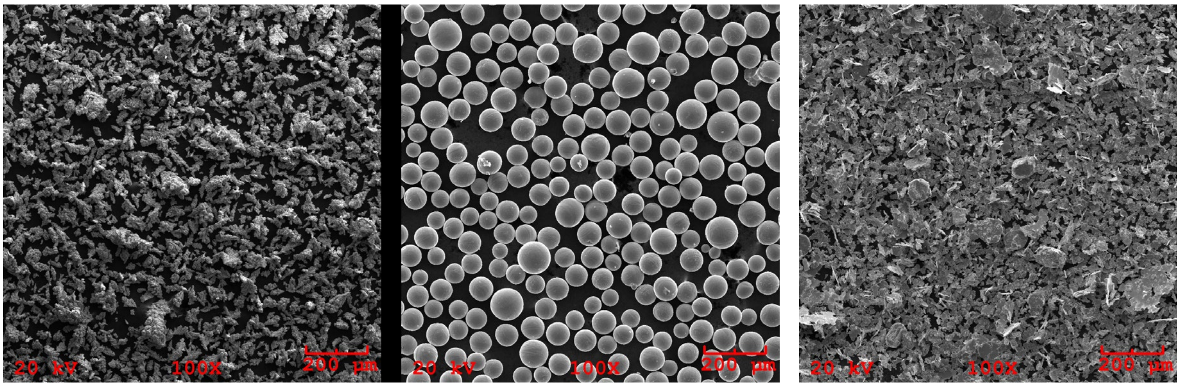

Fig. 1. SEM images of Cu powders (a), Ti powders (b), and ball milled Cu–2Ti mixture (c).

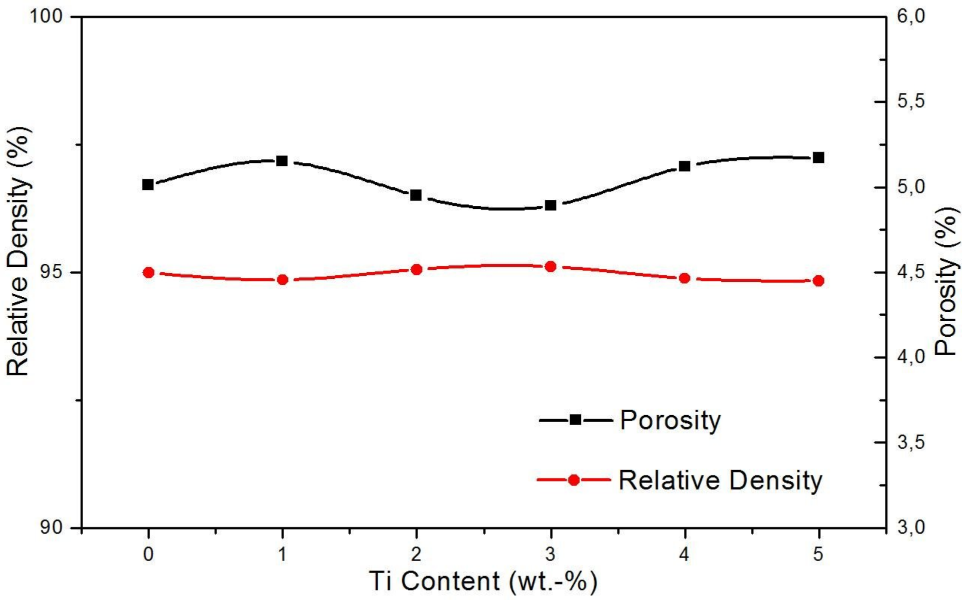

Fig. 2. Relative densities and amounts of porosity of sintered samples as a function of Ti content.

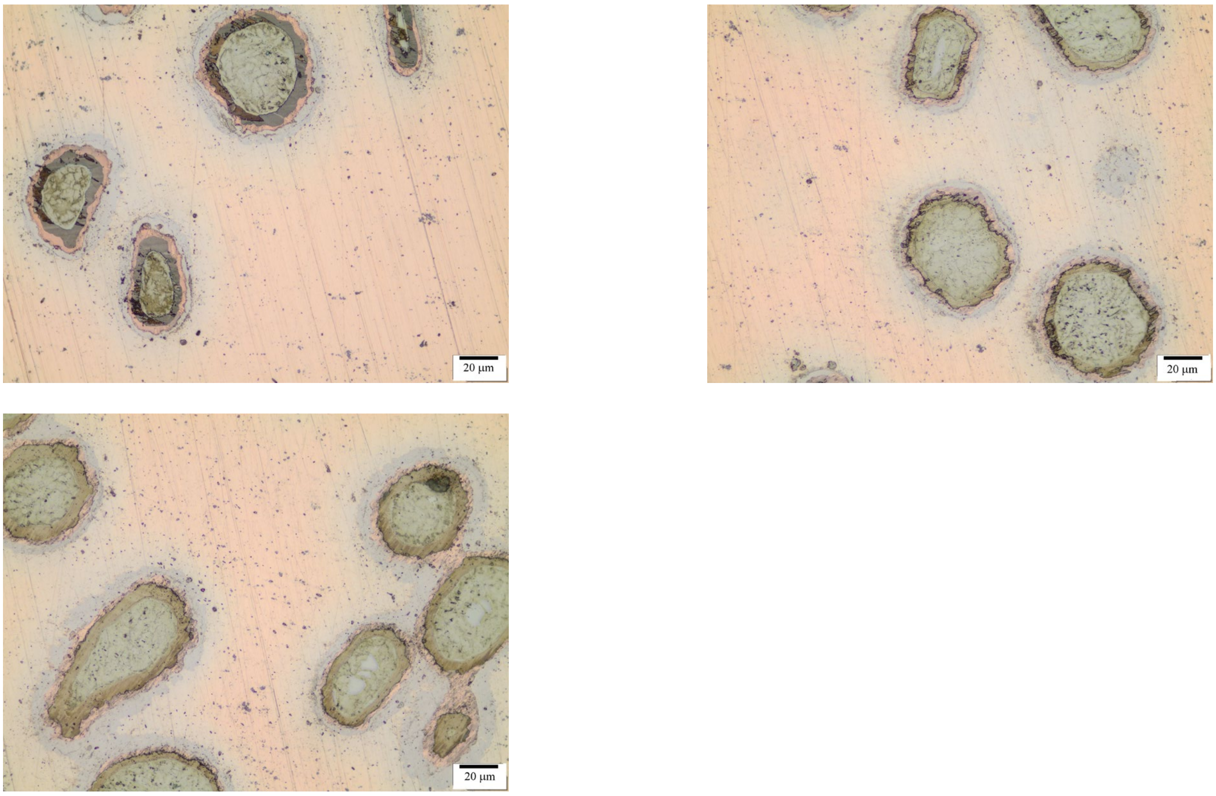

Fig. 3. Microstructures of sintered specimens: (a) Cu–2Ti; (b) Cu–4Ti; (c) Cu–5Ti.

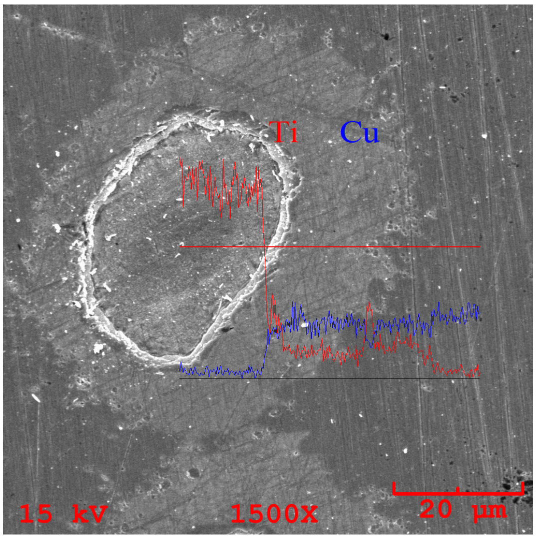

Fig. 4. EDX line scan analyses of phases around a Ti particle.

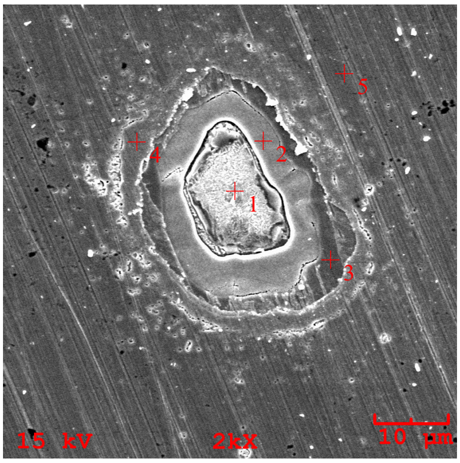

Fig. 5. Example of points where EDX analyses were taken.

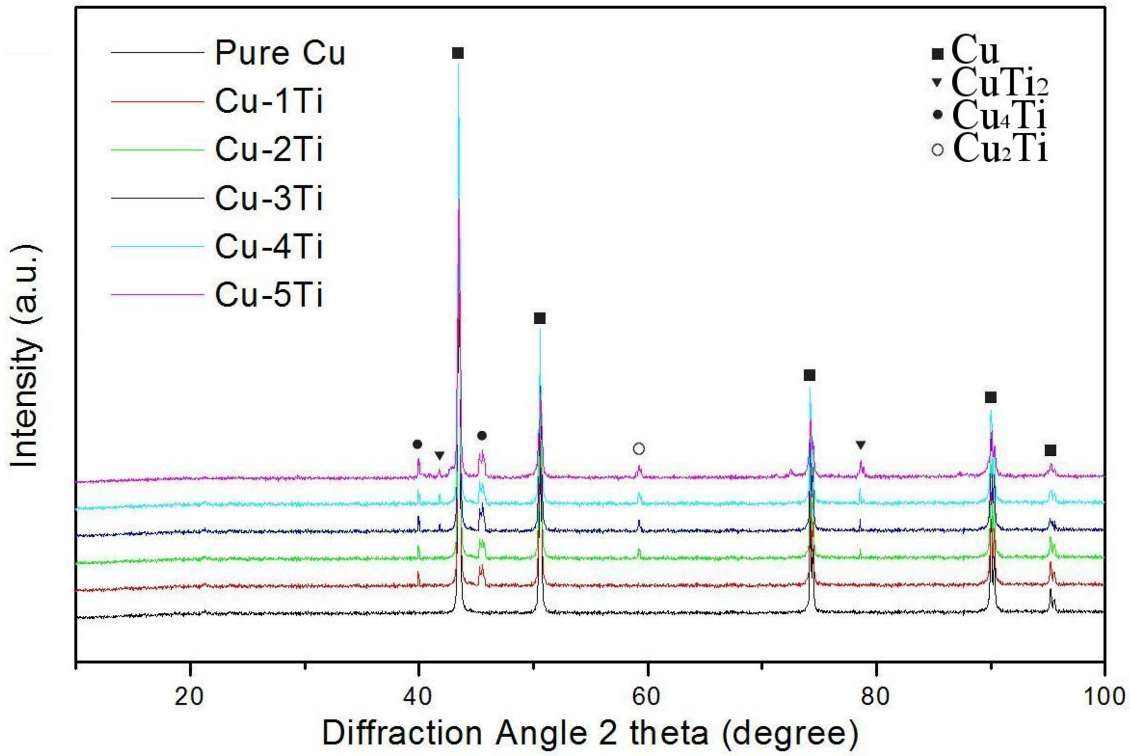

Fig. 6. XRD patterns of sintered samples with different Ti additions.

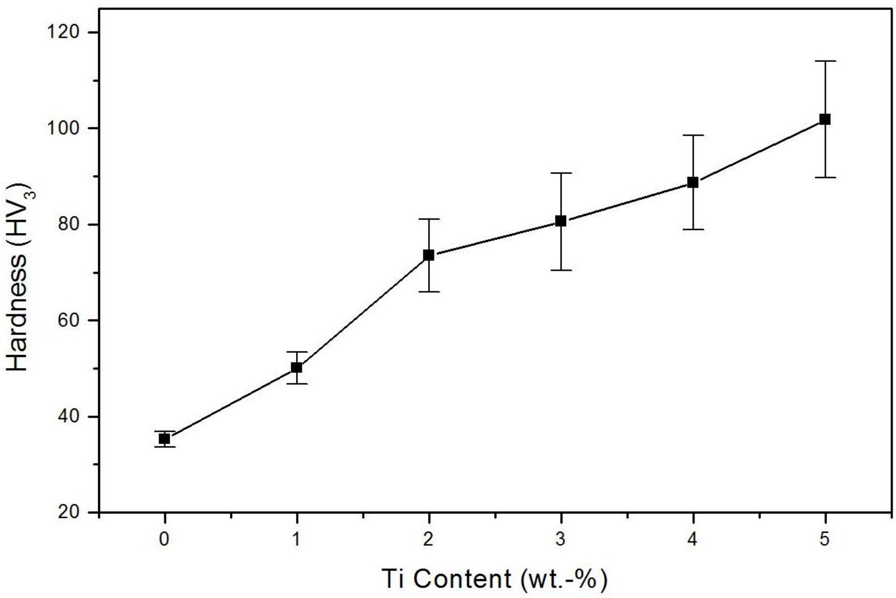

Fig. 7. Effect of titanium addition on the hardness of materials.

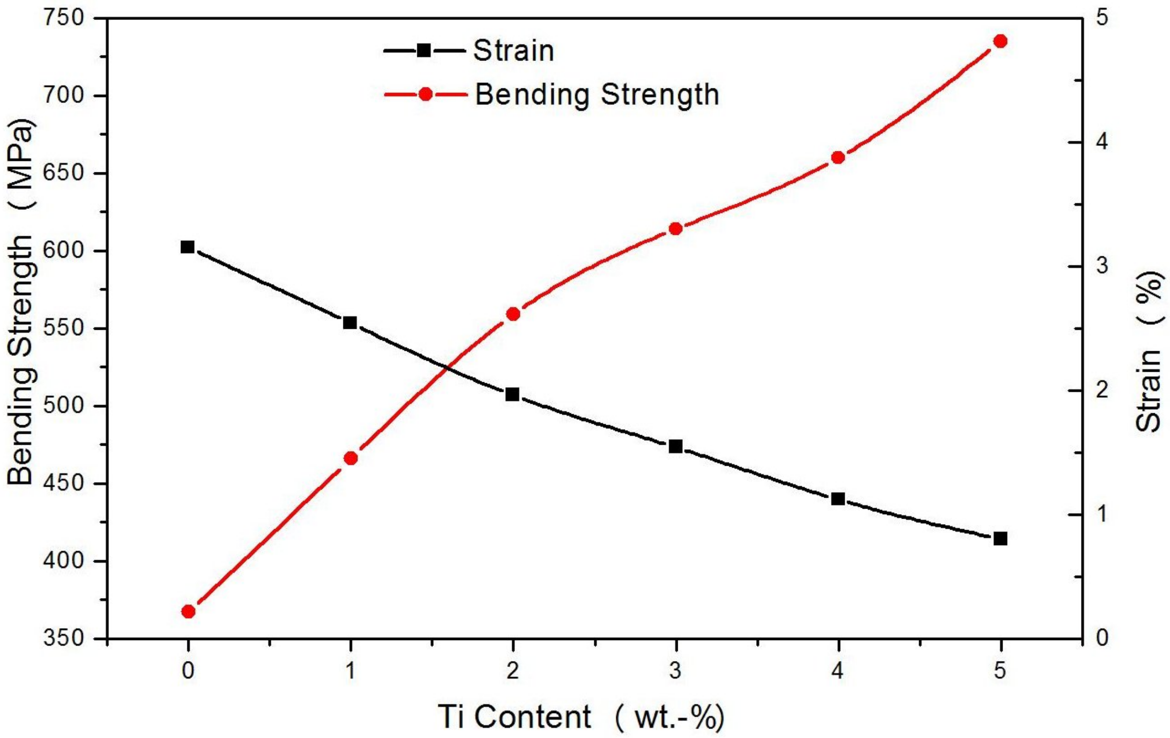

Fig. 8. Bending strength and strain of sintered specimens with different Ti contents.

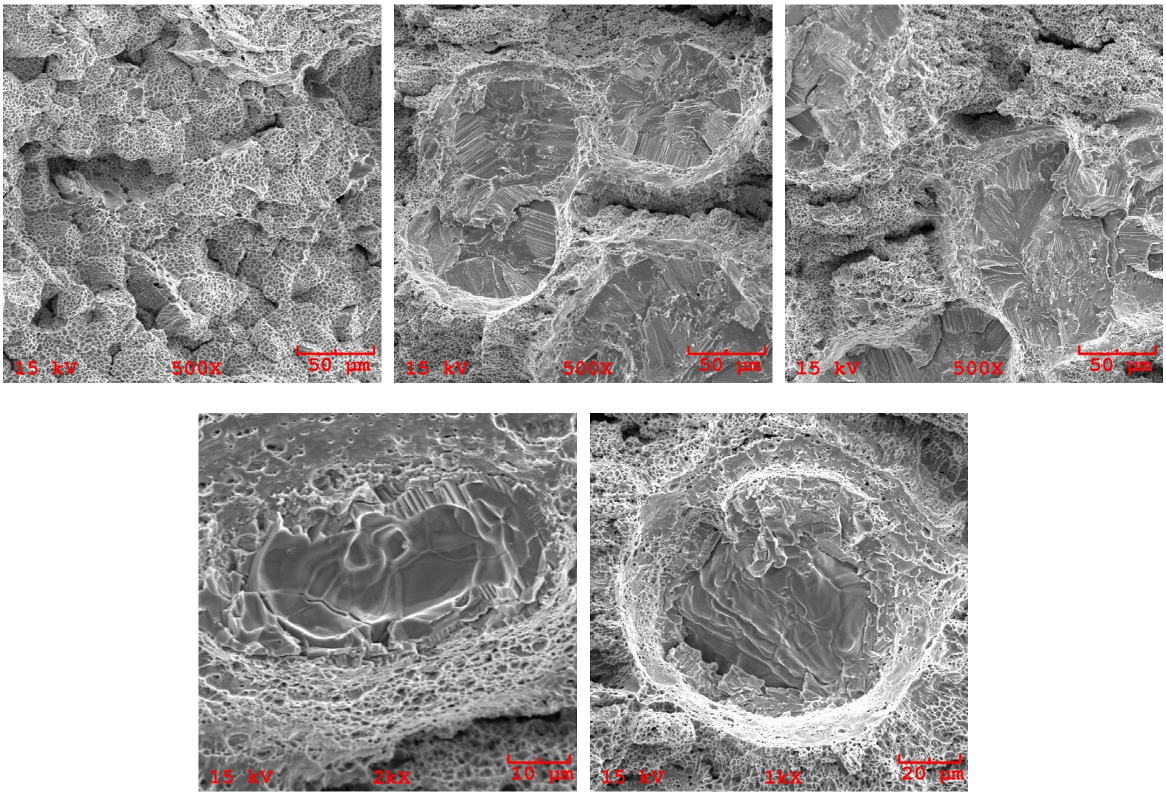

Fig. 9. Fracture surfaces of specimens after three-point bending tests: (a) pure Cu; (b) Cu–3Ti; (c) Cu–5Ti; (d) Cu–2Ti (high magnification); (e) Cu–4Ti (high magnification).

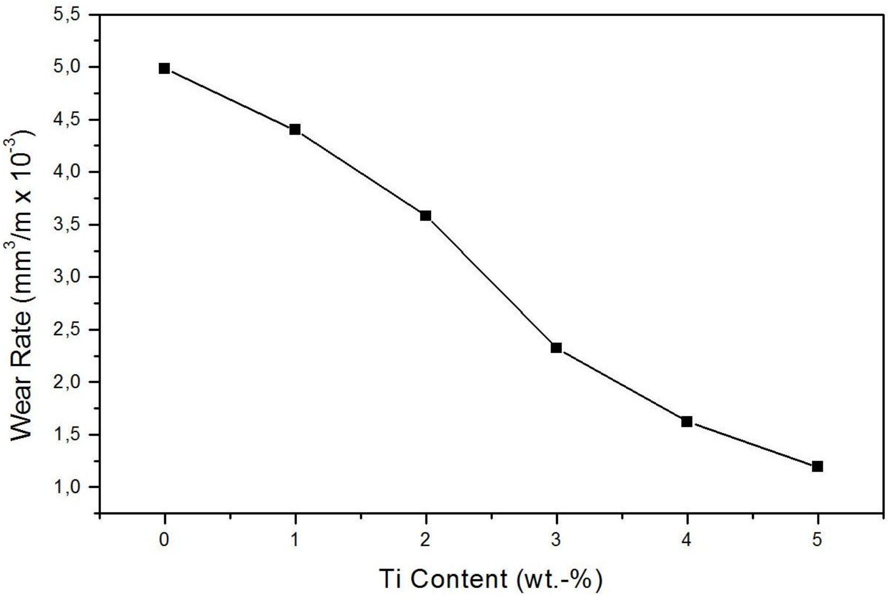

Fig. 10. Effect of Ti addition on the wear rate of specimens.

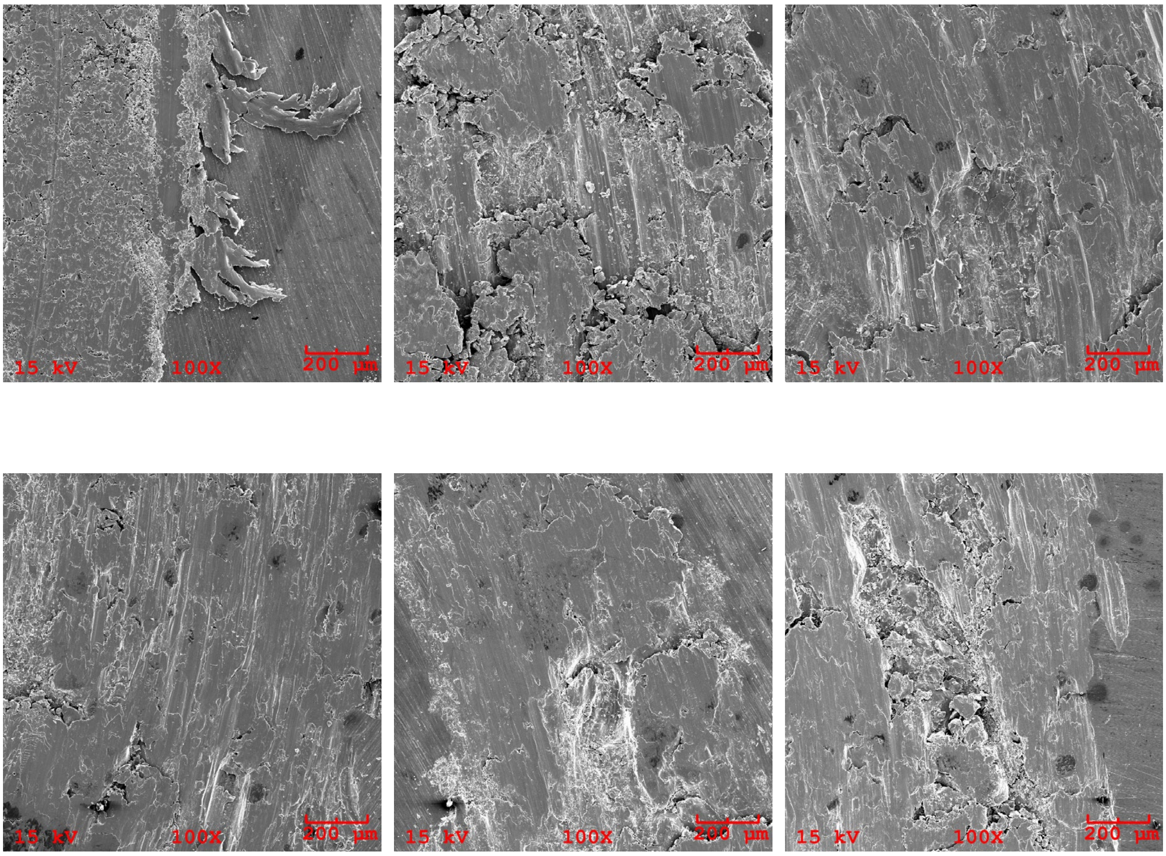

Fig. 11. SEM images of the worn surfaces of specimens: (a) pure Cu; (b) Cu–1Ti; (c) Cu–2Ti; (d) Cu–3Ti; (e) Cu–4Ti; (f) Cu–5Ti.

Table 1. Chemical compositions and possible phases of the analysed phases

Point in Fig. 5.	Chemical Comp. (wt.%)		Chemical Comp. (at.%)		Possible Phase
	Ti	Cu	Ti	Cu	
1	67.57	32.43	73.50	26.50	$CuTi_2$
2	28.24	71.76	34.27	65.73	Cu_2Ti
3	15.33	84.67	19.36	80.64	Cu_4Ti
4	5.91	94.09	7.69	92.31	Cu SS
5	3.12	96.88	3.94	96.06	Cu SS