

## Investigation on the wear behavior of Cu/TiO<sub>2</sub> Nano-composites Produced by Powder Metallurgy and internal oxidation

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### Abstract

Electrical contacts should have good thermal and electrical conductivity and certain strength. The copper base nano-composites reinforced with fine TiO<sub>2</sub> particles have almost identical electrical and thermal conductivity with copper; in addition, because of the dispersion of the fine TiO<sub>2</sub> particles, Cu/TiO<sub>2</sub> composite has more strength than pure Cu, which improves copper matrix strength through impeding dislocation movement. In this work, first Cu and Ti powders were mechanically alloyed for 60h under Argon atmosphere and then Cu<sub>2</sub>O powders were added as oxidant. The specimens, containing different amounts of TiO<sub>2</sub> were produced by in-situ oxidation of Cu-Ti pre-alloyed powders. For compaction, at the first step powders pressed under 30MPa pressure at 400°C and then pressed at 400MPa in room temperature. The compact was then sintered at 800°C for 1h under argon atmosphere. Physical and mechanical properties such as density, specific electrical resistivity and hardness of the products were altered with amount of TiO<sub>2</sub> in Cu matrix. Microstructure and composition of the specimens were studied before and after internal oxidation using SEM equipped with EDS analyzer.

**Keywords:** *Copper base nanocomposite, TiO<sub>2</sub> particles, internal oxidation, wear rate, pin on disk*

### Introduction

Oxide dispersion strengthened copper matrix composites have good thermal and electrical conductivity with high strength at room and at elevated temperatures [1]. Wear resistivity of the copper base composites with fine reinforcements is noticeably higher than pure copper [2]. The Cu/Al<sub>2</sub>O<sub>3</sub> composites have almost identical electrical and thermal conductivity with copper. In addition, they have the advantage of higher strength than pure copper. This is owing to the dispersion of the fine oxide particles, which improve copper matrix strength through impeding dislocations movement [3]. Cu/Al<sub>2</sub>O<sub>3</sub> composite is a representative of this kind of composites that is prepared in-situ by internal oxidation which includes preparing Cu(Al) solid solution by mechanical alloying and internal oxidation of Al by mixing pre-alloyed Cu-Al powder and Cu<sub>2</sub>O

powders as an oxidant agent [4]. Cu/Al<sub>2</sub>O<sub>3</sub> nanocomposites have many advantages to use as contact materials but the duration of oxidation is too long and the complete oxidation is difficult to achieve. The reason is that Al is dissolved in Cu therefore; the remained solute Al in Cu will lead to decrease electrical conductivity of the composite [5].

Internal oxidation has been the subject of numerous investigations during the past decade. This process has two major benefits, firstly, its occurrence during alloy oxidation can prevent the formation of a protective external scale and secondly, internal oxidation provides a method of introducing second phase particles into an alloy which can markedly affect the mechanical and other properties of the alloy [6]. Phase diagram of Cu-Ti shows limited dissolution of Ti in Cu (less than 6 weight percent). Since oxidation of titanium is faster than aluminum, if a small amount of Ti stays unoxidized in Cu, the titanium could be extracted from the copper's lattice using the precipitation hardening treatment. Therefore, titanium does not have negative effect on electrical conductivity of Cu/TiO<sub>2</sub> composite. In this work, Cu/TiO<sub>2</sub> nanocomposites is fabricated with in-situ internal oxidation of Cu-Ti pre-alloyed powder with different percent of Ti, in order to investigate the effect of various amounts of Cr<sub>2</sub>O<sub>3</sub> particles on the electrical conductivity, hardness and wear rate of Cu/TiO<sub>2</sub> nanocomposites.

### Materials and Method

The materials used in this work were copper and copper oxide powders having average grain size of less than 63μ made by Merck, GmbH. Titanium powder made by 'Xinnuo baoji' Co., China had the average grain size of less than 10μ. After weighing the powders, mechanical alloying was performed with the ball to powder ratio of 20 to 1 and rotational speed of 250 rpm.

The alloying method for synthesis of Cu/TiO<sub>2</sub> nanocomposite was milling a certain amount of the powders poured into a container according to the stoichiometric reaction (1). In order to prevent the powder's oxidation it was performed under the 1 bar argon pressure. Cu-Ti and Cu<sub>2</sub>O were milled together for 10h. The sampling was done in a glove box filled

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with argon to prevent powder oxidation. To investigate morphology of the powders in different mechanical alloying stages, SEM and X-ray diffraction analyses were made to ensure achieving of a homogenous solid solution of Cu-Ti. Amounts of Cu<sub>2</sub>O required for the reaction and the product, TiO<sub>2</sub>, were calculated from the following stoichiometric oxidation reaction:



**Table 1: Weight and Volume percent of TiO<sub>2</sub> in final nanocomposite with different quantity of Ti in Pre-alloyed powder.**

wt.% Ti	wt.% Cu <sub>2</sub> O	wt.% TiO <sub>2</sub>	vol.% TiO <sub>2</sub>
1	3.47	1.58	6
2	6.41	2.97	12
3	9.02	4.24	18

To prevent oxidation of very fine powder particles, compacting was firstly conducted in a hot press under 30MPa applied pressure at 400°C in glove box. For densification the specimens, a cold press was conducted at 400MPa. Sintering process was carried out at 800°C with the heating rate of 5 °C/min in order to complete the internal oxidation process and then they were cooled down to the room's temperature with cooling rate of 5°C/min.

X-ray diffraction analyses were determined progress of mechanical alloying process during milling and TiO<sub>2</sub> detection after sintering. The density value of specimen was calculated by usual Archimedes method with balance model CP324S made by 'Sartorius' company. The electrical resistivity was measured by micro ohmmeter LOM-D500 which works based on Kelvin Bridge. The Vickers's hardness was measured under applied load of 5N. Dry sliding wear tests were carried out according to ASTM G-99 standard using pin-on-disk equipment. The composite pins slide against the steel counter face with 67HRC hardness. The pins had a diameter of 5mm and a length of 10mm. The sliding speed and normal load were 0.25 m/s and 20N, respectively. The sliding distances were examined at 1000, 2000 and 3000m. The weight loss was measured by an electronic balance with an accuracy of 0.1mg and was converted into volume loss with the density of samples. The wear rate was given as volume loss per unit sliding distance. To study the wear mechanisms of the specimens, worn surface of the pins were investigated using SEM and EDS analysis. .

## Results and discussion

In order to determine the optimum mechanical alloying time, milling process was done in two different times of 40 and 60hr and in ball to powder ratio of 10 to 1 and 20 to 1. Fig. 1 shows SEM micrographs of powder Cu-2Wt. % Ti in different conditions. As in Fig.1 is shown average powder particle size after 60hr milling is less than after 40hr milling.

Also, after 40 hours of mechanical milling, still some of the powder grains have agglomerated together and more time is required to reach to an equilibrium state between cold welding and broken powder

particle. Milling for almost 60 hours with BPR 20 to 1 not only decreases average grains sizes but also causes relatively coaxial particle morphology. Decrease in powders' grain size and the distance between their layers makes the atoms to penetrate more easily in the common part of the layers and facilitates formation of alloys.

To make ensure that the time and ball to powder ratio of milling is suitable for mechanical alloying of Cu-Ti system, X-ray diffraction was applied for the Cu-Ti mixture after 60 hours mechanical milling with rpm 20 to 1. XRD results of the sample Cu-2Wt. % Ti is shown in Fig. 2. According to low amount of Titanium, peaks which are related to copper are only observable in these results. The reason for partial displacement of the copper's main peaks is the change of the copper's lattice parameter due to presence of titanium in it after making the solid solution of Cu-Ti during mechanical alloying process.

With comparing the samples diffraction in Fig. 2, it is can be seen that by increasing milling time, peaks' intensity decreases but increases their width which means that the particles are becoming smaller, in the other hand peaks' displacement to left and decrease in their intensities shows a more increase in the amount of solubility of Ti in Cu by increasing the milling time. Diffraction angle decrease and peaks displacement to the left is proportional to the increase in crystallite. according to the Bragg's law ( $n\lambda = 2d\sin\theta$ ) and the direct relationship of the amount of crystallite and lattice parameter, entrance of titanium atoms with atomic diameter of 2.93Å in copper's lattice with the atomic diameter of 2.56Å causes an increase in copper's lattice parameter.

Fig. 3 is the mapping picture of the powder Cu-2Wt. % Ti after 60 hours of mechanical alloying. Green and red spots are showing copper and titanium elements respectively. It can be observed a homogeneous solid solution has been formed and there is a good distribution of the solute element (titanium), in the solvent copper. Tables 2 and 3 show the physical properties of specimens, before and after sintering.

**Table2. Properties of samples before sintering**

Sample	Porosity (%)	Specific electrical resistivity (μΩ.cm)
Cu-1 wt.% Ti+Cu <sub>2</sub> O	16.18	3.34
Cu-2wt.% Ti+Cu <sub>2</sub> O	15.20	5.92
Cu-3wt.% Ti+Cu <sub>2</sub> O	14.95	7.22

**Table3. Properties of sample after sintering**

sample	Porosity (%)	Specific electrical resistivity (μΩ.cm)	Hardness(HV)
Cu-3.47vol.% TiO <sub>2</sub>	12	1.95	75.3
Cu-4.61 vol.% TiO <sub>2</sub>	15.56	2.79	87.8
Cu-9.02vol.% TiO <sub>2</sub>	18.2	7.19	96.5

It can be seen that before sintering, the density of samples increases with increasing of Ti in Cu-Ti pre-alloyed powder. But after sintering the specimen expansion with formation of oxides particles ( $\rho_{\text{TiO}_2}=4.23\text{gr/cm}^3$ ,  $\rho_{\text{Ti}}=4\text{ gr/cm}^3$ ) due to form more porosity. Since internal oxidation and sintering were simultaneously occurred, the green density of compact directly affects the composites properties. S. Liang [7] reported that in the case of high value of green density, the specimen expansion with formation of oxides particles is more sever. In addition, the entrapped gas in the compact may also expand during heating. The combined actions would raise the tendency of forming porosity in the interior of the composite. Due to presence of Ti in Cu- Ti solid solution and porosity, which act as an electron scattering agents, specific electrical resistivity of unsintered samples increases with increasing Ti content. Specific electrical resistivity of Cu/ TiO<sub>2</sub> composites is less than Cu-Ti alloys. It can also be seen that as the amount of TiO<sub>2</sub> increases, the porosity increases the effect of TiO<sub>2</sub> and lead to increasing of sintered specimens electrical resistivity that limited extent in comparison to unsintered specimens. It is seen in table 3 that hardness of nanocomposite specimen is increased as the amount of reinforcement increases. There are two important strengthening mechanisms to be considered in the Cu/TiO<sub>2</sub> nanocomposite produced by in-situ oxidation. The oxide dispersion strengthening according to Orowan mechanism and fine grains according to Hall-Petch that caused by the indirect effect of dispersoids as grain growth obstacles[8].

To investigate wear behavior of Cu/TiO<sub>2</sub> nanocomposites the results of weight decrease observed in the samples in the wear test were calculated and the samples densities which was measured before by the Archimedes method according to ASTM B3 28-9 standard, the samples volume decrease was calculated as in table 3 is shown.

As shown in Fig. 4-a, increasing the sliding distance, the amount of the samples' volume loss increases. As the reinforcement particles, TiO<sub>2</sub> increases, the volume loss decreases. Fig. 4-b shows the graph of the wear rate versus reinforcement particles of the nanocomposite which is derived by calculating the slope of the volume decrease-distance curve of the samples.

Fig. 5 shows SEM images for Cu-2.97wt%.TiO<sub>2</sub> nanocomposite wear in different sliding distances. In 1000m distance, grooves and channels parallel with the wear's direction are observed which shows a abrasive wear. As the sliding distance increases to 2000 meters the depth and width of the grooves increases and the results of the chemical analysis of EDS confirms the formation of a superficial layer different with the solvent which shows an increase in oxygen presence in the wear surfaces while increasing the sliding distance.

Due to the sample's friction on the disks surface the temperature of surface increases to the level in which an oxide phase forms. Increasing the sliding distance

causes some cracks perpendicular to the wear direction in the sample's surface in addition to wear lines and grooves which is indicative of the dominance of laminar wearing mechanism in high distances. As indicated in EDS analyses of worn surface of Cu-2.97wt%.TiO<sub>2</sub> in sliding distance of 3000m, oxidation wear mechanism was started.

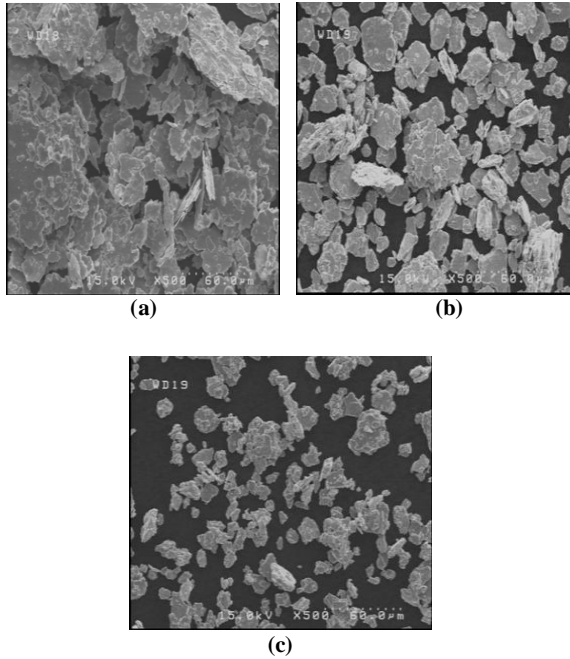
**Table 4: EDS analyses of worn surface of Cu-2.97 wt% TiO<sub>2</sub> in sliding distance of 3000m.**

Element	Series	[wt.-%]	[at.-%]
Oxygen	K series	0.75	2.89
Titanium	K series	1.89	2.49
Iron	K series	2.68	2.97
Copper	K series	94.68	91.65

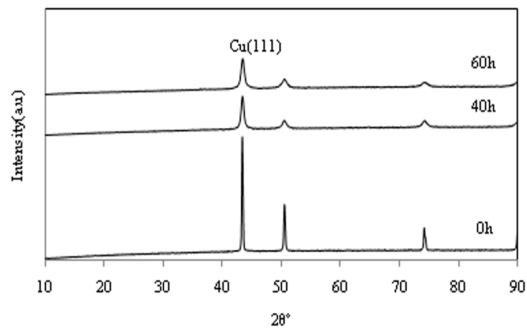
## Conclusion

- 1- In this present research according to powder's morphology, X-ray diffraction analysis and mapping, suitable time and ball to powder ratio of milling in order to fabrication of nanocomposite by mechanical alloying and internal oxidation are considered 60 hr and BPR 20 to 1.
- 2- The density of nanocomposite will decrease due to increasing of titanium quantity in initial pre-alloying powder because of increasing the porosities along production of TiO<sub>2</sub> in sample.
- 3- Specific electrical resistivity of Cu/TiO<sub>2</sub> nanocomposite increases with increasing the reinforcement particles because of increasing of interface between Cu and TiO<sub>2</sub> and electrons scattering.
- 4- Hardness of Cu/TiO<sub>2</sub> nanocomposite increased with the amount of TiO<sub>2</sub> increased.
- 5- In wear test with increasing of sliding distance, the rate of wear volume loss in samples is increased, also with increasing of reinforcement particles of TiO<sub>2</sub> the rate of wear volume loss and subsequently rate of wear will decrease.
- 6- In sliding distance less than 1000m dominant of wear mechanism is abrasive and with increasing of sliding distance to more than 2000 m, vertically cracks to direction of wear in surface of samples are observed that shows the majority of laminar wear. After sliding distance of 3000m, oxidation wear mechanism should be considered.

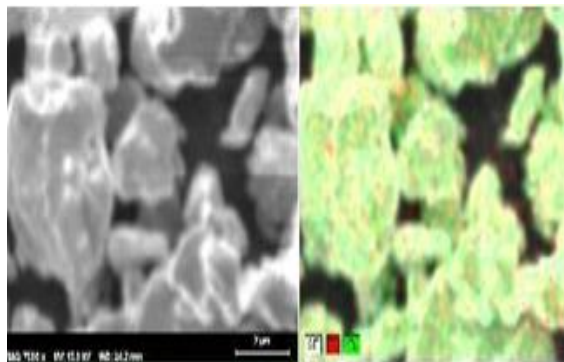
## Figures and Drawings



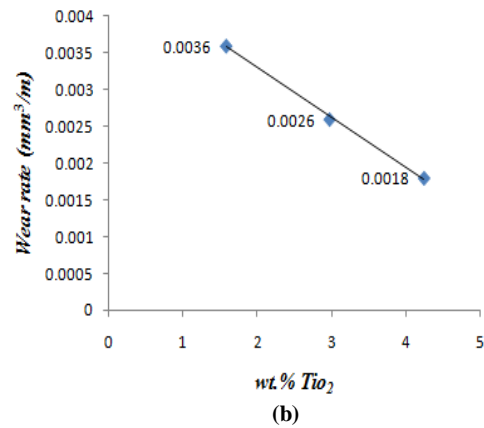
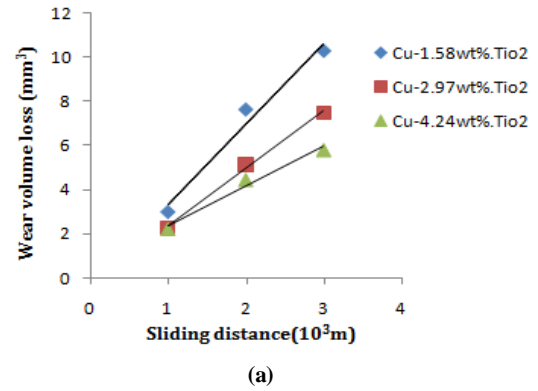
**Fig. 1:** Morphology of Cu-2wt. %Ti powder in different condition of mechanical milling (a) 60 hours with BPR 10 to 1, (b) 40 hours with BPR 20 to 1, (c) 60 hours with BPR 20 to 1.



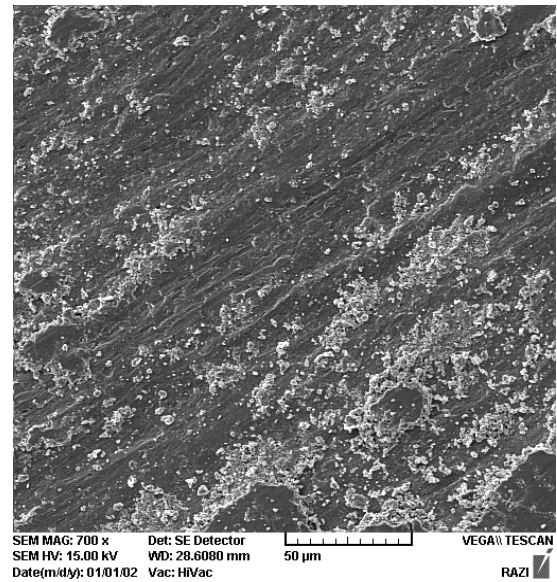
**Fig. 2:** XRD analysis of Cu-2wt. %Ti sample, after 0 hr (as mixed), 40 and 60 hr milling with BPR 20:1.



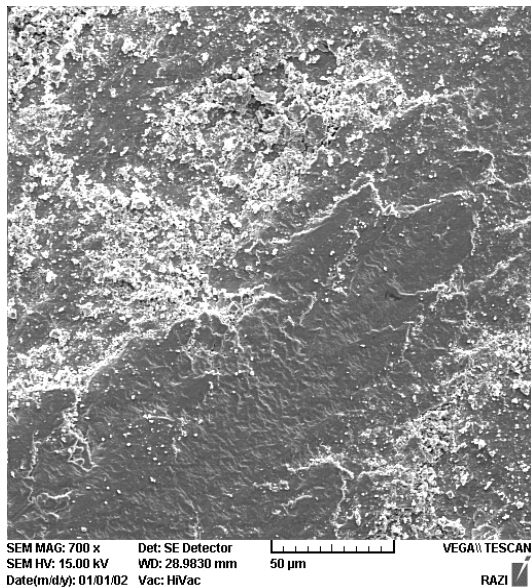
**Fig. 3:** Mapping image on Cu-2wt. %Ti powder that milled for 60 hours



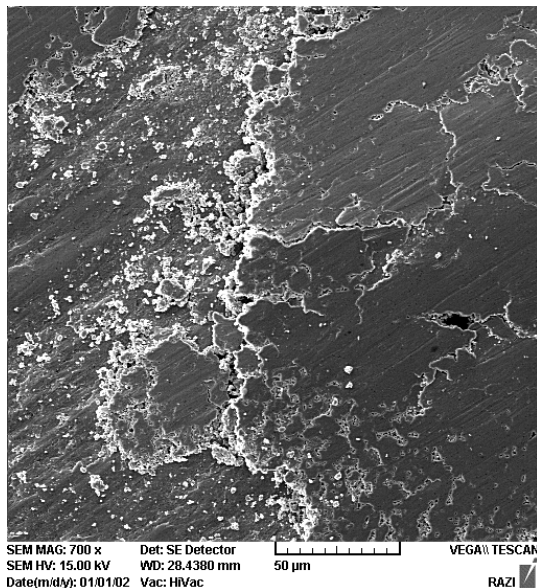
**Fig. 4:** (a) line of wear volume loss-sliding distance in three different sliding distances (b) Graph of wear rate-wt. %TiO₂.



(a)



(b)



(c)

**Fig. 5: SEM image of worn surface of Cu-2.97wt%.TiO<sub>2</sub> nanocomposite under 20 N force and sliding velocity of 0.25 m/s in sliding distance (a) 1000 m (b) 2000 m (c) 3000 m.**

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