FABRICATION OF TITANIUM CARBIDE REINFORCED COPPER MATRIX COMPOSITE BY *IN-SITU* PROCESSING

Nur Hawadah Mohd Subhi, Zuhailawati Hussain*, and Radzali Othman
School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia.
*E-mail address:zuhaila@eng.usm.my

ABSTRACT

Composite materials with copper matrix and ceramic particle reinforcements provide an alternative material for scope for producing relatively high thermal conductivity, electrical conductivity and hardness properties. Most of the work on copper-based composites has involved TiC reinforcement, which is introduced in the copper matrix through a powder metallurgy (P/M) route. TiC particle is an interesting candidate for the reinforcement of the Cu composite because of its high melting point, high hardness, good oxidation and corrosion resistance combined with good electrical and thermal conductivity. In this study, *in-situ* prepared copper-titanium carbide using high energy ball milling was addressed. Cu-Ti-C mixture powder was mechanically alloyed by high energy ball milling at 400 rpm speed for 4 to 80 hours to investigate the formation of TiC phase during milling. From the XRD result, after 5 h milling, TiC peak was found at 36.3˚ and 60.9˚.
Keywords: mechanical alloying, in-situ composite, phase analysis

INTRODUCTION

High-energy ball milling, also called mechanical alloying (MA), is a powder metallurgy technique that involves the mechanical milling of reactants to form product phase. It is one of the most promising technologies for obtaining compounds at room temperature [1]. The resultants powder developed through the repeated cold welding and fracturing of the powder particles with a final compositions corresponding to the percentages of the respective constituents in the initial charge [2]. *In-situ* composites can be formed via reaction between two or more components during MA. Most of *in-situ* process was focus on aluminum-based composites by liquid casting. In the present study, the formation of *in-situ* TiC in Cu-based composite synthesized via *in-situ* technique was investigated.

The basic principle of this technique is that the fine and thermodynamically stable ceramic phases are formed *in-situ* by the exothermal reaction between elements or between element and compound within the metal matrix. The advantage of the *in-situ* process is that the reinforcement surfaces tends to remain free of contamination, such as gas absorption, oxidation and other detrimental surfaces reactions, therefore, an improve

reinforcement-matrix interface bond can be achieved. *In-situ* composite exhibit improved mechanical strength, hardness as well as enhanced wear resistance [3]**.** Compared to other method, *in-situ* synthesis by MA offers advantages such as more uniform reinforcement particle distribution and finer particle size, leading to stronger and more heat-resistant material [4].

The Cu-Ti-C system was chosen to study the possibility of synthesis of tungsten carbide phases by different milling time. The aimed of this study was to determine the effect of MA time on the formation of *in-situ* TiC phase in copper composite.

EXPREIMENTAL PROCEDURE

The characteristic of the starting materials is reported in Table 1. The composition of Cu-20 vol% TiC is shown in Table 2. The elemental Cu and graphite powders were milled with ball to powder weight ratio (BPR) of 10:1 for 10 hours to produce a Cu-C pre-alloyed powder. N-heptane was added as a process control agent to prevent cold welding of the milling sample. At first attempt, milling was continued with addition of titanium powder for 4 hours. The as-milled powders were analyzed by XRD to determine the formation of titanium carbide phase at 4 hours milling time. For second attempt, milling was continued for 5, 10, 20, 40, 60 and 80 hours in order to optimize the formation of TiC during milling. MA was performed in planetary ball mill (Fritcsh, Pulverisette 5, Germany) under a high purity argon atmosphere at rotational speed of 400 rpm.

The characteristic of the milled powders were examined by different methods including: scanning electron microscopy (SEM), x-ray diffraction (XRD), laser particle size analyzer and energy dispersive x-ray (EDX).

After MA, powders were compacted in cylindrical die to produce green pellet. WD 40 was used as the die wall lubricant. The compacted pressure was fixed at 400 MPa. The pellet was sintered in vacuum furnace at 900˚C for one hour under vacuum pressure at 10^{-3} millitorr / Pa. The phase change and microstructure of sintered sample was determined by XRD and SEM.

Table 1. Characteristics of raw powders

Material	*Supplier*	*Ave particle size (µm)*	*Purity(%)*
Copper	Merck,Germany	**29.95**	**>99.7**
Titanium	Merck,Germany	**59.01**	**>98.0**
Graphite	Fluka,Switzerland	**15.91**	**>99.9**

Table 2. Compositions of Cu-20vol% TiC

Material	*Weight %*
Copper	**87.9**
Titanium	**9.67**
Graphite	**2.42**

RESULTS AND DISCUSSION

XRD spectra of the Cu-Ti-C system for 4 hours are shown in Fig. 1. After milling for 4 hours, Ti and Cu diffraction spectra can be clearly distinguished, while some C diffraction peak overlapped with Cu peaks (Figure 1a) due to solubility of C in Cu after pre-alloyed of Cu and graphite for 10 hours. TiC diffraction peaks was found after heat treatment at 900˚C (Figure 1b). The presence of TiC (111), (200) and (220) diffraction peaks can clearly be seen, indicating formation of *in-situ* TiC was assisted by heat treatment.

In order to produce *in-situ* TiC via MA, the milling was continued for 5, 20, 40, 60 and 80 hours. The XRD pattern of as-milled Cu- 20 wt% TiC is shown in Fig 2. As can be seen, the TiC phases start to form after 5 h of milling. The XRD result also propose that the milling conditions used in this research are adequate to produce *in-situ* a metal-matrix composite material consisting of titanium carbide phase, dispersed in copper matrix without additional heat treatment. The peak intensity of TiC diffraction peaks from 20 h up to 80 h of milling time did not change even at extended milling time. It is worth to be stated that milling up to 80 h did not induced more amount of TiC. *In-situ* formation of TiC composite also performed by Lu et. al. [5] by using selective laser melting (SLM). In their study, they was found TiC phase during melting process.

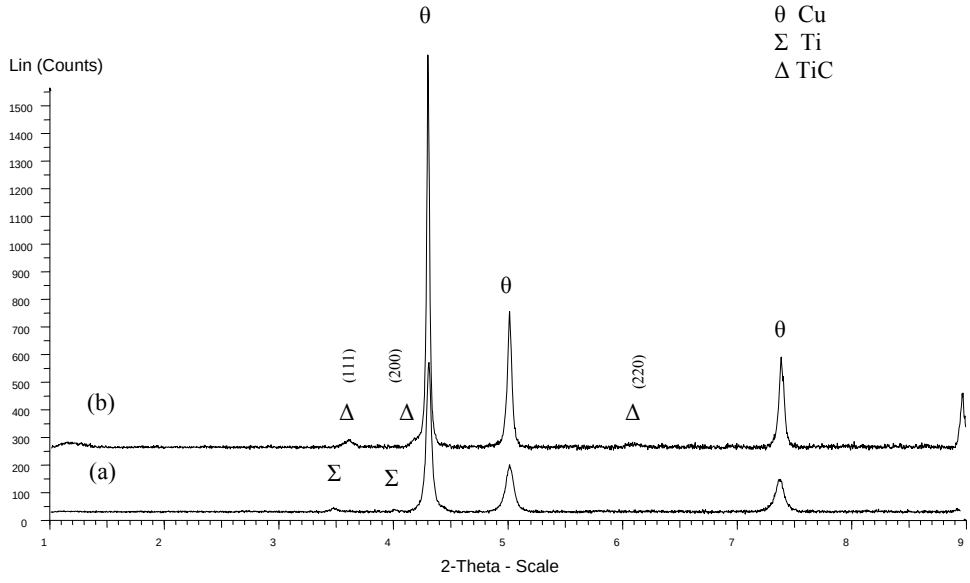


Figure 1 XRD spectra of Cu-Ti-C system for 4 hours milling (a) as-milled powder (b) after heat treatment

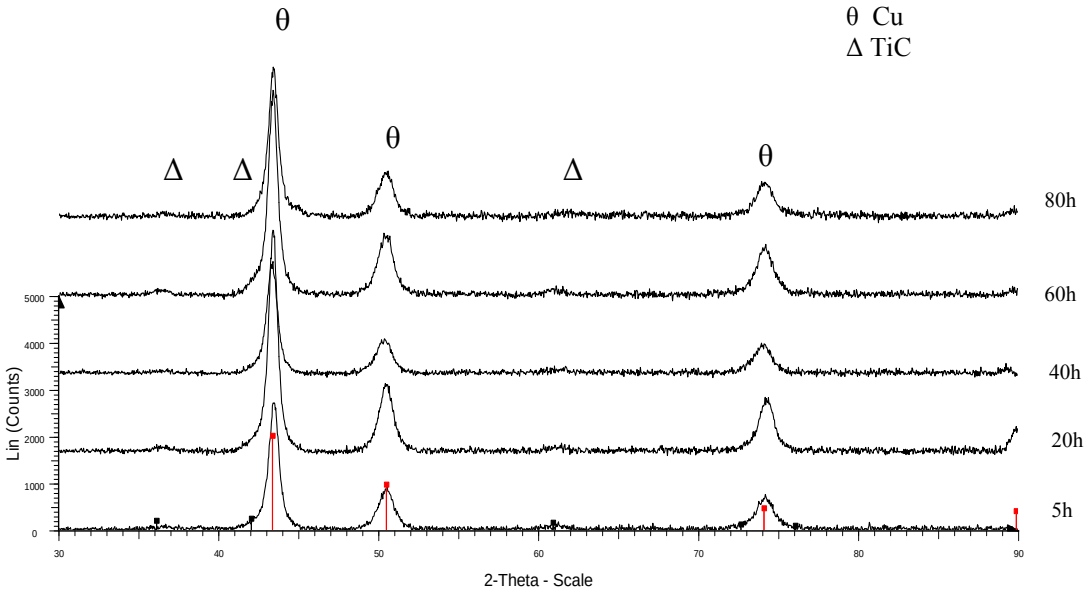


Figure 2 XRD spectra of Cu-Ti-C system for 5, 20, 40, 60 and 80 hours milling (as-milled powder).

XRD pattern after heat treatment as shown in Fig. 3. Titanium carbide phase can be clearly identified in the Cu-20wt%TiC composites. Fe_3C phase was started to form after 40 h of milling resulting from milling contamination by the milling media. At 80 h milling the Fe_3C diffraction peak become more intense and well defined showing an increase of Fe_3C volume fraction. Murphy and Courtney [6] show that the contamination content can be as high as 9 vol% Fe when Nb, graphite and Cu powders are simultaneously milled in a single step milling operation. In this work, previous milling of Cu and graphite probably prevented further contamination because graphite has good lubricant properties.

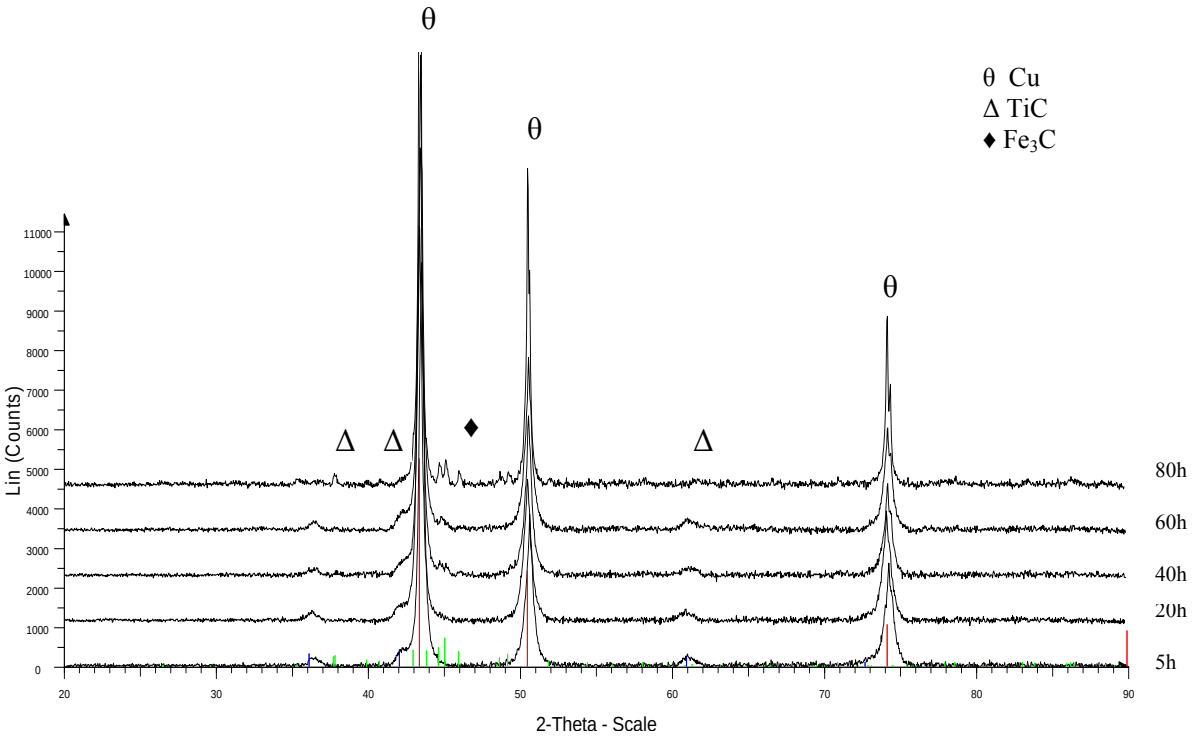
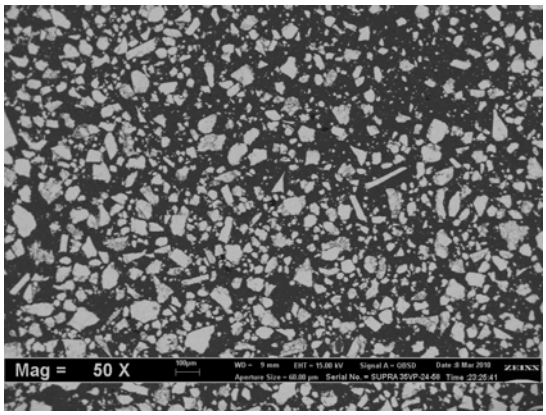
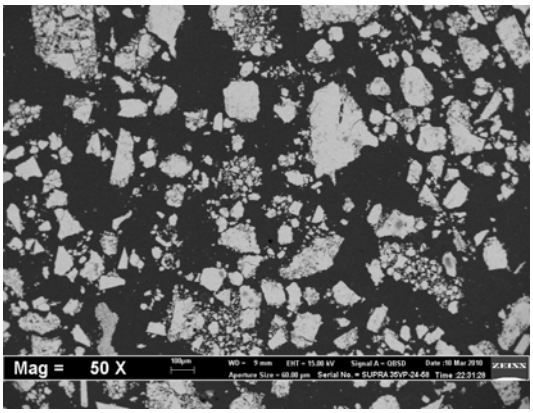


Figure 3 XRD spectra of Cu-Ti-C system for 5, 20, 40, 60 and 80 hours milling after heat treatment

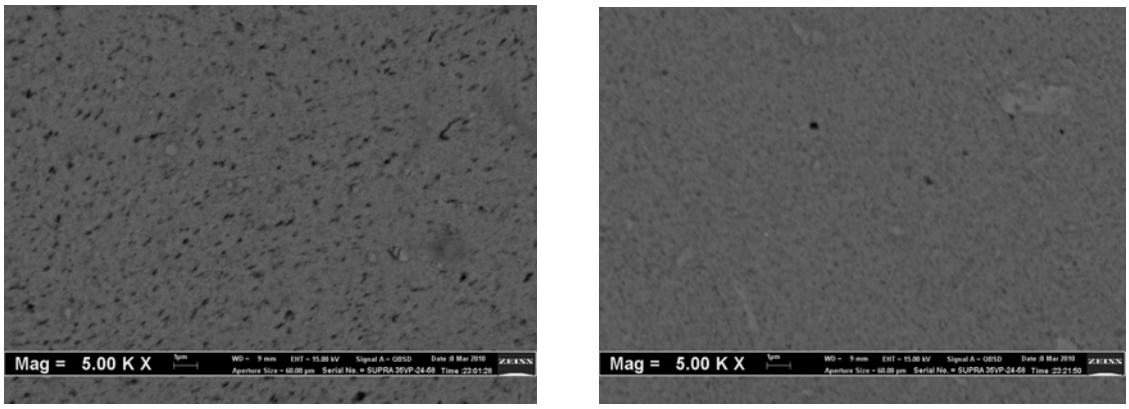
Fig. 4 shows the SEM micrograph of as-milled Cu- 20 vol% TiC powder for 4 and 5 h milling. For 4 h milling (Fig 4 (a)), the average particle size was 12 µm which is in good agreement with the one determined by particle size analyzer. Fig. 4 (b) shows as-milled Cu-TiC powder for 5 h milling. Average particle sizes was around 20 µm. Fig. 4 (c) was SEM micrograph of sintered Cu-TiC composite at 4 h milling. As can be seen, the pore is much more in sintered Cu-TiC for 4 h milling compared to 5 h milling (Fig. 4 (d)). The titanium carbide phase only formed after 5 h milling so that it was clearly seen that titanium carbide phase was uniformly dispersed into nanostructured copper matrix.



(a)



(b)



(c) (d)

Figure 4 (a) SEM picture of as-milled Cu-20 vol% TiC powder at 4 h milling, (b) as-milled Cu-20 vol% TiC powder at 5 h milling, (c) Cu- 20 vol% TiC at 4 h milling after heat treatment, (d) Cu- 20 vol% TiC at 5 h milling after heat treatment

Fig. 5 and Fig. 6 shows EDX area analysis of Cu-TiC at 4 and 5 h milling respectively. The reduction of graphite percentage in 5 h milling was due to diffusion of C in Cu matrix. Therefore, TiC formation was promoted because of low solid solubility of C in Cu compared to the solubility of Ti in Cu [5].

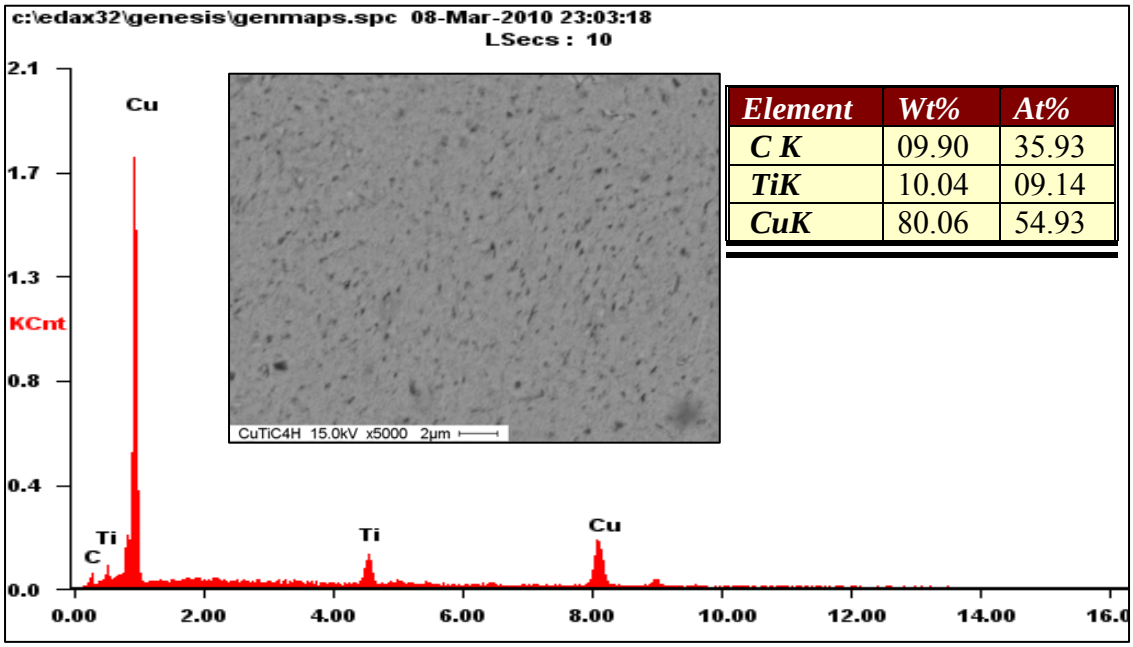
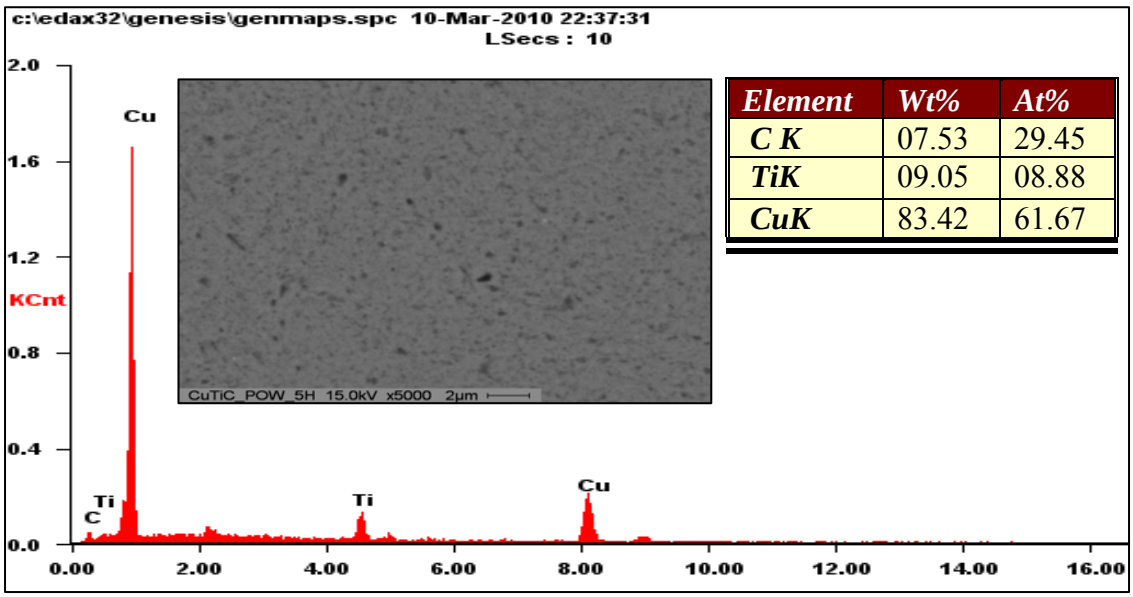


Figure 5 EDX analysis of as-milled Cu- 20 vol% TiC for 4 h milling.



Element	Wt%	At%
C K	07.53	29.45
TiK	09.05	08.88
CuK	83.42	61.67

Figure 6 EDX analysis of as-milled Cu- 20 vol% TiC for 5 h milling.

Figure 7 shows the average crystallite size determined for Cu- 20 vol% TiC for 4, 5, 20, 40, 60 and 80 h of milling in the as-milled and after heat treatment. Only Cu crystallite size could be determined because diffraction peaks corresponding to titanium carbides are very weak. As can be seen in the beginning, a rapid increase of average crystallite size occurs after 5 h of milling. This is believed to be due to plastic deformation and cold welding during initial milling. This variation is supported by the particle size measurement of 4 h and 5 h which is 12.23 µm and 111.5 µm, respectively. Average crystallite size of Cu in sintered *in situ* pellet was measured compared to the as-milled powder. This trend may be explained by the effect of sintering on green compact. In mechanically alloyed powders the crystallite size which is the size of the coherently diffracting domains is often equated with the grain size [7].

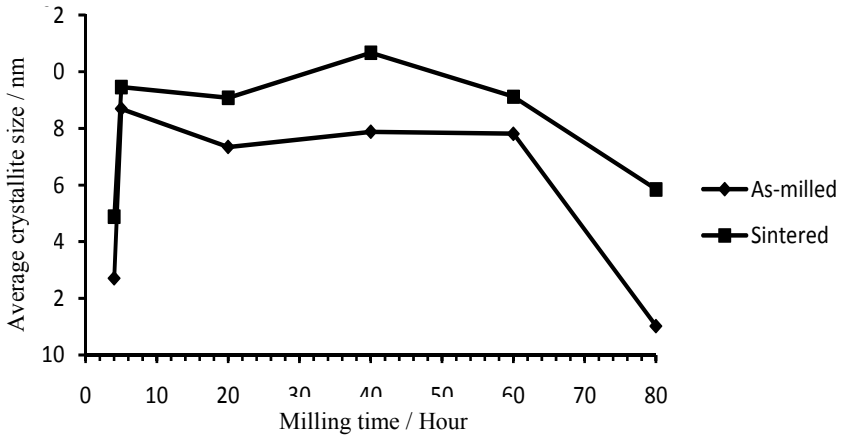


Figure 7 Average crystallite size of Cu- 20 vol% TiC as-milled powder and after heat treatment (sintered).

CONCLUSION

A study on effect of milling time on formation of *in-situ* TiC in Cu-based composite by MA, reveals the following result:

1. It was confirmed that a dispersion of TiC particles began to participate by solid state reaction induced by MA after 5 h milling.
2. The microstructure observation on as-milled powder at 5 h milling shows that TiC phase was totally induced in Cu matrix.
3. Average crystallite size of Cu was calculated using Scherrer equation ranged between 11-19 nm. Rapid increase of average crystallite size resulted after 5 h milling was due to plastic deformation and cold welding during initial milling.

ACKNOWLEDGEMENTS

This research was supported partly by The Japan International Cooperation Agency (JICA) under AUN-SEED/Net Program (account number 6050069) and a Science Fund Grant provided by the Ministry of Science, Technology and Innovation, Malaysia (account number 6013361).

REFERENCES

1. Yang. C, et al., *Synthesis of Ti3Al2C2 ceramic by high-energy ball milling of elemental powders of Ti, Al and C.* Journal of Materials Processing Technology, 2009. **209**: p. 871-875.
2. Davis, R., B. McDermott, and C. Koch, *Mechanical alloying of brittle materials.* Metallurgical and Materials Transactions A, 1988. **19**(12): p. 2867-2874.
3. J. P. Tu, N.Y.Y., W. X. Qi, F. Liu, X. B. Zhang, H. M. Lu, M. S. Liu, *Preparation and Properties of TiB2 Nanoparticle Reinforced Copper Matrix Composites by In-Situ Processing* Materials Letters, 2002. **52**: p. 448-452.
4. M. T. Marques, A.M.F., J. B. Correia, A. M. Botelho do Rego, R. Vilar, *XRD, XPS, and SEM Characterization of Cu-NbC Nanocomposite Produced by Mechanical Alloying.* Materials Chemistry and Physics, 2008. **109**: p. 174-180.
5. Lu, L., et al., *In situ formation of TiC composite using selective laser melting.* Materials Research Bulletin, 2000. **35**(9): p. 1555-1561.
6. Murphy, B.R. and T.H. Courtney, *Mechanochemically synthesized NbC cermets: Part I. Synthesis and structural development.* Journal of Materials Research, 1999. **14**(11): p. 4274-4284.
7. Suryanarayana, C., *Mechanical Alloying and Milling*. 2003: Marcel Dekker. 7-9.