MICROSTRUCTURE AND MECHANICAL PROPERTIES OF AN Al-CuO IN SITU COMPOSITE PRODUCED BY FRICTION STIR PROCESSING

G. L. You *, P. W. Kao and N. J. Ho
Department of Materials and Optoelectronics Science; Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaoshiung 804, Taiwan
* Corresponding author (kimmss@msn.com)

Keywords *Metal matrix composites (MMCs); Friction stir processing (FSP); Transmission electron microscopy (TEM)*

1. Introduction

Aluminum-based particulate reinforced metal matrix composites (MMCs) are of interest for structural applications. It is widely recognized that the mechanical properties of metal matrix composites (MMCs) are controlled by the size and volume fraction of the reinforcements as well as the nature of the matrix-reinforcement interface [1]. Superior mechanical properties can be achieved, when fine and stable reinforcements with good interfacial bonding are dispersed uniformly in the matrix.

In conventionally processed power metallurgy composites, the reinforcing particles are formed prior to addition to the matrix metal. In this case, the scale of reinforcing phase is limited by the starting powder size, which is typically of the order of microns to tens of microns and rarely below 1μm. A possible alternative is to synthesize the reinforcement in-situ in the metal matrix. It has been shown that aluminum reinforced with large amount of nanometer-sized particles could be fabricated from powder mixtures of Al and transition metals (TM), including Al-Cu [2], Al-Ti [3] and Al-Fe [4], by using friction stir processing (FSP).

Friction stir processing (FSP) was developed based on the principle of friction stir welding (FSW) [5, 6]. In FSP, a non-consumable rotating tool with a specially designed pin and shoulder is plunged into specimen, and the friction between the rotating tool and the workpiece can raise the local temperature of material to the range where it can be plastically deformed easily. The basic idea to form in-situ composites via FSP [2-4] has combined the hot working nature of FSP and the exothermic reaction between aluminum and transition metals. The FSP can provide the following functions in one-step: (a) severe plastic deformation to promote mixing and refining of constituent phases in the material, (b) hot consolidation to form fully dense solid.

The objective of this study is to produce Al-matrix composites reinforced with large amount of nanometer sized Al_2O_3 particles. Thermite reactions can occur between aluminum and an oxide of a less reactive metal, and consequently, aluminum matrix composites reinforced by Al_2O_3 particles can be produced by oxide-aluminum displacement reaction. A considerable heat release will accompany the Al-CuO reaction, since the heat of formation for CuO, Cu_2O and Al_2O_3 are 162kJ/mol, 173kJ/mol and 1676kJ/mol, respectively [7]. In this work, CuO was selected to react with Al to form the in-situ composite.

2. Experimental detail

Billet of powder mixtures of Al with 10 mol% CuO (denoted as Al-10CuO) was prepared by the use of conventional pressing and sintering route, which was used as a precursor for FSP. The powders used in this study are aluminum powder (ECKA-Granules, 99.7% purity, -325 mesh) and CuO powder (CERAC, 99.7% purity, -200 mesh). After mixing, the mixed Al-10CuO powders were cold compacted at 225MPa to form a billet of 12 × 20 × 88 mm^3. To improve the billet strength for easier handling in FSP, the green compact was sintered at 773 K for 1 hr.

The tool for FSP in this study has a shoulder of 16 mm dia. and a pin of 6 mm in both dia. and length. The tool pin used in FSP was standard M1.2*6 (diameter of 6 mm and pitch height of 1.2 mm). The tool spindle angle (angle between spindle

and workpiece normal) was 3°. The rotating tool was traversed along the long axis of the billet. For multiple FSP, the rotating tool was moved along the same line, and it was applied after the billet had been cooled down from the previous FSP pass.

In FSP, the major processing parameters are tool-rotating rate, and tool traversing speed. Basically, the temperature resulted from the combination of tool rotating and traversing speed must be high enough to initiate the reaction. But it should not be too high, because high temperature will promote the exothermic Al-CuO reaction that may cause excessive melting, which may result in large cavities in the stir zone.

Specimens taken from the stirred zone (SZ) of FSPed billet were used for the characterization of mechanical properties and microstructure. X-ray diffraction (XRD, CuK_α, 40 kV, 30 mA) was utilized to identify the phases present in the specimens. Scanning electron microscopy (SEM, JSM-6330) was used to study the distribution of second phase particles. Thin foils were studied by the use of an analytical electron microscope (AEM, JEOL 3010) operated at 200 kV. The Vickers microhardness was measured with 300g load for 15s. Mechanical properties of specimens machined from the stirred zone (SZ) were measured by the use of compression test on an Instron 5582 universal testing machine with an initial strain rate of 1×10^{-3} s^{-1}. Cylindrical specimens with dimensions of 4mm in diameter and 6mm in length were used for compression tests.

3. Results and discussion

The X-ray diffraction (XRD) patterns (Fig. 1) indicate that after sintering at 773 K, there is weak peak of Cu_2O indicating a partial reduction of CuO reduced from CuO, and after 4 FSP passes, there are diffraction peaks of Al, CuO, Cu_2O and Al_2Cu. Apparently, CuO was not fully reacted with Al after 4 passes of FSP. The presence of Al_2Cu in the FSPed sample indicates that the Cu reduced from CuO had reacted with Al to form the intermetallic phase. However, Al_2O_3 could not be found in the XRD patterns.

According to the XRD results, the Al-CuO reaction may be expressed as either of the following reactions:

(a) $2Al + 3CuO \rightarrow Al_2O_3 + 3Cu + \Delta H_1$ (1)

(b) $2Al + 6CuO \rightarrow 3Cu_2O + Al_2O_3 + \Delta H_2$ (2a)

$2Al + 3Cu_2O \rightarrow Al_2O_3 + 6Cu + \Delta H_3$ (2b)

The enthalpy changes associated with the above reactions are: ΔH_1=-1190kJ/mol, ΔH_2=-1223kJ/mol, and ΔH_3=-1157kJ/mol. The Cu reduced from CuO or Cu_2O can further react with Al to form Al_2Cu by the following reaction:

$2Al + Cu \rightarrow Al_2Cu$ (3)

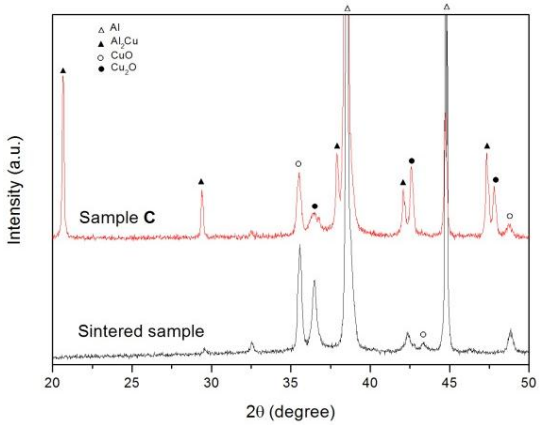

Fig. 1. XRD patterns of as-sintered sample and sample **C** produced by FSP with 500rpm and 45mm/min.

The typical microstructure in the stir zone of specimens after 4 FSP passes is shown in Fig.2a. It reveals a homogeneous distribution of second phase particles in the aluminum matrix, in which particles of relatively large size were identified as unreacted CuO/Cu_2O. The fine particles with size below 1 μm, which were mainly as Al_2Cu, are uniformly dispersed in the aluminum matrix as shown in Fig.2a. It is consistent with the XRD results that CuO and Cu_2O remain in the FSPed specimen. A higher magnification of an unreacted CuO/Cu_2O particle is shown in Fig. 2b, which consists of CuO and Cu_2O reduced from CuO. Relative to the core, the outer region of the particle contains larger amount of brighter phase. According to the EDS (energy dispersive spectrum) analysis, the bright phase in the particle shown in Fig. 2b is Cu_2O and the grey phase is CuO.

The microstructure was further examined by the use of TEM. The average size of aluminum grains is about 1.5 μm, and there is fine dispersion of

nanometer size particles within the aluminum grains (Fig. 3a). As shown in Fig. 3b, these intragranular particles are interacted with dislocations. The Al_2Cu particles of submicrometer size are well dispersed in the aluminum matrix. According to EDX (energy dispersive X-ray microanalysis) analysis, the composition of these intragranular particles was close to Al_2O_3. Selected area diffraction (SAD) shows a diffuse ring pattern, which means these particles are amorphous. After E-beam irradiation during the TEM observation, the clear rings of diffraction spots appear in the pattern and these particles shows the diffraction contrast. It implies that these particles start to crystallize. It is then proposed that these aluminum oxide particles were amphorous in the FSPed specimen, which started to crystallize after electron irradiation during TEM observation. This may explain that no diffraction peaks corresponding to Al_2O_3 was found in the XRD pattern. In summary, the microstructure of the FSPed specimen can be considered as a composite with the reinforcing phases identified as Al_2O_3 particles of nanometer size and Al_2Cu particles of submicrometer size.

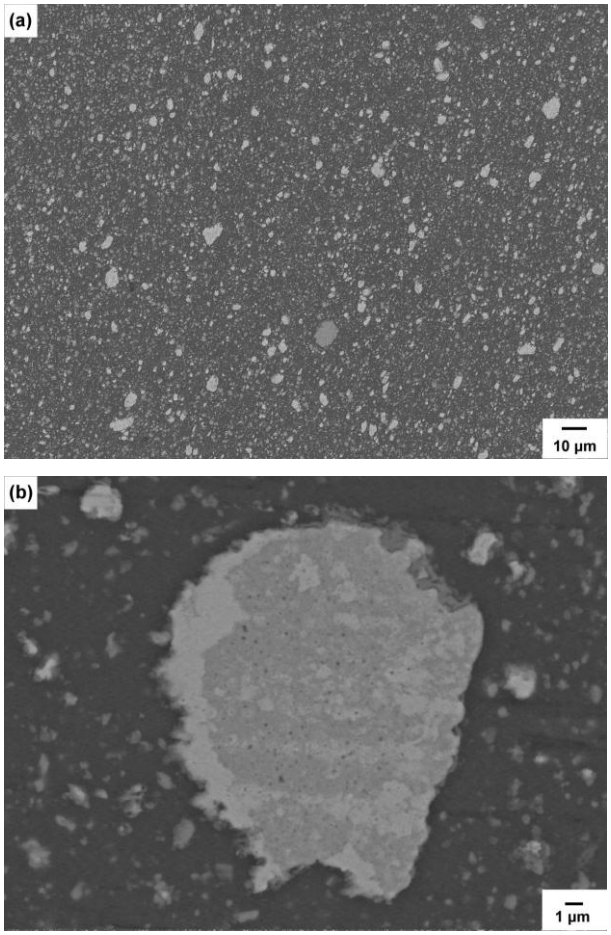

Fig. 2. SEM-backscattered electron image (BEI) of the stirred zone (SZ) of Al-10CuO specimen produced by 4 FSP passes showing (a) uniform dispersion of second phase particles in the aluminum matrix and (b) partially reacted CuO/Cu_2O particle.

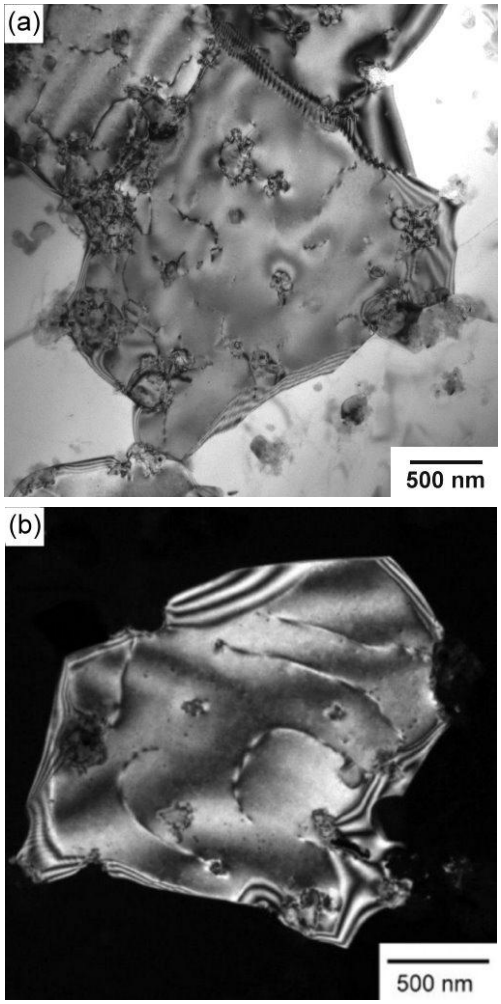

Fig. 3. (a) TEM bright field image (BFI) showing fine dispersion of nanometer size particles in aluminum grain of FSPed specimen. (b) TEM center dark field image (CDFI) showing interaction of dislocations with particles.

After 4 FSP passes, CuO was only partially reacted with aluminum. Figure 4 shows that the partially reacted CuO/Cu_2O particle has a core-shell structure, in which CuO/Cu_2O forming the core (**C**) is enclosed by a shell comprised of amorphous

aluminum oxide (**B**) and Al_2Cu (**A**). It is suggested that the aluminum oxide shell become a diffusion barrier, which rendered the reaction between aluminum and the CuO/Cu_2O containing core.

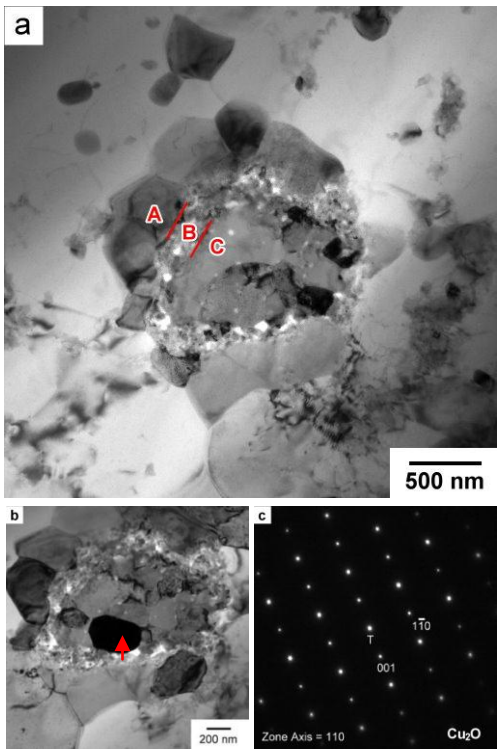

Fig. 4 (a) TEM bright field image (BFI) showing the core-shell structure of partially reacted CuO in FSPed Al-10CuO specimen, in which A, B, C are Al_2Cu, Al_2O_3 and CuO/Cu_2O core (b) BFI of Cu_2O in zone (indicated by arrow), (c) SAD pattern of Cu_2O.

The influence of FSP parameters on the hardness of the FSPed specimen is summarized in Table 1. According to Arbegast [8], the heat input in FSP may be related to the index w, which can be expressed as

$$w=R^2/(v\times 10^4) \quad (4)$$

The results shown in Table 1 may be summarized as follows.

(1) Specimen A, produced by the lowest v and low w, shows the highest hardness.
(2) Compared with specimen A, specimen B has much lower hardness, which might be due to a coarser microstructure in specimen B resulted from high heat input.
(3) Specimen E, produced by low w and the highest v, has the lowest hardness.
(4) Comparing specimens A, C, D and E, which have similar heat input, the hardness increases with decreasing v.

Compressive stress-strain curves of FSPed specimens (A, B, E) are shown in Fig. 5, which are consistent with the microhardness results. The compressive tested specimens were not fractured, when the test was stopped at strain about 0.22. It clearly shows that the Al-CuO in-situ composite produced by FSP exhibits very high strength and good ductility. The strength of the composites could be attributed to the fine Al grain size and Orowan strengthening due to the distribution of fine reinforcing particles, mainly Al_2O_3.

Table 1. The influence of FSP parameters on microhardness of FSPed specimens.

Sample	v (mm/min)	R (rpm)	w	H_v
A	30	500	8.3	138±1.0
B	30	1400	65.3	93.8±4.3
C	45	500	5.6	108±3.0
D	45	700	10.9	96.9±1.9
E	85	700	5.8	85.6±1.4

Although the higher heat input by FSP can enhance the in-situ reaction of Al-CuO, it also decreases the strength of the composite due to microstructure coarsening resulted from high heat input. The tool traverse speed can affect the time that the material is subjected to the thermo-mechanical action in FSP, which can be considered as the "processing time". A low tool traverse speed can increase the processing time or the time for reaction. Besides heat input, FSP also provides severe plastic deformation, which can effectively refine the microstructure of the processed material. In summary, a low tool traverse speed has the beneficial effect for both enhancing the in-situ reaction and refining the microstructure.

Post-FSP heat treatment was used to enhance the Al-CuO reaction. The heat treatment was carried in Ar atmosphere at various temperatures ranging from 773 to 923 K for 1 hour. As shown in Fig. 6, the CuO/Cu_2O difffraction peaks still remain in the XRD patterns of heat treated specimens. The

hardness values of the heat treated specimens are also indicated in Fig.6, which are similar to that of as-FSP specimen. Apparently, the reaction between CuO/Cu_2O and Al proceeds rather slowly even at 923 K for 1 hour. It implies that the shell of Al_2O_3 formed between CuO/Cu_2O and Al may act as a barrier to prohibit the reaction. However, the reaction could proceed rather rapidly during FSP. It is then suggested that the critical mechanism responsible for the rapid reaction and the formation of nanometer sized particles in FSP is the effective removal of the reaction product from the Al-CuO interface by the severe strain imposed in FSP.

The Al-CuO reaction in FSP is very rapid. The distinct advantage of FSP for the formation of fine intermetallic particles in Al is the concurrent action of high temperature and severe plastic deformation.

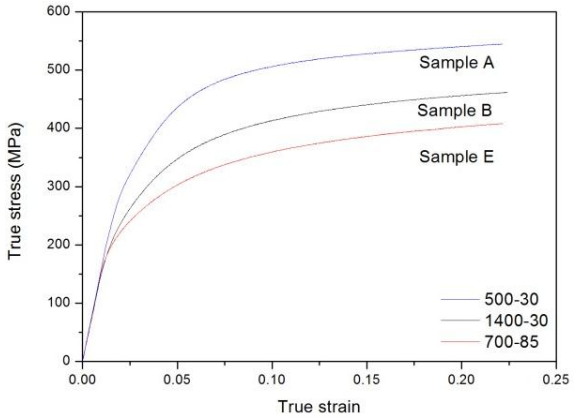

Fig. 5. Compressive stress-strain curves of FSPed specimens produced by various processing parameters.

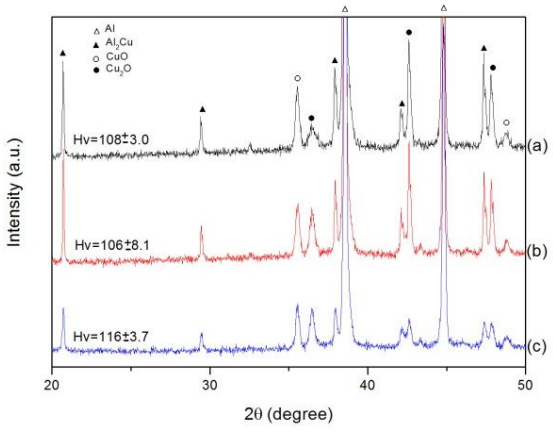

Fig. 6. XRD patterns of (a) as-FSPed sample C, and after post-FSP heat treatment at (b) 773K and (c) 823 K.

In FSP, the CuO particles could be effectively refined, which would increase the contact between CuO and Al, and promote the reaction. In addition, the reaction products can be removed from the Al/CuO interface and dispersed into the Al matrix due to the severe shear strain, and consequently, thus the reaction could proceed effectively at the interface.

4. Conclusion

In this study, friction stir processing (FSP) was applied to produce aluminum based nanocomposites from powder mixtures of Al and CuO. This technique has combined the hot working nature of FSP and the exothermic reaction between Al and CuO. The composites are reinforced with nanometer sized particles of Al_2O_3 and Al_2Cu, which were formed in-situ during FSP. The fine structure of these composites can be attributed to the severe deformation in FSP. The major contributions to high strength of the composite are the ultrafine-grained structure of aluminum matrix and the Orowan strengthening caused by the fine dispersion of nano-size Al_2O_3 particles inside aluminum grains.

References

[1] D.J. Lloyd "Particulate reinforced aluminum and magnesium matrix composites" *Intl Mater Rev*, Vol. 39, pp 1-23, 1994.

[2] C.J. Hsu, P.W. Kao and N.J. Ho "Ultrafine-grained Al-Al_2Cu composite produced in situ by friction stir processing" *Scripta Mater*, Vol.53, pp 341-345, 2005.

[3] C.J. Hsu, C.Y. Chang, P.W. Kao, and N.J. Ho and C.P. Chang "Al–Al_3Ti nanocomposites produced in situ by friction stir processing" *Acta Mater*, Vol. 54, pp 5241-5249, 2006.

[4] I.S. Lee, P.W. Kao and N.J. Ho "Microstructure and mechanical properties of Al–Fe in situ nanocomposite produced by friction stir processing" Intermetallics, Vol. 16 , pp 1104-1108, 2008.

[5] R.S. Mishra, M.W. Mahoney, S.X. McFadden, N.A. Mara and A.K. Mukherjee "High strain rate superplasticity in a friction stir processed 7075 Al alloy" *Scripta Materialia*; Vol.42, pp 163-168, 1999.

[6] R.S. Mishra and Z.Y. Ma "Friction stir welding and processing" Mater. Sci. Eng. R, Vol. 50, pp 1-78, 2005.

[7] O. Kubaschewski and C.B. Alcock, "Metallurgical thermochemistry". Oxford, 1979.

[8] W.J. Arbegast and P.J. Hartley "Friction Stir Weld Technology Development at Lockheed Martin Michoud Space Systems- An Overview" Proceedings of the Fifth International Conference on Trends in Welding Research, Pine Mountain, GA, Jun 1-5, pp 541-546, 1998.