

PREPARATION OF Cu MATRIX COMPOSITE REINFORCED WITH IN-SITU NANOSIZED Al_2O_3 PARTICLE POWDER FROM METAL NITRATES

Hai Minh Le¹⁾, Yen Ngoc Nguyen¹⁾, Duong Tien Hoang Truong¹⁾, Huy Duc Vu¹⁾, Hai Hong Nguyen¹⁾, Khanh Quoc Dang^{1)*}

¹⁾ School of Materials Science and Engineering, Hanoi University of Science and Technology, Hanoi, Vietnam

Received: 04.01.2019

Accepted: 28.02.2019

*Corresponding author: e-mail: khanh.danguoc@hust.edu.vn, Tel.: +84 24 3868 0355, School of Materials Science and Engineering, Hanoi University of Science and Technology, No.1, Dai Co Viet Street, Hai Ba Trung, Hanoi, Vietnam

Abstract

The objective of the present work is to investigate the feasibility of the synthesis of copper matrix composite reinforced with in-situ nanosized Al_2O_3 particle powder via combustion synthesis method from metal nitrates followed by reducing process at high temperature. The starting nitrates $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ composition corresponds to Cu-30% Al_2O_3 . X-ray Diffraction (XRD) patterns of the obtained powders indicated the presence of the oxides CuO and CuAl_2O_4 . The powder had the size of 75 ± 10 nm after deagglomerating by soft ball milling for 24h. After reducing in CO at 1000°C for 3h, the peaks of the oxides were no longer observed and were replaced by the peaks of Cu and α - Al_2O_3 . The morphology of the reduced powders observed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis showed well distribution of the α - Al_2O_3 particles within the Cu matrix with an average particle size of 40 nm.

Keywords: Cu- Al_2O_3 nanocomposite, CuAl_2O_4 , CuAlO_2 , combustion synthesis, reduction

1 Introduction

The aim of fabricating copper-based composites reinforced with dispersed ceramic particles is to enhance the mechanical properties of copper, in particular their higher specific strength and good elevated temperature mechanical properties while still maintaining the high electrical and thermal conductivities [1-8]. Currently, there are two main routes of producing such kind of composites, which are ex-situ and in-situ processes. In in-situ synthesis technique, the reinforcing ceramic phases are synthesized in the metallic matrix by a chemical reaction during the composite fabrication. Consequently, compared to ex-situ synthesis technique, in-situ routes introduce significant advantages such as nanosize, good distribution and thermodynamical stability of reinforcing particulate phases [9-13], which considerably enhance the properties of the composites.

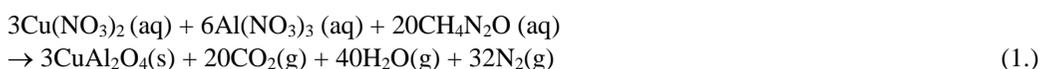
The Cu nanocomposite reinforced by in-situ Al_2O_3 have been developed through different synthesis routes such as mechanical alloying and rapid solidification. Ying and Zhang studied the synthesis of a Cu-20 vol.% Al_2O_3 nanocomposite via mechanical milling of a Cu-Al powder together with CuO powder [14]. Al_2O_3 particles in the consolidated composite material have a size smaller than 200 nm in diameter. Recently, chemical route has emerged as a newly developed method to prepare Cu nanocomposites reinforced with nanosized Al_2O_3 particles. Cu

nanocomposites reinforced by 5, 10, and 15 wt.% Al_2O_3 were prepared using mechano-chemical method [15-18]. This research reported that Cu was added to aqueous solution of aluminum nitrate or aqueous solution of aluminum nitrate and ammonium hydroxide. The average particle size of Cu and Al_2O_3 were 209 nm and 50 nm, respectively. Krakum et al. prepared Cu- Al_2O_3 composite via directly mixing of CuO and Al_2O_3 powders [19]. The powder mixture was then ball-milled in ethanol and sintered in an SPS apparatus to achieve highly dense CuAlO₂ sample. This bulk sample was then reduced by H_2 gas to obtain Cu- Al_2O_3 composite.

A new process to produce homogeneous Cu- Al_2O_3 nanocomposites from combustion reaction of metal nitrates was developed in the present study. The final Cu- Al_2O_3 nanocomposites was obtained by CO reducing and sintering process. The phases present, morphology and microstructure will be determined by X-ray Diffraction (XRD), Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy analysis (EDS) techniques.

2 Experimental procedure

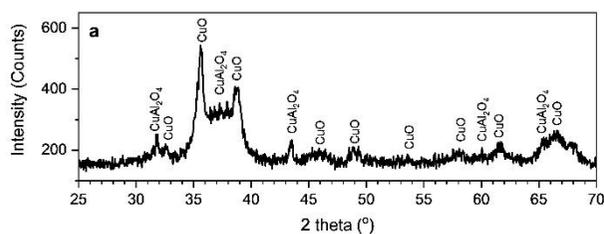
Copper nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (>99%) and aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (>99%) as oxidizers and urea $\text{CH}_4\text{N}_2\text{O}$ (>99%), as fuel were used to produce Cu-30 vol% Al_2O_3 nanocomposite, purchased from Xilong Scientific Co. Ltd., China. Precursor materials were mixed by a fixed ratio, and then dissolved in distilled water. Subsequently, the solution was placed in an electric resistance furnace (Linn HT1300, Germany) which was preheated at 500°C. The combustion reaction was performed according to the reactions (1) and (2).



The synthesized product was milled for 24 hours in a pure ethanol solution (96%) using alumina balls with ball-to-powder mass ratio of 20/1 then dried at 120°C for 24 hours and calcined at 1100°C for 2 hours. The reduction process was carried out at 1000°C for 3 hours by annealing in a forming gas (99.97% CO) environment. The green compacts were formed by uniaxial pressing in a 10 mm inner diameter cylindrical steel die under a uniaxial applied pressure of 500 MPa. The compacted samples were then sintered by a tube furnace (Linn HT1200, Germany) at 1000°C for 3 hours with a heating rate of 5°C/min in argon atmosphere.

The phase analysis was carried out by XRD (D5000 Siemens, Germany) using Cu $K\alpha$ radiation. The morphology of the synthesized powders and the sintered samples was characterized by a field-emitting scanning electron microscope (FE-SEM Hitachi S4800, Japan). The particle size and the size distribution were evaluated by ImageJ software through SEM images. In addition, EDS was performed to identify the elements that present in the synthesized powders.

3 Results and Discussion



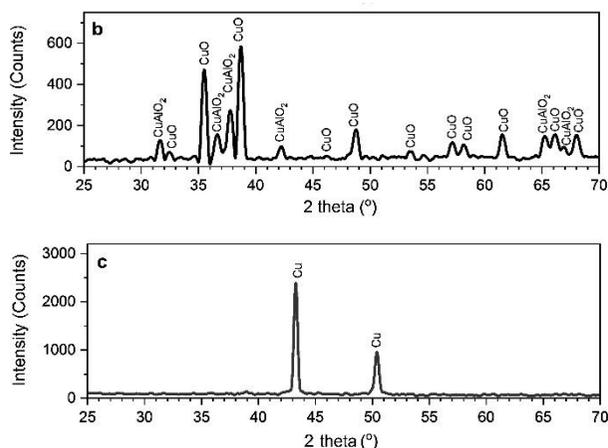


Fig. 1 The XRD patterns of (a) the combustion-synthesized powder, (b) after annealed at 1100°C in air for 2 hours and (c) after reduction in CO at 1000°C for 3 hours

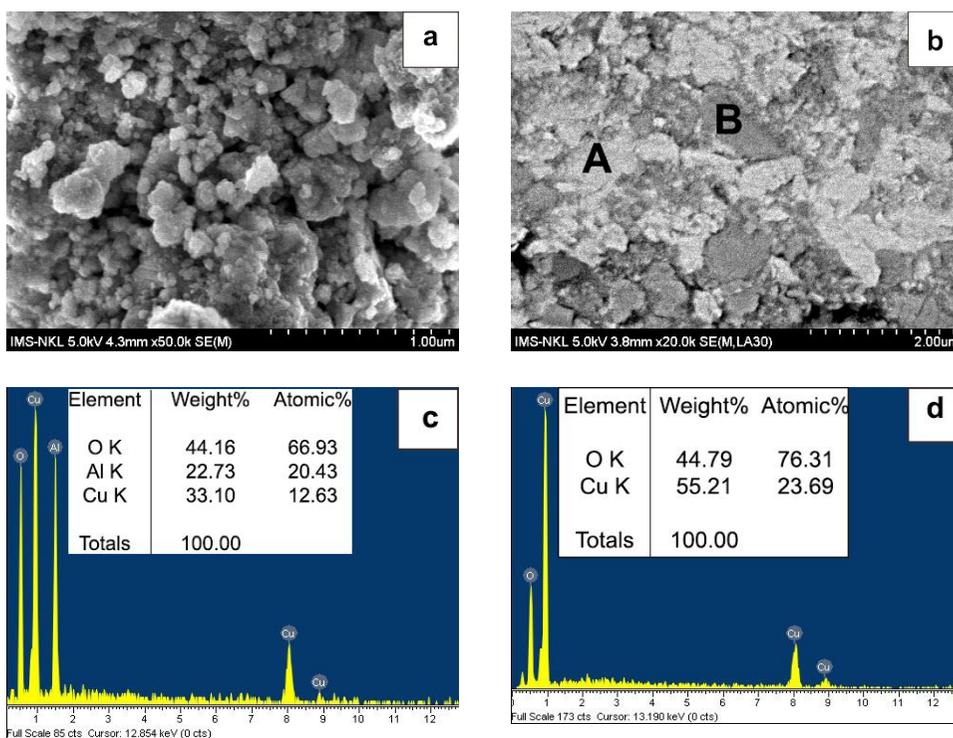


Fig. 2 SEM images of combustion-synthesized powder annealed at 1100°C in air for 2 hours in (a) SE mode, (b) BSE mode and its corresponding EDS patterns acquired on (c) A and (d) B areas

The evolution of the microstructure organization of the combustion-synthesized powder according to each step of the thermal treatment process can be deduced from XRD spectra (**Fig. 1**). The XRD spectrum of the combustion-synthesized powder exhibited almost all the main CuO and CuAl_2O_4

reflections (**Fig. 1a**). The appeared peaks were very broad indicating the poor crystalline nature of combustion synthesized product due to nanosized effect. After 2-hour annealing at 1100°C in air, the peaks of CuO phase was more intense and well-defined indicating a good crystallinity of the annealed product. However, the CuAl₂O₄ peaks disappeared and replaced by the peaks of CuAlO₂ (**Fig. 1b**). According to Hu et al., [20] the decomposition of CuAl₂O₄ at a temperature higher than 900°C led to the formation of CuAlO₂ and α -Al₂O₃ or γ -Al₂O₃ phases depending on the partial pressure of O₂. However, if the amount of CuO is excessive, the solid–solid reaction between CuO and CuAl₂O₄ can take place to form CuAlO₂. The XRD pattern of annealed powder after reduction in the presence of reducing gas CO at 1000°C for 3 hours showed the sharp and high intense peaks of metallic Cu (**Fig. 1c**). The small peak width indicated a good crystallinity with a large grain size of the formed Cu. However, no peaks of Al₂O₃ phase was observed in XRD spectrum. The invisibility of Al₂O₃ could be due to several reasons including poor crystallinity and small particle size of the generated Al₂O₃ and its much lower backscattering factor compared to Cu.

The SEM image in secondary electron mode of the combustion-synthesized powder after annealing was displayed in **Fig. 2** showing a monomodal particle size distribution with an average size of 100 nm. Back-scattered SEM images of the annealed powder illustrated the contrast between CuO and CuAlO₂ (**Fig. 2b**). EDS analysis (**Fig. 2c,d**) indicates that the bright area (marked as A) and the dark area (marked as B) are CuAlO₂ and CuO, respectively.

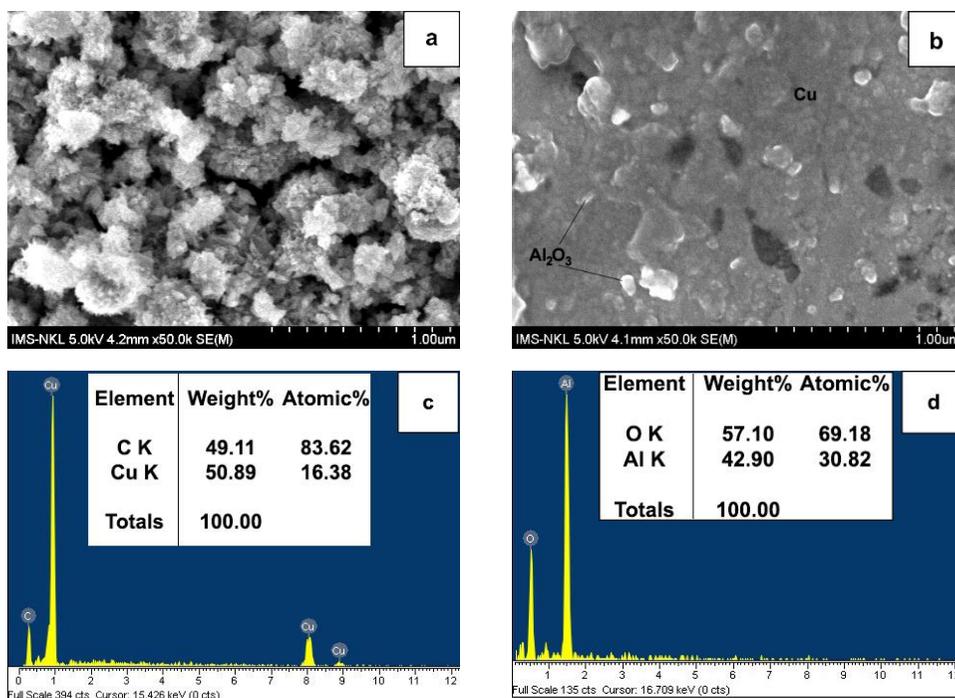


Fig. 3 SEM images of the composite powder reduced by CO at 1000°C for 3 hours in (a) powder, (b) its polished surface and corresponding EDS patterns acquired on (c) dark and (d) white areas

The reduction in the presence of reducing gas CO at 1000°C for 3 hours led to the formation of pores, which were uniformly distributed along the grain surfaces (**Fig. 3a**). In order to investigate

the distribution homogeneity of reinforcing particulates, back-scattered SEM (mode) and corresponding EDS of the composite powder are presented in **Fig. 3b–d**. The EDS spectra which acquired on the dark (**Fig. 3d**) and white (**Fig. 3c**) regions clearly demonstrated the existences of Cu matrix and Al_2O_3 particulate reinforcement. In the composites, the in-situ Al_2O_3 particles with an average size of 70 nm were uniformly dispersed throughout in the Cu matrix, as seen in **Fig. 3b**.

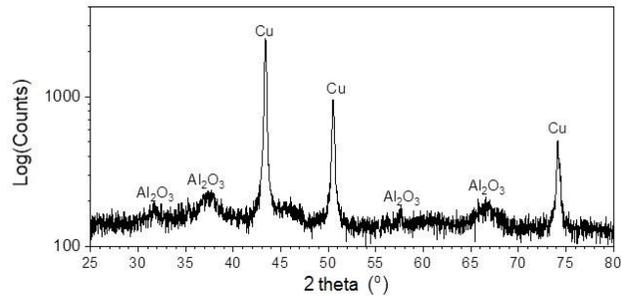


Fig. 4 XRD patterns of the Cu-30 vol% Al_2O_3 composite sintered at 1000°C for 3 hours

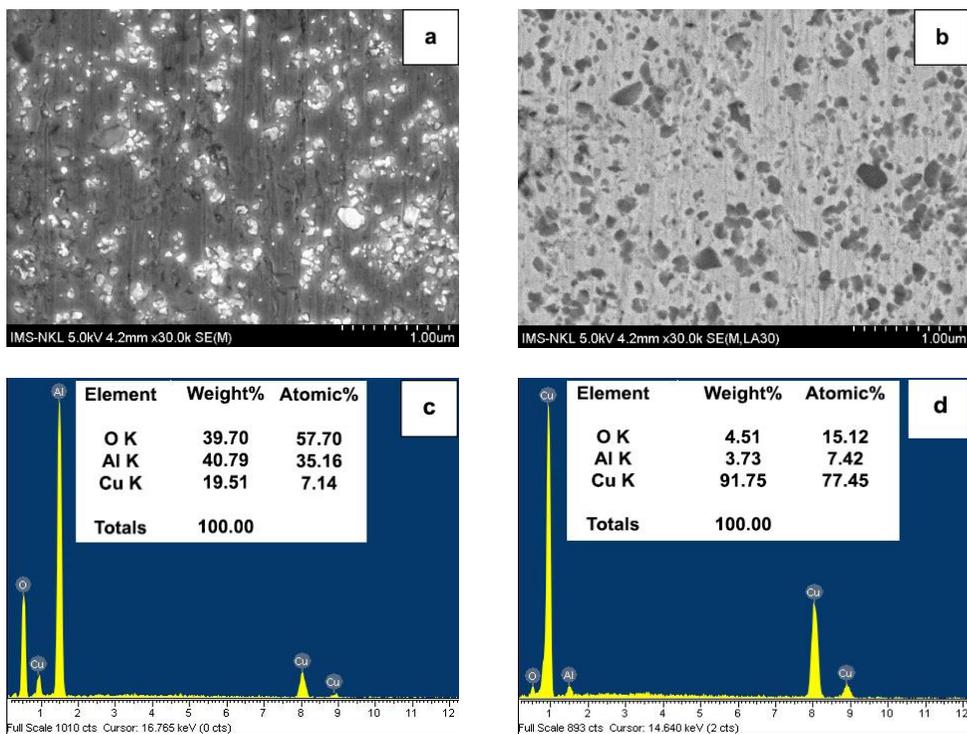


Fig. 5 The SEM images of the sintered composite in (a) SE mode, (b) BSE mode from the same area and its corresponding EDS patterns acquired on (c) bright and (d) dark areas

The XRD pattern of the sintered Cu-30 vol% Al_2O_3 composite is plotted on a logarithmic scale (**Fig. 4**) in order to observe the low-intense peaks. Apart from the peaks of copper matrix, the

XRD pattern shows the reflections corresponding to the hexagonal close-packed structure of α - Al_2O_3 . However, these Al_2O_3 peaks were not observed after reducing in CO. Their appearance could be due to that the heat treatment recovered considerably internal strains and made the crystallite size increase remarkably. SEM images of the sintered composite in both (a) secondary electron and (b) back-scattered electron modes from the same area and their corresponding EDS patterns acquired on (c) bright and (d) dark areas (**Fig. 5a-d**) proved a nanosized and well-dispersed Al_2O_3 particles within Cu matrix. The average size of the in-situ reinforced Al_2O_3 particles was about 40 nm. In the future works, the fabrication of bulk nanocomposite with different reinforcement composition and their mechanical and physical properties will be studied.

4 Conclusions

Cu-30vol.% Al_2O_3 nanocomposites have been successfully synthesized by chemical routes through combustion reaction of metal nitrates (i.e. $\text{Al}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$) followed by CO reduction and sintering. The obtained XRD spectra revealed that the mixture of CuO and CuAl_2O_4 powder formed after combustion reaction was transferred to CuO and CuAlO_2 after annealing and to composite powder of Cu/ Al_2O_3 after reducing by CO. SEM images in both SE and BSE mode and its corresponding EDS patterns showed nanosized and well-dispersed of Al_2O_3 particles within Cu matrix. The average size of the in-situ reinforced Al_2O_3 particles was 40 nm.

References

- [1] S. Sheibani, M. Khakbiz, M. Omidi: *Journal of Alloys and Compounds*, Vol. 477, 2009, No. 1-2, p. 683-687, DOI: 10.1016/j.jallcom.2008.10.095
- [2] C. Biseli, D. G. Morris, N. Randall: *Scripta Metallurgica et Materialia*, Vol. 30, 1994, No. 10, p. 1327-1332, DOI: 10.1016/0956-716X(94)90267-4
- [3] T. Takahashi, Y. Hashimoto: *Materials Transactions JIM*, Vol. 32, 1991, No. 4, p. 389-397, DOI: 10.2320/matertrans1989.32.389
- [4] M. T. Marques, V. Livramento, J. B. Correia, A. Almeida, R. Vilar: *Materials Science and Engineering A*, Vol. 399, 2005, No. 1-2, p. 382-386, DOI: 10.1016/j.msea.2005.03.090
- [5] M. T. Marques, V. Livramento, J. B. Correia, A. Almeida, R. Vilar: *Journal of Alloys and Compounds*, Vol. 434-435, 2007, p. 481-484, DOI: 10.1016/j.jallcom.2006.08.307
- [6] Z. Hussain, R. Othman, B. D. Long, U. Minoru: *Journal of Alloys and Compounds*, Vol. 464, 2008, No. 1-2, p. 185-189, DOI: 10.1016/j.jallcom.2007.10.026
- [7] H. Zuhailawati, T. L. Yong: *Materials Science and Engineering A*, Vol. 505, 2009, No. 1-2, p. 27-30, DOI: 10.1016/j.msea.2008.10.038
- [8] E. Botcharova et al.: *Journal of Alloys and Compounds*, Vol. 351, 2003, No. 1-2, p. 119-125, DOI: 10.1016/S0925-8388(02)01025-3
- [9] L. Froyen, J. D. Wilde: *Materials Science Forum*, Vol. 437-438, 2003, p. 141-144, DOI: 10.4028
- [10] T. Wang et al.: *Materials & Design*, Vol. 65, 2015, p. 280-288, DOI: 10.1016/j.matdes.2014.09.025
- [11] J. Ružić, J. Stašić, V. Rajković, D. Božić: *Materials & Design*, Vol. 62, 2014, p. 409-415, DOI: 10.1016/j.matdes.2014.05.036
- [12] N. Soltani et al.: *Materials & Design*, Vol. 53, 2014, p. 774-781, DOI: 10.1016/j.matdes.2013.07.084
- [13] S. C Tjong, Z. Y Ma: *Materials Science and Engineering: R: Reports*, Vol. 29, 2000, Issues 3-4, p. 49-113, DOI: 10.1016/S0927-796X(00)00024-3

- [14] D. Y. Ying, D. L. Zhang: *Materials Science and Engineering A*, Vol. 286, 2000, No. 1, p. 152-156, DOI: 10.1016/S0921-5093(00)00627-4
- [15] F. Shehata, A. Fathy, M. Abdelhameed, S. F. Moustafa: *Materials and Design*, Vol. 30, 2009, No. 7, p. 2756-2762, DOI: 10.1016/j.matdes.2008.10.005
- [16] F. Shehata, A. Fathy, M. Abdelhameed, S. F. Moustafa: *Journal of Alloys and Compounds*, Vol. 476, 2009, No. 1-2, p. 300-305, DOI: 10.1016/j.jallcom.2008.08.065
- [17] M. S. Motta, P. K. Jena, E. A. Brocchi, I. G. Solórzano: *Materials Science and Engineering: C*, Vol. 15, 2001, Issues 1-2, p. 175-177, DOI: 10.1016/S0928-4931(01)00272-7
- [18] P. K. Jena, E. A. Brocchi, M. S. Motta: *Materials Science and Engineering: A*, Vol. 313, 2001, Issues 1-2, p. 180-186, DOI: 10.1016/S0921-5093(00)01998-5
- [19] M. R. Kracum et al.: *Journal of the American Ceramic Society*, 2018, p. 1-10, DOI: 10.1111/jace.15801
- [20] W. Hu, F. Donat, S. A. Scott, J. S. Dennis: *RSC Advances*, Vol. 6, 2016, No. 114, p. 113016-113024, DOI: 10.1039/C6RA22712K

Acknowledgements

This research is funded by Hanoi University of Science and Technology (HUST) under project number T2017-PC-066.