Effects of electropulsing on microstructure and conductivity of nanofilms of Zn-Al alloys

Y.H.Zhu*, S.To*, W.B.Lee* and H.W.Zhang**
* State Key Laboratory of Ultraprecision Machining Technology, Dept. of Industrial & Systems Engineering, The Hong Kong Polytechnic University
**State Key Laboratory of Electronic Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu, 610054, China

ABSTRACT

Electropulsing induced microstructual changes and phase transformations in nanofilms of Zn-Al based alloys were studied by X-ray diffraction and scanning electron microscopy techniques. It was found that electropulsing affected considerably crystal orientation of nanophases. Also, electropulsing tremendously accelerated nanophase decomposition (such as formation of Z-zones and transitional phases). After electropulsing, the electric resistances of nanofilms of ZA22 and ZA27 reduced for 16.6% and 18.2%, respectively. Effect of electropulsing induced preferred crystal orientation changes on nanophase decomposition and electric conductivity of the Zn-Al based alloys is discussed.

Keywords: electropulsing; microstructure; conductivity; nanofilms; Zn-Al alloys

** corresponding author: yaohuazhu@hotmail.com*

1 INTRODUCTION

Because of their attractive thermal and physical properties, nanocrystalline materials have been studied for more than 40 years. Preparation, properties, structure and applications have been the main four aspects of nanomaterials science and technology. In the late 1980s, Glieiter, Suryanayana and Koch provided a comprehensive analysis of these materials.[1,2] Ruppin, Venkatasubramanian *et. al.,* Bux *et. al.* found that the thin film of the nanomaterials exhibited much better magnetic, dielectric, thermal-electric andphotonic properties.[3-7]

Our previous research studied nanophase decomposition of thin films of Zn-Al based alloys.[8-11] It was found that nanophases particles clustered to form Z-zones and transitional phases, which appeared as an important route in decomposition of the nanophase in the thin films of the Zn-Al based alloys (ZA7, ZA22, ZA27 etc.).[8-11] Also, nanophase η'_n possessed a strong preferred crystal orientation, which resulted in retardation of decomposition of nanophase significantly.[8-11]

However, few detailed studies of the thermal and electric properties of the nanofilms have been carried out from point of view of microstructural changes and phase transformations of the nanofilms. An understanding of correlation between those physical properties and nanophase decomposition is still lacking. It is vital to explore not only the new functional nanofilms, but also new processing based on the metallurgical background knowledge of the structural evolution and decomposition of nanophases involved.

As an advanced process, electropulsing treatment (EPT) has been proved to be a very effective process for improving the microstructures of materials and their properties.[12-14] Our previous work has shown that with adequate electropulsing, the elongation of the Zn-Al based alloys was increased by 437 % at ambient temperature under a high strain rate, whereas the instantaneous tensile stress remained unchanged, compared with that of the non-EPT alloy.[12] It was also reported that electropulsing tremendously accelerated phase transformations by a factor of at least 6000 times, compared with that achieved in the conventional ageing. [13,14]

In the present work, the electropulsing induced microstructural changes and their effects on electric conductivity of nanofilms of Zn-Al based alloys (ZA7, ZA22 and ZA27) are studied.

2 EXPERIMENTAL PROCEDURES

The nominal chemical compositions of the ZA alloys tested in the present study were $Zn_{90.7}Al_{7.0}Cu_{2.3}$, $Zn_{75.3}Al_{22.1}Cu_{2.6}$ and $Zn_{7.0.3}Al_{27.0}Cu_{3.0}$, respectively.

Small pieces of the previously rolled and solution treated alloys were cut and cleaned carefully before put into a melting pool in the chamber of an electron bean deposition facility. Glass-substrates coated with films of about 3μm of the ZA alloys were cut into pieces of 10 mm in width and 20 mm in length. Then the coated films were subjected to electropulsing treated (EPT) for various periods of time (2, 4, 6, 10, and 15 mins). The multiple positive electropulses were applied. Various operation parameters, such as pulse

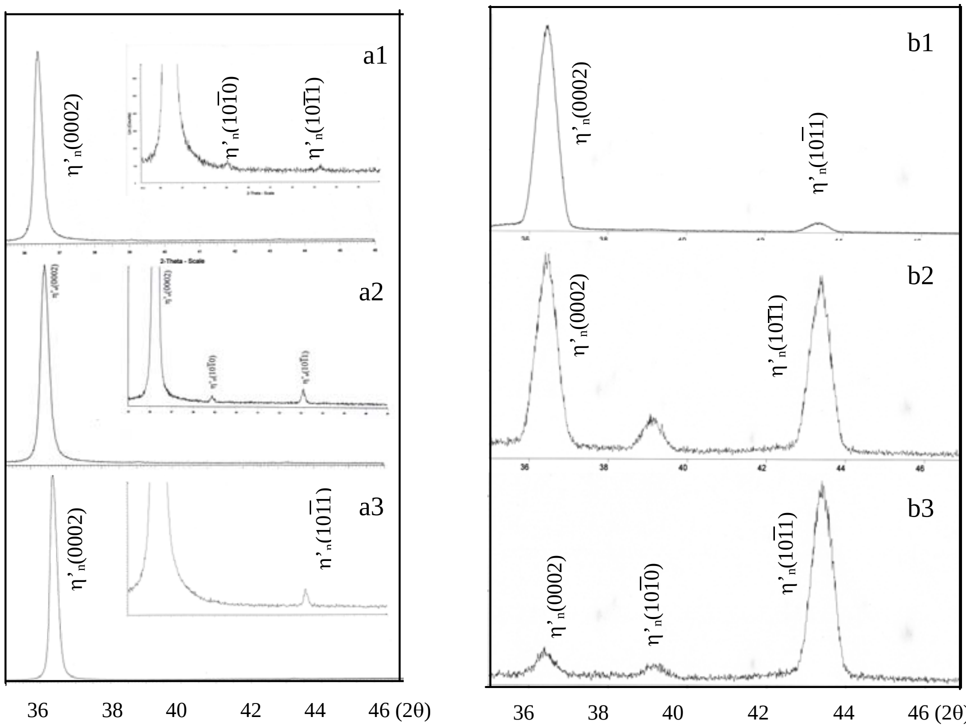

Fig.1 X-ray diffractograms nanofilms of ZA7, ZA22 and ZA27 alloys, as coated (a) and after EPT for 2 mins (b)

frequency, the root-mean-square value of current density (RMS), and the amplitude were 1.6 KHz, 540 mA and 10 A/mm^2, respectively. The EPT was carried out at room temperature (around 25-30°C), which was measured using a contact thermocouple for each test. The EPT operation procedure was reported in the previous articles.[8-11]

The microstructural evolution and phase decomposition of both nanifilms specimens were examined before and after EPT by X-ray diffraction (XRD) and secanning electron microscopy (SEM) techniques. Both routine operations of XRD and SEM were reported in the previous articles.[8-11]

The electric resistances of the specimens before and after EPT were measured by a R-chek-4 point meter made by ELECTRIC DESIGN TO MARKET, INC, USA. The results in ohms/ square received from the R-chek-4 point meter were the sheet resistance per square (R_s), which represented by “ OHMS/□ or Ω/□ “.

3 RESULTS AND DISCUSSIONS

3.1 Electrpulsing Induced Decomposition of Nanophase η'$_n$

Only one supersaturated nanophase was observed in the as coated films of the ZA alloys (ZA7, ZA22 and ZA27) being tested. One principle XRD peak of the nanophase was observed at an angle (2θ) of 36.4°, as shown in Fig.1a. Enhancing the heights of the XRD peaks, two peaks appear at 2θ 38.9 and 43.2°. The principle peaks appear at 2θ 38.9 and 43.2°. The principle XRD peak is from (0002) crystal planes, and the others are from $(10\bar{1}0)$ and $(10\bar{1}1)$ crystal planes of the nanophase. The as coated nanophase η'$_n$ had the hcp structure and possessed a very strong crystal preferred orientation (0002) planes.

The structural evolution of the films of the nanofilms of the alloys was examined by SEM technique. In the as coated films of ZA7 alloy, plenty of nano-particles of 60-80 nm in diameter accumulated to form “ pyramids “ due to the strong preferred orientation at (0002) planes, as shown in Fig.2a1. Under electropulsing, the amount of the “ pyramid “ reduced (Fig.2a2 and Fig.2a3).[8] After electropulsing for 15 mins, lots of the “ pyramid “ had been blown off along the direction of current, and the Z-zones had net been observed yet, as shown in Fig.2a4.

Shown in Fig.2b is the structural evolution of the films of ZA22 at the early stage of EPT. After electropulsing for 2 mins, nano-particles were observed to cluster to form Z-zones, as shown in Fig.2b2. With increasing time of EPT the zones developed, as shown in Fig.2ba and Fig.2b4. By comparison, the formation of the Z-zones was observed after ageing at 220°C for 5 hrs, as shown in Fig.3.[9] It is obvious that electropulsing considerably accelerated decomposition of the

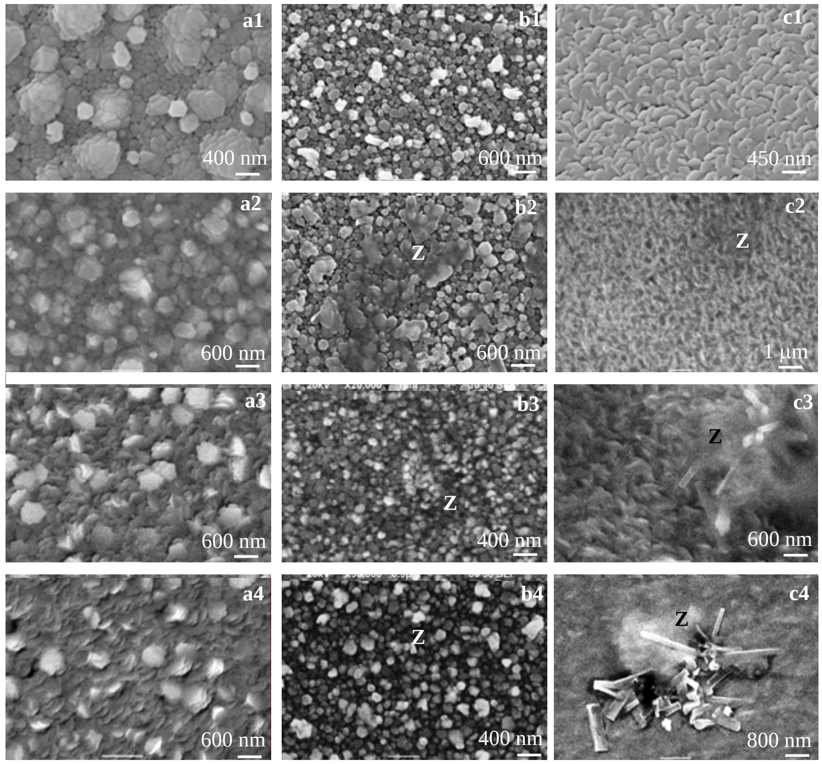

Fig.2 SEM images of nanofolms of ZA7 (a), ZA22 (b) and ZA27 (c) as-coated and after EPT

nanophase η’$_n$.

In the case of EPT of the nanofilm of ZA27, the Z-zones were observed after electropulsing for 2 mins. After electropulsing for 4 mins, the transitional phases were observed, which was quickly developed after electropulsing for 10 mins, as shown in Fig2b3 and Fig.2b4. In the previous studies, it was reported that Z-zones formed after ageing at 150 °C for 5 hrs, and the formation of the transitional phases were observed after ageing at 150°C for 15 hrs(Fig.3).[10] Apparently, the decomposition of the nanophase η’$_n$ was tremendously accelerated under electropulsing.

3.2 Electropulsing Induced Preferred Crystal Orientation Changes

Accompanying decomposition of nanophase η’$_n$, electropulsing induced preferred crystal orientation of the η’$_n$ phase changed gradually from (0002) planes to $(10\bar{1}1)$ planes in the nanofilms of alloys ZA7, ZA22 and ZA27. Fig.1b shows X-ray diffractograms of nanofilms of ZA7 (Fig.1b1), ZA22 (Fig.1b2) and Za27 (Fig.1b3c) after EPT for 2 mins. From Fig.1, it can be seen that under electropulsing changes of the preferred crystal orientation of η’$_n$ phase were significantly accelerated, compared with that in the ageing processes.[8-11] Meanwhile, it is seen that after 2 min of electropulsing, the preferred crystal orientation had slightly changed from (0002) planes to $(10\bar{1}1)$ planes in the nanofilms of ZA7 (Fig.1b1), while the crystal orientation of both (0002) and $(10\bar{1}1)$ became equivalent in strength in the nanofilms of ZA22 (Fig.1b2). In the nanofilms of ZA27, the preferred crystal orientation had changed almost completely from (0002) to $(10\bar{1}1)$ planes (Fig1b3). It is reasonable to conclude that electropulsing accelerated microstructural changes, i.e. the preferred crystal orientation of the nanophase η’$_n$ changed from (0002) to $(10\bar{1}1)$ with decreasing of the Zn-content

3.3 Driving Force of Mcicrostructural Changes and Phase Transformation

The driving force f mcicrostructural changes and phase transformation consists for the present study of mainly the chemical Gibbs energy, ΔG_{chem}, the orientation Gibbs energy, ΔG_{orien}, surface energy, ΔG_{surf} and the electropulsing induced Gibbs free energy, ΔG_{ep}, as described as: $\Delta G = \Delta G_{chem} + \Delta G_{orien} + \Delta G_{surf} + \Delta G_{ep}$.

During solidification of the alloy melt at the surface of a substrate, nanophases possess a strong preferred orientation in the films of the Zn–Al based alloys. Because the preferred crystal orientation is not identical with the orientation relationships, the ΔG_{orien} could be positive and makes the decomposition of the phases difficult in the alloy films. In the conventional ageing process, ΔG_{orien} plays a dominant role in driving microstructural change and phase transformation in nanofilms.[8-11]

Under electropulsing, the electron wind high rate formed due to the knock-on collision of electrons with atomic nuclei was beneficial to mobility of dislocations and vacancies. The transfer of energy from electrons directly to atoms was much more effective than that in the traditional thermal and thermo-mechanical processes.[15-17] In the case of electropulsing, ΔG_{ep} became strong enough to be the main driving force. Both the preferred crystal orientation change and the decomposition of nanophase were tremendously accelerated under electropulsing.

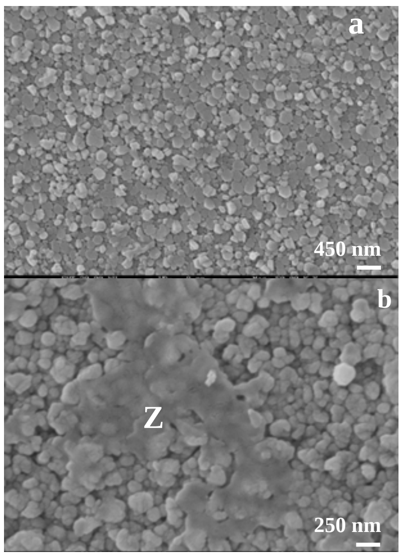

Fig3 SEM images of nanofilms of ZA22 alloy as-coated (a) and after ageing at 220C for 5 h (b)

3.4 Enhancement of Conductivity by Electropulsing

After EPT for 2 mins, the electric sheet resistances of nanofilms of ZA22 and ZA27 decreased from 1.2 Ω/□ and 1.1 Ω/□ to 1.1 Ω/□ and 0.9 Ω/□ (i.e. the resistances reduced for 16.6% and 18.2%), respectively. While the sheet resistance of the nanofilm of ZA7 remained unchanged.

In comparison with XRD and SEM results, it is seen that electric conductivity of nanofilms of Zn-Al based alloys was closely related with the preferred crystal orientation at $(10\bar{1}1)$ planes of the nanophase η'_n. The stronger the $(10\bar{1}1)$ orientation (i.e. the less Zn content), the better conductivity of the nanofilms would have. An adequate electropulsing may improve electric conductivity by increasing the preferred crystal orientation of $(10\bar{1}1)$ of the nanophase η'_n.

4 Conclusions

4.1. Electropulsing tremendously accelerated phase decomposition through formations of Z-zones and transitional phases.

4.2. Electropulsing tremendously accelerated microstructural changes, i.e. the preferred crystal orientation of the nanophase η'_n, changed from (0002) to $(10\bar{1}1)$.

4.3. Electric conductivity of nanofilms of Zn-Al based alloys was closely related with the preferred crystal orientation at $(10\bar{1}1)$ planes of the nanophase η'_n. The stronger the $(10\bar{1}1)$ orientation (i.e. the less Zn content), the better conductivity of the nanofilms would have. In the present study, after electropulsing for 2 mins the resistances of nanofilms of ZA22 and ZA27 reduced for 16.6% and 18.2%, respectively.

REFERENCES

[1] H.Gleiter, Prog. Mater. Sci. 33, 223, 1989.
[2] C.Suryanarayana, C.Koch. in: C.Suryanarayana (ed.), NanoEqulibrium Processing of Materials , Pergamon, 313,1990.
[3] R.Ruppin, J. Appl. Phys, 59, 1355, 1986.
[4] R. Venkatasubramanian, E.Siivola, T.Colpitts and B.O'Quinn, Nature 413,597, 2001.
[5] R.J.Hong, X.Jiang, B.Szyszka, V.Sittinger, S.H.Xu, W.Werner, G..Heide, J. of Crys. Growth, 253, 117, 2003.
[6] S.K.Bux,J.P.Fleurial,R.B.Kaner,Chem.Commu.46 8311, 2010.
[7]. L. Castaneda, Mater. Sci. Appli, 2, 242, 2011.
[8] Y.H.Zhu, W.B.Lee and S.To, Mater. Charact., 52, 217, 2004.
[9] Y.H.Zhu, W.B.Lee, C.Y.Chung and S.To, Applied Surface Science, 236, 106, 2004.
[10] Y.H.Zhu, W.B.Lee, Z.Mei, S.To and Y.K.Sze, Applied Surface Science, 242, 236, 2005.
[11] Y.H.ZHU, W.B.LEE and S.TO, JMST, 20, 687, 2004.
[12] Y.H.Zhu, S.To, W.B.Lee X.M.Liu, Y.B.Jiang and G.Y.Tang, Mater.Sci.Eng. A, 501, 125, 2009.
[13] Y.H.Zhu, S.To, W. B.Lee, X.M.Liu, .B.Jiang and G.Y.Tang: J. Mater. Res., 24, 2661, 2009.
[14] Y.H.Zhu, S.To, X.M.Liu and G.L.Hu: Metall. Mater. Trans. A. 42, 1933, 2011.
[15] A. F. Sprecher, S. L. Mamnna and H. Cornad: Acta Metall. 34, 1145, 1986.
[16] K. Okazaki, M. Kagawa and H. Conrad: Mater. Sci. Eng. A 45, 109, 1980.
[17] F. R. Nabarro: Theory of crystal dislocation, (Clrendon Press, Oxford), 529, 1976

Acknowledgements

Authors would like to express their gratefulness to The Research Grant Council of Hong Kong Special Administration Region of the People's Republic of China for providing financial support (Project No.PolyU5316/09E).