Al-Mg 합금 박막의 압축응력 완화를 위한 어닐링 공정상의 입자 발달

Evolution of grains to relieve additional compressive stress developed in Al-Mg alloy films during thermal annealing

이준성[a*], 양지훈[b], 정재인[b], 정용화[c], 곽영진[c], 김상섭[a]
[a*]인하대학교 신소재공학과(E-mail:leejunseong88@gmail.com), [b]포항산업과학연구원, [c]포스코

초 록: In this work, a possible mechanism for grain evolution in Al-Mg alloy films during thermal annealing is suggested on the basis of the phase transition and the related residual stress. Al-Mg alloy films with compositions of 14.0 and 18.0 wt% Mg content were deposited on cold-rolled steel substrates by the direct current co-sputtering method using Al and Mg targets. After the deposition, the samples were thermally annealed at 400 ℃ for 10 min. The featureless, dense cross-sectional microstructure of the as-deposited films turned into a grainy microstructure after the thermal annealing. According to the residual stress evaluated by using the XRD-sin2ψ technique and the phase analysis by XRD, it is likely that grains were created in order to relieve the additional accumulation of residual stress originating from the phase transition from face-centered cubic Al (α) to Al_3Mg_2 (β) and Mg (δ) phases, suggesting interplay between the microstructure and residual stress.

1. 서론

Al-Mg alloy films have been used in diverse areas thanks to their beneficial properties, including low density, high strength/weight ratio, and good corrosion resistance [1-4]. The properties of Al-Mg alloy films are known to vary depending not only on the deposition conditions but also on the chemical composition. For instance, in a study of the effects of Mg content, electrolyte temperature, and current density on the properties of electrodeposited Al-Mg alloy films, no intermetallic phase evolved in spite of the wide variation of Mg content [5]. In another example, magnetron sputter-deposited Al-Mg alloy films prepared with a wide range of Mg content showed that the film phase strongly relied on the chemical composition [6]; an Al-rich face-centered cubic (fcc) phase evolved when the Mg composition was less than 35%. However, a Mg-rich hexagonal close-packed (hcp) phase was formed when the Mg content was greater than 35%. Recently, the current authors reported the relationship between the film properties, including microstructure and phase, and the deposition conditions, such as powder density and working pressure, in magnetron sputtering [4]. According to the report, two distinctive microstructure domains were found to have been created in relation to the sputtering conditions: a smooth surface with a dense, featureless cross section, and dome-shaped, rough surface with a columnar structure.

In general, the physical and chemical properties of metal films are closely associated with the film microstructure that evolves during deposition and/or post treatment. In particular, one of the important parameters governing the film microstructure is the stress created in the film, which will eventually have a strong influence on its mechanical, electrical, and chemical properties [7-9]. There is ample literature showing the role of stress on the microstructure evolution in films [7-9]. For example, the microstructure of tungsten films has been shown to be highly dependent on the film stress [7]; under compressive stress, a dense microstructure with a body-centered cubic phase was formed, whereas under tensile stress, a columnar structure with a two-phase mixture was evolved. In ZnO films, the compressive stress induced grain growth [8]. In addition, the transition from tensile to compressive stress resulted in a change in the preferred orientation, lattice parameters, surface roughness, and grain size of CrN films [9].

It is thus likely that microstructure is strongly related to the residual stress of films. Accordingly, the mechanism of microstructure evolution and the relationship between microstructure and residual stress need to be investigated in order to take the best advantage of Al-Mg films. To the authors’ knowledge, there are few such reports so far. In this study, Al-Mg alloy films of two compositions were prepared on cold-rolled steel substrates by using the direct current (DC) magnetron co-sputtering method. Before and after thermal annealing at 400 ° C for 10 min, the microstructure and residual stress were investigated. A mechanism for the grain evolution after the thermal annealing is proposed on the basis of the residual stress and phase formation.

2. 본론

1) Experimental

Al-Mg alloy films with either 14.0 or 18.0 wt% Mg were deposited on cold-rolled steel substrates by the DC magnetron co-sputtering technique. Before being loaded in the sputtering chamber, the substrates were cleaned as follows: washing with detergent, cleaning ultrasonically in acetone and ethanol, and finally drying by blowing with N2.For the sputter deposition, the chamber was first evacuated to a base pressure of less than 5 × 10-6 Torr (0.66mPa) using a turbomolecular pump. Ar was then introduced into the chamber as the working gas to the target pressure using a mass flow controller. The chamber pressure was measure dusing ion and convection gauges in combination. Pure Al and Mg metal were used as the sputtering targets. The DC power applied to the Al target was fixed at 8 kW and the DC power applied to the Mg target was 0.7-1.9 kW. Different compositions of Al-Mg alloy films could be deposited solely by changing the DC power applied to the Mg target. The as-deposited films were thermally annealed at 400 ° C for 10 min in air.

The surface and cross-sectional microstructures of the films were observed by field-emission scanning electron microscopy (FE-SEM). The phase and crystal structure were examined by X-ray diffraction (XRD) using Cu Kα radiation (1.5406 Å) in θ-2θ mode. The chemical composition of the films was determined by energy dispersive X-ray spectroscopy (EDS) installed in FE-SEM. The residual stress of the films was evaluated by using the XRD-sin2ψ technique [10-12], which is recognized as a reliable method for calculating the residual stress in polycrystalline films. The XRD-sin2ψ technique is based on Equation (1).

$$d_{\varphi\psi} = \left[\frac{1+\nu}{E}\cdot sin^2\psi - \frac{2\nu}{E}\right]\cdot\sigma\cdot d_0 + d_0 \qquad (1)$$

where is the angle between the surface normal and the bisector of the incident and diffracted X-ray beam, is the lattice spacing under the residual stress , is the lattice spacing at the free-standing state, and E and are Young’ s modulus and Poisson’ s ratio of the film, respectively. Equation (1) can be converted to a linear function, that is, in the form of Y = a · X + b, as shown in Equation (2). Then the slope “a” allows us to calculate the residual stress by using Equation (3).

$$Y = \mathbf{a}\cdot X + \mathbf{b};\; Y = d_{\varphi\psi} = \frac{\lambda}{2\cdot\sin\theta};\;\; X = \left[\frac{1+\nu}{E}\cdot sin^2\psi - \frac{2\nu}{E}\right] \qquad (2)$$

$$\mathbf{a} = \sigma\cdot d_0 \qquad (3)$$

2) Results and discussion

The microstructures of the as-deposited and annealed Al-Mg films were investigated and the results are shown in Fig. 1. The insets are the corresponding surface images. As shown in Figs. 1a and 1b, the surfaces of the as-deposited films are smooth but indistinct grain structures are visible. The cross-sectional images of the as-deposited films show a featureless, dense microstructure, with no significant evidence of grains or columnar structures. This film microstructure changed significantly during the thermal annealing, as shown in Figs. 1c and 1d. The surface microstructures of the annealed films are quite similar to those of the as-deposited films. In contrast, in the cross-sectional microstructure, a grainy microstructure clearly evolved after the thermal annealing.

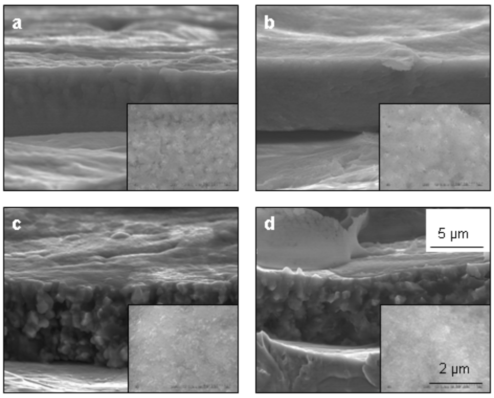

Fig. 1. Representative cross-section microstructures observed by FE-SEM of Al-Mg alloy films of two different compositions before and after the thermal annealing: the as-deposited films of (a) 14.0 and (b) 18.0 wt% Mg and the annealed films of (c) 14.0 and (d) 18.0 wt% Mg. Insets are the corresponding surface microstructures.

To understand the microstructural evolution, we investigated the crystalline phases of the films using XRD. Representative XRD patterns of the Al-Mg alloy films are shown in Fig. 2. As shown in the figure, all the peaks of the as-deposited films were well indexed to an fcc Al (α) phase [JCPDS 89-4037]. Taking the peak intensity into consideration, it is reasonable to conclude that the films consisted of only an Al (α) phase. However, the presence of a negligible amount of a Mg (δ) phase cannot be excluded. On the other hand, the annealed films reveal the formation of an Al_3Mg_2 (β) intermetallic phase [JCPDS40-0903] and an hcp Mg (δ) phase [JCPDS89-5003], along with the pre-existing α phase.

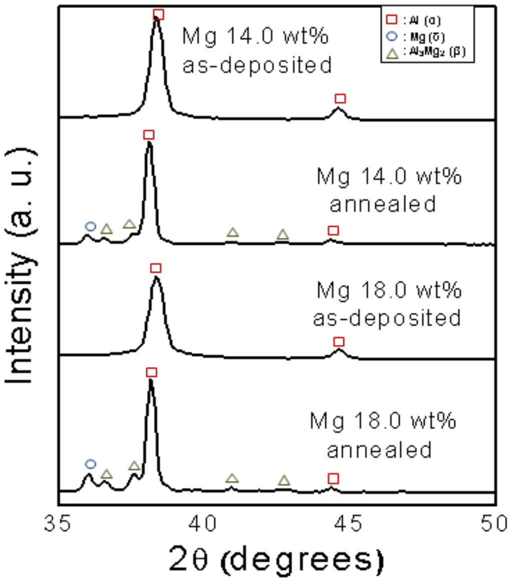

Fig. 2. X-ray diffraction patterns of Al-Mg alloy films of two different compositions before and after the thermal annealing.

The lattice constant of fcc Al (α) is ~4.03 Å and four atoms are present in one unit cell. Consequently, the volume of one atom is considered to be 16.35 Å3/atom. The lattice constant of intermetallic Al3Mg2 (β) is 28.23Å and 1168 atoms exist in one unit cell [13,14], leading to the conclusion that the volume of one atom is ~19.26 Å3/atom. For the δ phase, a = 3.208 Å and c = 5.209 Å and two atoms are in one unit cell, and thus the volume of one atom is 23.21 Å3/atom. Namely, the phase transformation from α to β + δ causes a significant volume change according to the changes in the atomic structure, resulting in corresponding compressive stress in the film during the thermal annealing.

The residual stress of the films before and after the thermal annealing was evaluated by using the XRD-sin2Ψ technique and the results are summarized in Fig. 3. Fig. 3a, taken from the Al-Mg alloy film with 14.0 wt% Mg, demonstrates the process of evaluating the residual stress, i.e., the patterns in relation to Ψ and the converted linear function. With the slope, one can calculate the residual stress. As shown in Fig. 3b, the as-deposited films were in a state of compressive stress ranging from 75 to 100 MPa. Surprisingly, the thermally annealed films show similar compressive stress values. It is quite common that compressive residual stress in as-deposited films tends to be relieved by thermal annealing [15-18]. However, the Al-Mg films exhibit almost the same compressive stress state regardless of the thermal annealing.

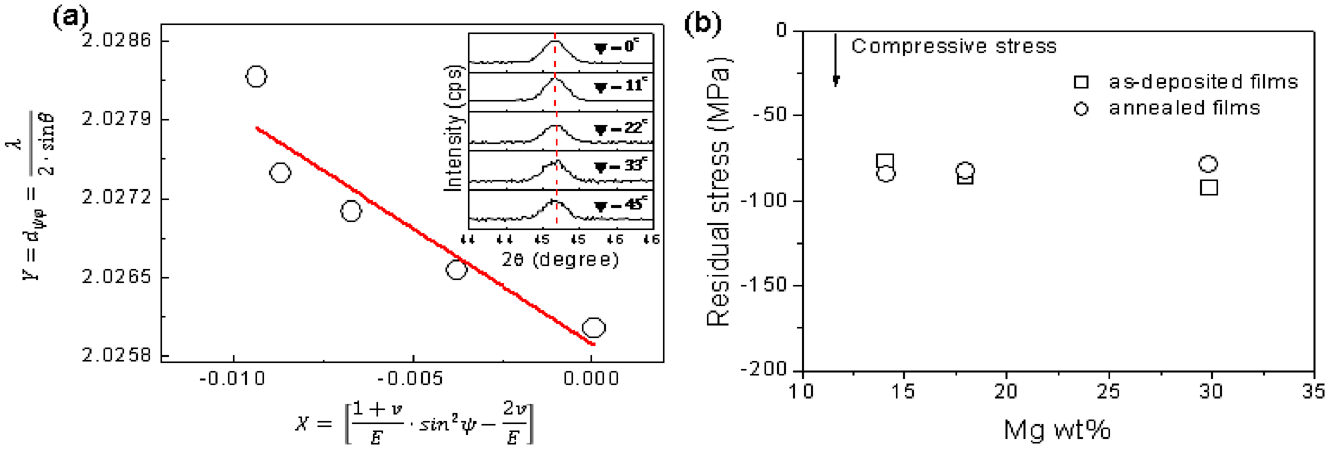

Fig. 3. (a) Example showing how to calculate the residual stress by using the XRD-sin$^2\psi$ technique. The results were taken from the Al-Mg alloy film with 14.0 wt% Mg. (b) Summary of calculated residual stresses for the Al-Mg alloy films before and after the thermal annealing.

The reason why the residual stress state remained almost the same before and after the thermal annealing is most likely to be linked to the microstructural evolution. As shown in Fig 1, the featureless, dense films turned into grainy ones after the thermal annealing. The newly created β and δ phases during the thermal annealing apply more compressive stress to the Al-Mg alloy films. Such addition of more compressive residual stress is not favorable for the films in terms of thermodynamics. One efficient way to relieve the additional compressive stress that results from the phase transition is to create grains instead of maintaining the featureless, dense microstructure, as schematically illustrated in Fig. 4.

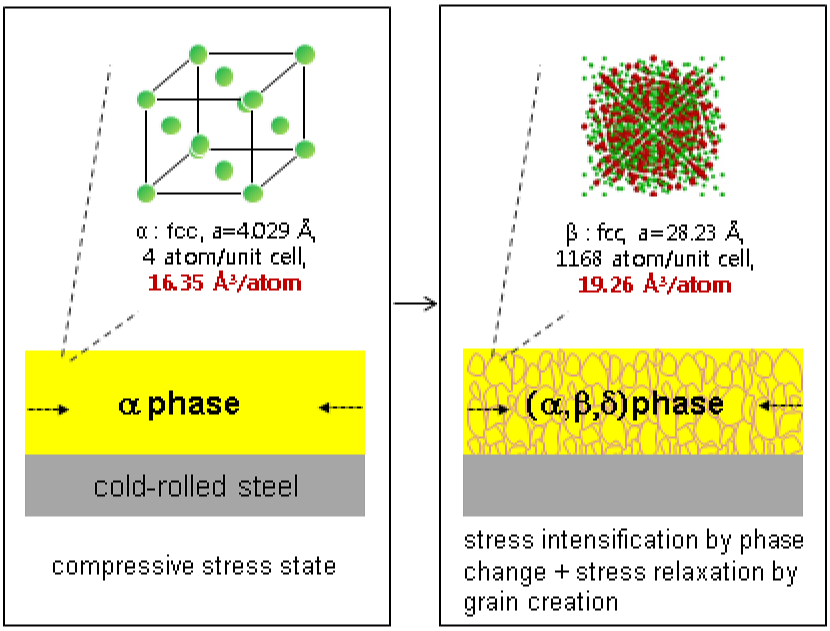

Fig. 4. Schematic illustration of the mechanism for the evolution of the grainy microstructure in the Al-Mg alloy films after the thermal annealing.

3. 결론

In summary, Al-Mg alloy films with compositions of 14.0 and 18.0 wt% Mg content were deposited on cold-rolled steel substrates by the co-sputtering method. The samples were then post-annealed at 400 °C for 10 min. Their microstructure, phase, and residual stress were examined. The as-deposited films showed a featureless, dense cross-sectional microstructure with an fcc Al (α) phase under compressive stress. In contrast, during the thermal annealing, grains were created as a result of the formation of Al_3Mg_2 (β) and hcp Mg (d) phases. The need to compensate for the additional accumulation of stress originating from the phase transition is responsible for the evolution of grains In the films after the thermal annealing.

참고문헌

1. A. Griguceviciene, K. Leinartus, R. Juskenas and E. Juzeliunas, J. Electroanal. Chem. 565 (2004) 203.
2. F. Liu, R. Liu, Z. Hou, H. Liu, Z. Tian and L. Zhou, Ann. Phys. 324 (2009) 332.
3. S. Toros and F. Ozturk, Comp. Mater. Sci. 49 (2010) 333.
4. G.-J. Sun and S. S. Kim, Met. Mater. Int. 19 (2013) 211.
5. S. S. V. Tatiparti and F. Ebrahimi, J. Electrochem. Soc. 155 (2008) 363.
6. B. A. Shedden, M. Samandi and B. Window, Surf. Coat. Tech. 97 (1997) 557.
7. Y. G. Shao, Y. W. Mai, Q. C. Zhang, D. R. McKenzie, W. D. McFall and W. E. McBride, J. Appl. Phys. 87 (2000) 177.
8. S. Shao, Z. Fan, J. Shao and H. He, Thin Solid Films, 445 (2003) 59.
9. Q. Kong, L. Ji, H. Li, X. Liu, Y. Wang, J. Chen and H. Zhou, Materials Science and Engineering B, 176 (2011) 850.
10. H. Ljungcrantz, L. Hultman, J.-E. Sundgren, S. Johansson, N. Kristensen, J.-A. Schweitz, and C. J. Shute, Journal of Vacuum Science & Technology A, 11 (1993) 543.
11. Q. Luo, and A. H. Jones, Surface & Coatings Technology, 205 (2010) 1403.
12. C. Ma, S. C. Wang, R. J. K. Wood, J. Zekonyte, Q. Luo, and F. C. Walsh, 19 (2013) 1187.
13. S. Samson, Acta Crystallographica, 19 (1965) 401.
14. V. Firouzdor, and S. Kou, Metallurgical and Materials Transactions A, 41 (2010) 3238.
15. O. Vohringer, Advances in Surface Treatments, 4 (1986) 367.
16. H. Holzapfel, V. Schulze, O. Vohringer, and E. Macherauch, Materials Science and Engineering: A, 248 (1998) 9.
17. X. Zhang, T.-Y. Zhang, M. Wong, and Y. Zohar, Sensors and Actuators A, 64 (1998) 109.
18. L. Karlsson, A. Horling, M. P. Jahansson, L. Hultman, and G. Ramanath, Acta Materialia, 50 (2002) 5103.

감사의 글

본 연구는 산업통상자원부의 WPM(World Premier Materials) 사업을 수행하는 스마트 강판소재 사업단의 연구비 지원을 받아 수행되었으며 이에 감사를 드립니다.