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Nanostructured Thin Films β-Al-Mg Obtained Using PLD Technique

A. Radziszewska[a,*], S. Kąc[a] and M. Feuerbacher[b]

[a]Faculty of Metals Engineering and Industrial Computer Science, AGH University of Science and Technology al. Mickiewicza 30, 30-059 Kraków, Poland

[b]Institut für Mikrostrukturforschung, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

In this work, the pulsed laser deposition (PLD) technique was used to grow AlMg thin films from a β-Mg_2Al_3 target with nominal composition: 39.09 at.% Mg and 60.91 at.% Al. The paper presents the study of β-Mg_2Al_3 thin films deposited using the pulsed laser deposition technique. AlMg thin films were prepared on Si (400) substrates and deposited by means of using a QS-Nd:YAG laser (λ = 266, 355 nm). Samples were prepared with laser fluence (1.1 J/cm^2 and 1.6 J/cm^2) and at two different substrate (Si) temperatures (25 °C and 200 °C). The target possessed columnar structure and changes in chemical composition took place as a result of the influence of the laser irradiation. Investigations focused on structure and chemical composition showed that the films generally had nanocrystalline structure and that the quantity of Al and Mg varied in the films.

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1. Introduction

As the lightest materials, Al–Mg alloys, are applied in various industries because of their desirable features, e.g. low mass density, better corrosion resistance, especially when they cover magnesium. Cubic β-Al_3Mg_2 phase is a very attractive material, of great interest for aeronautics [1, 2]. Therefore, the β-Al_3Mg_2 thin films were produced using pulsed laser deposition technique. Laser ablation process is the most recent technique used to deposit thin films from a wide range of target materials [3]. The PLD technique is very useful, because the spot size of the focused laser beam which is small and the target area may be less than 1 cm^2. In this technique, it is easier to prepare samples for research purposes or for applications in other techniques [3, 4].

In the case of pulsed laser deposition (PLD) of metals, the produced plume of vapor is significantly ionized. Photon energy of the nanosecond laser pulse is immediately converted into heat in the target and the quantity and composition of the laser ablated vapor are governed by the principle of thermodynamics in the low power density region [5]. Fractional vaporization in metals is dependent on the laser beam energy density [5].

Therefore, this research was aimed at determining the influence of process parameters (substrate temperature, laser fluence) on morphology, structure, chemical composition and such properties as the hardness and elasticity of deposited Al_3Mg_2 thin films. The paper also shows changes of the structure and chemical composition of the target after laser ablation process.

2. Experimental details

All films discussed in this paper were grown by a pulsed laser deposition technique using the QS-Nd:YAG laser. The QS-Nd:YAG laser emits pulses characterized by the wavelength (λ) of 266 nm and 355 nm and duration of 18 ns and 10 Hz pulse repetition rate. The laser fluence (q) was fixed at 1.1 J/cm^2 (for wavelength of 266 nm) and 1.6 J/cm^2 (for wavelength 355 of nm). Thin films were deposited on polished Si (400) substrates (wafers). Silicon wafers were positioned inside a vacuum stainless steel chamber, onto which ablated material was deposited. The reaction chamber was turbo pumped to $\leq 5 \times 10^{-4}$ Pa. The experiments were conducted in vacuum. All depositions were performed at the substrate temperature of 200 °C (for λ = 266 nm) and 25 °C (for λ = 355 nm). The deposition process involved the use of a target with the nominal composition of 60.9 at.% Al and 39.1 at.% Mg (Fig. 1c). The target grew by the flux-growth technique [6]. The experimental conditions used in the PLD process were presented elsewhere [7]. After deposition, microstructural analyses of the target and thin films were conducted by means of the scanning electron microscopy (SEM — Hitachi 3500N) and the transmission electron microscopy (TEM — JEOL JEM-2010 ARP) techniques. The presence of nanocrystalline structure was confirmed by the selected area diffraction (SAD) pattern analysis. In addition, energy dispersive spectroscopy (EDS) microanalysis was carried out to study

* corresponding author; e-mail: radzisze@agh.edu.pl

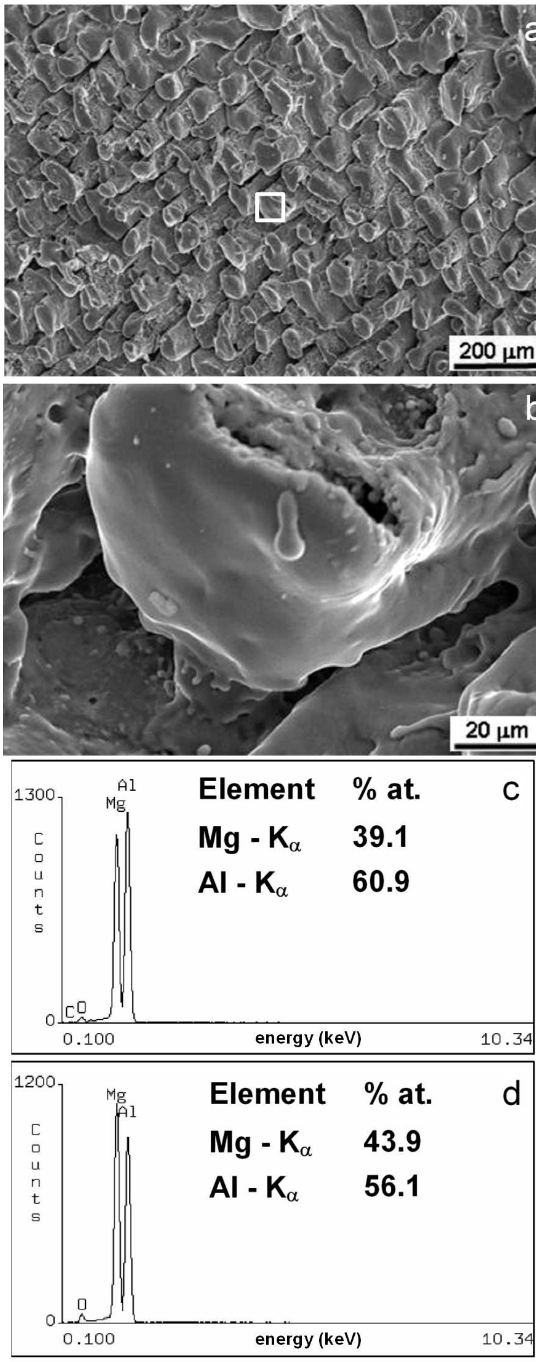

Fig. 1. Micrographs of the β-Al-Mg target after ablation process: (a) a top view of the target by SEM; (b) SEM image of the β-Al-Mg target — a higher magnification of the area shown in Fig. 1a; (c) the energy dispersive X-ray spectrum of the β-Al-Mg target before deposition process; (d) the energy dispersive X-ray spectrum of the β-Al-Mg target after laser ablation.

the content of Al and Mg in deposited films and in the target. The hardness and elastic modulus were measured by CSM Instruments Nanoindentation Tester at the load of 5 mN.

3. Results and discussion

Figure 1 shows the microstructure (Figs. 1a,b) and chemical composition (Figs. 1c,d) of the target after laser ablation process. A columnar structure was formed on the target surface. The columns were oriented along the laser beam propagation and they have a flat top surface. Its diameter averaged to 100 μm. Pits related to the ejection of particulates were also observed in the target surface. The appearance of the pits is mainly related to the density of the target [5]. The thermal conductivity is lower for the target and in this connection a local irregularity can quickly heat material up before transferring the energy to the rest of the target. This causes a higher local temperature and results in an explosive effect and leads to the formation of a hole [5]. Changes in the chemical composition of the target were observed after ablation process. The quantity of Mg amounted to 43.9 at.%, and 56.1 at.% Al (Fig. 1d).

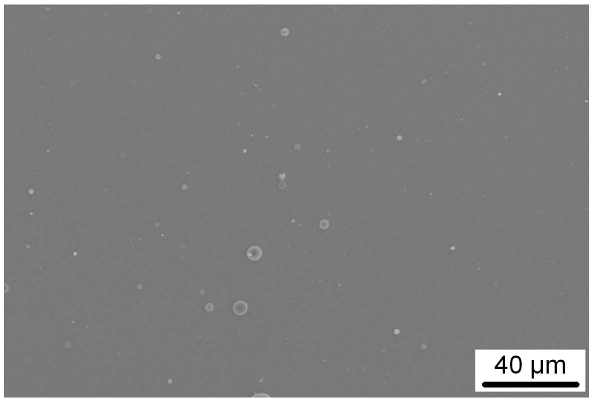

Fig. 2. Micrographs of the β-Al-Mg film; a top view of the film by SEM — produced with the laser fluence of 1.1 J/cm^2 (266 nm); substrate temperature: 200 °C.

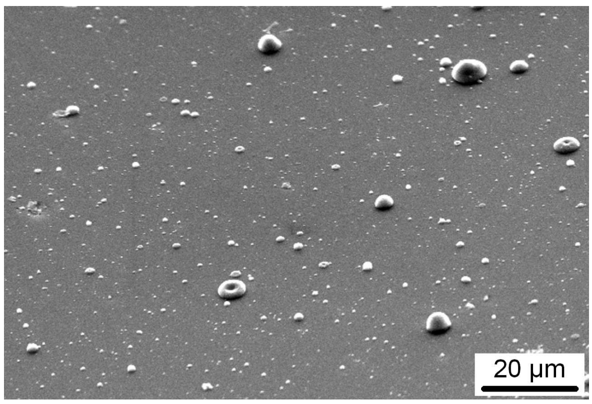

Fig. 3. Micrographs of the β-Al-Mg film; a top view of the film by SEM — produced with the laser fluence of 1.6 J/cm^2 (wavelength: 355 nm); substrate temperature: 25 °C.

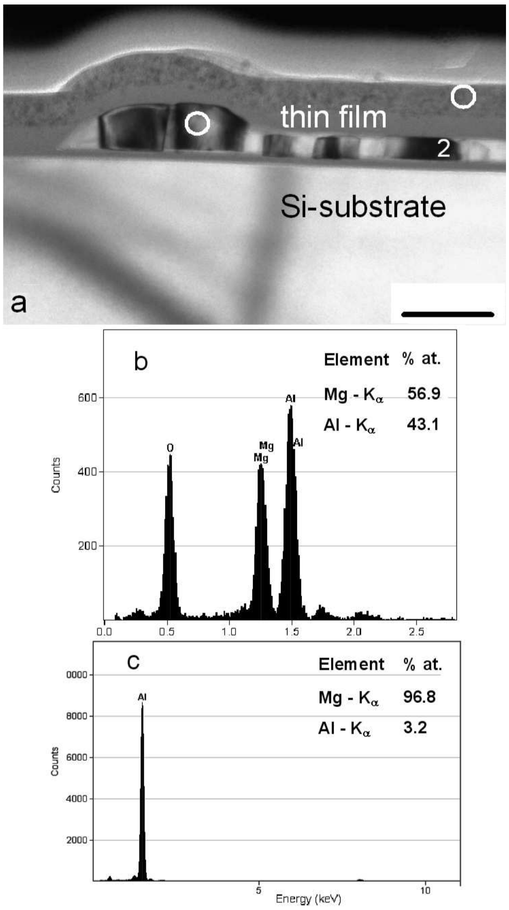

Fig. 4. (a) TEM bright-field micrograph of the β-Al-Mg film deposited with the fluence of 1.1 J/cm^2 — cross-section; (b) the energy dispersive X-ray spectrum of Al–Mg film denoted by 1 in Fig. 4a; (c) the energy dispersive X-ray spectrum of Al–Mg film denoted by 2 in Fig. 4a.

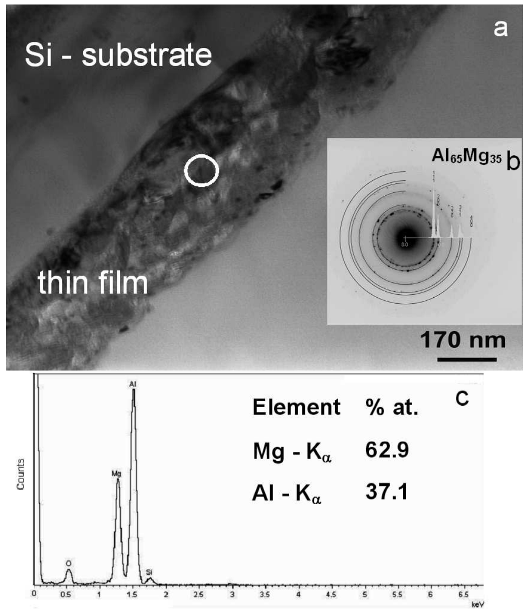

Fig. 5. (a) TEM bright-field micrograph of the β-Al-Mg film deposited with the fluence of 1.6 J/cm^2 (355 nm) — cross-section; (b) a selected area diffraction pattern from the nanocrystalline film; (c) the energy dispersive X-ray spectrum of Al–Mg film.

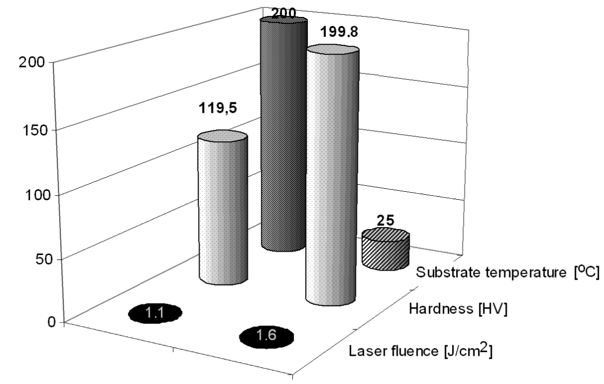

Fig. 6. Nanohardness of β-Al-Mg thin films deposited at different PLD process parameters: laser fluence: 1.1 J/cm^2 (266 nm) and 1.6 J/cm^2 (355 nm); substrate temperature: 25 ℃ and 200 ℃.

Figures 2 and 3 show the surface morphology and structure of Al_3Mg_2 films. Films had similar thickness, namely 120 nm and 260 nm ($\pm$5 nm), when grown at 200 ℃ and 25 ℃, respectively. The structure of the films changed as a consequence of the modification of the deposition conditions, namely substrate temperature and laser fluence in this particular case. Droplets (Fig. 3) formed as a result of laser ablation-in films obtained at the substrate temperature of 25 ℃. The average diameter of droplets amounted to 3–6 μm. However, while substrate temperature reached 200 ℃ the density of the spherical droplets decreased and their size reached values from 1 to 4 μm (Fig. 3). Simultaneously, the concentration of droplets can increase together with a considerable growth of the number of laser pulses from the same place of the target. Figure 4 shows the TEM micrograph and EDS spectra of this film deposited at 1.1 J/cm^2. This film was composed of three layers with different structure. The first one, the nearest to the Si substrate, is characterized by an amorphous structure and its thickness reached 40 nm (Fig. 4a). A nanocrystalline structure was observed on the top of the film. It proves that this film has a nanocrystalline structure. Moreover, aluminium crystals (Fig. 4a) grew in some regions of the and assumed the shape of the letter "V". The film prepared at 1.6 J/cm^2 had defected nanocrystalline structure (Fig. 5a), which is confirmed by the selected area electron diffraction (SAED) technique (Fig. 5b). The chemical composition of this film was calculated from EDS spectra (Fig. 5c) and was homogeneous in the bulk. In the case of the films deposited at the substrate temperature of 25 ℃, the Al/Mg ratio is close to that expected

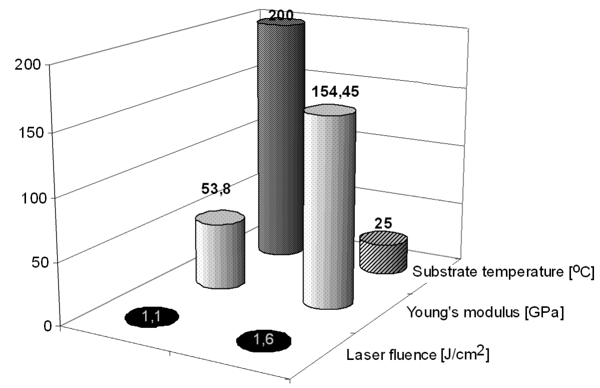

Fig. 7. Young's modulus of thin films β-Al-Mg deposited at different PLD process parameters: laser fluence: 1.1 J/cm^2 (266 nm) and 1.6 J/cm^2 (355 nm); substrate temperature: 25 ℃ and 200 ℃.

from the nominal composition of the target (37.1 at.% Mg and 62.9 at.% Al) (Fig. 5c). Arnold [5] ascertained that the appearance of the nonstoichiometric behavior can be relevant to the sputtering effect of several elements or preferential ablation from the target and also thermal evaporation at low energy due to different vapor pressure.

Hardness and elastic modulus measurements were carried out for these films (Figs. 6, 7). The hardness of thin films amounted to 119.5 HV for a thin film deposited at 25 ℃ (1.6 J/cm^2) and 199.8 HV for the one deposited at 200 ℃ (1.1 J/cm^2). Simultaneously, Young's modulus for thin film obtained for 1.1 J/cm^2 and 1.6 J/cm^2 reached 53.8 GPa and 154.45 GPa, respectively.

4. Conclusions

In conclusion, pulsed laser deposition is very promising, as far as the deposition of very high quality β-Al-Mg thin films at different substrate temperatures and laser fluence values is concerned. After ablation, the target had columnar structure. The content of Al and Mg changed, compared to the initial state. Structural examinations of the deposited thin films by SEM, TEM and EDS showed that the films had generally nanocrystalline structures. Droplets were observed on the surface of thin films. The size and density of these droplets changed depending on the substrate temperature. Modification of substrate temperature and laser fluence led to changes in the chemical composition of received films as well as of their hardness and elastic modulus.

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