Characterization of Al-Mg thin film deposited using pulsed laser deposition technique

INTRODUCTION

One of the most important changes in the domain of current surface engineering consists in the discovery and application of modern materials and techniques of the production, as well as their application in nanotechnology, biophysics, optoelectronics and other, dynamically developing field of science and common applications of the technology. Therefore, to produce thin films, which are widely used in the above-mentioned industries the new technology namely pulsed laser deposition (PLD) was applied.

Complex Metallic Alloys (CMA) are characterized by the presence of a hundred up to over a thousand atoms in one unit cell. They are exceptional intermetallic phases. The first pioneering work concerning the structure of intermetallic compounds was published by Pauling in 1923 [1]. It was focused on the NaCd₄ compound (1152 atoms in a unit cell). There are some other examples of such materials: the Bergman phase: Mg₆(Al, Zn)₆ (162 atoms in a unit cell) [2], or the Samson phase: β-Al₃Mg₂ (1168 atoms in a unit cell) [3]. According to Samson, the β-Al₃Mg₂ phase is a light material (density: 2.2 g/cm³) with exceptionally large unit cells that crystallize in a face centered cubic (FCC) lattice with the crystal lattice parameter a = 2.82 nm.

The basic elements and simple intermetallic compounds, compared to CMA materials [5, 6] with giant unit cells, are generally characterized by unit cells consisting of only a single atom or several tens of other atoms. On the other hand, in the giant unit cells that are found in β-Al₃Mg₂, and that are characterized by lattice parameter values in the order of several nanometers, there is a shift of the crystal lattice at the scale of interatomic distances. In such cases, atoms are arranged into polytetrahedral clusters and the structure of CMA materials is characterized by a certain duality, namely: at the nanometric scale, the structure of CMA materials is similar to that of crystals, while at atomic scale, they are similar to quasicrystals [7]. The local icosahedric ordering in the structure that is incompatible with the periodic shift in the crystal lattice is slightly parameterized from two or more targets.

Moreover, it is possible also depositing films of different chemical composition from two or more targets.

The present study is focused mainly on the characterization of the morphology and chemical composition of Al-Mg thin films deposited by the pulsed laser deposition (PLD), as well as their microstructure and phase composition. The research was carried out by scanning electron microscope (SEM) and the transmission electron microscope (TEM). For the purpose of determining the phase composition of the obtained films the X-ray diffraction and electron diffraction techniques were used.

MATERIAL AND METHODS

The examined material was Al-Mg thin films, produced by the laser ablation technique that was deposited on a silicon substrate (100). The β-Al₆₀.₉Mg₃₉.₁ alloy was used as target. Thin films were deposited with the Q-switching laser with the pulse frequency ω 12±15 Hz, and the single pulse duration τ 10±12 ns and the wavelength λ 1064 nm. Thin films were deposited at the laser beam energy density q = 13.8 J/cm² and at the substrate temperature Tₛ of 25°C. The substrate material was positioned parallel to the target surface, which the laser beam was directed at. The incident angle of the laser beam relating the target was equal to 45°, while the time of thin films deposition was 60 min. The pressure in the reaction chamber amounted to 5×10⁻⁴ Pa. More detailed information on the procedure of thin films deposition can be found in the previous publications [9].

The examinations of the morphology and chemical composition of the thin films were performed by SEM, Hitachi S-3500N, equipped with Noran energy dispersive X-ray spectrometer (EDS). The detailed investigation of the films microstructure was performed by transmission electron microscopy (TEM). The TEM investigation was carried out by a JEOL JEM-2010 ARP microscope. Thin foils from the cross-section of the sample were prepared by ion-beam thinning using Gatan Precision Ion Polishing System (PIPS). Investigations of phase composition of thin films were performed in TEM by selected area electron diffraction (SAED) and by Siemens D500 X-ray diffractometer (XRD) equipped with a copper anode tube (λ = 1.54 Å). The electron diffraction patterns were interpreted by means of the JEMS software [10]. The phase identification was supplemented by TEM-EDS results.

RESULTS AND DISCUSSION

Figure 1 shows the SEM images of Al-Mg thin films surface deposited at room temperature (Tₛ = 25°C) on (100) Si substrate. Observations revealed the presence of multiple droplets of different sizes. They form during the interaction of laser beam with the target material that also remains in close contact with the generated plasma. In the process, the material experiences the influence of a recoil force that exceeds 10⁶ N [11]. The influence of the force on the target material leads to the ejection of macroscopic droplets. Their presence may result from subsurface boiling process inside the target material, where the time required for the transformation of the laser energy into heat and for the transport of the heat into the material is...
shorter than the time required for evaporating the surface layer of the target [11-13]. However, the authors of Ref. [14] conclude that the influence of shorter laser wavelengths (within the UV range) leads to the reduction of the number and size of the droplets during deposition, which could be observed in YBa$_2$Cu$_3$O$_{7-δ}$ films deposited on SrTiO$_3$ (100).

In the case of an Al-Mg film deposited at temperature of 25°C, the size of droplets was in the range from about 1 to 15 μm (Fig. 1). The formation of droplets is related to the influence of the first harmonic of the laser (λ = 1064 nm), which leads to increased penetration of a laser pulse into the target material. The transport of macroparticls of the target material in the plasma plume results in overlapping of the droplets (Fig. 1). SEM-EDS was implemented to analyze the chemical composition of Al-Mg thin films. Table 1 and Figure 2 present the results of these examinations. They proved that there are considerable changes in the content of aluminium and magnesium, as compared to the target material (Al: 60.9 at. %, Mg: 39.1 at. %). The film contained 57.5 at. % of Al and 42.5 at. % of Mg (Tab. 1, Fig. 2).

The detailed investigation of thin Al-Mg film microstructure was performed by TEM on cross-section thin foil (Fig. 3). It was found that the Al-Mg film obtained at room substrate temperature (25°C) was about 1 μm thick (the dimension of the film with the droplet). Film growth started in zone 1 (about 170 nm thick) (Fig. 3) that was characterized by the presence of nanocrystalline structure (ring character of SAED pattern). This was followed by the growth of another zone with nanocrystalline structure (zone II, the SEAD pattern of area marked as 2 in Figure 3). Then followed the growth of column-shaped aluminum crystals (zone III; the SEAD pattern of area marked as 3, 4 in Figure 3). In this zone droplet crystallization started. In these zones, some grains assumed the characteristic “V shape”. Similar “V shape” grains were also observed and presented in other Refs [15, 16]. This type of structure forms by competitive growth of differently oriented neighboring crystals and was attributed to zone T described by Barna [17]. Near the droplet surface, however, a zone with nanocrystalline structure was formed. The near-surface zone was about 150 nm thick and it consisted of the Al$_{65}$Mg$_{35}$ phase [10] with the crystalline FCC structure (zone 5 in Figure 3). The following phases were identified in the Al-Mg film:

- in zone I – Al$_{65}$Mg$_{35}$ phase with a crystalline FCC structure [10],
- in zone II and IV – Al$_{65}$Mg$_{35}$ phase with a crystalline FCC structure [10],
- in zones III – Al (FCC) crystals.

Additionally, the phases presented in thin films were also identified by means of the XRD phase analysis (Fig. 4). However, the analysis showed only the potential presence of primarily two phases in Al-Mg films, namely a non-stoichiometric Mg$_{x}$Al$_{1-x}$ compound and the pure aluminum.

Additionally, due to the applied measuring methodology and the nanometric thickness of the film, XRD patterns showed mainly peaks generated by the Si substrate (100) (Fig. 4) and silicon oxide (SiO$_2$) that was present on the silicon substrate.

**CONCLUSIONS**

The investigation of the microstructure of thin Al-Mg films showed that numerous droplets were present on their surfaces. The droplets size fitted within the range from 1 to 15 μm. Due to this fact, there were considerable divergences between the chemical composition of a film and the original chemical composition of the target. The film showed higher content of magnesium than aluminium in Al-Mg thin film then in the target.
TEM investigation showed the presence of nanocrystalline zones and zones with column-shaped crystals in the film. The occurrence of the following phases was identified: $\text{Al}_{30}\text{Mg}_{23}$, $\text{Al}_{65}\text{Mg}_{3}$ and $\text{Al}$. On the other hand, the XRD phase analysis showed the presence of a non-stoichiometric $\text{Mg}_{1-x}\text{Al}_x$ compound and also $\text{Al}$ to be confirmed.

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