

A study of r.f.-sputtered Al and Ni thin films on AZ91D magnesium alloy

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Abstract

Pure Al and Ni thin films have been successfully r.f.-sputtered on AZ91D substrate. After 350 °C×24-h heat treatment in a high vacuum, the 2 μm thickness of the Al film reacted completely with the substrate to form Al₁₂Mg₁₇ phase. However, the Ni film was not observed to form a reactive layer after 350 °C×48-h treatment. Scratch test results indicate that the cohesive strength exhibits a significant improvement after the 350 °C×48-h treatment for the Ni film. The hardness tests demonstrated that the Ni film is harder than the Al film, AZ91D and Al₁₂Mg₁₇ phase. The sliding wear tests also showed that the Ni film has a lower wear rate than the others. The intrinsic brittleness of Al₁₂Mg₁₇ phase has a low cohesive strength with the substrate and a poor wear resistance to grinding.

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1. Introduction

The demand for lightweight designs and recyclable materials have led to a great increase in the research and development of magnesium alloys for practical industrial applications. Among these alloys, AZ91D, which is used as a die-casting material, is highly important due to its wide applications in computers, communication and consumer electronics. However, poor corrosion resistance and the low wear resistance of magnesium alloys have limited their widespread applications [1,2]. It is well known that surface modifications by depositing metal coatings are feasible to improve the surface properties of magnesium alloys. For example, evaporating high purity magnesium on AZ91E [3] and arc-spray a coating of pure aluminum, as well as hot-pressing and anodizing on AZ31 [4], have considerably improved the corrosion resistance in saline

environments. However, there has been little study of whether the aforementioned surface metal coatings can improve the wear resistance of magnesium alloys. Hiraga et al. [5] indicated that surface modification of AZ91D by laser alloying using Si powder can improve its wear resistance by suitable powder feeding. Harada et al. [6] also pointed that lining AZ31B and AZ91D with pure Ti and Ni foils using shot peening can effectively improve their wear resistance. Clearly, surface metal coatings can also improve the wear resistance.

Senf et al. [7] reported that Cr and CrN films could be reactive-sputtered on AZ91 alloy. Brookes et al. [8] indicated that an Al–Mg/Mg multilayer foil with 50 μm thickness could be produced by the closed-field unbalanced magnetron sputtering [8]. However, to the best of our knowledge, there has been no previous report regarding sputtered Al and Ni thin films on AZ91D alloy. In this study, r.f. magnetron sputtered aluminum and nickel thin films on AZ91D alloy are investigated. At the same time, some of the as-sputtered films are heat-treated at 350 °C in a high vacuum for the purpose of improving the cohesive strength in between the films and substrate. Thereafter, the

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mechanical properties of the films, such as cohesive strength, hardness and wear rate are also investigated.

2. Experimental procedures

2.1. Specimen preparation

AZ91D alloy was die-cast to plates ≈ 0.8 mm thick. The as-cast plates were cut using a diamond saw to a specimen size of 10×10 mm, then ground and polished to a # 1200 grit finish and well cleaned with acetone for sputtering. The final thickness of specimens was 0.6 mm. Pure aluminum or pure nickel thin films were deposited on the specimens by r.f. magnetron sputtering apparatus with a turbo-pumped vacuum system using a 2-in. disk of pure aluminum (purity 99.99 wt.%) or pure nickel (purity 99.9 wt.%) in an argon atmosphere. A schematic diagram of the r.f.-sputtering apparatus used in this study was reported in our previous paper [9]. The sputtering conditions are: the distance between the target and substrate was 8 cm, the base pressure was about 6×10^{-7} Torr. The working

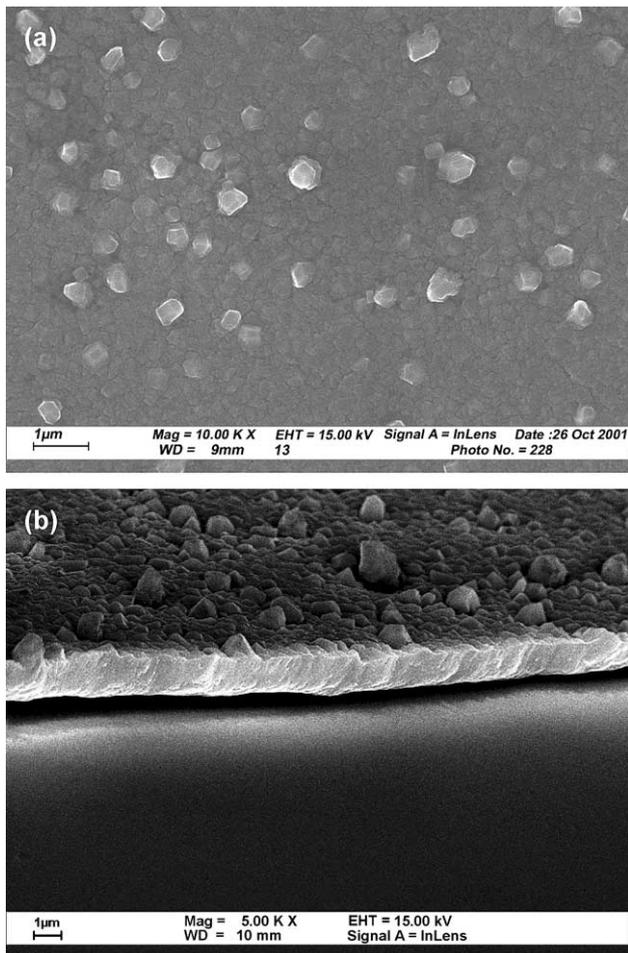


Fig. 1. SEM photographs of as-sputtered Al film (a) surface morphology, (b) cross-sectional microstructure.

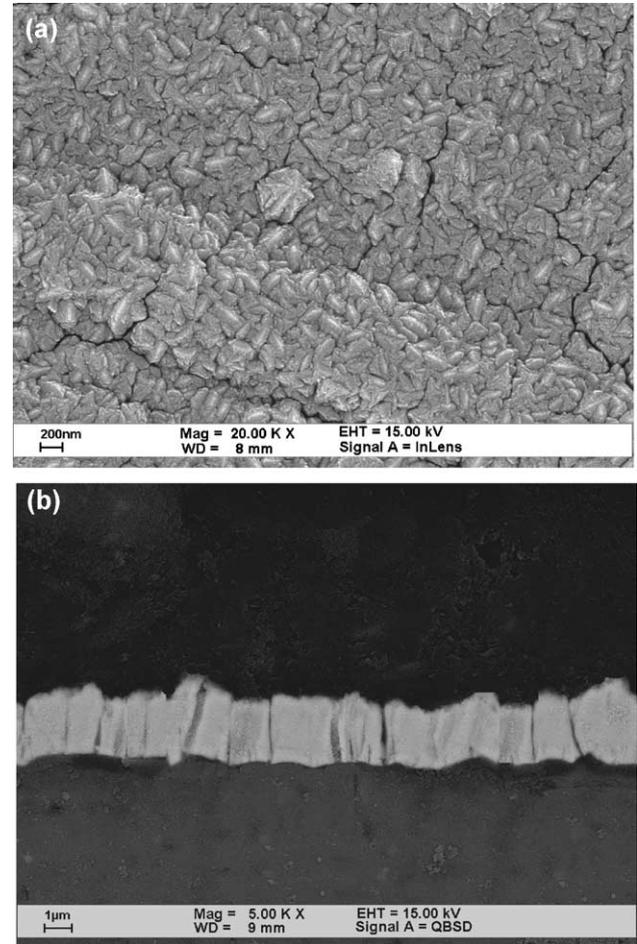


Fig. 2. SEM photographs of as-sputtered Ni film (a) surface morphology, (b) cross-sectional microstructure.

pressure was set at 5×10^{-3} Torr with ultrahigh purity argon. The r.f. power was 100 W (Advanced Energy RFX600) and the substrate was unheated and unbiased during the sputtering. The sputtering time varied from 10 to 240 min. After sputtering, the thicknesses of sputtered films were measured by an α -stepper (Surface Profiler, Dektak³ ST, Veeco, USA) and the sputtering rates of pure aluminum and nickel are calculated as 3.5 Å/s [10] and 1.6 Å/s, respectively, in which both metals exhibit a linear relationship with time. In order to prevent the thin films from peeling off the substrate due to the inherent residual thermal stress, the film thickness of pure aluminum and nickel was set at 2 μm in this study. Furthermore, in order to improve the interfacial adhesion between the thin film and substrate, some of the sputtered specimens were heat-treated at 350 °C in a high vacuum (below 6×10^{-6} Torr) for 24-h (Al thin film) or 48-h (Ni thin film).

2.2. Characterization of pure Al and Ni films

The sputtered Al and Ni thin films were studied for their crystal structures using a glancing angle X-ray diffractometer, GAXRD (Siemens D5000) or an XRD

(Philip PW1710) using $\text{CuK}\alpha$ radiation. The power was 40 kV \times 30 mA for GAXRD and 30 kV \times 20 mA for XRD, and for both the 2θ scanning rate was 0.03 $^\circ$ 2 θ /s. For GAXRD, the range of scanning angle was 5 $^\circ$. In order to quantitatively analyze the chemical composition of the phase formed at the interface of thin film and substrate, an electron probe microanalyzer (EMPA, JEOL 8800M) measurement was performed with a wavelength dispersive X-ray spectrometer (WDXS) analysis system. The operating power of EPMA was 15 kV \times 20 mA with 1 μm probe size. The surface morphology and cross-sectional microstructure of sputtered films were observed by a field-emission scanning electron microscopy (FESEM, LEO 1530) with an X-ray dispersive spectrometer (EDXS).

2.3. Mechanical properties

All sputtered specimens were measured for their hardness by Vicker's microhardness tester (Akashi MVK-E II) with an applied load of 300 g for the substrate and 25 g for the films. For each specimen, the average hardness value was taken from at least 10 test readings. To prevent the effects of substrate and film thickness on the film

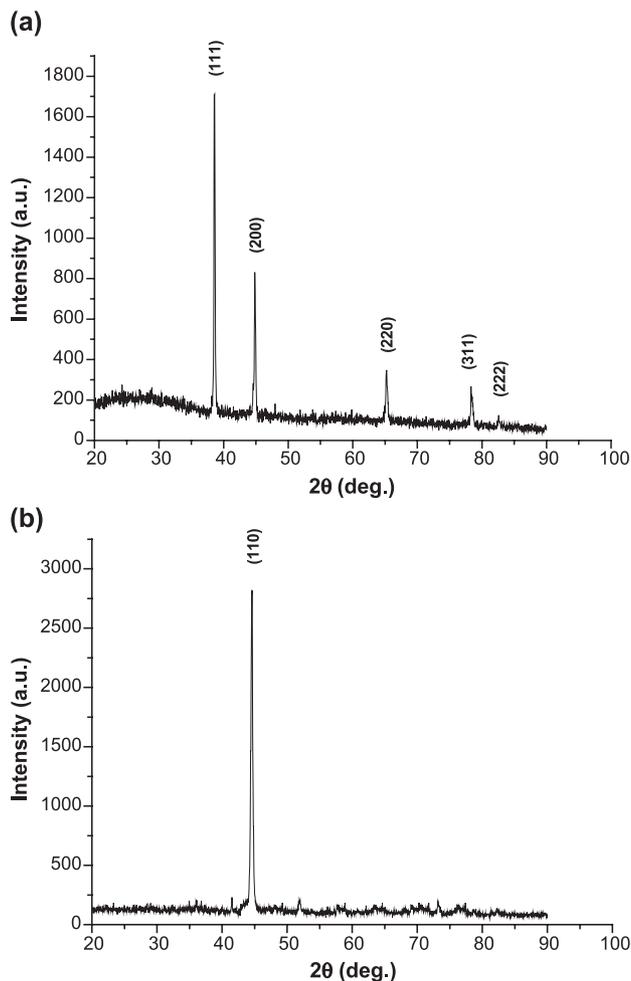
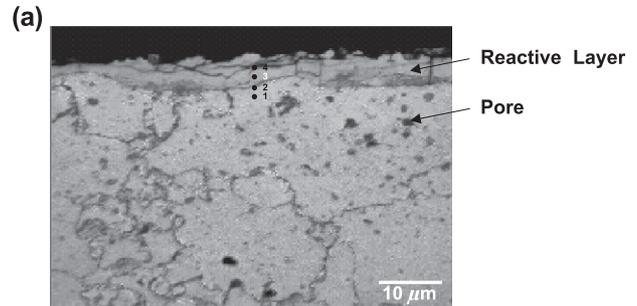


Fig. 3. GAXRD results of as-sputtered (a) Al film, (b) Ni film.



Location	Mg (at.%)	Al (at.%)
point 1	62.75	37.25
point 2	62.70	37.30
point 3	62.70	37.30
point 4	63.00	37.00

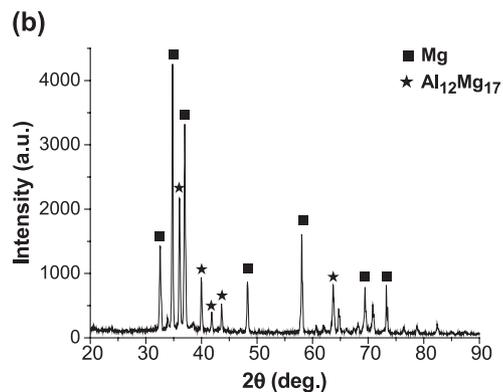


Fig. 4. (a) Optical micrograph of Al film after heat treatment at 350 $^\circ\text{C}\times$ 24-h, during which $\text{Al}_{12}\text{Mg}_{17}$ phase is formed. The attached table shows the EMPA results for the $\text{Al}_{12}\text{Mg}_{17}$ layer. (b) The XRD results for (a).

hardness, the equation proposed by Jonsson and Hogmark [11] was used to calculate the intrinsic hardness of the film based on these test readings:

$$H_f = H_s + \frac{H_c - H_s}{2C_{1,2}(t/D) - C_{1,2}^2(t/D)^2} \quad (1)$$

where H_f , H_s and H_c are the hardnesses of film, substrate and composite, respectively; t is the film thickness; D is the indenter depth; C_1 is $\sin^2 22^\circ$ for the case of films softer than the substrate; C_2 is $2\sin^2 11^\circ$ and is used for films harder than the substrate. The interfacial adhesion between thin film and substrate was determined from the scratch test, which was carried out using a Rockwell C indenter (Teer ST2200). The scratching speed was set at 10 mm/min with an applied load, which was varied from 10 to 40 N at an increment rate of 100 N/min. The sliding wear test was performed using a dimple grinder (GATAN model 656) with an applied load of 11 g and a speed of 40 rpm in which a bronze grinding wheel contacted the sputtered specimen. During the grinding, the specimen was set on a rotating mount with a speed of 6 rpm and diamond paste (GE Micron Product, model CBN, size 0–2 μm) was used as the grinding powder. Details of the

dimple grinder used in this study are as previously published [12].

3. Results and discussion

3.1. Microstructures of as-sputtered films

Fig. 1a and b shows the SEM photographs of surface morphology and cross-sectional microstructure, respectively, of as-sputtered Al film. Those of as-sputtered Ni film are shown in Fig. 2a and b. Fig. 1 shows that the Al film is dense with very fine columnar grains, and no observable cracks. Fig. 2 indicates that the Ni film is also dense and its columnar grains are also fine. However, there are many cracks on the film that penetrate the whole film thickness, as shown in Fig. 2b. As discussed in Section 3.3, these cracks do not affect the cohesive strength of Ni film and substrate because these cracks are grown in a direction nearly normal to the substrate. The cracks appearing in the Ni film but not in the Al film are proposed to be from the different coefficients of thermal expansion (α)

among AZ91, pure Ni and pure Al. At room temperature, α of AZ91, pure Ni and pure Al are 26.0 , 13.3 and $23.6 \times 10^{-6} \text{ K}^{-1}$, respectively [13]. The large α difference between AZ91 and pure Ni causes the cracks to occur after sputtering.

Fig. 3a and b shows the GAXRD results of as-sputtered Al and Ni films, respectively, in which only aluminum and nickel diffraction peaks are observed in each diagram. According to the data of JCPDS [14], the diffracted plane (hkl) corresponding to each peak is indicated in Fig. 3. This figure shows that there is a texture formed in the sputtered film, especially in the case of as-sputtered Ni film, where a strong (110) texture occurs, as shown in Fig. 3b.

3.2. Sputtered thin films heat-treated at 350 °C in high vacuum

In order to form the reactive phase at the interface of Figs. 1 and 2, the as-sputtered specimens were heated at 350 °C for 24- or 48-h in a high vacuum. Fig. 4a shows an optical micrograph of heat-treated Al film specimen, in which the pure Al film with 2 μm thickness disappears and

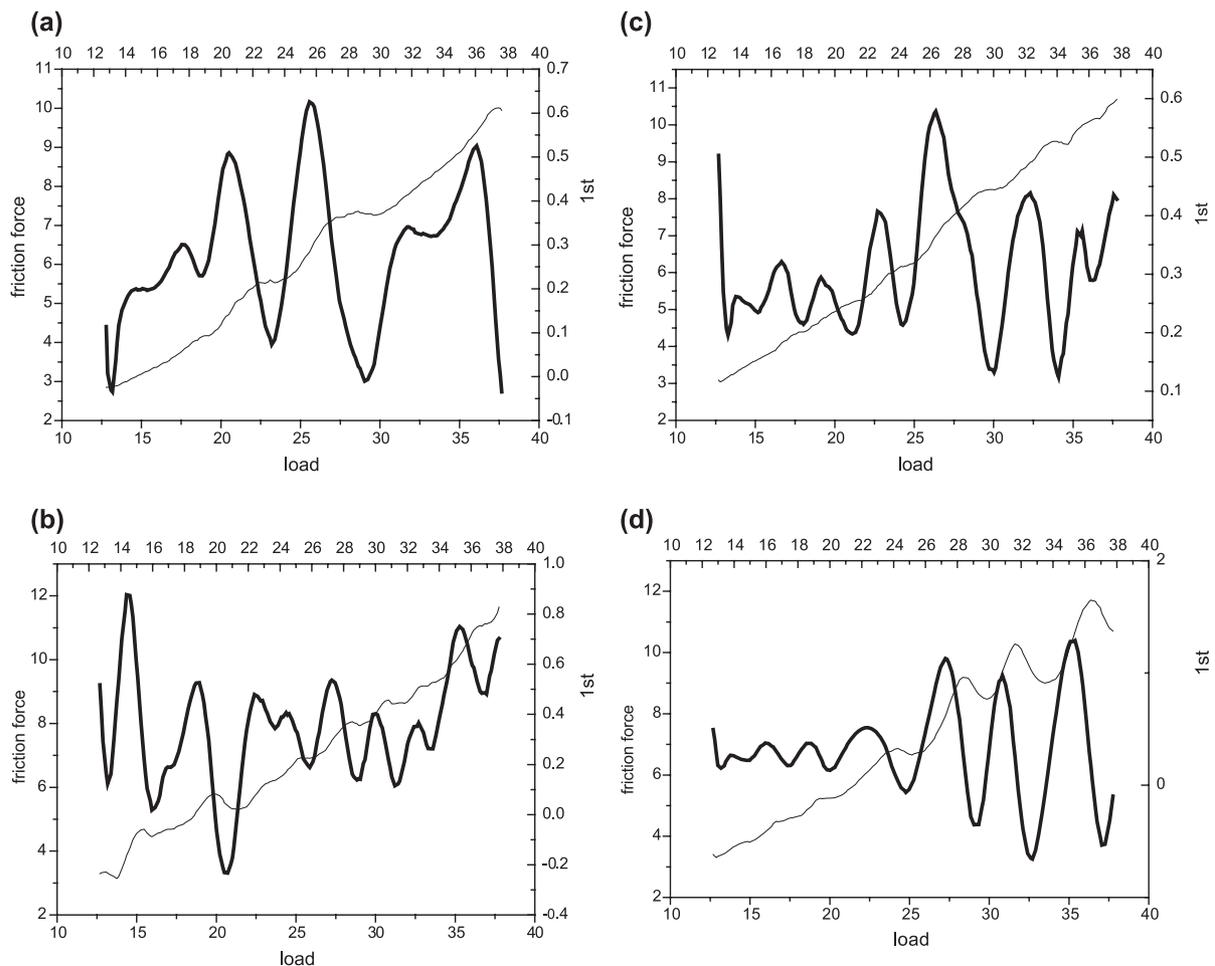


Fig. 5. Scratch test results of sputtered Al and Ni films before and after heat treatment at 350 °C in high vacuum. (a) The as-sputtered Al film, (b) Al film heat-treated at 350 °C×24-h, (c) the as-sputtered Ni film, and (d) Ni film heat-treated at 350 °C×48-h.

Table 1
Results of Vicker's microhardness tests and those of calculated from Eq. (1) for Al and Ni films with and without heat treatment at 350 °C

	H_s (Hv)	t (μm)	H_c (Hv)	H_t (Hv)
As-sputtered Al film	88.3	2	87.6	84±5
Ni film with or without heat treatment at 350 °C×48 h	88.3	2	99.4	209±10
Al film heat-treated at 350 °C×24 h (Al ₁₂ Mg ₁₇ phase)	88.3	5	102.0	140±10

a reactive layer 5 μm thick is formed on the surface. The composition of this reactive layer is measured by EPMA, and the results are shown in the table attached to Fig. 4a with the detected points 1–4 being indicated in Fig. 4a. From the EPMA results, the reactive layer shown in Fig. 4a is Al₁₂Mg₁₇ phase. This conclusion is further confirmed by the XRD results, as shown in Fig. 4b, in which peaks corresponding to magnesium and Al₁₂Mg₁₇ can be identified. This reactive layer is quite brittle since many cracks are observed during the preparation for metallographic examination, as shown in Fig. 4a.

The aforementioned 350 °C heat treatment in high vacuum was also conducted on the specimens of as-sputtered Ni film. However, no reactive layer can be observed by SEM, even though the heating time was prolonged to 48 h. This may be because 350 °C is not hot enough to form the intermetallics of Mg₂Ni or MgNi₂ between the Ni film and AZ91D substrate.

3.3. Mechanical properties

Fig. 5a–d shows the scratch testing results of sputtered Al and Ni films before and after the heat treatment at 350 °C in high vacuum. In Fig. 5, the thin curves represent the results of scratch loading with load from 10 to 40 N vs. the scratch friction with having 200 data points, and the thick curves are the first derivative of the thin curves. The highest peak occurring on the thick curve corresponds to

the critical load, L_c , which indicates that the film begins to initiate the cracks between the film and substrate [15]. From Fig. 5a and b, the L_c values are 25 and 15 N for Al films before and after 350 °C×24-h treatment, respectively. The dramatic decrease of L_c value is due to the formation of Al₁₂Mg₁₇ phase after heat treatment, in which Al₁₂Mg₁₇ is intrinsically brittle. The results of Fig. 5c and d indicate that the L_c values of Ni films before and after 350 °C×48-h treatment are 26 and 35 N, respectively. The significant improvement of the cohesive strength between the Ni film and substrate after heat treatment may be due to two reasons. The first reason is that the thermal stress induced by different α_s between Ni and AZ91D may be reduced by the heat treatment. The second is the nanoscale interaction layer that may be formed at the interface of Ni film and substrate due to the heating, although the microscale reactive layer cannot be observed by SEM in the last section. From Fig. 5a and c, the as-sputtered Al and Ni films have almost the same cohesive strength with the AZ91D substrate.

The Vicker's microhardness of AZ91D substrate is measured as 88.3 Hv (average value of 10 readings). According to Eq. (1), the Vicker's microhardness of Al and Ni thin films calculated with and without heat treatment at 350 °C are listed in Table 1. Table 1 shows that the Ni film is hardest, the Al film is softest and Al₁₂Mg₁₇ is in between. The hardness of Al₁₂Mg₁₇ shown in Table 1 is similar to that previously reported study [16]. The inherent higher hardness of the Ni film implies that it has a better wear resistance than the Al film, as discussed below.

Table 2 shows the results of sliding wear tests of the specimens of AZ91D alloy, Al films and Ni films, with or without heat treatment, at 350 °C. Before the wear test, the reading of the dimple grinder was set at 140 μm . During the test, the reading (in μm) was recorded every 5 min until 30 min, when the test was completed. The data shown in Table 2 are plotted in Fig. 6. From Fig. 6, the slope of each line is the same after 15-min testing. This means that the thin film on the substrate has been worn through after 15-min testing. Therefore, the wear rate is calculated by the data of the beginning 15-min test for

Table 2
Results of sliding wear tests of AZ91D alloy, Al and Ni films with and without heating at 350 °C

Time (min)	Specimens				
	AZ91D	As-sputtered Al film	As-sputtered Ni film	Al film heat-treated at 350 °C×24 h (Al ₁₂ Mg ₁₇ phase)	Ni film heat-treated at 350 °C×48 h
0	140.0	140.0	140.0	140.0	140.0
5	138.5	138.5	139.25	138.0	139.25
10	137.0	137.5	138.5	136.0	138.5
15	135.5	136.0	137.5	134.0	137.5
20	134.0	134.5	136.0	132.5	136.0
25	132.5	133.0	134.5	131.0	134.5
30	131.0	131.5	133.0	129.5	133.0
Wear rate ($\mu\text{m}/\text{min}$)	0.30	0.27	0.17	0.40	0.17

The calculated wear rate for each case is also listed.

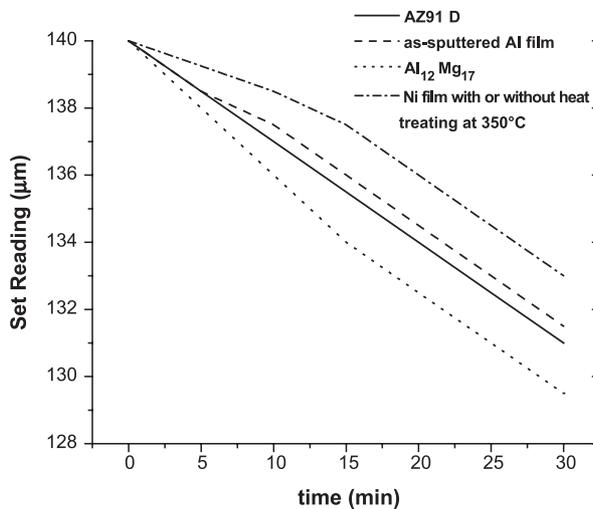


Fig. 6. Results of sliding wear test for AZ91D, Al and Ni films with or without heat treatment at 350 °C. The data (in µm) are obtained from Table 2.

each specimen and the results are shown in Table 2. From Table 2 and Fig. 6, the Ni film with or without heat treatment has the best wear resistance among the as-sputtered Al film, Al₁₂Mg₁₇ and AZ91D substrate. The Al₁₂Mg₁₇ has the worst wear resistance due to its brittleness. The lowest cohesive strength between Al₁₂Mg₁₇ and AZ91D substrate may be another reason for its poor wear resistance. Clearly, from the viewpoint of improving the wear resistance of AZ91D, the Ni film is superior to the Al film.

4. Conclusions

In this study, pure Al and Ni thin films are successfully r.f.-sputtered on the ground and polished AZ91D substrate. These films are bright and smooth. After 350 °C×24-h heat treatment in high vacuum, the 2 µm thickness of Al film reacts completely with substrate to form Al₁₂Mg₁₇ phase about 5 µm thick. However, the Ni film is not observed from SEM to form the reactive layer between Ni film and substrate after 350 °C×48-h treatment, although a nanoscale interaction layer may exist, as the scratch test results indicate that the cohesive strength has significant improvement after the 350 °C×48-h treatment for the Ni

film. The hardness tests demonstrate that the Ni film is harder than the Al film, AZ91D and Al₁₂Mg₁₇ phase. The sliding wear tests also show that the Ni film, with or without 350 °C heat treatment, has the lowest wear rate than the others. The intrinsic brittleness of Al₁₂Mg₁₇ phase possesses a low cohesive strength with the substrate and a poor wear resistance to grinding. From the viewpoint of surface modification, the r.f.-sputtered Ni film is superior to that of Al film.

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