DLC Coating on Magnesium Alloy Sheet by Low-Temperature Plasma

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Magnesium alloy sheets were coated with diamond-like carbon (DLC) using low-temperature plasma for the improvement of formability. For the better adhesion between Mg and DLC, Si-containing intermediate layer was necessary. In SEM observation, Si-containing layer formed by tetraethoxysilane (TEOS) plasma exhibited very tight and regular waving pattern, which was inherited to DLC layer deposited successively, and showed good adhesion. From the X-ray photoelectron spectroscopy (XPS) measurement, Si-C bond was found at the interface after DLC coating. Concerning the surface chemical structure, both sp^3 fraction and hydrogen content measured by XPS and glow discharge spectroscopy, respectively, decreased with increasing CH_4 concentration in the mixed gas with H_2 in DLC coating. The friction coefficient was reduced by the TEOS and DLC coating to a compatible level with MoS_2 lubricated one, but its clear dependence on CH_4 concentration was not found. The formability by deep drawing of DLC coated Mg alloy sheet was as good as that of MoS_2 lubricated one.

Keywords: Magnesium alloy sheet, DLC coating, Low-temperature plasma, Adhesivity, Surface composition

1. Introduction

Magnesium is a promising material as a light metal for various application fields because of its unique features such as an extremely small density and the greatest specific strength among all the metals. However, because of its poor formability, in particular, a high surface friction coefficient, Mg sheet is difficult to be processed by press-forming. For the press-forming of Mg sheet, the use of lubricant, usually molybdenum disulfide (MoS_2)-containing grease, on the surface is necessary.

We have tried to increase formability of Mg alloy sheet by manipulating the condition of press-forming and obtained some good results [1,2],

but we also coated diamond-like carbon (DLC) films on Mg alloy sheet directly using low-temperature plasma to reduce the surface friction coefficient [3,4].

DLC is a general term of amorphous carbon or hydrocarbon, expressed as a-C or a-C:H, which is stable in chemically and physically and has a low friction coefficient. Plasma surface modification and coating is not a new technique, but it has been regaining more expectation recently as an environmentally friendly system and many applications have been proposed. DLC coating on Mg alloy sheet surface is one of them [5-8]. In our previous report, we have reduced the friction coefficient of the Mg alloy sheets by DLC coating

and suggested a possibility of press-forming without MoS₂ [3,4].

In this paper, we examine basically the structure and adhesivity of DLC coated at various plasma conditions on Mg alloy sheets.

2. Experimental

2.1. Materials

Mg alloy sheet (AZ31B-O), purchased from Osaka Fuji Corp., was cut into suitable sizes for each testing and characterizing method, and cleaned ultrasonically in distilled ethanol before use. The Mg alloy contains about 3% of Al, 1% of Zn, and trace amounts of Mn and Si.

As gases for plasma CVD, methane (Nihon Tennengasu Kogyo), hydrogen (Nitto Bussan), and tetraethoxysilane (TEOS, special grade, Wako Pure Chemical Industries) were used.

2.2. DLC Coating

DLC coating and silicon-layer coating were carried out with a plasma polymerization apparatus (Samco International, PD-S10) [3]. Most of the cases, silicon layer was coated first, then DLC was coated continuously without breaking the vacuum. A capacitively coupled plasma was created with an rf generator (13.56 MHz) between a pair of stainless-steel electrodes (160-mm d., 60-mm gap). Mg alloy sheet samples were placed underneath of the top electrode, to which the power was supplied. The electrode was not heated intentionally. The reactor was evacuated with both a rotary vacuum pump and a mechanical booster for 30 min for the pressure to be less than 1 Pa and then the mechanical booster was turned off.

The flow rate of TEOS was controlled with a needle valve while CH₄ and H₂ were introduced into the reactor through a mass flow controller (Tylan FC-770A). The pressure of the system was monitored with an absolute pressure gauge (MKS Baratron 122AA). During the coating, deposition rate and total thickness were monitored with a deposition monitor (Leybold Inficon, XTM/2) that had a quartz oscillator sensor coated with gold.

The standard plasma condition for TEOS coating was 150 W, 3 sccm, 3 min, and that for DLC coating was 150 W, 10 min, 25 sccm of the mixture of CH₄ and H₂.

2.3. Cross-Cut Peeling Test

For the evaluation of the adhesivity of the DLC coatings on Mg alloy sheet, cross-cut test was carried out. In the test, the surface layer of DLC coated Mg alloy sheet was cut straight with 1-mm

interval for X- and Y-axes to make one-hundred 1-mm squares in a 10-mm square. An adhesive tape (Nichiban, Serotepu) was placed on it with a good contact. Then the tape was pulled back toward 180° angle. The adhesivity was evaluated from the number of unpeeled squares out of 100.

2.4. Surface Analysis

Surface chemical composition of DLC coated Mg alloy sheets were analyzed with X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9200). The operation condition was: X-ray source, Mg K α ; X-ray gun, 10 kV and 20 mA; pass energy, 50 eV, chamber pressure <10⁻⁷ Pa.

In compensation for the data of XPS, glow discharge spectroscopy (GDS, Rigaku GDA750) was used for the analysis of surface concentration of hydrogen. The operation condition was: frequency, 6.78 MHz pulse; Ar pressure, 350 Pa; voltage 800 V; measurement area, 2.5-mm d.

Surfaces of DLC coated Mg alloy sheets were observed with scanning electron microscope (SEM, Elionix, EXM-3500).

2.5. Friction Test

Friction test was carried out using a

(a) Non-coated Mg

(b) DLC coated

(c) TEOS coated

(d) TEOS and DLC coated

(e) TEOS and DLC
(30 min) coated

Figure 1. SEM photographs of (a) non-coated, (b) TEOS coated, (c) DLC-coated, and (d, e) Si and DLC coated Mg alloy sheet surfaces.

(d, e) DLC, CH₄ 60%; (e) DLC, 30 min.

ball-on-disk type tribometer. The DLC coated Mg alloy sheet (30-mm d.) on the turntable was pressed with a stainless-steel ball (6-mm d.) with 0.5-N load. The friction coefficient was measured up to 2-m integrated distance at the rotation speed of 30 rpm.

2.6. Deep Drawing

Deep drawing was carried out using an originally developed control compact deep drawing machine. The condition of the deep drawing was as follows: blank-holder force, 100-300 N; punch diameter, 9.5 mm; drawing ratio, 2.0-2.3; die diameter, 11.1 mm; punch speed, 0.5 mm/s; temperature, 200 °C. The outer side of the Mg alloy sheet (19.00-21.85-mm d.) was coated with DLC for this experiment.

3. Results and Discussion

3.1. Surface Morphology

In general, the adhesion between DLC and metal (Mg) is poor. Therefore, usually, Si-containing intermediate layer is inserted between them. As we have reported previously, we used TEOS plasma coating for the intermediate layer, and found that the adhesion and friction coefficient of Mg alloy sheet surfaces were improved [3,4].

The adhesivity can be judged by the close observation of the surfaces coated. Figure 1 shows SEM photographs of the surfaces of Mg alloy sheet coated by different manner. When DLC was coated directly on Mg (Fig.1b), oriented long flakes are found, which are obviously ready to come out. When only TEOS was coated on Mg

Figure 2. The number of unpeeled squares in the adhesion test of TEOS and DLC coated Mg alloy sheet. Percentages in the figure denote CH₄ concentration in DLC coating.

(Fig.1c), a regular waving pattern was found, which looked tight and rigid and seems to have

good adhesion. When DLC was coated after TEOS coating (Fig.1d), the appearance did not change from TEOS coating (Fig.1c), keeping the waving pattern, and the adhesivity seems to be good. When DLC was coated thicker (30 min) after TEOS coating (Fig.1e), a high internal stress caused peeling, but it is interesting to refer that the waving pattern of TEOS coating has been inherited.

3.2. Effect of TEOS Layer on Adhesivity of DLC Coatings

We measured the adhesivity of TEOS and DLC coatings deposited at various conditions on Mg alloy sheets by cross-cut test. Figure 2 shows the results of the cross-cut test for the samples coated with various TEOS flow rates (1 to 4.5 sccm) and various CH₄ concentration (10% to 80%) in the total flow rate of 25 sccm with H₂. As far as

Figure 3. Si2p XPS spectra of (a) TEOS coated and (b) TEOS and DLC coated Mg alloy sheet surfaces.

Si-O bond; Si-C bond.
(b) DLC, CH₄ 60%, ca. 5 nm.

deposition rate is concerned, higher TEOS flow rate and higher fraction of CH_4 were greater. Therefore, since the other plasma parameters are fixed, the thicknesses of the layers for the tested samples were different.

From this figure, for any given CH_4 concentration, the higher TEOS flow rates show better adhesivity. Regarding the CH_4 concentration, it is interesting that the lower concentration showed better adhesivity although the thickness of the layer is smaller.

3.3 Chemical Structure of DLC Coatings

The adhesivity of DLC coatings was improved by the TEOS intermediate coatings. One of the reasons of the improved adhesivity is a formation of Si-C covalent bond [9]. Figure 3 shows Si2p XPS spectra of (a) TEOS coated and (b) TEOS and DLC coated Mg alloy sheet surfaces. In this

Figure 4. C1s XPS spectrum of TEOS and DLC coated Mg alloy sheet surface.

sp^2 ; sp^3 ; C-O. DLC, CH_4 60%.

Figure 5. Ratio of sp^3/sp^2 on the surface of DLC coated Mg alloy sheet estimated by deconvoluted C1s XPS spectra as a function of CH_4 concentration in DLC coating.

particular case, DLC was coated for only 5 nm in order for the interface to be analyzed. In TEOS coated surface (a), only Si-O peak was found, while in DLC coated surface on TEOS coating (b), Si-C peak was newly found, which is effective in the adhesivity.

In XPS measurement, many researchers deconvolute narrow spectra to conduct precise analysis. Even for a hydrocarbon peak, the deconvolution enables us to distinguish sp^3 and sp^2 carbons, in which the peaks for sp^3 and sp^2 are located at around 285.2 and 284.3 eV, respectively [10,11]. Figure 4 is an example of deconvoluted C1s XPS spectrum of DLC coating. The relationship between sp^3/sp^2 and CH_4 concentration in DLC coating is shown in Figure 5. As is expected, sp^3 decreases as the CH_4 concentration increases.

When we deal with organic materials, we are always reminded the defect of XPS: hydrogen cannot be detected. ATR-FTIR is often used for the analysis of surface chemical structure along with XPS, but GDS may be the easiest technique to compensate XPS analysis. In GDS measurement, simply the relative amounts of most of the elements including H that constitute the surface are obtained by the analysis of emission in plasma. Figure 6 shows the relationship between H content and CH_4 concentration in DLC coating. The results can be naturally explained that H was found less for the DLC coated at higher CH_4 concentration.

Figure 6. Surface H concentration on DLC coated Mg alloy sheet measured by GDS as a function of CH_4 concentration in DLC coating.

3.4. Friction Coefficient

Figure 7 shows a comparison of friction coefficient. The friction coefficient of non-coated Mg alloy sheet ($\bullet\cdots\bullet$) is high, about 0.3-0.5. By

Figure 7. Results of friction test for the surface of Mg alloy sheets.

(.....) Non-coated; (- - -) MoS₂ lubricated; (—) TEOS and DLC coated.
DLC, CH₄ 60%.

the MoS₂ application (- - -), the friction coefficient was lowered to less than 0.2. That of TEOS and DLC coated one (—) was also reduced to compatible level with MoS₂ lubricated one. As a DLC coating, in general, the friction coefficient of 0.2 is not very low, but for the present application we are seeking, it is low enough, and other factors besides the friction coefficient may be involved for better formability of Mg alloy

Non-coated MoS₂ lubricated DLC coated

Figure 8. Relationship between punch load and punch stroke in deep drawing for non-coated, MoS₂ lubricated and DLC coated Mg alloy sheets, and photographs after deep drawing. x : Fracture.

sheet.

In the results presented so far, all properties have simple dependence of CH₄ concentration in DLC coating. However, a clear dependence of the friction coefficient on CH₄ concentration has not been found. The adhesivity and surface chemical composition do not necessarily correspond to the friction coefficient.

3.5. Deep Drawing

Figure 8 shows the relationship between punch load and punch stroke for Mg alloy sheets of non-coated, MoS₂ lubricated, and DLC coated, along with photographs after the deep drawing. Lower punch load means better formability. “x” indicates fracture of the sheet. The formability of non-coated Mg is very poor and fractured shortly, while that of the both MoS₂ lubricated and DLC coated Mg was good enough to complete the deep drawing. Most of the case, the formability of DLC coated ones are as good as MoS₂ lubricated ones, and sometimes they are better as shown in Fig.8.

4. Conclusion

TEOS intermediate layer, exhibited rigid regular waving pattern, was found to be necessary for a sure adhesion between Mg alloy sheet and DLC coating. The formation of Si-C bond at the interface was confirmed by XPS measurement. The adhesivity was increased at the plasma condition of higher TEOS flow rate and lower CH₄ concentration. Chemical structure of the DLC coating was dependent on the CH₄ concentration: sp³ fraction and H content decreased with increasing CH₄ concentration. The friction coefficient of TEOS and DLC coated Mg alloy sheet was reduced to the level for MoS₂ lubricated one. Also, the formability of DLC coated Mg alloy sheet by deep drawing was improved to be as good as MoS₂ lubricated one. The correlation between the surface properties and formability has not been fully understood.

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