The Corrosion Behavior of Sputter-Deposited Magnesium-Valve Metal Alloys

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Eiichi Hirota, Hiroki Habazaki, Asahi Kawashima, Katsuhiko Asami
and Koji Hashimoto

Institute for Materials Research

Synopsis

An attempt was made for preparation of magnesium alloys with valve metals, such as titanium, zirconium, niobium and tantalum whose melting points far exceed the boiling point of magnesium. These alloys became single phase solid solutions in wide composition ranges, but were crystalline in contrast to the fact that other alloys with valve metals such as nickel-, copper-and aluminum-base alloys were amorphous in wide composition ranges. The alloys containing sufficient amounts of valve metals showed high corrosion resistance due to spontaneous passivation in 1 M HCl at 30°C. The high corrosion resistance was attributed to the formation of passive oxyhydroxide films in which valve metal cations were remarkably concentrated. However, because of crystalline alloys and because of the presence of active magnesium, their corrosion resistance is lower than that of valve metals.

1. Introduction

Magnesium is the representative of high strength light metals. However, the corrosion resistance is considerably impaired by the presence of small amounts of impurities, such as iron, nickel and copper [1]. In particular, the presence of iron is detrimental. Mg-Al, Mg-Zn and Mg-rare earth alloys with low impurities have been used as high strength light alloys but their corrosion resistance is rather low. Accordingly, new magnesium alloys with high corrosion resistance are expected to be realized, although alloying of magnesium is difficult mostly because of low solubility limits of corrosion-resistant metals along with the low boiling point of magnesium.

One of the most attractive advantages of sputtering is no necessity of melting for preparation of alloys. This enables new alloys to be prepared in which the melting point of one of alloy constituents is higher than the boiling

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point of another alloy constituent. By utilizing this advantage it has been possible to prepare successfully amorphous copper alloys with tantalum [2,3] and niobium [2,4] and various amorphous aluminum alloys with tantalum [5], niobium [5], tungsten [6], molybdenum [6], titanium [7-10] and zirconium [7,9]. All sputter-deposited alloys showed higher corrosion resistance than copper and aluminum.

Magnesium is the widely used lightest metal but has poor corrosion resistance. Alloying of magnesium with valve metals such as tantalum, niobium, zirconium and titanium is to improve the corrosion resistance. Although melting points of these valve metals are higher than the boiling point of magnesium, these alloys can be prepared by sputtering.

Accordingly, the purpose of this work is to prepare magnesium-valve metal alloys by sputtering and to study their corrosion behavior in 1 M HCl where magnesium dissolve quite rapidly.

2. Experimental

D.C. Magnetron sputtering was used for preparation of alloys [2,5]. For the purpose of homogenization of the sputter-deposits, the water-cooled substrates were revolved around a central axis of the sputtering chamber in addition to revolution of the substrates themselves around the center of each substrate disc. The target consisted of a magnesium disc of 6 mm thickness and 100 mm diameter, on the sputter erosion region of which valve metal discs of 1 mm thickness and 20 mm diameter were symmetrically placed. The composition of the sputter-deposited alloy was varied by the number of the valve metal discs on the target. Because the present work was not for the protective coating but to study the corrosion behavior of the sputter deposits, glass plates were used for the substrate. The substrates were rinsed by immersion in water containing a commercial detergent for cleaning of aluminum metal at 75°C. After the target and substrates were installed in the sputtering machine the vacuum chamber was evacuated to about 1×10^{-6} torr. Sputtering was carried out at 2×10^{-3} torr of argon gas which was prepared by removal of oxygen, water and dust from high purity argon gas of 99.9995% purity.

The alloys prepared were 2-3 μm thick. Their composition was determined by electron probe microanalysis and their structure was identified by X-ray diffraction at θ-2θ mode with Cu K_α radiation.

Prior to corrosion and electrochemical measurements the specimen surface was polished by SiC paper in cyclohexane. The corrosion rates of the alloys in 1 M HCl solution at 30°C were estimated from ICP analysis of dissolved elements after immersion for 24-120 h. Electrochemical measurements were also carried out in the same solution.

X-ray photoelectron spectra were measured by SSI-100 with Al K_α excitation for the specimens before and after immersion or potentiostatic polarization for 1 h in 1 M HCl at 30°C. Binding energies of electrons were calibrated by a method described elsewhere [11,12]. Quantitative determination of the alloy surfaces was performed by the method reported previously [13,14] by using the integrated intensities of respective photoelectron spectra and Mg $KL_{2,3}L_{2,3}$ Auger spectrum. For the quantitative determination, the photoionization cross-section ratios of the Cl 2p and Zr 3d electrons to the O 1s electrons used was 1.017 [15] and 2.403 [16], respectively. The sensitivity factor of the Mg $KL_{2,3}L_{2,3}$ Auger electrons against the O 1s photoelectrons used was 3.710 [17]. The photo-ionization cross-section ratios of the Ti $2p_{3/2}$, Nb 3d and Ta 4f electrons to the O 1s electrons were determined by the method described previously [2] from TiO_2, Nb_2O_5 and Ta_2O_5 formed by high temperature oxidation of metals as 1.278 [18], 2.981 [4] and 2.617 [19], respectively.
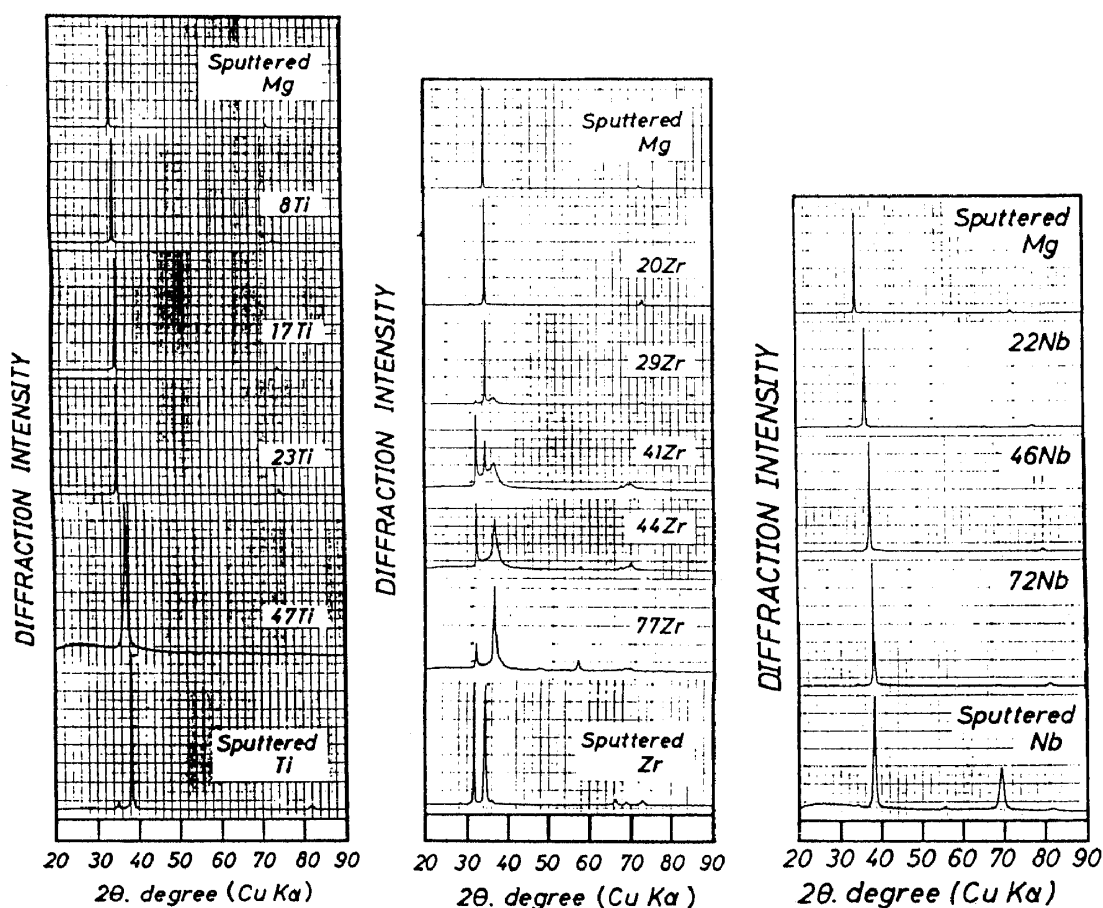
3. Results

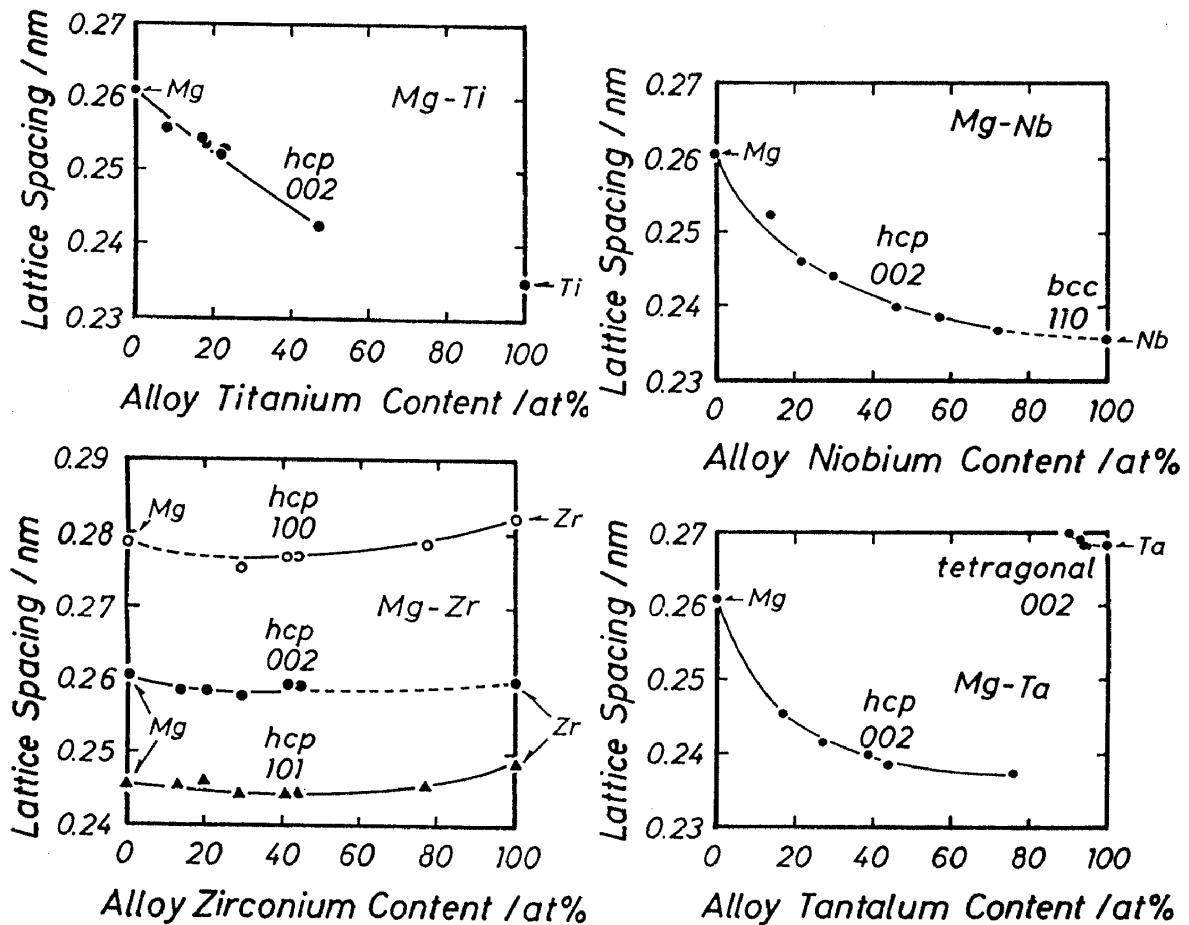Figure 1 X-ray diffraction patterns of Mg-Ti, Mg-Zr and Mg-Nb alloys

Figure 2 Change in lattice spacing by alloying

Magnesium alloys containing 8-47at%Ti, 13-77at%Zr, 14-72at%Nb and 17-95 at%Ta were prepared. Because of a low sputtering yield of titanium, the maximum concentration of titanium attained by this sputtering method was 47 at%. X-ray diffraction patterns of various alloys are given in Figure 1. The diffraction patterns of Mg-Ta alloys were similar to those of Mg-Nb alloys. All alloys prepared showed diffraction patterns typical of crystalline single phase alloys. Figure 2 shows the change in lattice spacing as a function of alloy composition. The addition of titanium, niobium and tantalum with smaller Goldschmidt radii than that of magnesium results in continuous decrease in 002 spacing of hcp magnesium. In particular, extrapolation of the lattice spacing of Mg-Nb alloy reaches 110 spacing of bcc niobium. Sputtered tantalum forms the high temperature tetragonal phase and hence the spacing of the most intense diffraction line gives rise to discontinuous change at 80-90 at% Ta. The continuous change in lattice spacing suggests

the formation of a single phase solid solution by supersaturation of alloying elements. Lattice spacings of magnesium are not greatly different from those of zirconium. Accordingly, it is difficult to confirm the formation of single phase solid solution for Mg-Zr alloys by continuous change in lattice spacings, but because of no diffraction lines of other phases the alloys seem to consist of a single hcp phase.

Figure 3 Potentiodynamic polarization curves of Mg-Ti alloys, magnesium and Titanium

The corrosion rates of alloys containing about 40 at% of titanium, zirconium, niobium and tantalum in 1 M HCl at 30°C were about 3 x 10^{-2}, 1 x 10^{-2}, 2 x 10^{-3} and 1.5 x 10^{-3} mm/year. These corrosion rates are remarkably lower than that of magnesium which dissolves almost instantaneously in 1 M
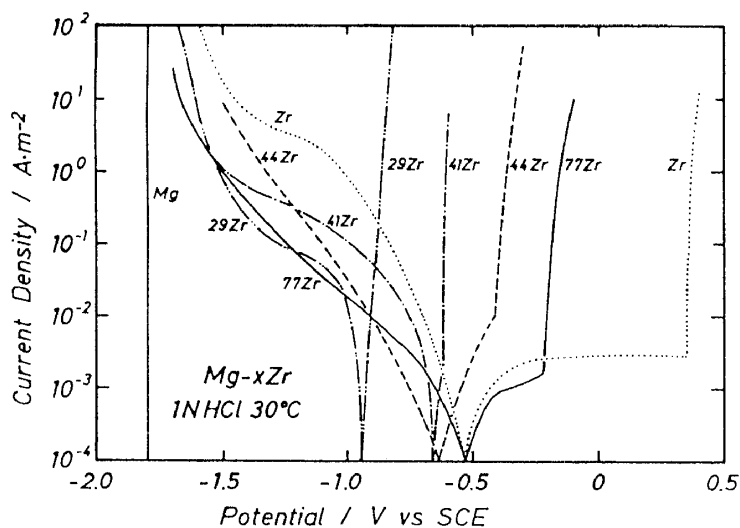

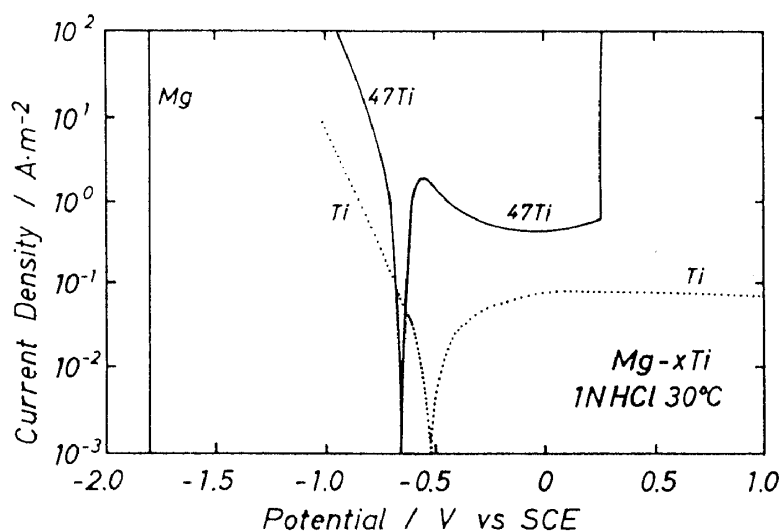Figure 4 Potentiodynamic polarization curves of Mg-Zr alloys, magnesium and zirconium

HCl. However, because of formation of crystalline alloys their corrosion rates are much higher than those of aluminum-valve metal alloys which become amorphous by sputtering [5-8]. Figure 3 shows potentiodynamic polarization curves of Mg-47Ti alloy, magnesium and titanium. The alloys with 23 at% or less titanium dissolved immediately when immersed in 1 M HCl, and hence their polarization curves in 1 M HCl were not measured. Magnesium metal dissolves, being accompanied

by violent hydrogen evolution, while titanium metal is spontaneously passive. The open circuit potential of the Mg-47Ti alloy is close to titanium. Figures 4-6 show potentiodynamic polarization curves of Mg-Zr, Mg-Nb and Mg-Ta alloys along with those of alloy constituents. Alloys with 20 at% or less zirconium, 30 at% or less niobium and 17 at% tantalum dissolved immediately in 1 M HCl and their polarization curves were not measured. The additions of zirconium, niobium and

Figure 5 Potentiodynamic polarization curves of Mg-Nb alloys, magnesium and niobium

tantalum ennoble the open circuit potential and lead to spontaneous passivation. The zirconium containing alloys suffer pitting by anodic polarization similarly to zirconium metal, but the pitting potential is ennobled by increasing alloy zirconium content. By contrast, the additions of sufficient amounts of niobium and tantalum prevent pitting corrosion.
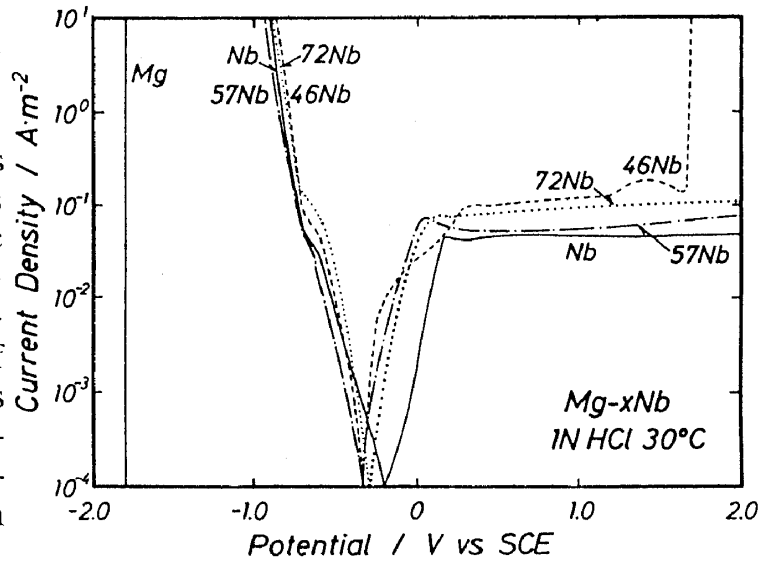
For a better understanding of enhancement of corrosion resistance by alloying, the alloy surfaces before and after immersion or potentiostatic polarization in 1 M HCl were analyzed by X-ray photoelectron spectroscopy. In addition to spectra of alloy constituents, spectra of oxygen and carbon were observed. The C 1s spectrum arose from a contaminant hydrocarbon layer covering the specimen surface. The O 1s spectrum was composed of two peaks; the lower binding energy peak was assigned

Figure 6 Potentiodynamic polarization curves of Mg-Ta alloys, magnesium and tantalum

to O^{2-}, and the higher binding energy peak arose from OH^- ions and bound water in the surface film [12,13]. The former peak was substantially stronger than the latter one after immersion or polarization. Spectra from alloy constituents were composed of the oxidized state for the surface film and the metallic state for the underlying alloy. Cations in the films were assigned to Mg^{2+}, Ti^{4+}, Zr^{4+}, Nb^{5+} and Ta^{5+}. After integrated intensities of photoelectron spectra were obtained for individual species, the thickness and composition of the surface film and the composition of the underlying alloy surface were quantitatively determined.

Figure 7 Thickness of surface films of Mg-57Nb and Mg-39Ta alloys

Figure 7 shows the change in the thickness of the surface film on spontaneously passive Mg-57Nb and Mg-39Ta alloys. As-prepared alloys were cove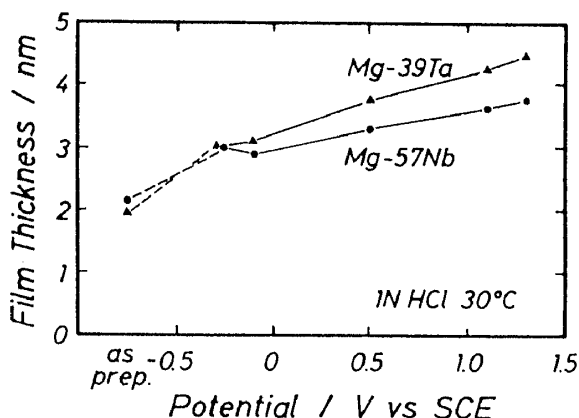red by air-formed oxide film of about 2 nm thickness. Immersion in 1 M HCl resulted in the formation of the passive film of about 3 nm thickness, and anodic polarization gave rise to further thickening of the passive film. This is a general trend of valve metals.

Figures 8-10 show compositions of surface films formed on Mg-47Ti, Mg-57Nb and Mg-39Ta alloys. As S. corresponds to the surface film formed on the alloys by air exposure after sputtering. As P. denotes the surface film formed by air exposure after mechanical polishing in cyclohexane before immersion or electrochemical measurements. Ec denotes the films formed by open circuit immersion in 1 M HCl. Air exposure of the specimens resulted in the formation of magnesium-enriched oxyhydroxide film in which the OH^-
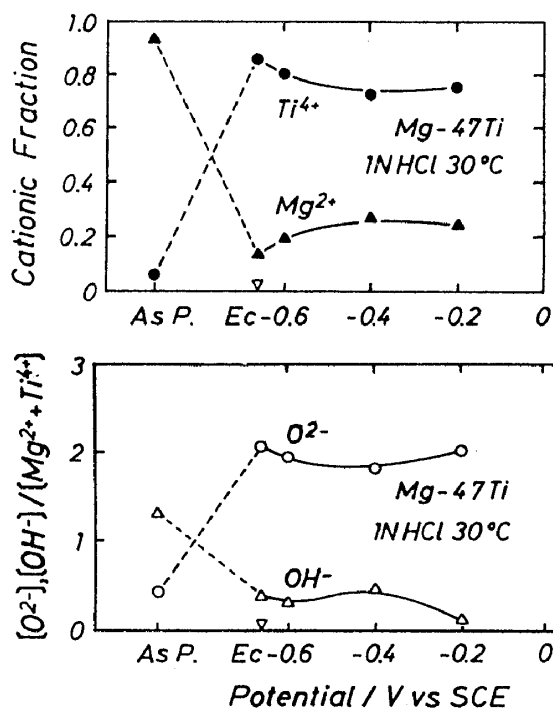

Figure 8 Change in cationic fractions and concentrations of oxygen species in the surface film on Mg-47Ti alloy

content was far higher than the O^{2-} content . By contrast, the cationic fractions in the air-formed films on the Mg-Zr alloys were almost the same as atomic fractions in the underlying bulk alloys. Immersion and anodic polarization of these alloys led to significant enrichment of valve metal cations in the passive films and the films consist of valve-metal oxyhydroxide in which the OH⁻ contents were very low, although magnesium ions were always contained in the films.
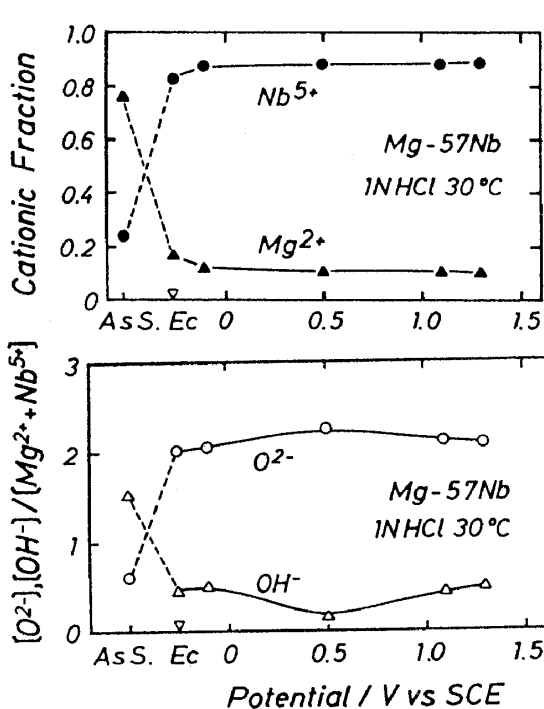

Figure 9 Change in cationic fractions and concentrations of oxygen species in the surface film on Mg-57Nb alloy
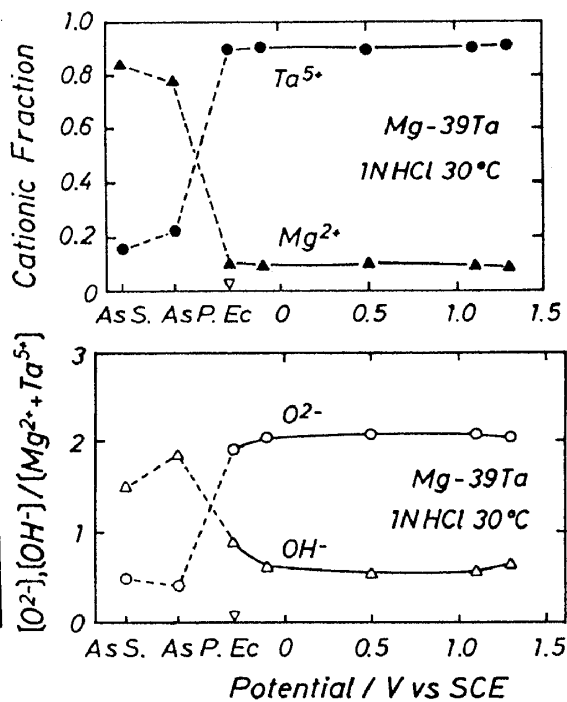
Figure 10 Change in cationic fractions and concentrations of oxygen species in the surface film on Mg-39Ta alloy

4. Discussion

Alloying of magnesium with sufficient amounts of valve metals such as titanium, zirconium, niobium and tantalum enhanced the corrosion resistance in 1 M HCl at 30°C in which magnesium metal dissolves immediately, being accompanied by violent hydrogen evolution. These alloys were spontaneously passivated in this aggressive solution. XPS analysis revealed the fact that the

spontaneous passivation resulted from the formation of the passive oxyhydroxide film in which valve metal cations were remarkably concentrated. The air formed films were composed of magnesium-enriched oxyhydroxides with higher concentrations of OH$^-$ ions, whereas the passive valve metal oxyhydroxide films contained low concentrations of OH$^-$ ions.

Because of a high dissolution rate of magnesium in 1 M HCl, the enrichment of valve metal cations in the surface occurs readily. The high corrosion resistance of magnesium-valve metal alloys in this aggressive solution is attributable to the formation of the passive valve metal oxyhydroxide films containing low concentrations of OH$^-$ ions. However, the corrosion resistance of magnesium-valve metal alloys is lower than that of valve metals themselves. Magnesium cannot form a protective passive film in any aqueous environments. Furthermore, these alloys are crystalline and cannot be expected to form a uniform passive film even if they consist of single phase solid solutions. Consequently, the presence of active magnesium in crystalline alloys is responsible for the fact that the corrosion resistance of Mg-valve metal alloys is inferior to that of valve metals themselves.

5. Conclusions

Magnesium-valve metal alloys, such as titanium, zirconium, niobium and tantalum whose melting points far exceed the boiling point of magnesium were successfully prepared by D.C. magnetron sputtering. These alloys consisted of single phase solid solutions in wide composition ranges. However, they were crystalline in contrast to the fact that other sputter-deposited valve metal alloys with copper, nickel and aluminum were composed of amorphous single phase in wide composition ranges.

The magnesium alloys containing sufficiently high concentration of valve metals showed remarkably high corrosion resistance in 1 M HCl at 30°C where magnesium metal dissolves readily being accompanied by violent hydrogen evolution. The high corrosion resistance was attributed to the formation of the passive oxyhydroxide films in which valve metal cations are significantly concentrated. However, their corrosion resistance is lower than that of alloy constituting valve metals themselves, because of the presence of active magnesium which is not capable of forming the passive film in any aqueous solutions and because of crystalline alloys on which a uniform passive film cannot be formed.

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