Amorphous and nano-structured alloys of increased corrosion resistance deposited by magnetron sputtering

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Abstract
The following alloys were deposited on glass and quartz substrates by MS: Al-Mg, Al-Mg-Zr, Fe-Cr-Ni, Fe-Cr-Ni-Ta, Au-Pd-In, Co-Cr-Mo, Ni-Cr-Mo [1-6]. The micro-topography, structure, electrochemical behaviour and anticorrosive stability of the sputtered alloys were studied using XPS, XRD, AFM, EIS, QCM, dc-voltammetry. XRD measurements indicated an amorphous (Ni-Cr-Mo, Co-Cr-Mo, Fe-Cr-Ni-Ta) or nanocrystalline (Al-Mg, Al-Mg-Zr, Fe-Cr-Ni) structure of the deposits. Microgravimetric (QCM) evaluation of corrosion resistance of the alloys was performed, which appeared to be an advantageous approach to express-evaluation, especially in gaseous environments. Electrochemical measurements indicated a superior anticorrosive resistance of the sputtered films when compared to that of the conventional alloy counterparts. The increased stability was attributed to a higher passivation capability of the surface films due to their more homogeneous and uniform structure. The alloys with refractory metals exhibited an exceptionally high corrosion resistance in acids (Fe-Cr-Ni-Ta). The refined structure of Mg-Al-Zr alloy led to the improvement of mechanical performance of the coatings.

Introduction

Alloy deposition by magnetron sputtering (MS) is of increasing interest because the deposits exhibit properties of great technological significance. MS coatings usually have superior corrosion resistance when compared to their casting counterparts. Sputtering procedure provides a possibility to create alloy compositions with refractory metals, whose melting point is much higher than the boiling point of other components. It is also possible to obtain by MS technique a single phase alloys supersaturated with the metals of limited solubility. Another advantage is possibility to form the coatings on non-conductive substrates.

This paper summarizes the properties of some magnetron sputtered alloys whose casting counterparts are of technical importance in such fields as medicine, food-equipment, chemical processing, automotive and aircraft industry: Al-Mg, Fe-Cr-Ni, Co-Cr-Mo, Au-Pd-In, Ni-Cr-Mo. Attention was also given to the alloys with refractory metals (Al-Mg-Zr, Fe-Cr-Ni-Ta), which exhibited an exceptionally high corrosion resistance.

Al-Mg and Al-Mg-Zr alloys

The Mg-Al alloys due to their low specific weight and high strength/weight ratio are attractive in a variety of technical applications, especially where weight reduction is of importance – aerospace, automotive, computers industry, etc. However, these alloys are susceptible to pitting corrosion, the primary reason of which is the low protective capacity of the magnesium hydroxide film.

Al-Mg films with Mg content in a wide concentrations range (0 % - 98 %) were formed on glass substrates by magnetron sputtering [1-3]. The voltammetric studies in 3.5% NaCl and 3.5% NaCl+50 ppm Cu(II) solutions showed that the corrosion resistance of samples increased with increase in Al content; this was evident from higher both open circuit and breakdown potentials.

Sputtered films of Mg-3Al, Al-4Mg and Al had a superior resistance to corrosion when compared to their cast counterparts, which are widely used for practical applications. XRD data showed that the increase in magnesium content caused the change in deposit structure from cubic to hexagonal. The grain size of sputtered samples was less than the size of cast counterparts (100-170 nm for sputter deposits and 225-300 nm for casts depending upon chemical composition). The superior corrosion resistance of magnetron sputtered Al-Mg films was attributed to a higher passivation capacity of the (hydro)oxide layer developed on the sputtered deposits with reduced grain size and more uniform microstructure.

Due to the limited solubility of Zr in Mg (*ca*. 1 at. %), the alloys formed by chemical reduction or melting procedures usually contain a large number of undissolved zirconium particles with dimensions over 10 μm, which increases the alloy susceptibility to corrosion. Sputter deposition provides a possibility to obtain a single phase alloys supersaturated with the metals of limited solubility.

Zirconium showed an exceptional grain-refining effect when added to magnesium-aluminium alloy. Nanocrystalline Mg-Al-Zr alloys with the grain size in the order of ca. 30-50 nm were formed in a wide Zr concentration range. Figure 1 shows a surface morphology change with zirconium concentration. The grain refining effect seems to be an effective approach to improve the mechanical properties of the coatings.

The valve metals, such as Al and Zr, may promote formation of barrier-type films thus improving corrosion performance of magnesium alloys. The anodic behaviour of the alloys was studied in 3.5% NaCl and 3.5% NaCl+50 ppm Cu(II) solutions in order to evaluate anticorrosive resistance. The alloys with zirconium concentrations of 4% and 15% exhibited an increased corrosion resistance when compared to their Zr-free counterparts. By contrast, the resistance decreased at higher zirconium concentrations (32 % and 50%). It has been shown by XRD measurements that the systems Mg-4Al-4Zr and Mg-3Al-15Zr represent the solid solutions supersaturated with zirconium. The sample containing 50% of Zr was composed of two phases, viz. Mg-Al and nanostructured Zr.

Quartz crystal microbalance indicated that zirconium containing alloys produce during corrosion thinner passive layers when compared to that of zirconium-free counterpart. The superior corrosion resistance of magnetron sputtered Mg-Al-Zr films was attributed to promotion of formation of barrier-type surface film and more uniform surface microstructure due to the grain refinement effect.

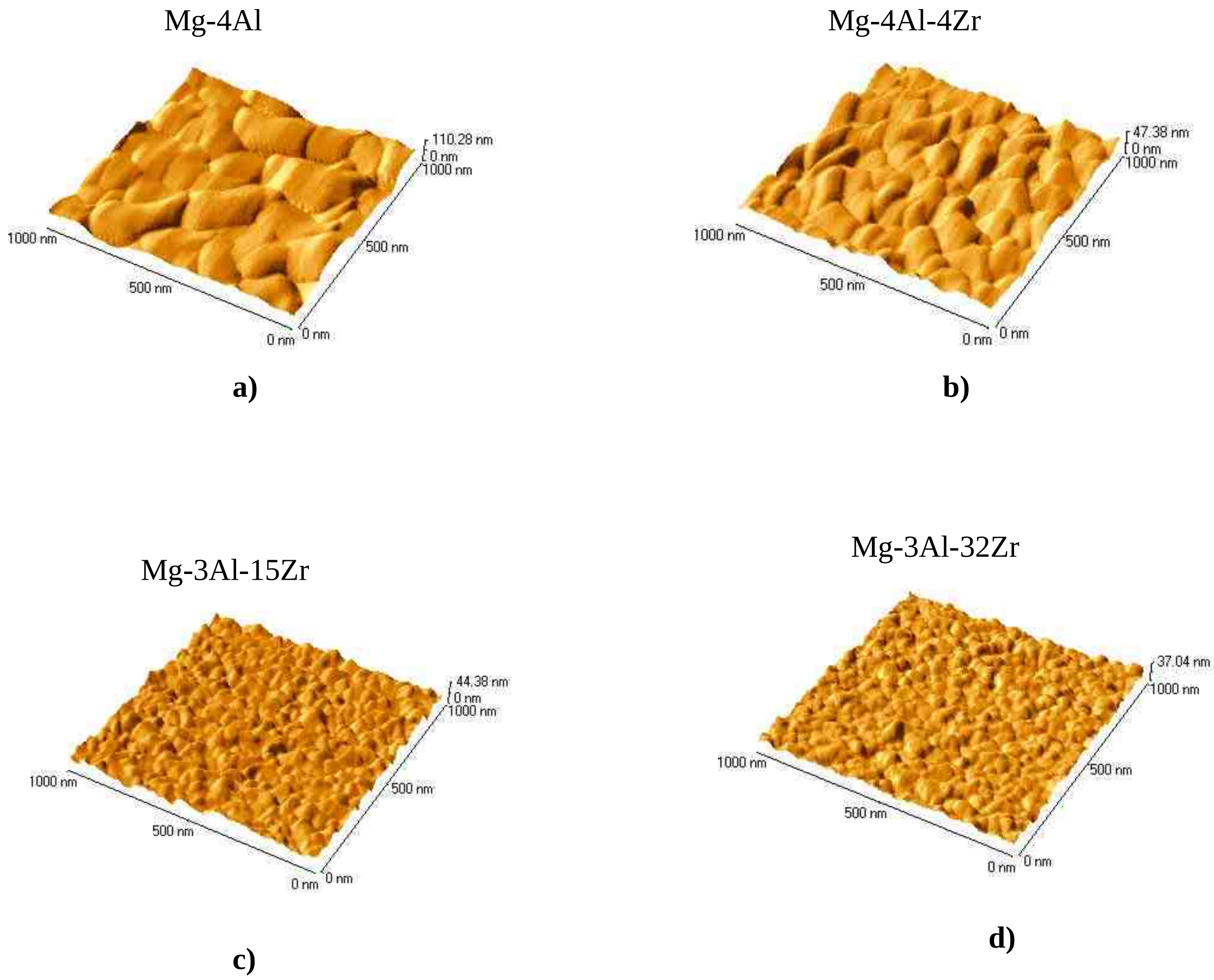

Fig. 1. Surface morphology change with Zr concentration as studied by AFM.

Fe-Cr-Ni and Fe-Cr-Ni-Ta alloys

It has been shown that Fe-Cr-Ni-Ta has an extremely high corrosion resistance in strongly acidic media. The corrosion rates in 12 M HCl were found to be more than six orders of magnitude lower than those of tantalum-free stainless steel [4]. The Fe-Cr-Ni and Fe-Cr-Ni-Ta alloys were deposited on quartz substrates by MS using targets of AISI 316 stainless steel and in combination with pure tantalum [5-7]. Formation of the Ta containing alloy by conventional melting is virtually impossible because the melting point of Ta is higher than the boiling points of the other components.

XRD results indicated a fine crystalline structure of the sputtered Fe-Cr-Ni alloy film, which contained both martensitic and austenitic phases. The Fe-Cr-Ni-Ta alloy film had an amorphous structure. AFM images have shown morphology of both alloys with characteristic pits, which had dimensions in the order of microns. The average depth of the pits in the tantalum-containing film was greater than that for the tantalum-free film (350-400 nm and 80-160 nm, respectively).

A time resolved *in-situ* information about corrosion behaviour of the magnetron sputtered coatings provides quartz crystal microgravimetry (QCM). Fig. 2 represents the data on mass changes during alloy corrosion in strongly acidic medium (10 M HCl). The distinctive mass growth during the first stages after Fe-Cr-Ni immersion implies accumulation of barely soluble products on the surface. In time, decrease in electrode mass is observed, which indicates that metal dissolution prevails.

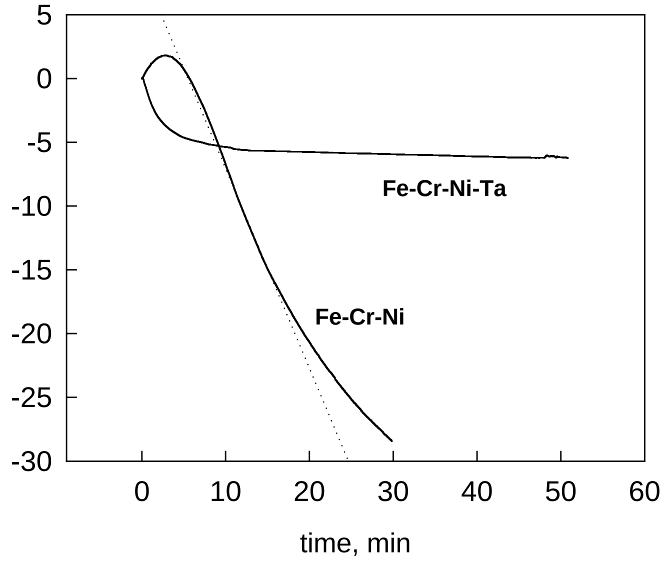

Fig. 2. Fe-Cr-Ni-Ta and Fe-Cr-Ni mass changes during alloy corrosion in 10 M HCl determined by QCM.

The QCM measurements indicted active dissolution of the Fe-Cr-Ni-Ta alloy during the first corrosion stages, however, with the corrosion time, the corrosion resistance became about two orders of magnitude higher than that of the Fe-Cr-Ni. In general, the microgravimetric measurements appeared to be an effective approach to evaluate the corrosion resistance of MS coatings.

Co-Cr-Mo and Ni-Cr-Mo alloys

Co-Cr-Mo and Ni-Cr-Mo alloys are of great importance in various technical and medical applications. The alloys prepared by magnetron sputtering had an amorphous structure with a superior corrosion resistance when compared to conventional crystalline alloys [8]. The corrosion monitoring has been performed by QCM in an oxygen-containing atmosphere and in NaCl solution. Corrosion has been initiated by supplying an oxygen gas into wet argon atmosphere and QCM detected corrosion with nanogram resolution as increase in mass. Corrosion currents were calculated from the mass vs. time curves. QCM appeared to be an effective tool for corrosive characterization of sputtered alloys in gaseous environments. The increased corrosion resistance of sputter deposited alloys indicated also the studies performed by electrochemical impedance spectroscopy.

Au-Pd-In alloy

Au-Pd-In alloys are known as metallic biomaterials, which are used in the production of implants in body tissues, especially in dentistry. The magnetron sputtered Au-Pd-In coatings had chemical composition similar to that of the casting alloy used as a sputtering target [9,10]. The deposits on quartz crystal substrates had a crystalline (not amorphous) structure. The corrosion behaviour of MS alloy was characterized by using electrochemical and QCM techniques in simulated physiological solutions. QCM reflected corrosion dynamics with nanogram resolution as an increase in electrode mass, which was due to oxygen bonding to the corroding surface. This approach appeared to be informative to characterize the corrosivity of simulated physiological solutions. The experiments, however, did not provide unambiguous indications of superior corrosion resistance of the sputtered coatings when compared to the casting alloy.

CONCLUSIONS

The magnetron sputtered alloys with an amorphous or nano-crystalline structure exhibited an increased corrosion resistance when compared to conventional crystalline counterparts. The alloy sputtering, therefore, is of increasing interest to produce highly resistant coatings. The alloys with refractory metals exhibited an exceptionally high corrosion resistance in acids (Fe-Cr-Ni-Ta) and had a refined structure (Mg-Al-Zr), which leaded to improvement of mechanical performance of the coatings. Limitations of dc-voltammetry (Tafel plots, breakdown potentials) and EIS (polarization resistance) were highlighted to evaluate corrosion resistance of magnetron sputtered alloys. In certain cases, quartz crystal microgravimetry was demonstrated to be an advantageous approach, especially in gaseous environments.

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