Electrochemical study of Mg-Nb alloy films in Hank’s solution

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Nanocrystalline Mg-Nb alloy films were sputter-deposited on glass substrates in a wide range of Nb concentrations. XRD studies revealed substitutional solid solutions of Nb in hcp Mg lattice when Nb concentrations were up to 26 at.%. At higher Nb concentrations, a bcc structure of Nb lattice was determined. An increase in Nb concentration led to contraction of the lattice as well as refining of the alloy, which was evident from reduced crystallographic c-parameter along with the grain size. Voltammetric studies in Hank’s solution showed that corrosion rate of the alloys decreased with Nb concentration. This was due to reduction of the active electrode area with preferential inhibition of partial anodic reaction. Application of the studied systems as biodegradable materials in vivo is discussed.

Key words: Mg-Nb alloy films, Hank’s solution, magnetron sputtering

INTRODUCTION

High intrinsic susceptibility to corrosion of magnesium is considered as a drawback when applying this metal (or alloys) in numerous technical fields, such as automotive and aircraft industries, computers and portable electronics. In biomedical applications, however, corrosion activity could be a beneficial property, which makes it possible to dissolve implants in vivo. Due to inherent biocompatibility of Mg and valuable mechanical properties, which are similar to those of human bones, Mg alloys are appreciated for fabrication of biodegradable implants for osteosynthesis, cardiovascular stents or tissue scaffolds [1–29]. This novel class of biomaterials is expected to support a healing process of a tissue and degrade thereafter. This means no need for secondary surgery to remove the implant when only temporary presence of it is necessary.

Magnesium is one of main constituents of human bone and the essential element in a muscle or soft tissue. Mg2+ ions are most common in the human body after Na+, Ca2+ and K+. These ions stabilize structure of DNA and RNA and are important for several metabolic enzymes [11]. A deficiency in magnesium causes dysfunction of cell membrane and increases incidence of cancer, heart disease and oxidative stress. The toxic dose of magnesium is unknown. Cytotoxic activity of released Mg2+ from Mg on osteoblast cells was not

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determined [12]. To the contrary, magnesium in damaged loc-
us supports activity of surrounding bone cells and promotes
bone growth [2, 9]. Also, mechanical properties of Mg based
alloys are superior to support the human bone when com-
pared to such permanent materials as Ti, stainless steel or
Co-Cr alloy [9, 12, 13].

From the viewpoint of biodegradability, Mg alloys are at-
ttractive candidates as well. The important requirement is a
uniform corrosion at sufficiently low rates especially during
initial stages after implantation. For instance, for stents, ap-
preciable degradation start is after some 6 months followed
by the vessel reconstruction period completed within next
6 months [7]. The total degradation of the implant during a
period of 12 to 24 months is desired [7, 26]. It is important
to adjust the degradation rate so that to avoid an intolerable
accumulation of the degradation products such as hydrogen
or alloying components. There are several ways proposed to
control the corrosion behavior of Mg alloys in vivo: alloying
and tailoring the composition, application of coatings made
of more resistant materials such as ceramics, polymer, com-
posite layers [3, 4, 9, 10, 15–26]. Biocompatibility and toxicity
are main issues regarding the modified surfaces and the ad-
itives. For instance, widely used alloying elements such as
Al, Zn, Mn may cause harmful effects [17, 25, 28–31]. Studies
have shown that Al may induce dementia, Mn can cause neu-
rotoxicity leading to Parkinsonism, Zr is closely associated
with liver, lung, breast or nasopharyngeal cancer.

Although degradable Mg biomaterials are actively inves-
tigated, new effective products are still in great demand. In
particular, biocompatible and non-toxic alloying elements
are a matter of great relevance. In this study we investigate Nb
as a possible candidate. This valve metal readily forms protec-
tive surface oxide and, therefore, has excellent corrosion re-
stance in most aqueous environments. Nb does not dissolve
in Mg matrix neither form intermetallic phases with it [32,
33]. Nb is known to be non-toxic and physiologically inert
[34, 35]. When treated with sodium hydroxide, Nb forms a
bonelike oxide layer that aids osteointegration [34] and pre-
vents corrosion [35].

Little is known about electrochemistry and corrosion be-
avour of Mg-Nb alloys, although first report on sputter co-
deposition of Mg and Nb was reported about two decades ago
[36]. Recently such alloys attracted attention as perspective
materials for hydrogen storage devices or switchable mirrors
[37]. There is very limited knowledge about electrochemical
and corrosion properties of Mg-Nb alloys in biological envi-
nronments. Our study aims to fill this gap.

EXPERIMENTAL

Magnetron sputtering of Mg and Nb targets was performed
using a Univex 350 vacuum system from Leybold Vacuum
GmbH (Germany) equipped with two confocal DC mag-
netsrons. Primarily the sputtering chamber was evacuated up
to ~2.2 × 10⁻⁶ mbar and then filled with working gas (Ar),
maintaining a constant pressure at 1.6 × 10⁻³ mbar. Targets
were prepared from high purity Mg (99.9%) and Nb (99.9%)
both from Alfa Aesar GmbH (Germany). During deposition
the samples (glass discs of 14 mm in diameter were used as
substrates) were kept at constant temperature of 60 °C by an
integrated infrared heater. The sputtering power used was 95
to 110 W for Mg target and 5 to 90 W for Nb one. The holder
of substrates was rotated at a constant velocity of 13 rpm to
ensure uniform coating distribution. The ratio of components
in Mg-Nb alloys was changed by means of varying sputtering
power of both magnetrons. Thickness of as-deposited thin
film Mg-xNb alloys was ca. 400–500 nm. After sputtering the
samples were kept in a chamber in N₂ atmosphere at ambient
conditions for 24 hours.

Composition of Mg-Nb alloys was examined by the mi-
croscope of a scanning electron microscope (SEM) using an
EVO-50EP device from Carl Zeiss SMT AG (Germany)
equipped with a secondary electron detector. Compositions
of the alloys in the paper are given in atomic %, e. g. Mg-4-
Nb.

Crystallographic structures of deposited alloys were studied
by X-ray diffraction (XRD) using a D8 Advance dif-
fractometer from Bruker AXS (Germany) equipped with the
Goebel mirror – a primary beam monochromator for CuKα
radiation. A step-scan mode was used in the 2Θ range from
30 to 70° with a step length of 0.02° and a counting time of
5 seconds per step.

Open circuit potential (E_{ocp}) and voltammetric mea-
surements were carried out using a P/G/FRA system PARSTAT
2273 from Princeton Applied Research Instr. (USA). Elec-
trochemical studies were performed in a naturally aerated
Hank’s Balanced Salt Solution (HBSS) from Sigma Aldrich
(Germany). Composition of Hank’s solution was (g/l)
0.185 CaCl₂ × 2H₂O, 0.097 MgSO₄, 0.4 KCl, 0.06 KH₂PO₄,
0.35 NaHCO₃, 8.0 NaCl, 0.048 Na,HPO₄, 1.0 Glucose and
0.011 Phenol Red, pH 7.2–7.6. Phenol Red is used for vis-
cual control of HBSS pH. All electrochemical measurements
were performed at 20 ± 1 °C. Ag/AgCl (in saturated KCl)
was used as a reference electrode and all potential values
throughout the paper are referred to this electrode. Plati-
num plate of ~4 cm² area was used as a counter electrode.
The working electrode (glass disc with deposited Mg-xNb
alloy) was mounted in a special holder and placed into a
three-electrode electrochemical glass cell. The area of work-
ing electrode surface exposed to electrolyte was 0.5 cm². The
measured and/or calculated kinetic parameters in the pa-
per are given in respect to the geometrical area of electrode.
Tafel polarization curves were measured in the potenti-
dynamic mode at the potential scan rate 5 mV/s and were
used for determination of corrosion current densities (j_{corr})
of studied alloys.

Optical inspection and images of as-prepared and corro-
sion damaged surfaces were performed by a B-353 Met mi-
croscope from Optika Microscopes (Italy), equipped with a
digital camera Optikam B 2.0.
RESULTS AND DISCUSSIONS

Crystallographic structure of the sputter-deposited alloys was studied by XRD (Figs. 1 and 2). Figure 1 shows the patterns obtained for Mg-Nb systems with different Nb content (4, 9, 14, 26 and 32 at.%). The pronounced peaks of diffractograms indicate a crystalline structure of the deposits with the prevailing crystallite orientation <001>. The alloys are substitutional solid solutions of Nb in Mg lattice when Nb concentration is up to 26 at.%. This does not hold, however, at higher concentrations (e.g. Mg-32Nb). It is well known that structural parameters of a solid solution depend on those of solute metal. Figure 1 shows that XRD peaks of Mg shift towards higher 2θ values when Nb concentration is

Fig. 1. XRD patterns of magnetron sputtered Mg-xNb alloys. Nb content (x) is given in the Figure in atomic %

Fig. 2. Dependences of parameter \( c_{\text{hcp}} \) of Mg hcp lattice and average grain sizes of coatings (in insert) on Nb content
increased. The shift is caused by a decrease in lattice parameters of Mg due to the partial substitution of larger Mg atoms by smaller Nb ones. The atomic radii of these atoms are 0.15985 and 0.14318 nm, respectively [38]. A hexagonal closed packed \((hcp)\) structure is characteristic of Mg and it is also retained for the alloys with the concentration up to ~26 at.% of Nb (Fig. 1). The lattice parameter \(c_{Mg}\) of the \(hcp\) structure decreases with increase in Nb concentration (Fig. 2). According to the Vegard's law, the crystal lattice parameter of alloy linearly depends on the concentration of constituent elements. However, some deviation from linearity is true for the system studied. It is obvious that the contraction of Mg lattice implies superior strength and hardness of Mg-Nb alloys when compared to those of pure magnesium. Introduction of Nb atoms into Mg lattice also induces grain-refinement effect. Average grain sizes of coatings were evaluated from XRD data according to the Scherrer's formula:

\[
D = \frac{0.94\lambda}{\beta \cos\Theta},
\]

where \(D\) is the grain size in nanometers, \(\lambda\) is the X-ray wavelength (\(\lambda = 0.154062\) nm for CuK\(_{α}\) radiation) and \(\Theta\) is the diffraction angle of the peak. The \(\beta\) stands for the width of the pure diffraction profile on the 2\(θ\) scale in radians, which has been obtained according to

\[
\beta = B - b,
\]

where \(B\) is the integral width at a half of the maximum intensity for a sample, and \(b\) is that for a standard (LaB\(_6\), for which \(b = 0.016\) rad was used). The \(\beta\) value was calculated according to the width of the Mg 002 peak. It was found that the alloys are nanocrystalline ones with the grain sizes (\(D\)) of the order of several tens of nanometers (Fig. 2). The grain size clearly decreases with increase in Nb content. It is noteworthy that shapes of both \(c\)- and \(D\)-curves are similar. The refinement is important from the viewpoint of corrosion resistance of metals. Fine-grained sputtered alloys usually exhibit higher passivity than the cast counterparts, as it was demonstrated, for instance, for sputtered Mg-Al alloys [39].

It is important that at higher Nb concentrations the alloys show the presence of cubic body centred \((bcc)\) structure (e. g. 26 and 32 at.%, curves 4 and 5 in Fig. 1). Only minor quantity of the \(bcc\) phase was found for Mg-26Nb alloy, whereas for Mg-32Nb alloy the \(bcc\) phase of Nb was prevailing. Probably, a transition from the \(hcp\) structure to \(bcc\) is the reason why the \(c\)-curve in Fig. 2 is not linear, at low Nb concentrations alloy has a prevailing \(hcp\)-phase and at high concentrations alloy has a prevailing \(bcc\) structure. The most probable cause of deviation from linearity is that formation of Nb \(bcc\) lattice in coating led to lesser quantity of Nb in Mg \(hcp\) lattice.

Open circuit potential \((E_{ocp})\) provides information on electrochemical (corrosion) stability of the alloys. The curves \(E_{ocp}\) vs. exposure time are given in Fig. 3. The initial \(E_{ocp}\) values are within the ranges ~–1.4 to ~–1.2 V (Ag/AgCl). A positive potential shift is observed during the exposure, which means an increase in electrode passivity. A quasi-steady-state value is attained after some 10–20 min of exposure. These values do not differ greatly for the alloys with 4 to 26 at.% of Nb. Substantial ennoblement exhibits alloy

![Fig. 3. Dependence of \(E_{ocp}\) of magnetron-sputtered Mg-xNb alloys in Hank’s solution on Nb content in alloy](image-url)
with 32 at.% of the additive. The most probable reason of such ennoblement is an enrichment of the alloy surface by Nb oxide, which has much higher protective capability when compared to Mg oxide.

Electrochemical behaviour of the systems in Hank’s solution was studied by dc-voltammetry (Fig. 4). Anodic and cathodic curves (Tafel plots) were recorded after a quasi-steady-state has been attained (Fig. 3). Obviously, when increasing Nb concentration, the $E-j$ plots shift down and open-circuit potential increases. The slope of cathodic Tafel plots is observed about 120–140 mV, which implies cathodic hydrogen evolution with a charge transfer control. On the contrary, anodic slopes change significantly when Nb concentration is increased: from ~200 mV for Mg-4Nb to ~130 mV for Mg-32Nb (curves 1 and 4). The last value is in line with the Mg corrosion mechanism according to which formation of the intermediate Mg$^+$ ions is the first step of dissolution [40, 41]. At the same time, considerably higher values of measured anodic slopes for alloys with low Nb concentration are due to the Negative Difference Effect, i.e. the increase of hydrogen evolution rate with the increase of anodic potential. It can be concluded that Nb acts as an inhibitor, which reduces the active surface area without changing remarkably the corrosion mechanism, i.e. electrochemical reactions of water decomposition and Mg dissolution. The positive $E_{ocp}$ shift implies that the inhibiting influence is more pronounced in respect to the anodic process.

As commonly known, extrapolation of Tafel plots to $E_{ocp}$ (or corrosion potential) gives the corrosion current density ($j_{corr}$). Such data are provided in the insertion in Fig. 4. It can be seen that introduction of 32 at.% of Nb leads to reduction of corrosion activity of about one order of magnitude. The $j_{corr}$ values (mA cm$^{-2}$) may be converted to mm per year (mm/year). Such data are given in Table. These corrosion rates are only a rough approximation as they assume corrosion process to be uniform. For exact evaluation of Mg corrosion rate the method of Tafel extrapolation must be complemented by other ones: weight loss and hydrogen evolution.

Figure 5 shows optical views of the surfaces. As-deposited samples are compared with those exposed in Hank’s solution. Obviously, at lower Nb concentrations, the surface is severely affected by corrosion. At higher Nb concentration, substantial mitigation of the corrosion attack is evident. In this case, there are no continuously corroded areas; just some localized corrosion sites are visible (Fig. 5e, f).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg-4Nb</th>
<th>Mg-14Nb</th>
<th>Mg-26Nb</th>
<th>Mg-32Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$j_{corr}$ mA cm$^{-2}$</td>
<td>$2.68 \times 10^{-5}$</td>
<td>$1.12 \times 10^{-5}$</td>
<td>$3.0 \times 10^{-6}$</td>
<td>$1.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>Corrosion rate, mm/year</td>
<td>0.61</td>
<td>0.25</td>
<td>0.068</td>
<td>0.036</td>
</tr>
</tbody>
</table>

Fig. 4. Tafel dependences of magnetron-sputtered Mg-xNb alloys in Hank's solution. Insert: dependence of $j_{corr}$ on Nb content. An extrapolation from Tafel regions to $E_{ocp}$ is shown for Mg-4Nb and Mg-32Nb alloys.
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CONCLUSIONS

1. Mg-xNb alloys with Nb content ranging between 4 and 32 at.% were formed by magnetron sputtering. The alloys had crystalline structures with grain sizes of the order of several tens of nanometers.

2. Increase in Nb content leads to higher corrosion resistance of the alloys in Hank’s solution. Corrosion rates of Mg alloy decreased almost tenfold when the concentration of Nb was increased from 4 to 32 at.%.

3. Corrosion process of Mg-Nb alloys could be tailored to \textit{in vivo} needs by proper selection of Nb concentration.

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38. XRD database “Powder Diffraction File-2” (integrated part of DB Advance Diffactometer software).

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Mg-Nb LYDINIO ELEKTROCHEMINIAI TYRIMAI HANK‘O TIRPALE
S a n t r a u k a
Plonus nanokristalinių Mg-Nb lydinių dangos buvo formuojamos ant stiklo substratų pastoviosios srovės magnetroniniu dulkinimo metodu. Rentgeno spindulių difrakcijos metodu nustatyta, kad lydinių, kuriose Nb koncentracija yra iki 26 at.%, suformuoja Nb centruoto tūrio kubinė kaitinius kietus tirpalus Mg heksagoninėje tankioje niai, kuriuose Nb koncentracija yra iki 26 at.%, suformuoja Nb patenkimą (nustatyta pagal kristalografinio c parametro mažėjimą) gardelė. Nb koncentracijos didėjimas Mg gardelėje lemia jos susituokimą (nustatyta pagal kristalografinio c parametro mažėjimą) ir dangos kristalinių dydžio mažėjimą. Voltampereometriniais matavimais Hank‘o tirpale nustatyta, kad didėjant Nb koncentracijai lydiniuje mažėja jų korozijos greitis. Tai sietina su elektrodo aktyviausiu ploto sumažėjimu ir preferenciniu anodinės reakcijos lėtinimu. Apačiose pasaulyje panaudoti tirtus lydinius kaip biodegraduojančias medžiagas.