Characterization of Some Master Mg-X System (Ca, Mn, Zr, Y) Alloys Used in Medical Applications

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Ultralight magnesium alloys are wide used in the medical field, especially for biodegradable implants. Although they are wide used, magnesium has low corrosion resistance. To improve this resistance, different types of alloys based on magnesium and Ca, Mn, Zr and Y can be developed. The main goal of the present paper is to investigate the properties of some master alloy based on Mg-X system (Ca ,Mn, Zr, Y) used in the development of biodegradable based alloys of Mg. The surface morphology was characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and optical microscopy. After the XRD analysis, there was observed that some specific compounds were formed of Mg2Ca, Mg0.97Mn0.025, MgZr, Mg_2Y, Mg24Y5 having the main Mg phase formed in the hexagonal structure. There were also evaluated the master alloys micro-hardness values in the range of 58.41 HV (Pure Mg), 67.97 HV (Mg-3Mn), 85.12 HV (Mg-25Zr), 131.8 HV (Mg-15Ca) and 291.45 HV (Mg-30Y). The corrosion resistance was developed using electrochemical testing in specific medium and there is shown that the corrosion rate increased significantly for the master alloys investigated, rather than pure magnesium. As a final conclusion structural properties of these alloys recommend them for usage as medical implants.

Keywords: optical microstructure, SEM, XRD, Micro-Hardness, Electrochemical tests

The potential benefits of magnesium (Mg) over other non-resorbable biomaterials, especially for orthopaedic applications, are obvious. When fully realized, functional bioresorbable implants based on Mg alloys can be unique to the field, offering the mechanical advantages of a metal combined with the degradable and biological advantages of polymers and biomaterials [1]. However, despite recent significant research, there are still challenges for the successful implementation of Mg-based materials in a variety of applications in the body. The notion that implants made of Mg and its alloys from a bio perspective are designed to degrade also means that their shape and mechanical properties constantly change over the life of the implant, adding another layer of complexity to Complete life cycle design [2-5].

Many of these challenges are related to corrosion, whether rate, morphology, or products, as discussed below, the main advantages Mg has over current materials such as low specific biodegradability [6-11], also presents some of the greatest challenges for its use in a wider context. Such multiple and competing considerations require careful management and an interdisciplinary approach to research (involving metallurgists, corrosion scientists, toxicologists, mechanical modellers, and surgeons). The pure Mg has no mechanical anticorrosive properties [12-14].

Properties required for a wide range of medical implants. Therefore, potential alloying elements must be carefully considered. Common elements that alloy with Mg include aluminium (Al), zinc (Zn), calcium (Ca), rare earth (RE), lithium (Li), manganese (Mn), and last but not least zirconium (Zr). An innovative and topical side in the literature is the Mg alloy with RE elements (ie Ce, La, Nd, Pr, Y, Gd). This is required for the field of biomaterials in general and not just for Mg-related work. Similarly, although Li has been used in medicine for nearly 150 years [15, 16], it has not been widely used in implanted materials - where continuous exposure to mg / day can be produced 0.39. The two elements Which are probably the most biocompatible with Mg are Ca and Zn [5,6].Mg alloys can be used as implants and have a degradation in time (12-18 weeks) after bone replacement [15,17]. The breaking strength of the MgCa alloy which is most commonly found in the specialized books is 210-240 MPa, and MgZr has a traction resistance of 125 MPa [18]. MgZn and MgZr have better mechanical properties than pure Mg because of the very small grain size (0.02 mm diameter), [19,20], unlike MgMn alloys that have very large grains. Zr has a monocyclic ceramic tensile strength in the range of 220-745 MPa [21]. It is very difficult to estimate biodegradability or showed that bio ceramics could provide osteointegration improvements and controlled biodegradability [22,23].

As coating phosphate (Ca-P) can delay the onset of magnesium corrosion and at the same time slow down the degradation process [24, 25]. MgCa alloys containing 0.6 to 3 percent by weight appear to be compatible for orthopaedic implants, but degradation is faster than bone healing [26,27].

The addition of Y has been used in Mg alloys for biodegradable implants due to its beneficial effects on corrosion resistance and lack of toxicity [28,29]. It is also known that Y2O3 has a high thermodynamic stability and Has been shown to reduce the rate of degradation of Mg-based alloys [28,30]. Recently, the biocompatibility studies of Mg-Y alloys show that a 3% Y concentration is sufficient to form a corrosive protective wall, while maintaining a Low corrosion rate [31]. In this paper we investigated the alloys acquired to check the biocompatibility with the

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Table 1
CHEMICAL COMPOSITION OF THE MAGNESIUM MASTER ALLOYS - HUNAN CHINA Co

Alloys	Mg/Y	Fe	Ni	Cu	Si	Al
Pure Mg	Mg(99%)	-	-	-	-	-
Mg15Ca	Ca(15.29%)	0.004%	0.001%	0.003%	0.013%	0.011%
Mg3Mn	Mn(2.79%)	0.002%	0.004%	0.001%	0.005%	0.035%
Mg25Zr	Zr(27.33%)	0.008%	0.001%	0.001%	0.007%	0.012%
Mg30Y	Y(28.05%)	0.010%	0.001%	0.001%	0.006%	0.011%

human body, the corrosion resistance, the hardness and elasticity of each alloy, and the morphology of the surface.

Experimental part

Materials and methods

For the experimental data, was purchased alloys with the chemical composition shown in Table 1. These alloys were purchased from Hunan China, pure Mg and 4 types of alloys: Mg15Ca, Mg3Mn, Mg25Zr, Mg30Y. Microscopy samples were cut from ingots, mechanically sanded using abrasive paper up to 2000 sand, and polished with 0.3 alumina slurry, cleaned with distilled water, exposed in the open air and chemically attacked to highlight the microstructure .

In order to highlight the microstructures there have been used the Leica 5000DMI optical microscope, and to obtain clearer images and larger magnification there is used a Quanta 3D scanning microscope (FEI, Hillsboro, OR, USA) -SEM equipped with a detector EDX.We used a XRD Expert Pro MPD diffractometer for diffraction analysis. The microhardness was done using a tribometer with indentation and scratch tests. The microscratch test was carried out thus a constant load of 5N was applied at a distance of 4mm with a travel speed of 3mm/s. For corrosion alloys there were kept in the Ringer solution then analyzed and investigated in order to obtain SEM images.

Results and discussions

Optical microscopy

In the figures below are presented images at different magnification powers from 100x to 500x for each alloy. An unique microstructure is the Mg-30Y alloy where *Y* grains can be highlighted, taking the specific form of magnesium grain change. It should also be noted that Mn forms very large grains with a specific structure of Mg-Mn alloys.

Scanning electronic microscopy

The electron microscope images at different magnification range, from 500x to 5000x, show each analysed alloy and there can be seen the microstructural differences between them.

At magnification of 5000x, the microstructures were more clearly observed and the magnesium grains highlight a modified microstructure form, depending on the element

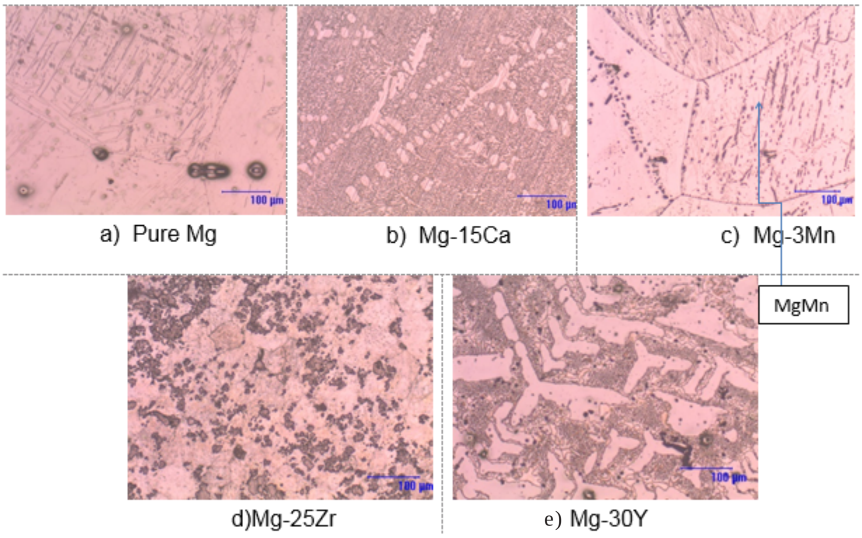


Fig.1(a,b,c,d,e): Optical microstructures of Mg alloys

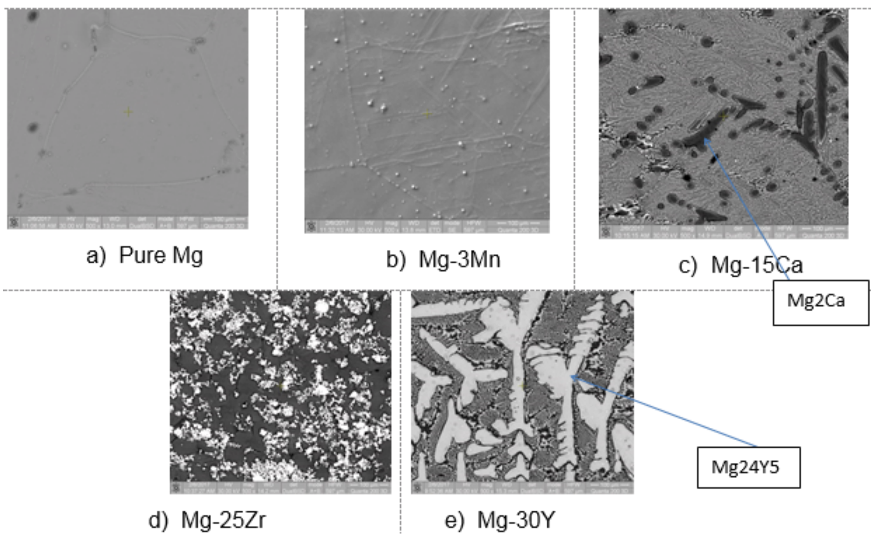
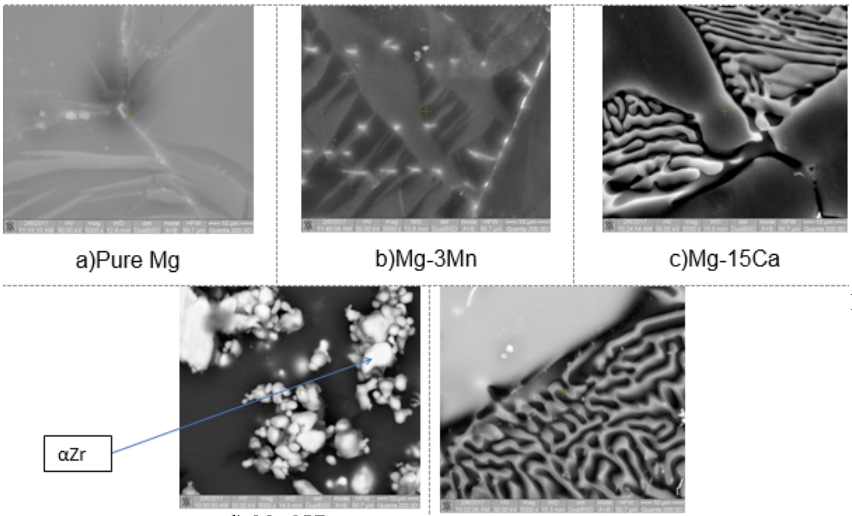


Fig.2(a,b,c,d,e): SEM images of Mg alloys



d) Mg-25Zr   de) Mg-30Y

Fig.3.(a,b,c,d,e): SEM images of Mg alloys

that Mg is alloyed. It is noted that MgZr forms spherical structures of different conglomerate granulations. The structure differs from other materials that form mechanical lamellar mixtures at the limit of separation of the magnesium grains.

XRD analysis

XRD analysis were performed on a Panalytical diffractometer XPERT Pro MPD, CuKα X-ray Tube. XRD patterns are revealed in figure 4. Pure magnesium is highlighted at 33.46 2Theta degree- as majority peak. Also, in comparison it were determined the compounds from the master alloys, like Mg2Ca, M24Y5, Mg-Mn, and α-Zr, as minority peaks. The crystallographic system of the Mg is hexagonal type, and for the rest of the compounds are the same, only Mg24Y5 has a cubic crystallographic type.

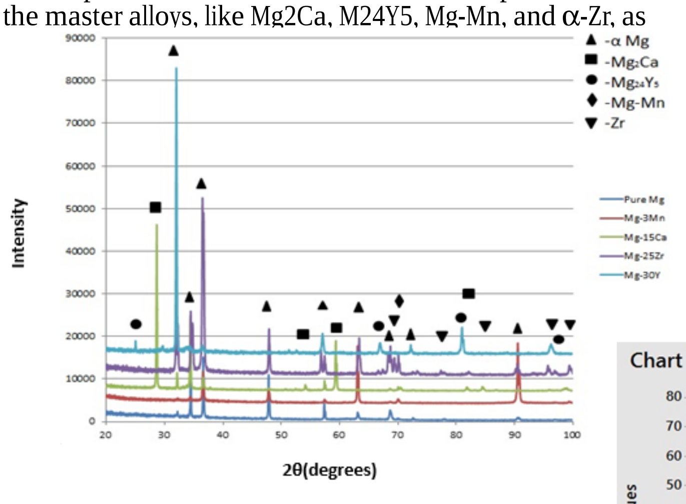


Fig.4. Curves of the alloys of Mg

Fig.5.Chart of alloys

Microhardness test

In figure 5 it is observed that pure Mg has the lowest hardness value of 58.47 HV, butthe hardness increases with a very small difference when it isalloyed with Mn, resulting67.97 HV hardness,according to table 2. When it is alloyed with Zr, the hardness rises up to 85.12 HV, yet low when compared to Mg-15Ca alloy (131.80 HV) or Mg-30Y alloy, having the highest hardness value of the alloys studied, 291.45 HV, nearly 6 times larger than Mg base material. Also, the pure Mg has the lowest value of modulus of elasticity, and the highest is found in the Mg-3Mn alloy 29.491 N/mm^2, very close to that of the Mg-30Y alloy 29.107N / mm^2.

Following the micro-scratch test, on the surface of specimens were observed material damages on Mg-Mn and Mg-Zr.This is due to the influence of the Mn and Zr alloying elements, which make the Mg alloy more fragile, which translates into high COF values (1.53-Mg3Mn and 1.31Mg-25Zr respectively) indicating the need of a higher load to remove the material.

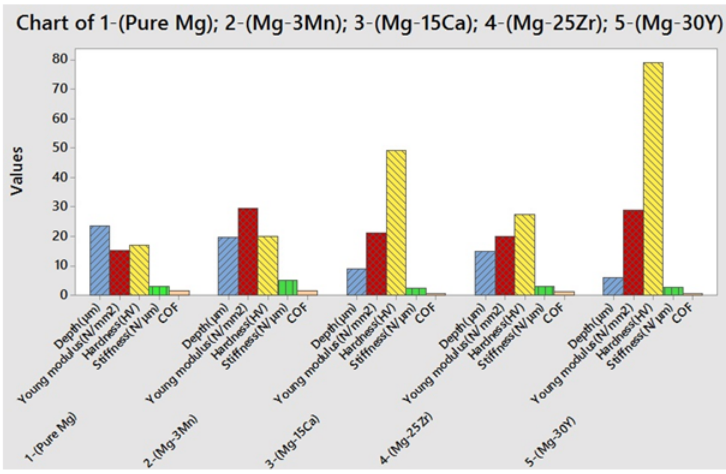


Table 2
MECANICAL PROPERTIES OF Mg ALLOYS

Master alloys	Depth(μm)	Young(N/mm^2)	Hardness (HV)	Stiffness(N/μm)
Mg-15Ca	8.961 (5.928)	21.076	49.23	2.376
Mg-3Mn	19.837(17.886)	29.421	20.15	5.164
Mg-25Zr	14.839(12.547)	20.145	27.54	3.036
Mg-30Y	5.984 (3.689)	29.107	79.18	2.580
Pure Mg	3.707 (21.149)	15.096	17.1	2.903

Alloys	Scratch trace dimension	Units of measure	COF
Mg-pur	433.61	µm	1.47
Mg-3Mn	438.28	µm	1.53
Mg-15Ca	297.82	µm	0.68
Mg-25Zr	427.20	µm	1.31
Mg-30Y	191.75	µm	0.51

Table 3
TRACE DIMENSIONS LEFT ON ALLOYS THE SCRATCH TEST

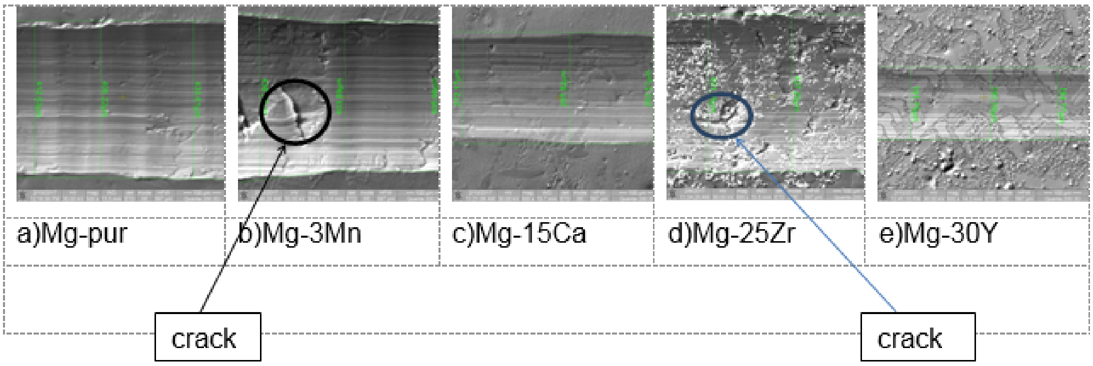


Fig.6(a,b,c,d,e); SEM images of traces produced after microscratch test with 500x magnitude

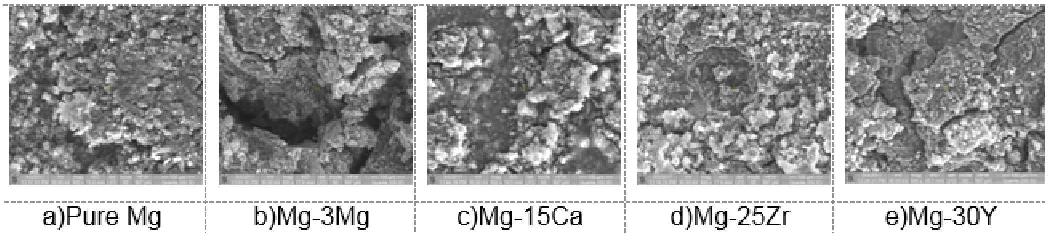


Fig.7(a,b,c,d,e); SEM images of surface morphology after immersion in Ringer's solution

The hardness is inversely proportional to the trace size left by the tribometer penetrator. Thus, at the highest value, 79.18HV the width of the trace is 191.75µm, and the lowest hardness, 17.1HV, the width of the trace is 433.6mm.

Corrosion analysis

For corrosion resistance, the linear voltammetry test was used and the curves obtained from the test are shown in figure 9. It is noted that the best corrosion resistance is alloy Mg-3Mn, and the lowest resistance value is Mg-15Ca.In the figures below we can see surface morphology after corrosion tests.

Electrochemical corrosion studies and corroded surface characterization were performed with a PGZ 301 device (VoltaLab 40) (Radiometer Analytical SAS - France). This is a dynamic performance system that ensures multiple results and easy to use.The device, together with the VoltaMaster 4. operating system, allows the evaluation of polarization resistance, long-term corrosion potential, torque potential and corrosion detection tests in points. Under these conditions, the device is ideal for electrochemical corrosion studies. In addition to this, it is also possible to obtain Electrochemical Impedance Spectroscopy (EIS) data. For measurements, a three-electrode cell having a useful volume of 100 mL was used. As a reference, a saturated calolome electrode was used, and a platinum electrode was used as an auxiliary electrode (measuring electrode).Work electrodes made of the studied materials were assembled by the measuring cell after they were sanded on SiC paper with 500 grains; 1000; 1500; 2000 and 4000 grains, degreased in ethyl alcohol and acetone, then washed with distilled water.

Theused cell allowed for all samples to provide the same surface as that one exposed to contact with the electrolyte used: S = 0.283 cm^2.Corrosion of alloys was studied in Ringer's solution, having the composition: NaCl-9.0; KCl, 0.43; $CaCl_2$-0.25; $NaHCO_3$-0.20 g / L. In order to assess the corrosion potential, the linear polarization method was used, with the current-potential curves in the potential range (PCD - 200 mV) - (PCD + 300 mV), with a potential scanning potential of 0.5 mV / s . The open circuit potential (PCD) was previously determined by measuring directly with respect to the reference electrode and following its variation for 4 min until a constant value was reached.

In the present paper, sweeping the potential was made with the speed of 10 mV/s on the potential interval +1…+2…-1 V, at a temperature of 20 C degrees. In figures 8,9 we can see the cyclic polarizing curves for the Mg alloys analyzed in Ringer solution.

Table 4 shows the parameters of the corrosion process evaluated based on these data.

Noteworthy is that only for the Mg-15Ca alloy the cyclic voltamogram branches are continuous curves, while for the other voltograms, the curves show a series of steps that seem to be passivation's and repeated activations of the process is corrosion. In fact, the discontinuous aspect of these curves may be due to the evolution of gas following the corrosion process; The gas bubbles partially accelerate the surface of the alloy and this returns to the initial value after bubble release.

Conclusions

Biodegradable alloys successfully replace classical alloys of Co-Cr stainless steel and Ti alloys.Regarding microstructural perspective, specific types of Mg hexagonal compounds and the analysis of cubic Mg24Y5 were emphasized.Regarding mechanical perspectiv, the alloys analysed have values close to the bone elasticity module. The hardness of the alloys lies between 17.1 HV for pure Mg and 79.18 HV for Mg-30Y. Regarding electrochimical tests,there were noted the corrosion speeds of 4 alloys, the most reduced corrosion speed being

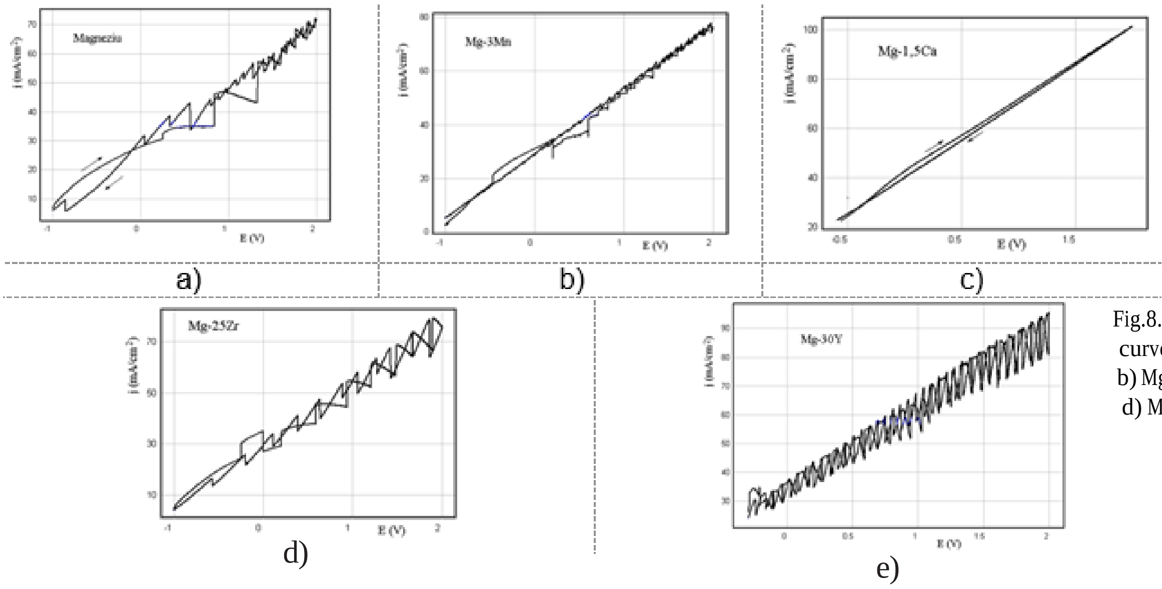


Fig.8. Cyclic polarizing curves of:a) pure Mg, b) Mg-3Mn,c)Mg-15Ca, d) Mg-25Zr,e) Mg-30Y

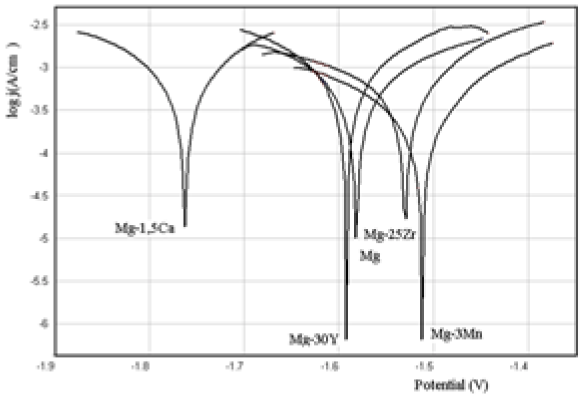


Fig. 9. Tafel curves for the five alloys studied in the Ringer solution

Table 4
DATA REGARDING Mg ALLOYS CORROSION IN RINGER SOLUTION

Alloys	Pure Mg	Mg-15Ca	Mg-3Mn	Mg-25Zr	Mg-30Y
OCP, mV	-1602	-1777	-1548	-1582	-1604
E(j=0), mV	-1581	-1762	-1512	-1530	-1592
R_p, ohm.cm^2	51.9	38.9	111.2	54.0	37.8
j, mAcm^{-1}	0.690	0.532	0.207	0.525	0.695
v, mm/an	8.07	6.22	2.43	6.14	8.13
E(i=0, mV (M.S.)	-1582	-1762	-1512	-1530	1592
R_p, ohm.cm^2 (M.S)	52.0	38.7	110.5	52.2	37.8

for the Mg-3Mn, as it has the lowest alloying level and the most accelerated speed being for Mg-15Ca. For these pre-alloys there can be emphasized that these alloys are suitable for medical implants. The alloying process should be moderate regarding concentration ratios.

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