Politechnika Śląska

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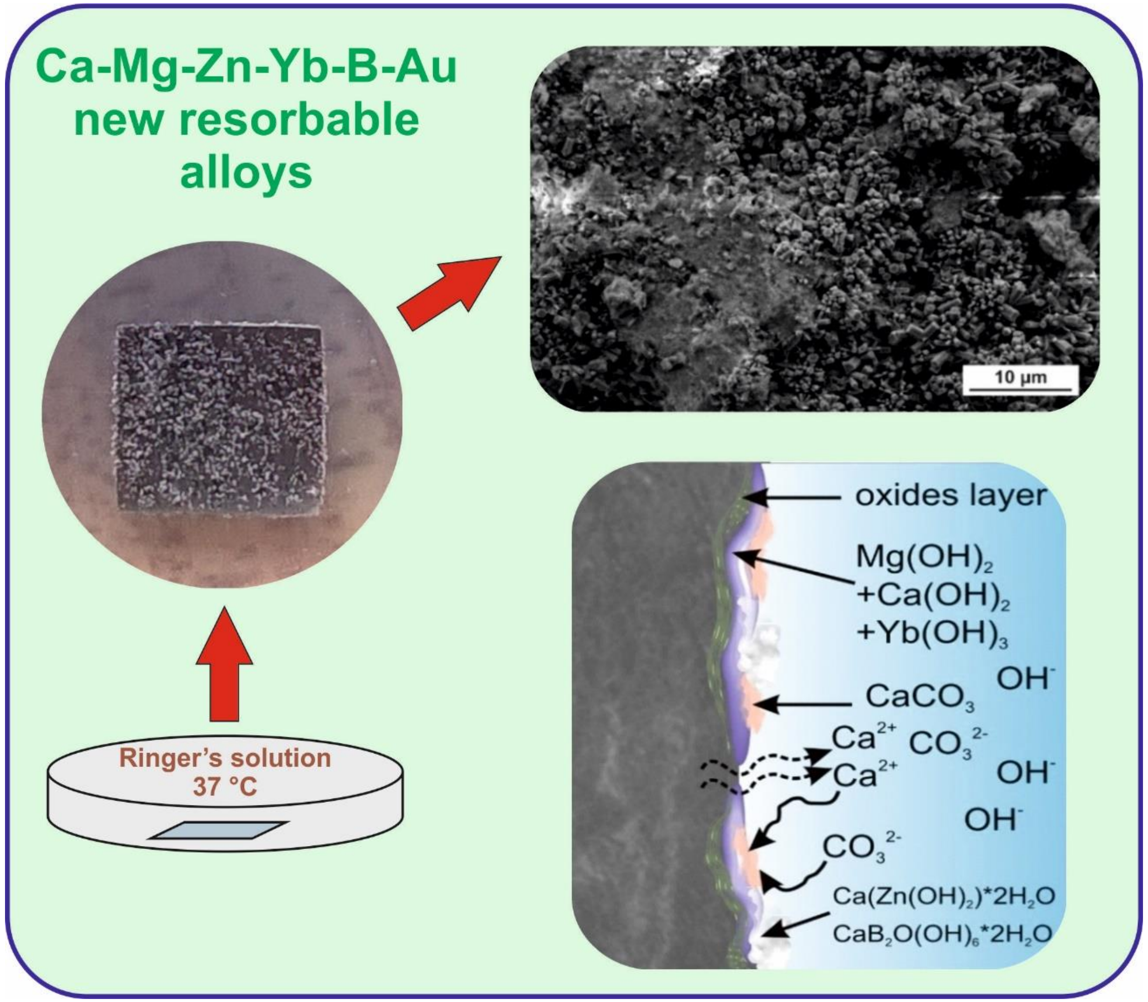
Structural and corrosion behavior characterization of bioresorbable Ca-Mg-Zn-Yb-B-Au alloys

Rafał Babilas

Gliwice, 30.06.2022

Ca-Mg-Zn alloys are expected as promising engineering materials. They can be used as resorbable materials in medicine.



The problem of Ca-Mg-Zn alloys is high rate of dissolution and low corrosoion resistance in aqueous solutions!

The **proposed methods** to reduce the **corrosion activity of calcium alloys Ca-Mg-Zn** is achieve of:

- **the homogeneous amorphous structure,**
- **modification of the chemical composition** by alloying additions such as **noble metals** (e.g. Au), **rare earth elements** (e.g. Yb) and **metalloids** (e.g. B).

Task: Limit of hydrogen evolution for Ca-based alloys in aqueous solutions

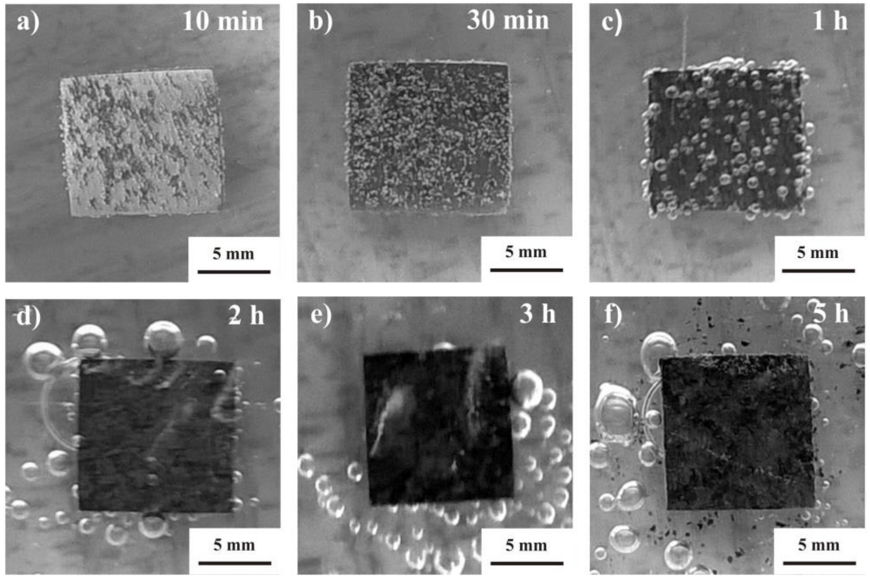
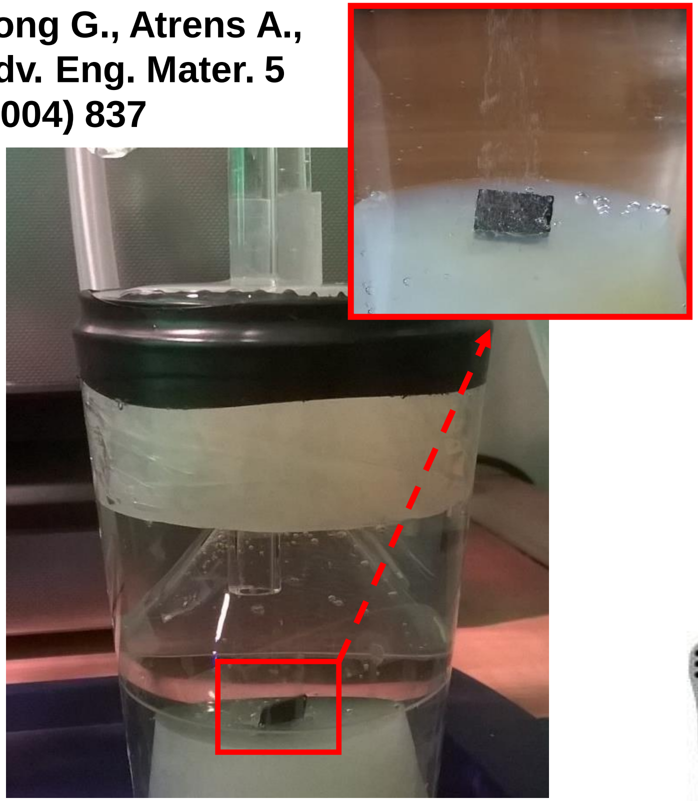


Fig. Changes of surface morphology and hydrogen evaluation of $Ca_{60}Mg_{15}Zn_{25}$ glassy plates versus immersion time in Ringer's solution at 37°C

Song G., Atrens A., Adv. Eng. Mater. 5 (2004) 837



$$Ca + 2H_2O \rightarrow Ca(OH)_2 \downarrow + H_2 \uparrow$$

Possible?

Ca-based implants

How to limit the corrosion activity of Ca-Mg-Zn alloys?

Au addition?

Gold is known as the most inert of metals with immunity to corrosion. Often used for dental items.

Materials Chemistry and Physics 226 (2019) 51–58

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

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Effect of Au addition on the corrosion activity of Ca-Mg-Zn bulk metallic glasses in Ringer's solution

Check for updates

Rafał Babilas[a,*], Anna Bajorek[b], Patryk Włodarczyk[c], Wojciech Łoński[a], Dawid Szyba[a], Dorota Babilas[d]

XRD results and volume of H_2 evolution in Ringer's solution

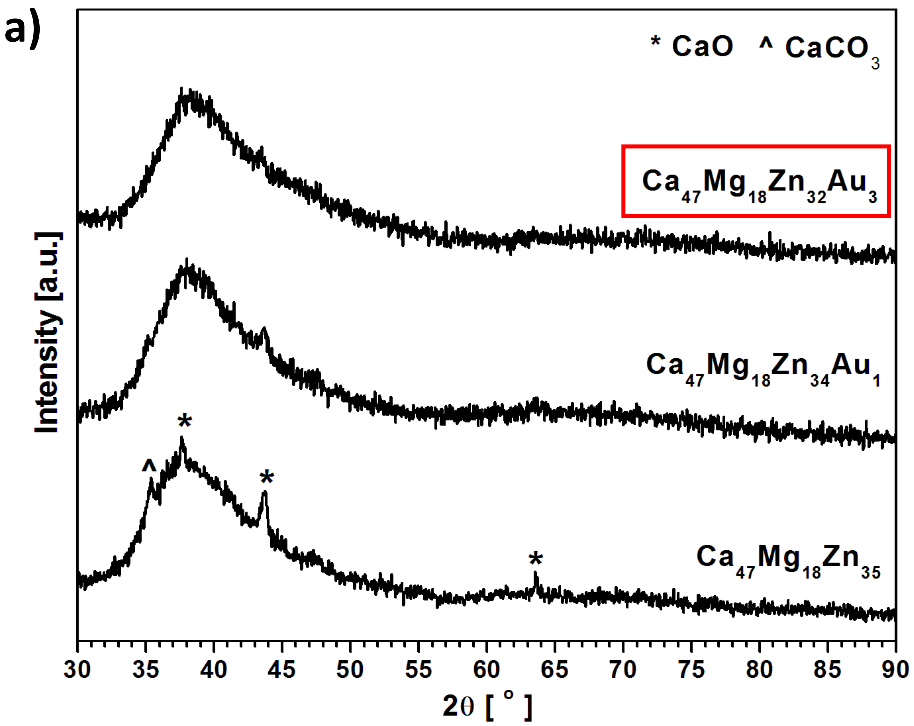


Fig. XRD patterns of $Ca_{47}Mg_{18}Zn_{35-x}Au_x$ (x=0,1,3 at.%) alloys in a form of plates

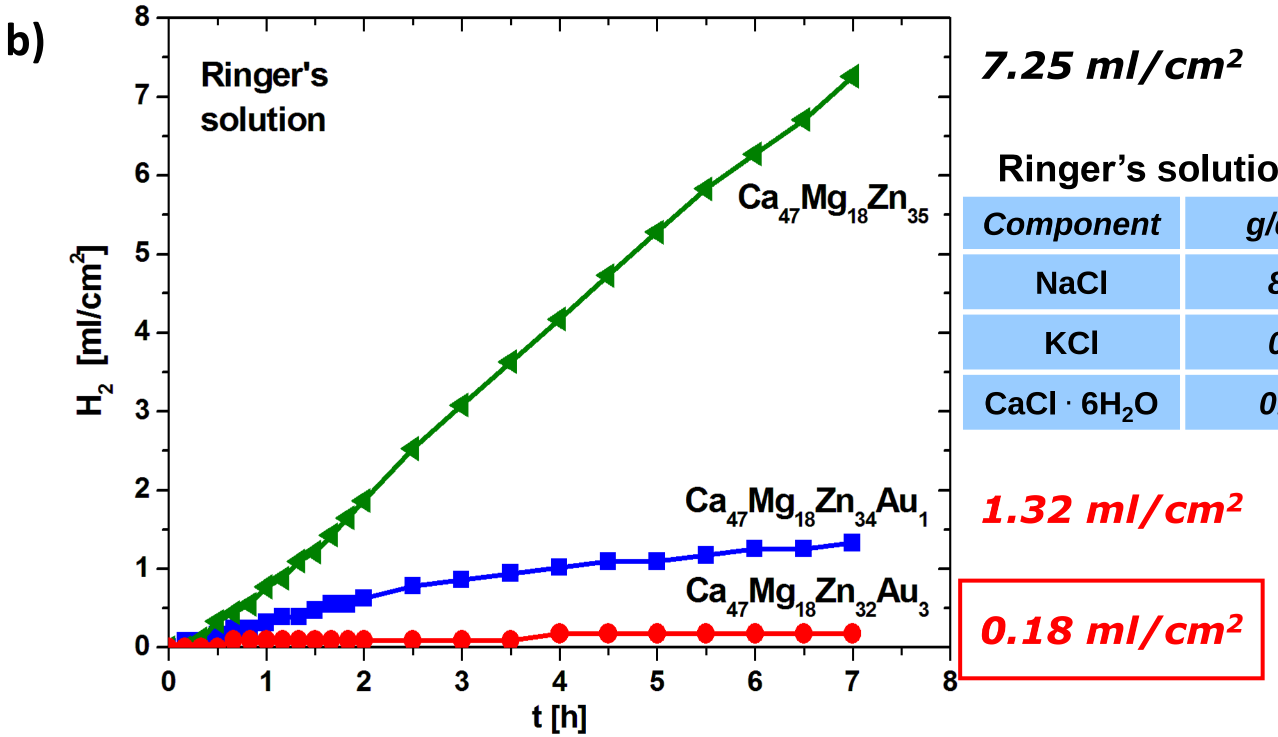


Fig. Hydrogen evolution volume as a function of time during tests in Ringer's solution at temperature of 37°C

Ringer's solution

Component	*g/dm³*
NaCl	*8.6*
KCl	*0.3*
$CaCl \cdot 6H_2O$	*0.48*

~1 ml/cm² per hour - this amount is permitted for rats with a weight of 240 g (https://doi.org/10.1152/jappl.1962.17.2.268)

Electrochemical results in Ringer's solution

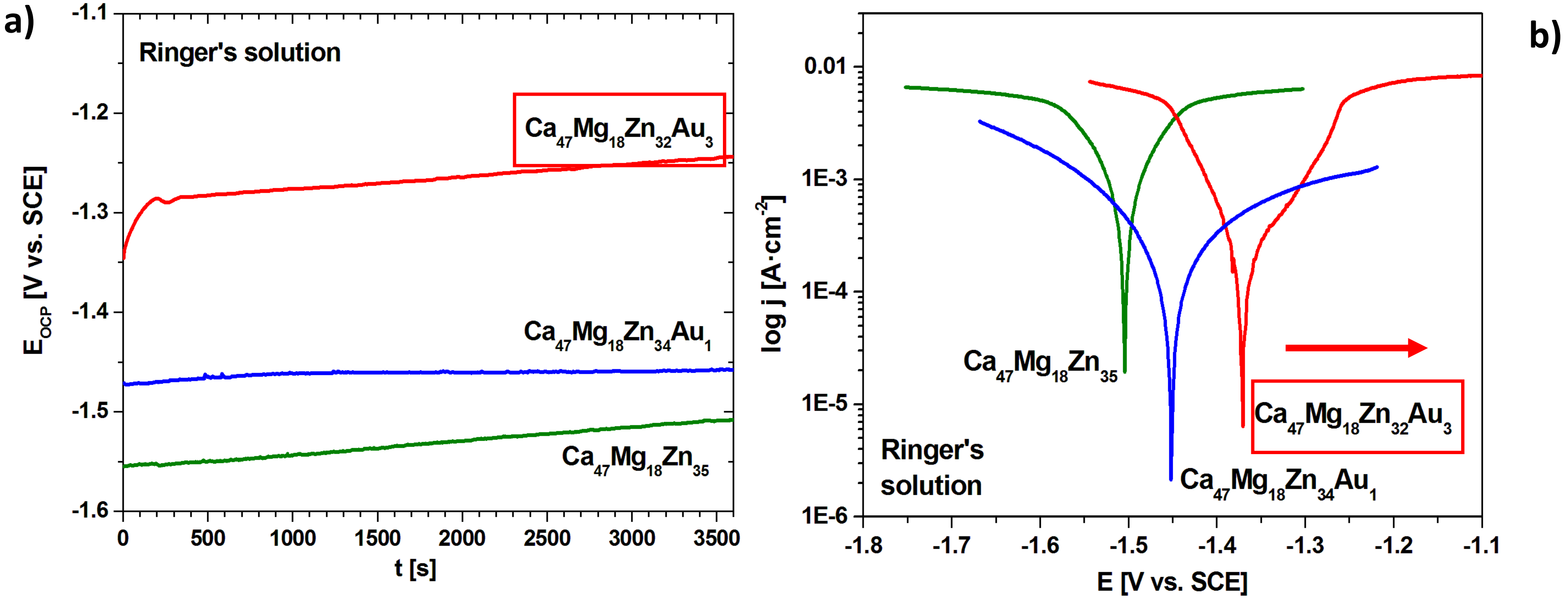
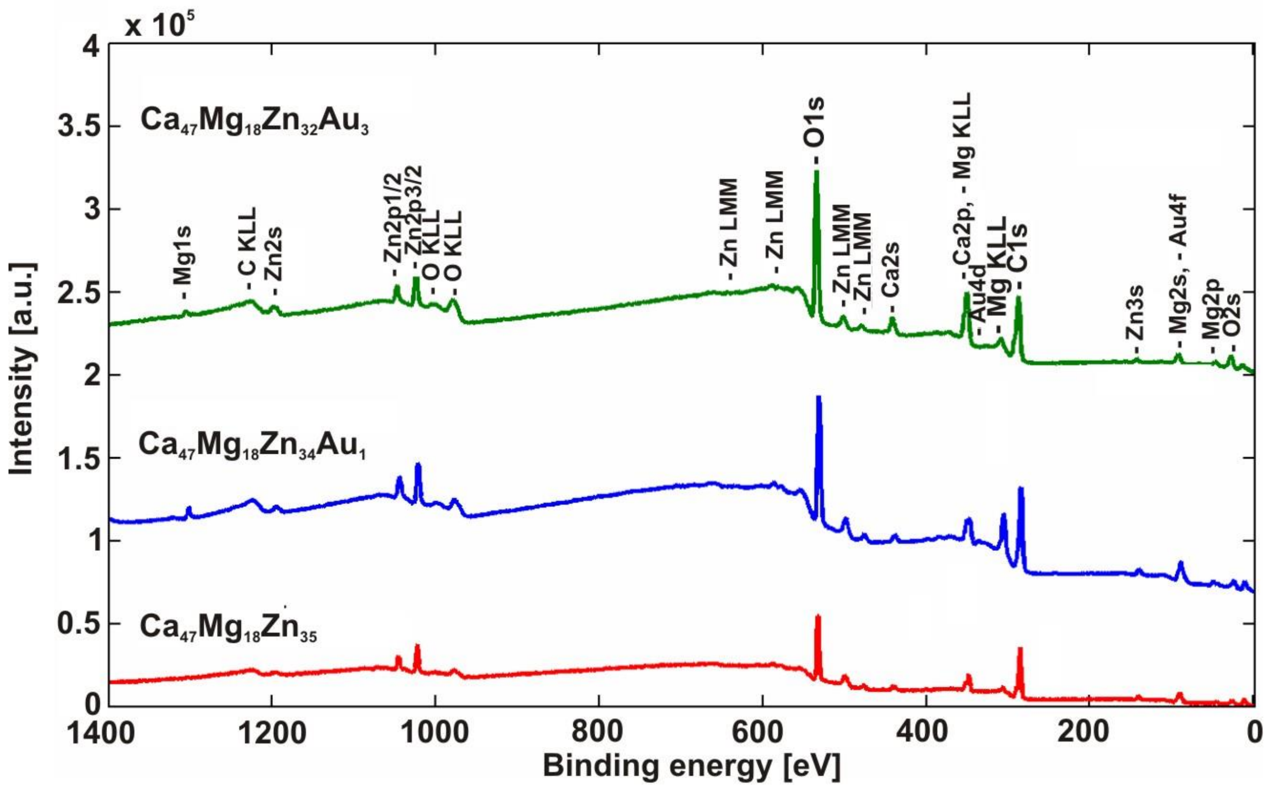


Fig. Changes of open circuit potential in a function of time (a) and polarisation curves (b) of $Ca_{47}Mg_{18}Zn_{35-x}Au_x$ (x=0,1,3) alloy in Ringer's solution at temperature of 37°C

XPS spectroscopy – survey spectra after electrochemical measurements



Oxides

Hydroxides

Carbonates

Fig. XPS survey spectra for the surface of $Ca_{47}Mg_{18}Zn_{35}$, $Ca_{47}Mg_{18}Zn_{34}Au_{1}$ and $Ca_{47}Mg_{18}Zn_{32}Au_{3}$ after corrosion in Ringer's solution

Analysis of corrosion products after 7 h of immersion in Ringer's solution

a) b)

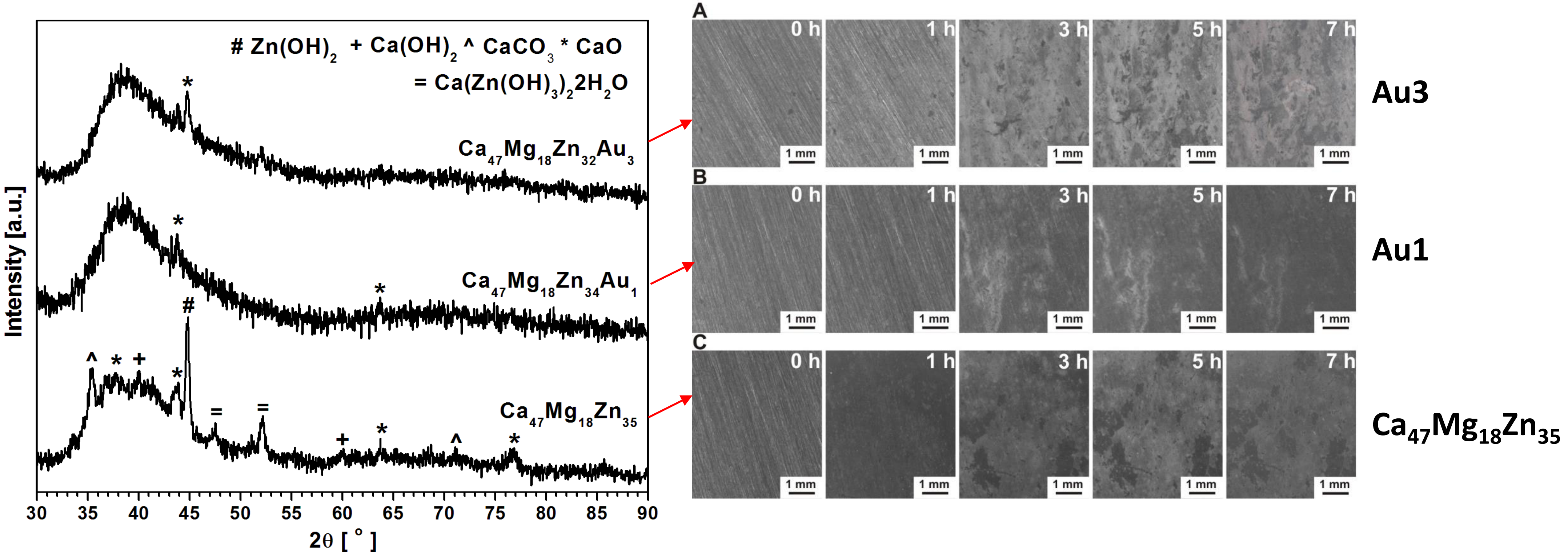


Fig. XRD patterns after 7 h of immersion (a) and changes of surface morphology of samples (b) after tests in Ringer's solution at 37°C

What about Yb addition in Ca-Mg-Zn alloys?

Ytterbium is the REE element, which has unlimited solubility in calcium and has been found to be effective in improving corrosion resistance.

Journal of Non-Crystalline Solids 488 (2018) 69–78

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Corrosion resistance of resorbable Ca-Mg-Zn-Yb metallic glasses in Ringer's solution

Rafał Babilas[a,*], Anna Bajorek[b], Piotr Sakiewicz[a], Aneta Kania[a], Dawid Szyba[a]

XRD patterns and electrochemical tests

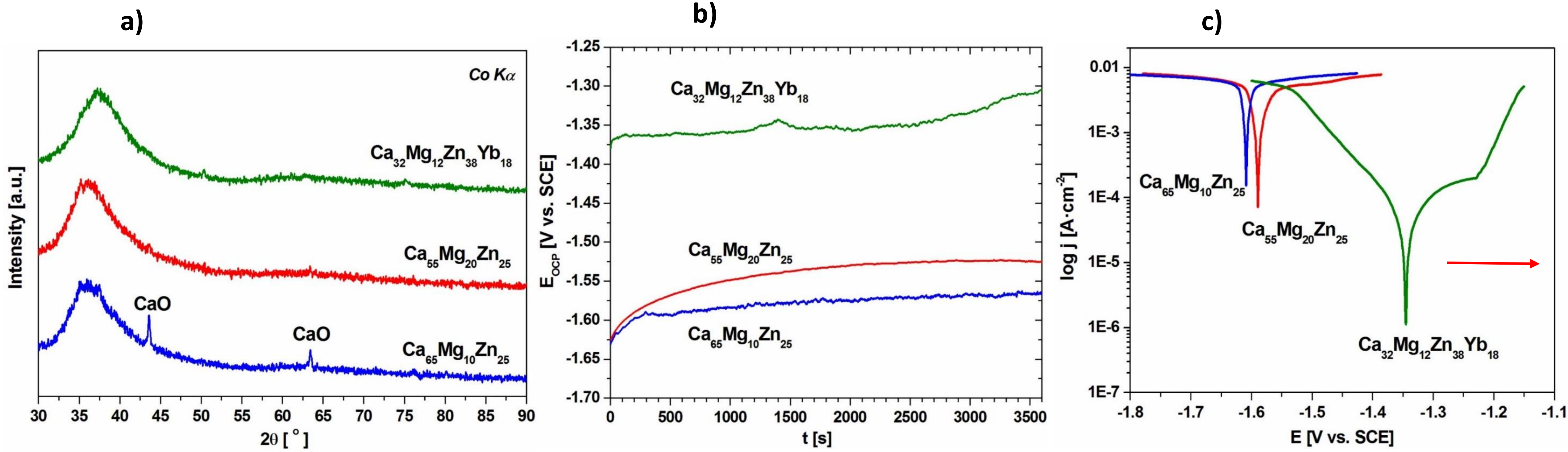
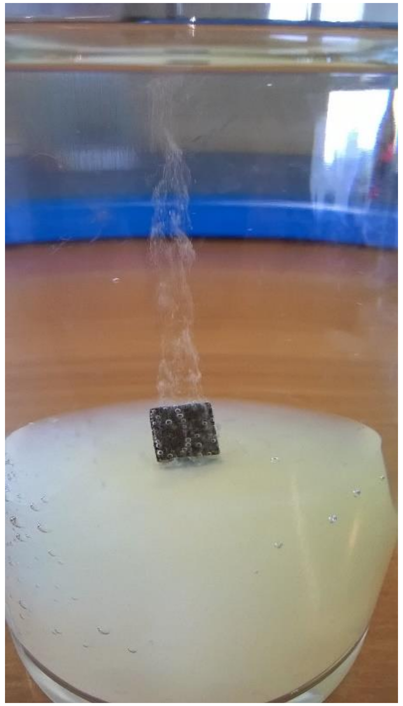
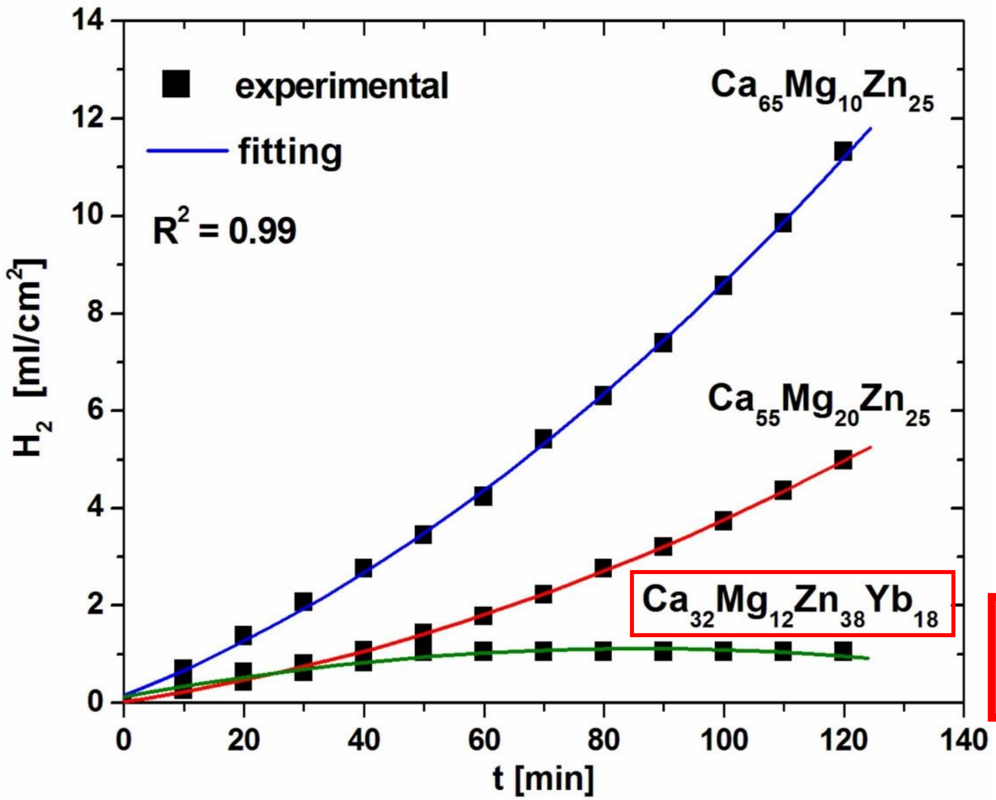


Fig. XRD patterns (a) changes of open circuit potential (b) and polarisation curves (c) for $Ca_{65}Mg_{10}Zn_{25}$, $Ca_{55}Mg_{20}Zn_{25}$ and $Ca_{32}Mg_{12}Zn_{38}Yb_{18}$ alloys in Ringer's solution at 37°C

Hydrogen evolution in a function of time in Ringer’s solution





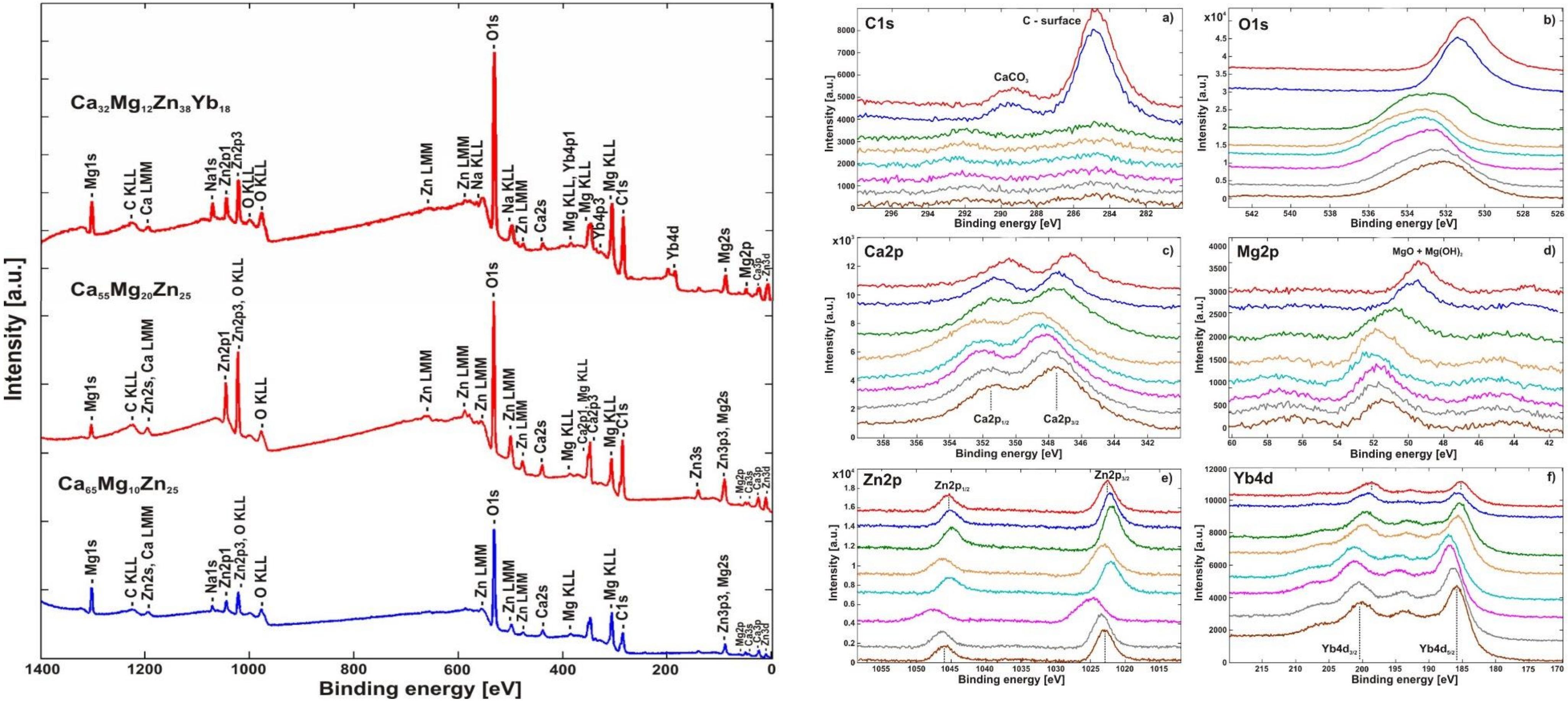
11.32 ml/cm²

4.98 ml/cm²

1.05 ml/cm²

Fig. Hydrogen evolution volume in a function of time in Ringer’s solution at 37°C

XPS spectroscopy – survey and core level spectra



Rys. XPS survey and core level spectra of C1s, O1s, Ca2p, Mg2p, Zn2p and Yb4d for $Ca_{65}Mg_{10}Zn_{25}$, $Ca_{55}Mg_{20}Zn_{25}$ and $Ca_{32}Mg_{12}Zn_{38}Yb_{18}$ alloys after corrosion tests in Ringer's solution at 37°C

Corrosion products analysis after 5 h of immersion in Ringer’s solution

a) b)

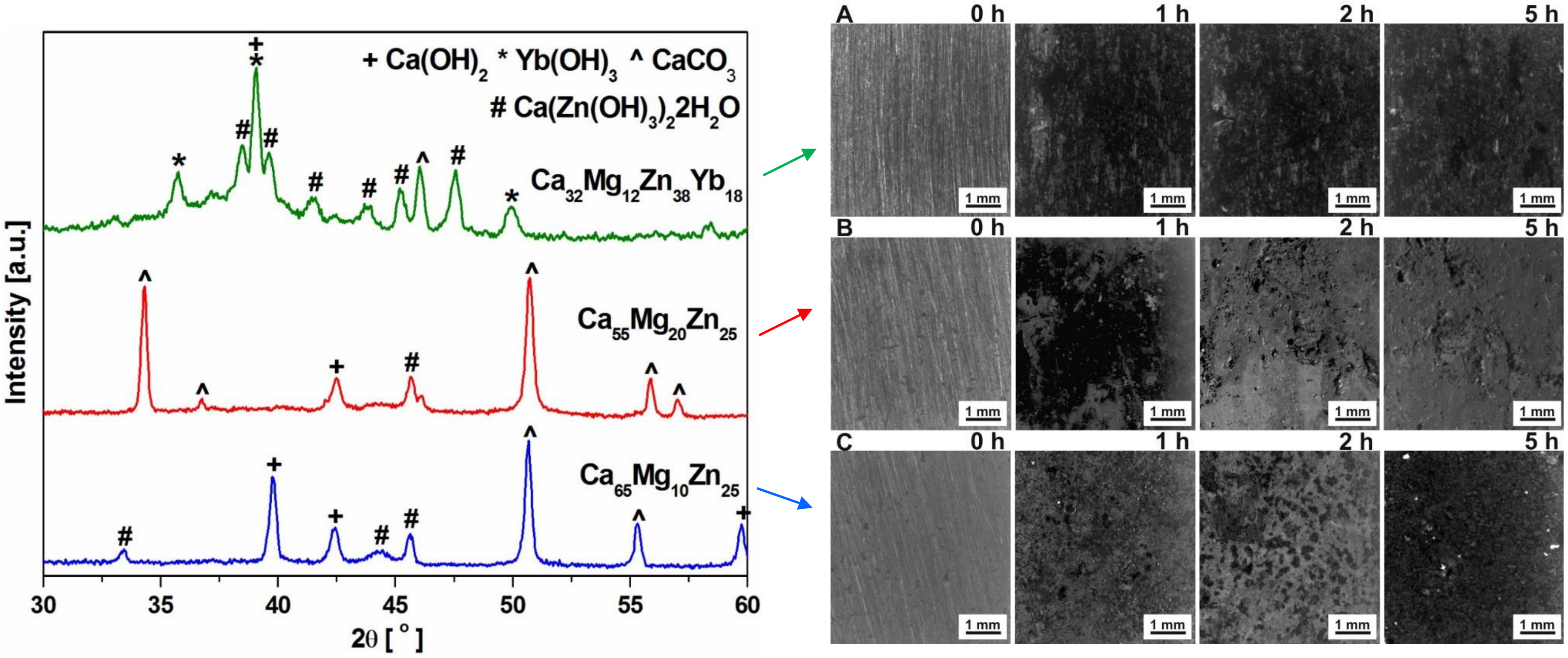


Fig. XRD patterns after 5 h of immersion (a) and changes of surface morphology of samples (b) after tests in Ringer’s solution

Boron addition?

Boron is a biocompatible element with a positive effect on the growth of bones and is required for the maintenance of human health.

Journal of Alloys and Compounds 815 (2020) 152313

Contents lists available at ScienceDirect

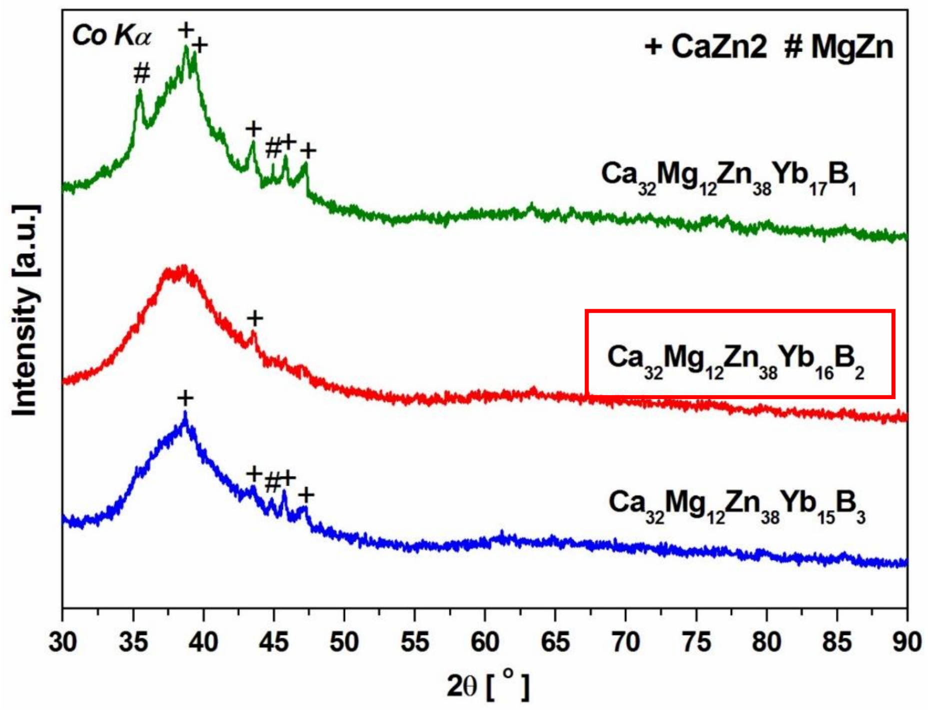
Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Structural and electrochemical study of resorbable $Ca_{32}Mg_{12}Zn_{38}Yb_{18-x}B_x$ (x=1, 2, 3) metallic glasses in Ringer's solution

Dawid Szyba [a], Anna Bajorek [b], Rafał Babilas [a, *]

XRD patterns and HRTEM images



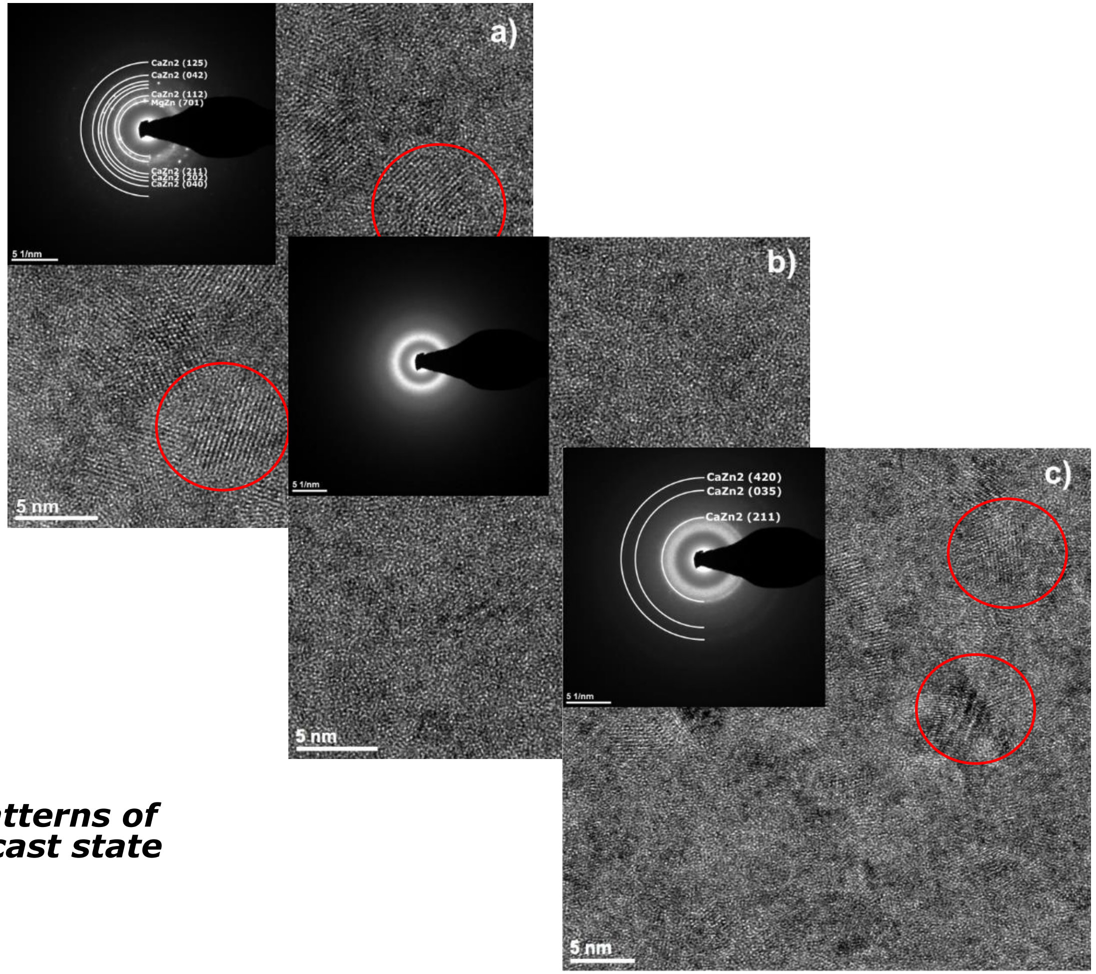


Fig. XRD patterns, HRTEM micrographs and SAED patterns of $Ca_{32}Mg_{12}Zn_{38}Yb_{18-x}B_x$ (x=1,2,3 at.%) samples in as-cast state

Electrochemical measurements in Ringer's solution

a) b)

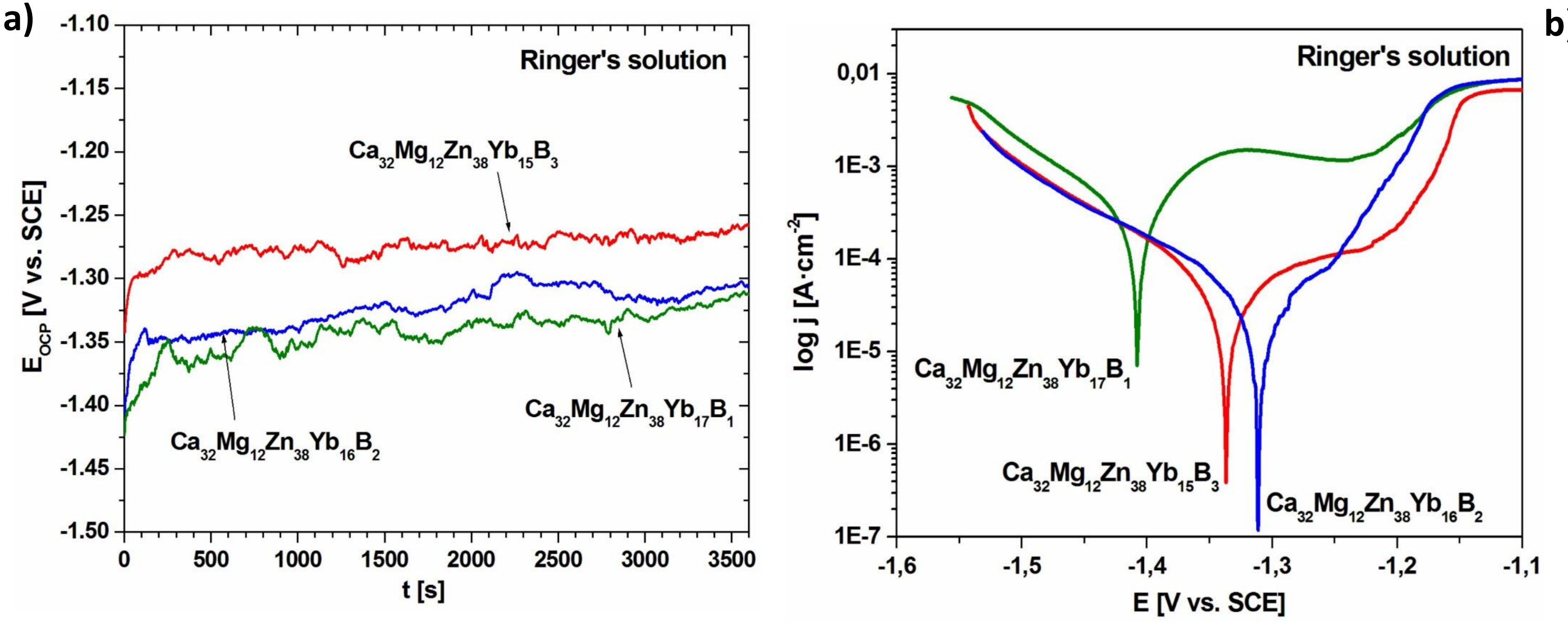
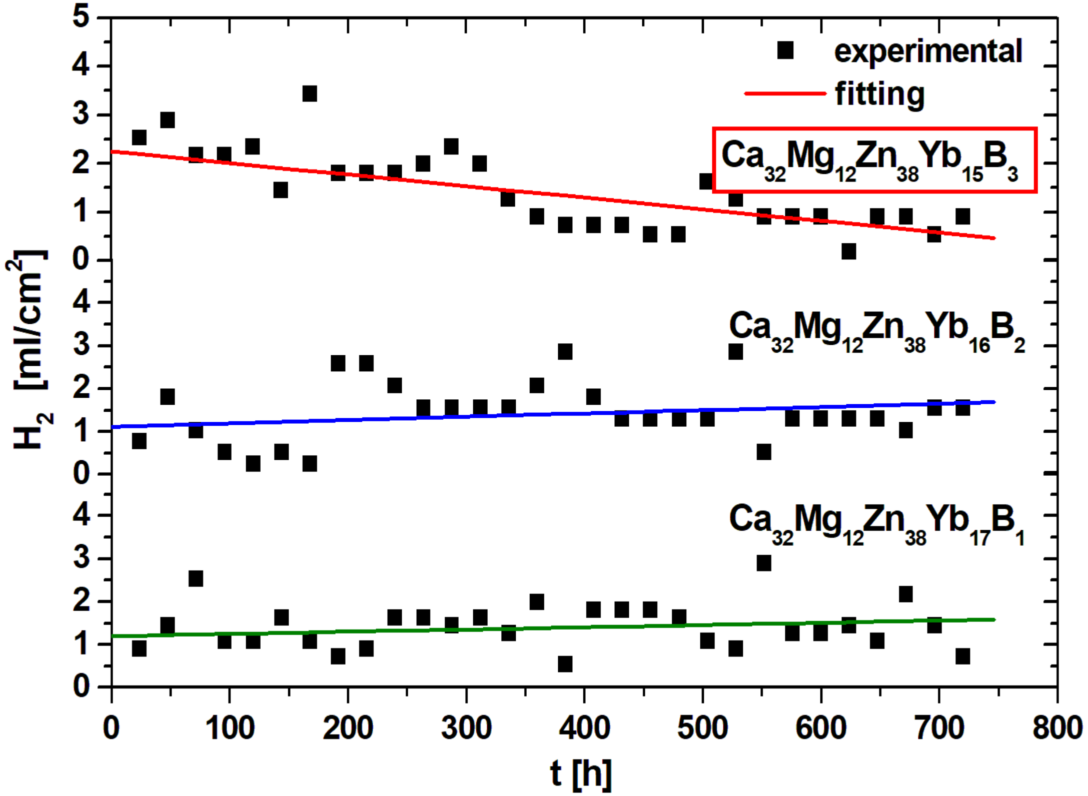


Fig. Changes of open circuit potential (a) and polarisation curves (b) of $Ca_{32}Mg_{12}Zn_{38}Yb_{18-x}B_x$ (x=1,2,3 at.%) alloys in Ringer's solution at temperature of 37°C

Hydrogen volume after 30 days of immersion in Ringer's solution



0.47 ml/cm²

1.69 ml/cm²

1.58 ml/cm²

Fig. Hydrogen evolution volume in a function of time during immersion in Ringer's solution at temperature of 37°C

B, Yb and Au addition together?

Materials & Design 213 (2022) 110327

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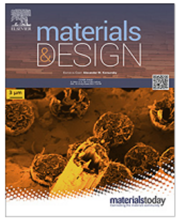


New resorbable Ca-Mg-Zn-Yb-B-Au alloys: Structural and corrosion resistance characterization

Check for updates

Dawid Szyba [a,*], Anna Bajorek [b], Dorota Babilas [c], László Temleitner [d], Dariusz Łukowiec [a], Rafał Babilas [a,*]

XRD results and DSC analysis

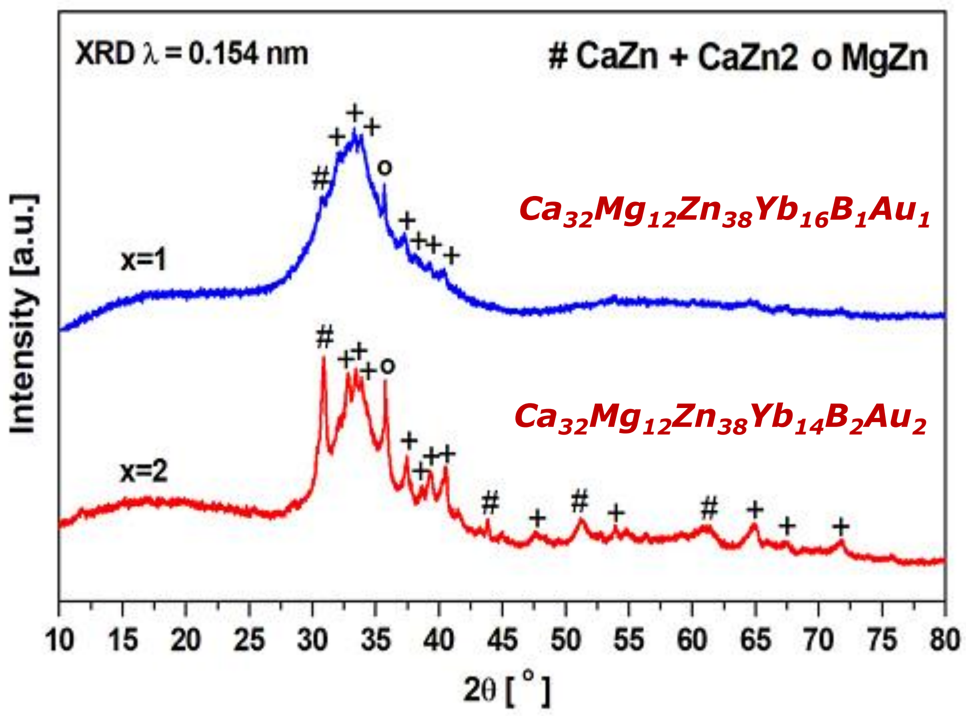


Fig. XRD patterns of $Ca_{32}Mg_{12}Zn_{38}Yb_{18-2x}B_xAu_x$ (x = 1, 2 at.%) alloys in a form of plate

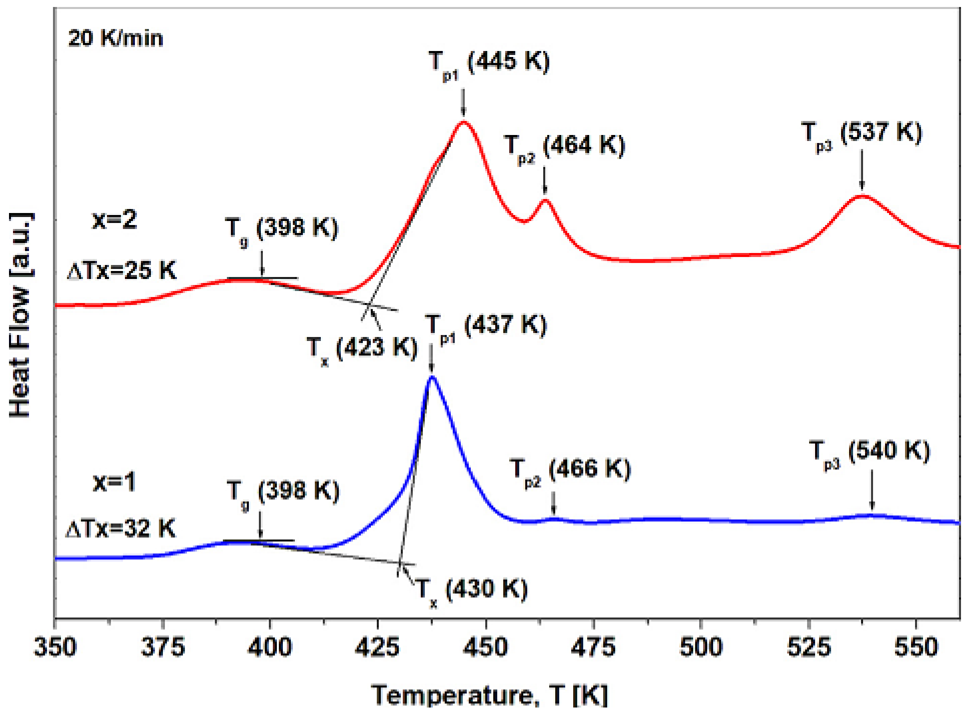
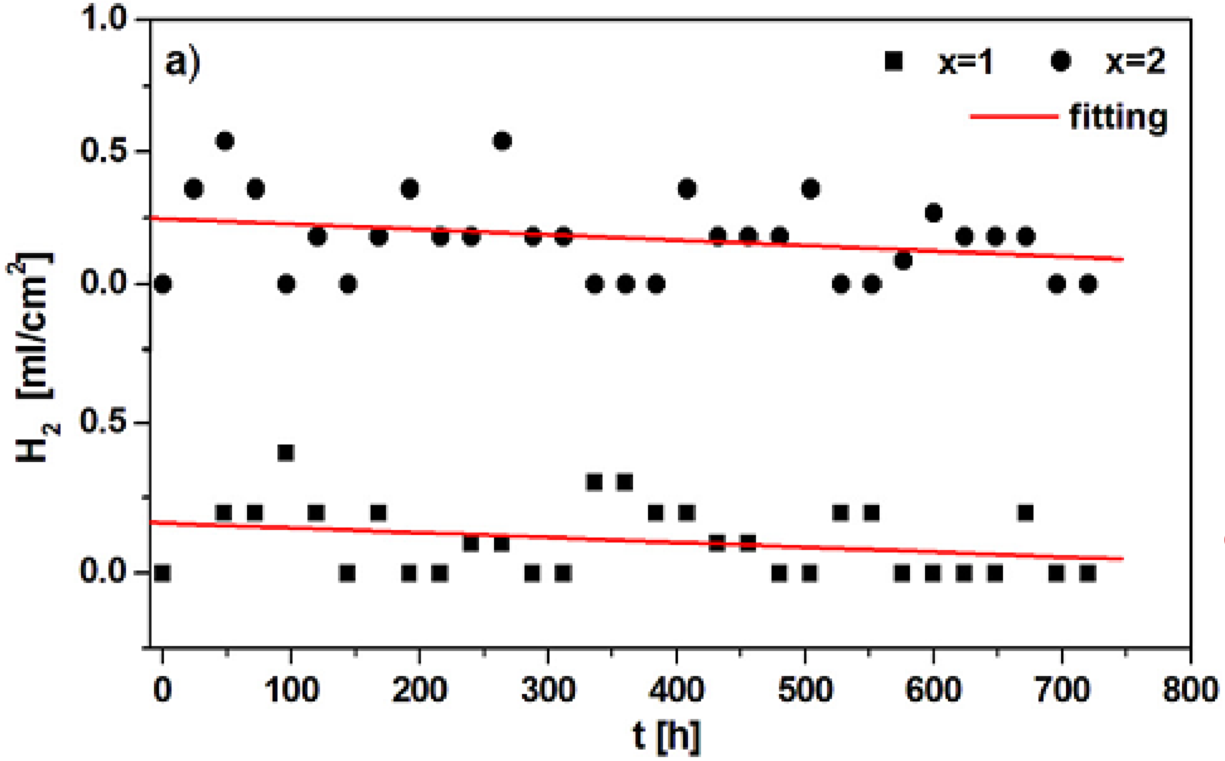


Fig. DSC curves of $Ca_{32}Mg_{12}Zn_{38}Yb_{18-2x}B_xAu_x$ (x = 1, 2 at.%) alloys in a form of plate

Evolution of hydrogen in Ringer's solution

30 days

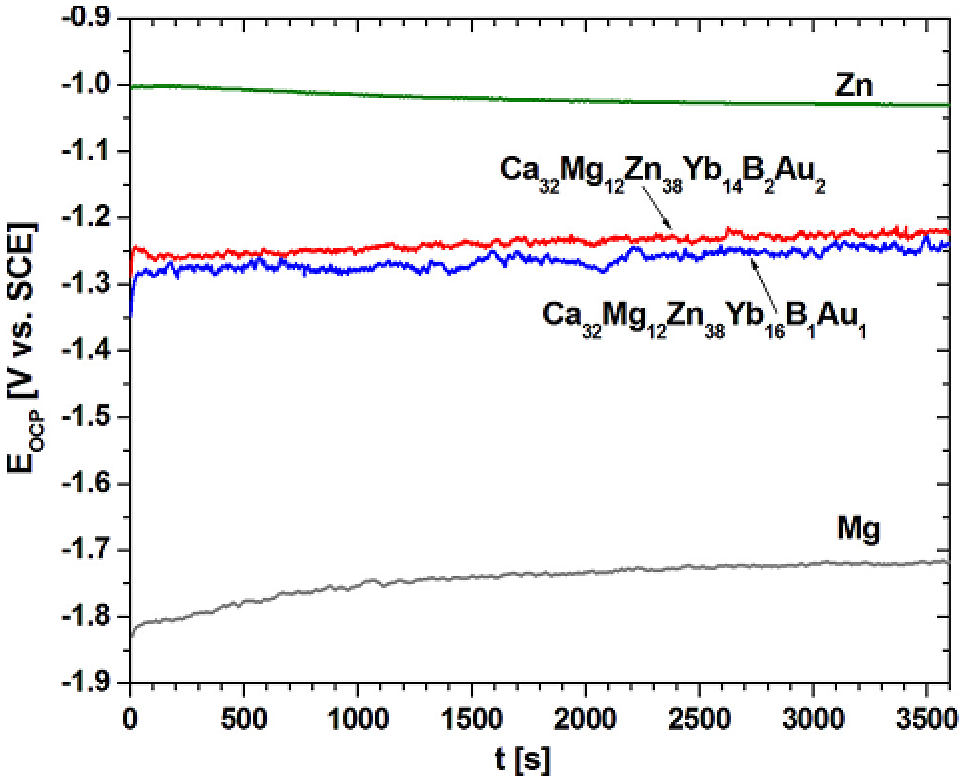


$Ca_{32}Mg_{12}Zn_{38}Yb_{16}B_1Au_1$

$Ca_{32}Mg_{12}Zn_{38}Yb_{14}B_2Au_2$

Fig. Hydrogen evolution volume over time for $Ca_{32}Mg_{12}Zn_{38}Yb_{18-2x}B_xAu_x$ (x=1, 2) plates in Ringer's solution at 37°C

Electrochemical measurements in Ringer's solution



Rys. E_{OCP} measurements for $Ca_{32}Mg_{12}Zn_{38}Yb_{18-2x}B_xAu_x$ (x=1, 2) plates compared with Mg and Zn

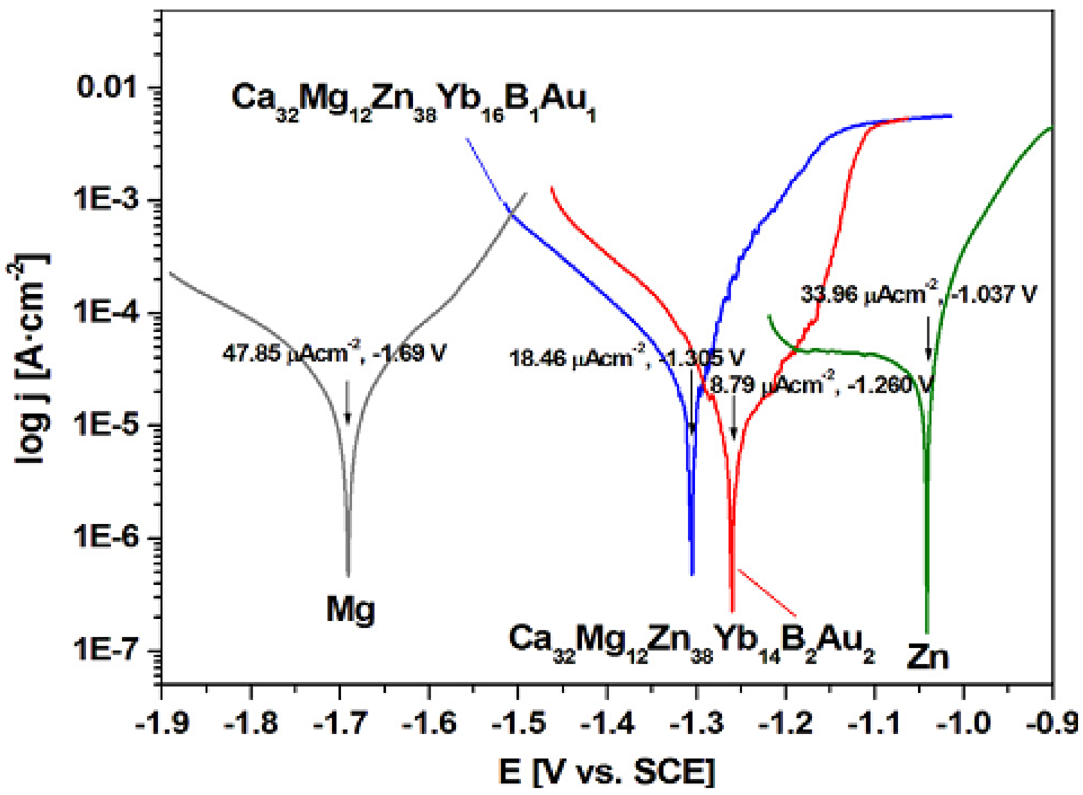


Fig. Tafel plots for $Ca_{32}Mg_{12}Zn_{38}Yb_{18-2x}B_xAu_x$ (x=1, 2) plates compared with Mg and Zn in Ringer's solution at 37°C

Analysis of corrosion products

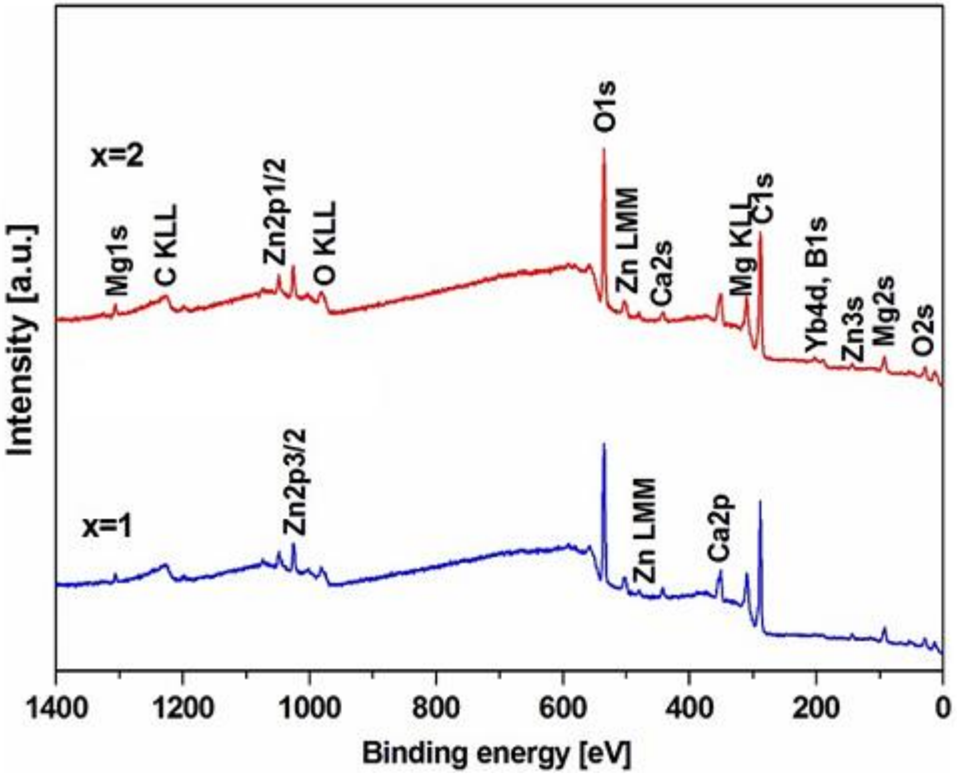


Fig. XPS survey spectra for $Ca_{32}Mg_{12}Zn_{38}Yb_{18-2x}B_xAu_x$ (x=1,2) plates after corrosion test in Ringer's solution at 37°C

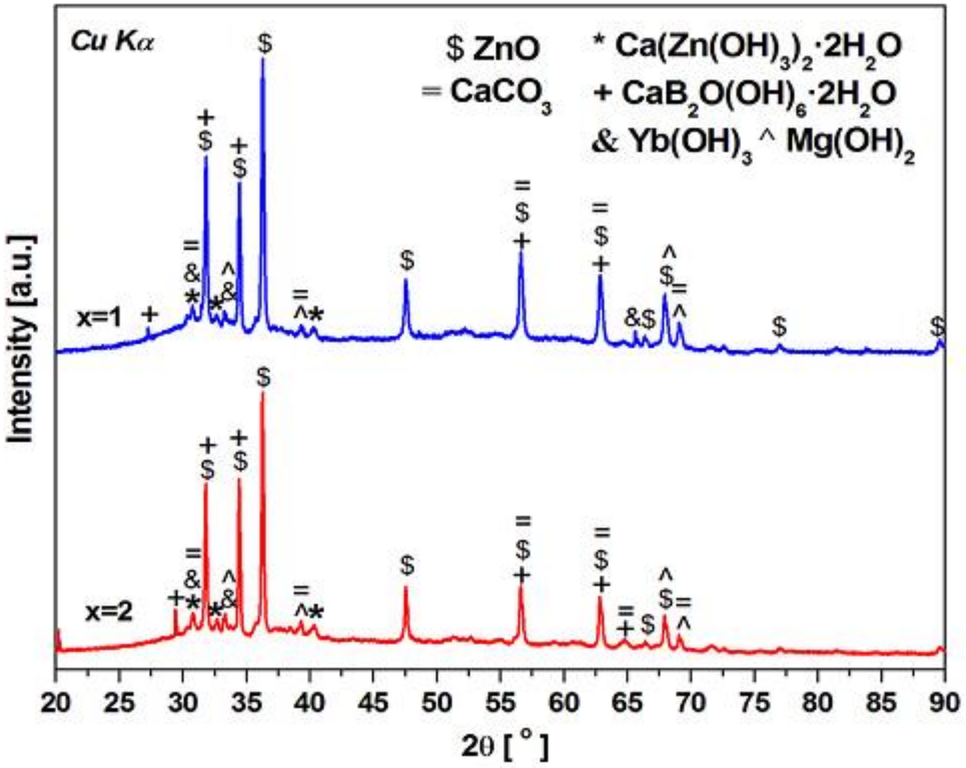


Fig. XRD patterns of corrosion products of $Ca_{32}Mg_{12}Zn_{38}Yb_{18-2x}B_xAu_x$ (x=1, 2) plates after immersion in Ringer's solution at 37°C over 30 days

Surface morphology of the plates after immersion in Ringer’s solution

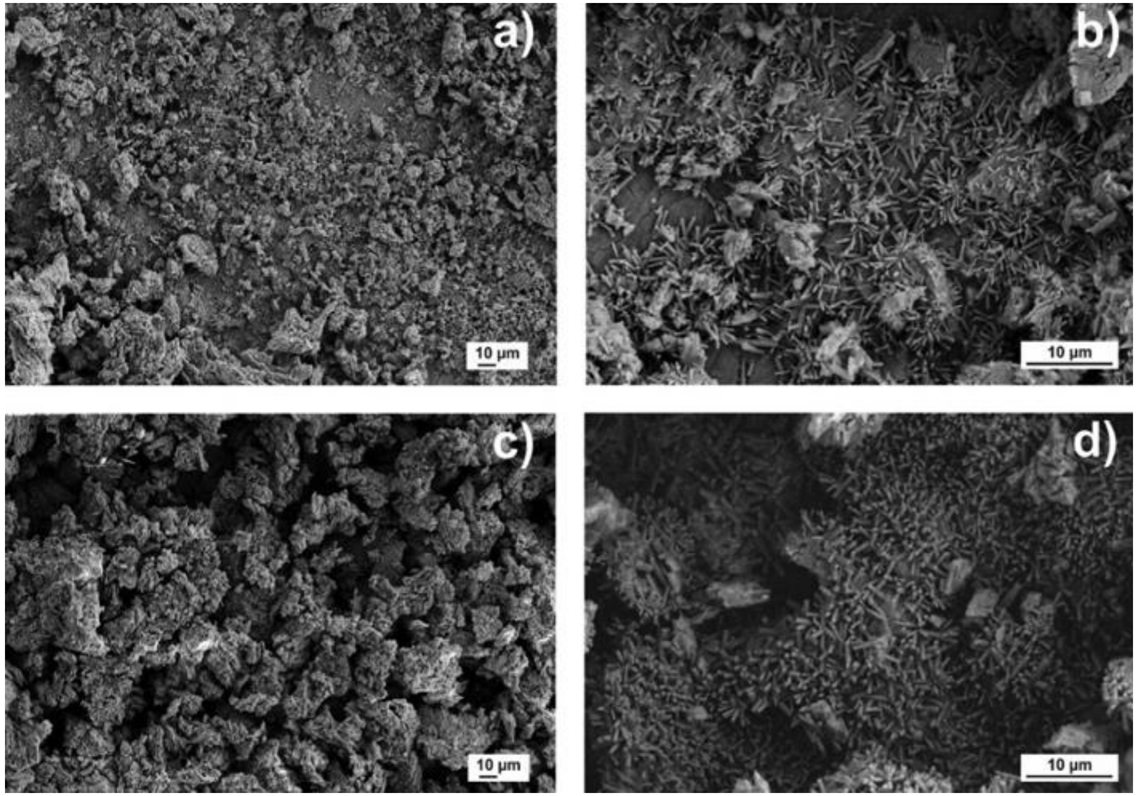


Fig. Surface morphology of $Ca_{32}Mg_{12}Zn_{38}Yb_{18-2x}B_xAu_x$, x=1 (a, b), x=2 (c, d) plates after immersion in Ringer’s solution at 37°C over 7 days

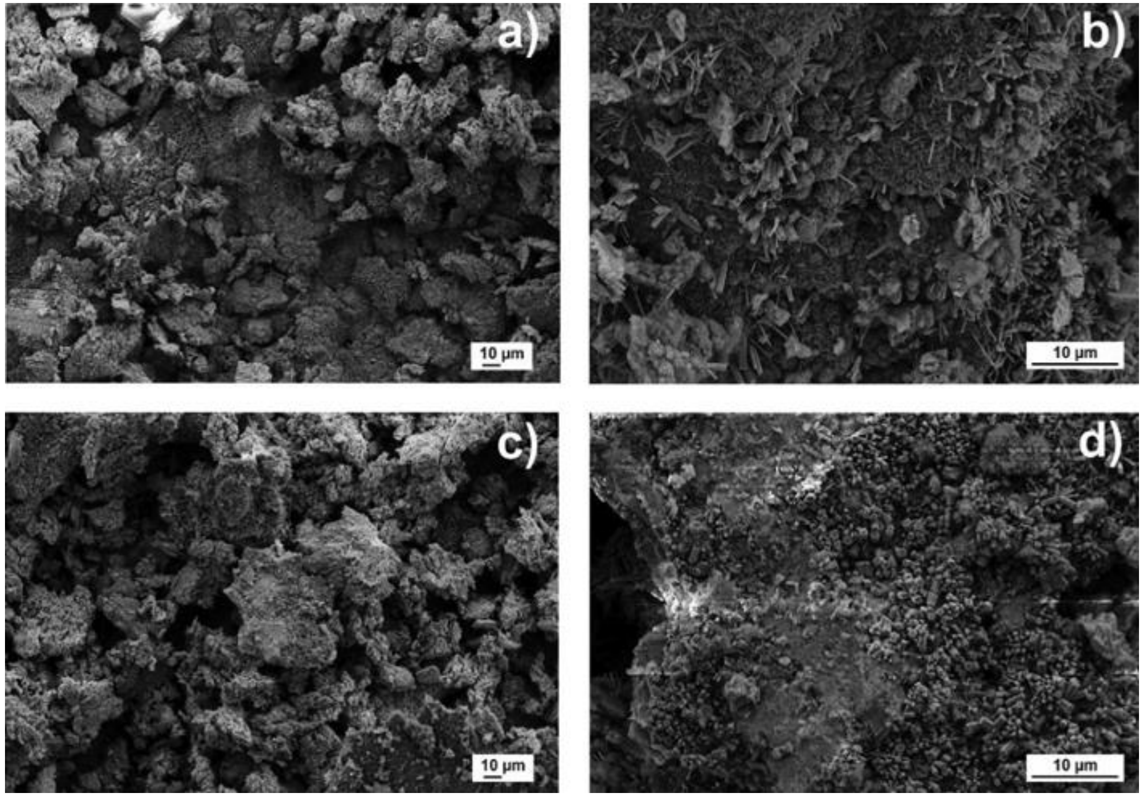
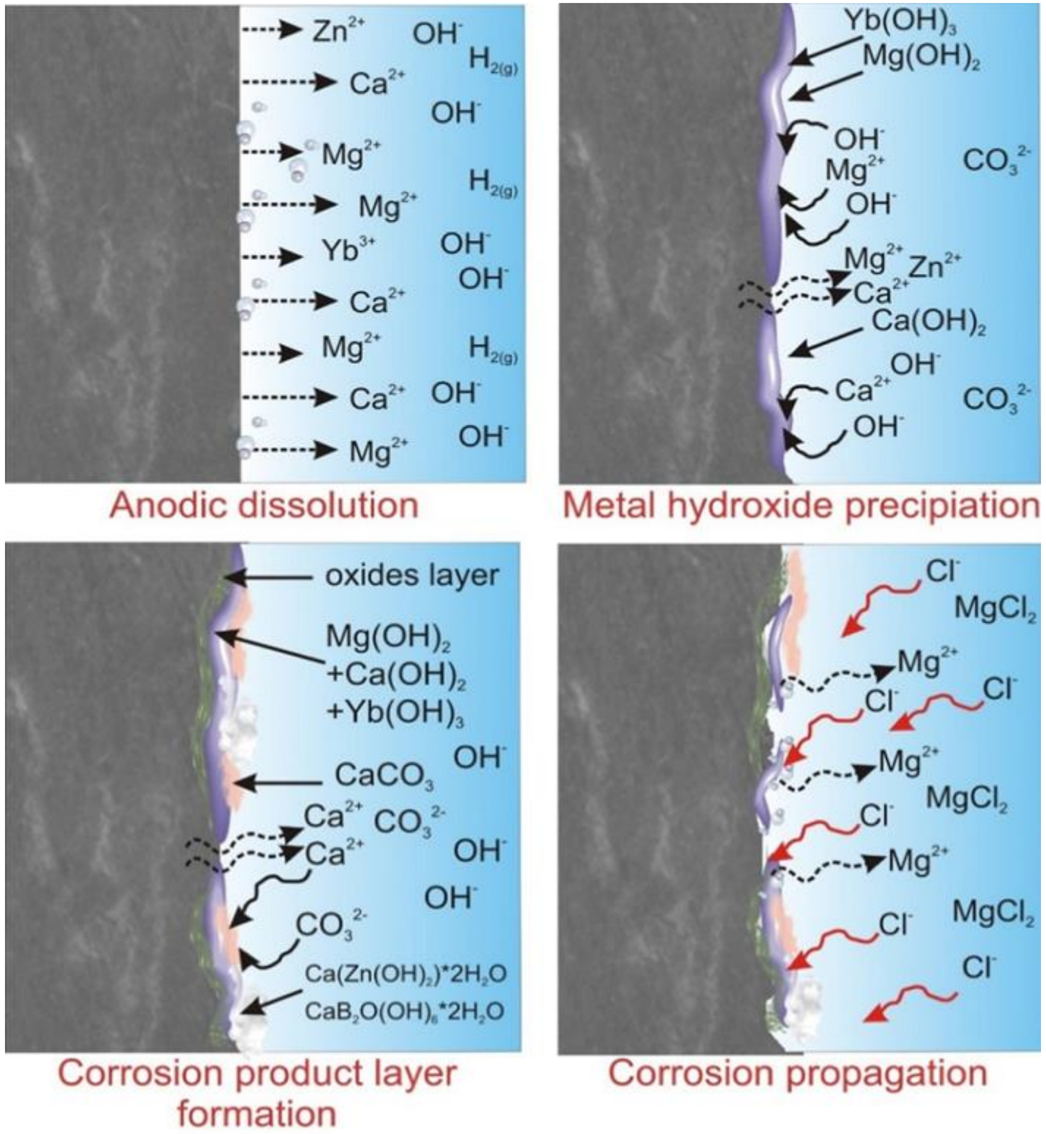


Fig. Surface morphology of $Ca_{32}Mg_{12}Zn_{38}Yb_{18-2x}B_xAu_x$, x=1 (a, b), x=2 (c, d) plates after immersion in Ringer’s solution at 37°C over 30 days

The corrosion mechanism of *Ca-Mg-Zn-Yb-B-Au alloys in Ringer's solution*



1. ***Anodic dissolution***
2. ***Hydroxide precipitation***
3. ***Corrosion product layer formation***
4. ***Corrosion propagation stage***

Schematic presentation of a corrosion mechanism of the Ca-Mg-Zn-Yb-B-Au alloys in Ringer's solution