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Biodegradable magnesium alloys for medical applications

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Plan of the speech

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2. Why these alloying elements?
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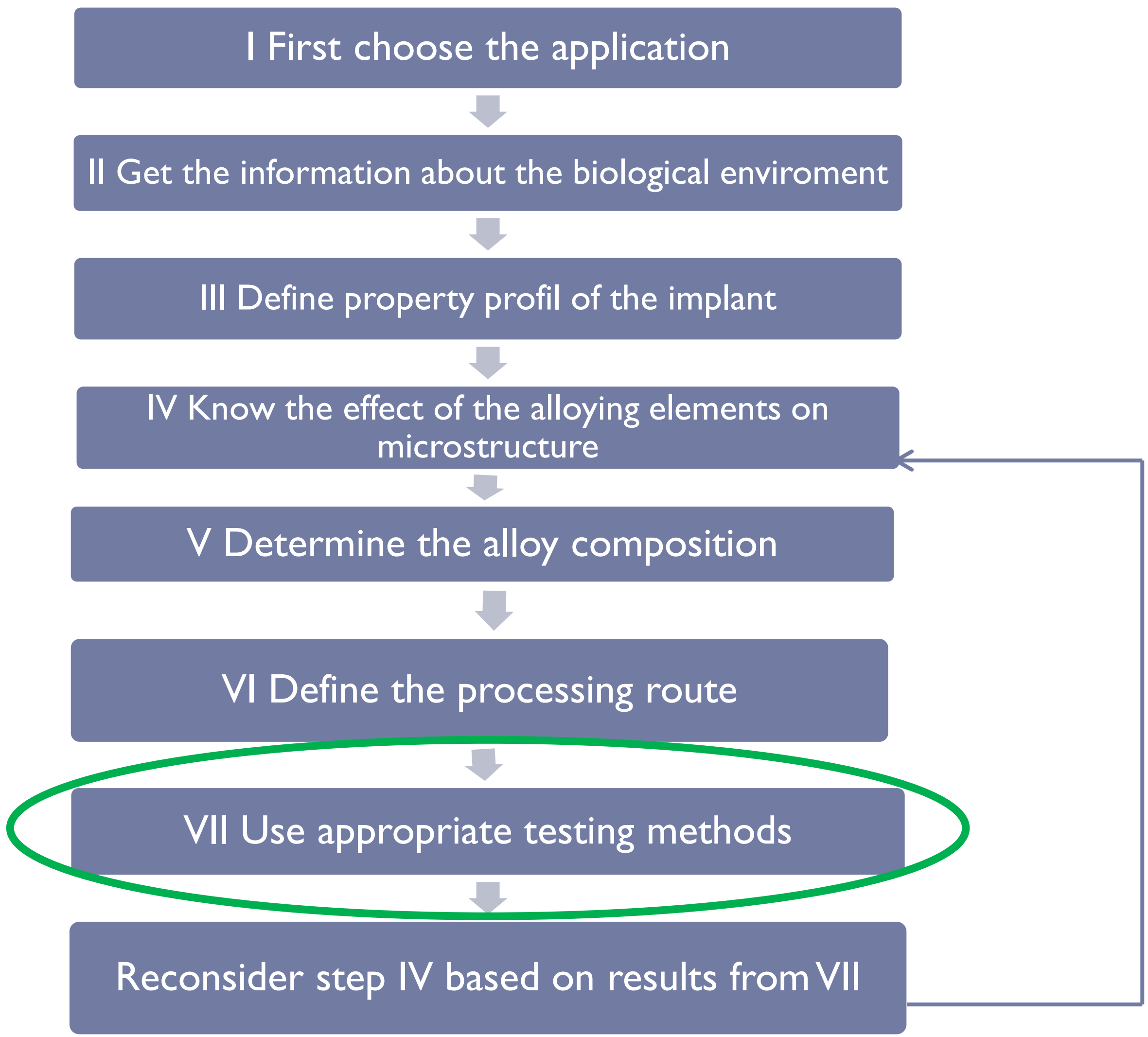
How to choose the right magnesium alloys?

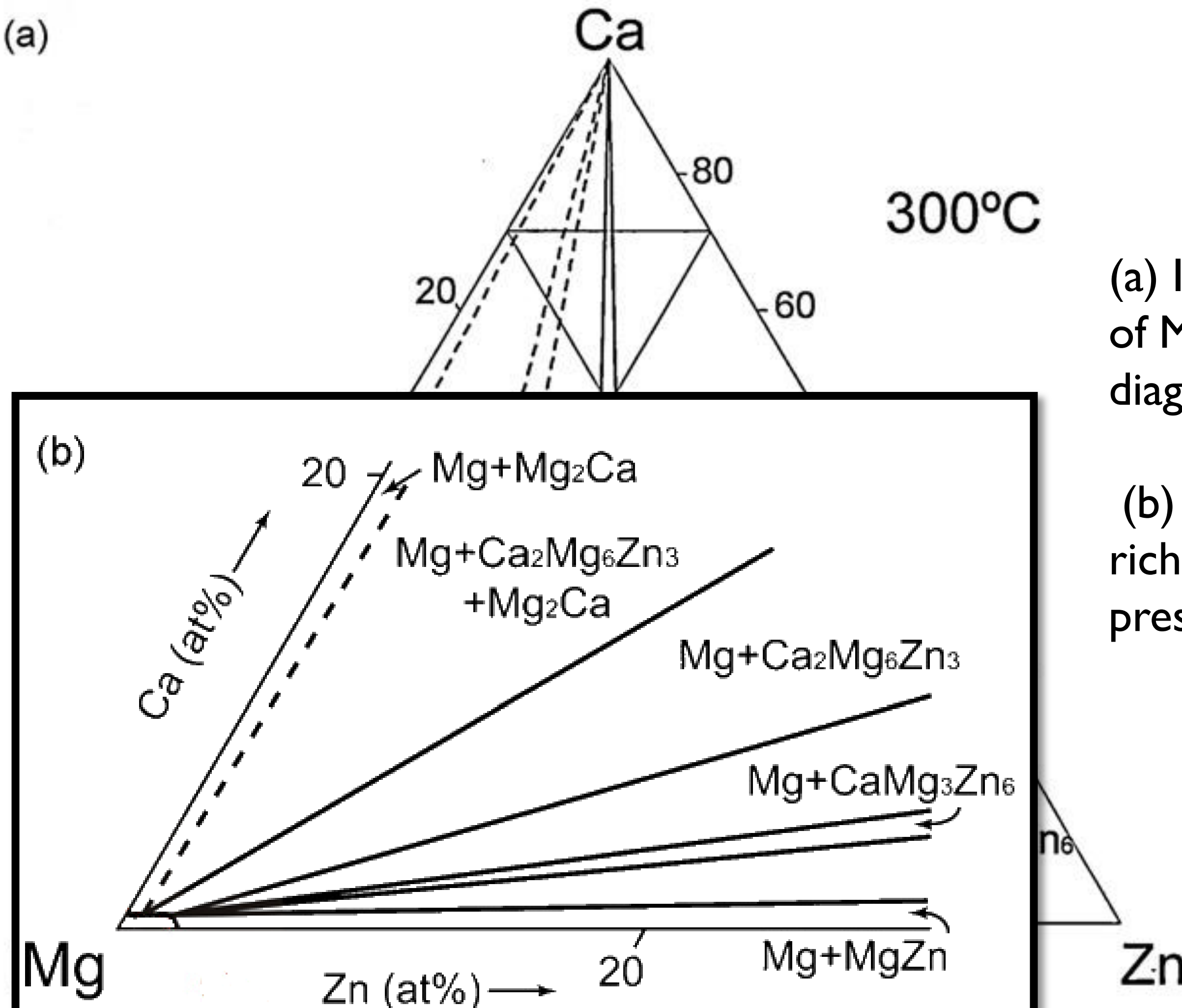


- [Degradable biomateirlas based on magnesium corrosion; F. Witte *et al.; Current opinion in Solid State and Materials Science* 2008; 63-72]

Why these alloying elements?

- **Zn**
  - biocompatible
  - ambient and artificial age-hardening response of Mg-Zn system – precipitation hardening
- **Ca**
  - biocompatible
  - grain refiner
  - better castability – increases the ignition temperature of molten Mg
  - higher creep resistance and hardness if added to Mg-Zn
  - age-hardening response of Mg-Zn is enhanced by trace Ca addition

Isothermal sections of Mg-Zn-Ca system at 300 ^{o}C



(a) Isothermal cross section of Mg–Ca–Zn ternary phase diagram at 300 ◦C,

(b) enlargement of the Mg-rich corner including present alloy compositions

Modified from: Oh-ishi, K., Watanabe, R., Mendis, C. Hono, K., (2009). Age-hardening response of Mg-0.3 at.%Ca alloys with different Zn contents. *Materials Science and Engineering: A*, *526*(1-2), 177-184

Compositions of the alloys

- Based on the isothermal sections of the Mg-Zn-Ca system and literature review we have chosen six types of alloys composition (wt.%):

- Mg-3Zn (ref. sample)
- Mg-3Zn-0.2Ca
- Mg-3Zn-0.5Ca
- Mg-3Zn-0.7Ca
- Mg-3Zn-1.0Ca
- Mg-3Zn-1.3Ca

Tab. 1 Composition of the investigated alloys

Alloy	Composition (wt %)			Composition (at %)			Zn/Ca	Ca/Zn
	Mg	Zn	Ca	Mg	Zn	Ca		
1	97	3	-	98.86	1.14	-	-	-
2	96.8	3	0.2	98.74	1.14	0.12	9.50	0.11
3	96.5	3	0.5	98.55	1.14	0.31	3.68	0.27
4	96.3	3	0.7	98.43	1.14	0.43	2.65	0.38
5	96	3	1	98.24	1.14	0.62	1.84	0.54
6	95.7	3	1.3	98.05	1.14	0.81	1.41	0.71

Ca changes the solid solubility of Zn in Mg

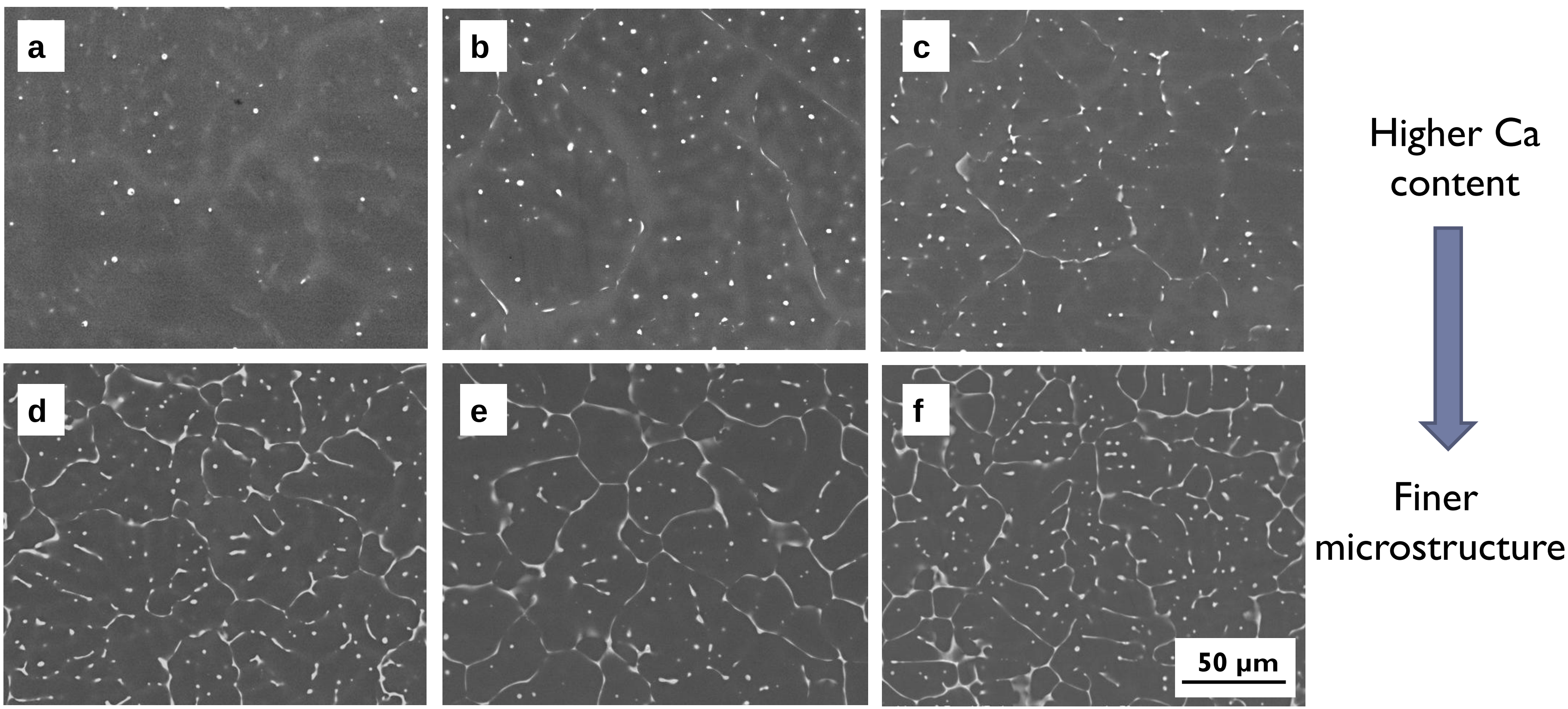
Techinques

- Resistance melting and casting under the protective argon atmosphere (K. Kubok)
- Metalographic sample preparation techniques (K. Kubok)
- Twinjet electro-polishing (K. Kubok)
- Ion beam milling system (M. Szlezinger and K. Kubok)
- Scanning electron microscopy (dr J. Wojewoda-Budka with K.Kubok)
- X-ray diffraction spectroscopy (dr A. Góral with K.Kubok)
- Microhardness tester (K. Kubok)

- Main method: **Transmission electron microscopy** (dr hab. L. Lityńska-Dobrzyńska and K. Kubok)

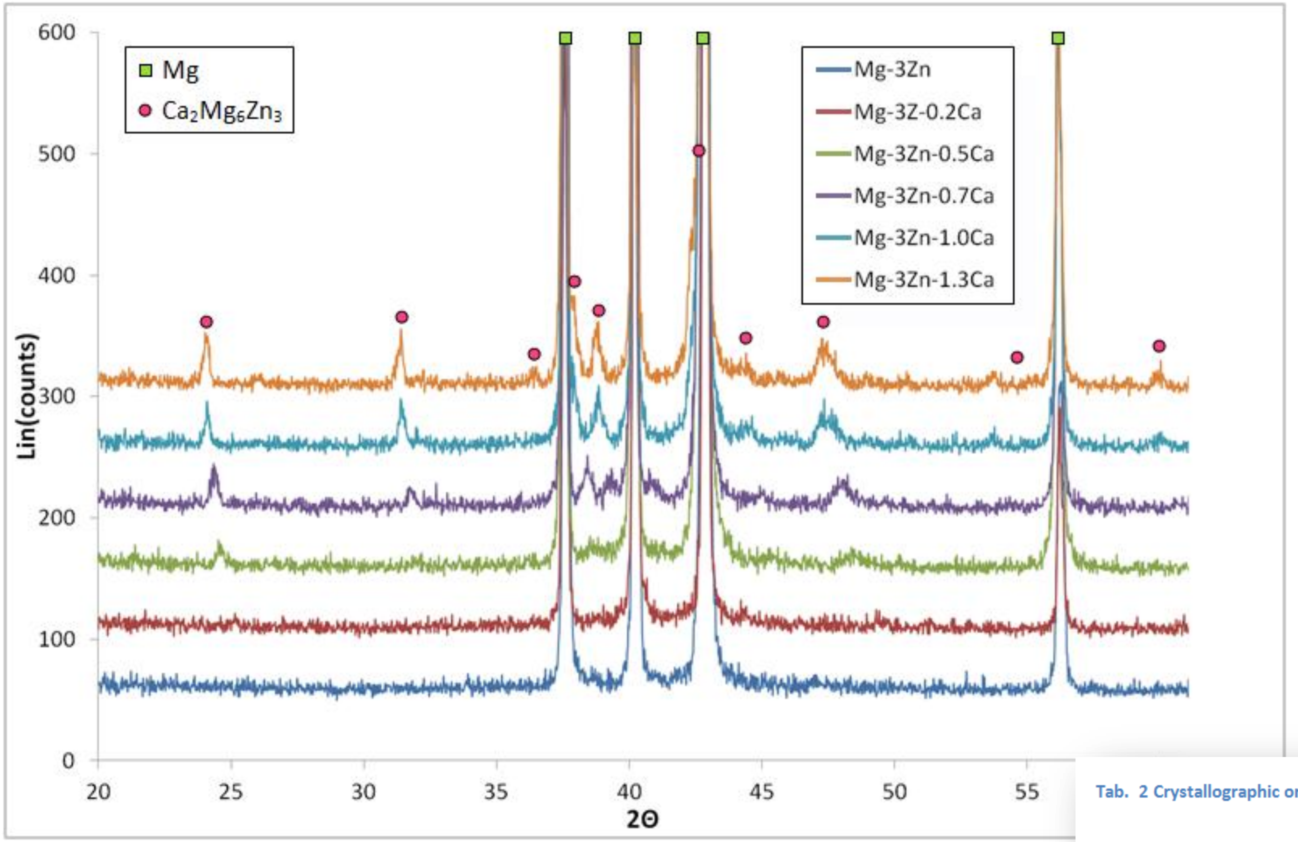
Results: SEM, examples

All investigated alloys have revealed α(Mg) dendritic microstructures with secondary phases distributed in interdendritic spacing and within the dendrities. The Mg_4Zn_7 has been identified as the main intermetallic phase in the Mg-3Zn wt.% alloy.



- Microstructures of a) Mg-3Zn; b) Mg-3Zn-0.2Ca; c) Mg-3Zn-0.5Ca; d) Mg-3Zn-0.7Ca; e) Mg-3Zn-1.0Ca; f) Mg-3Zn-1.3Ca; BSE; 20kV

Results: XRD spectrum of all samples



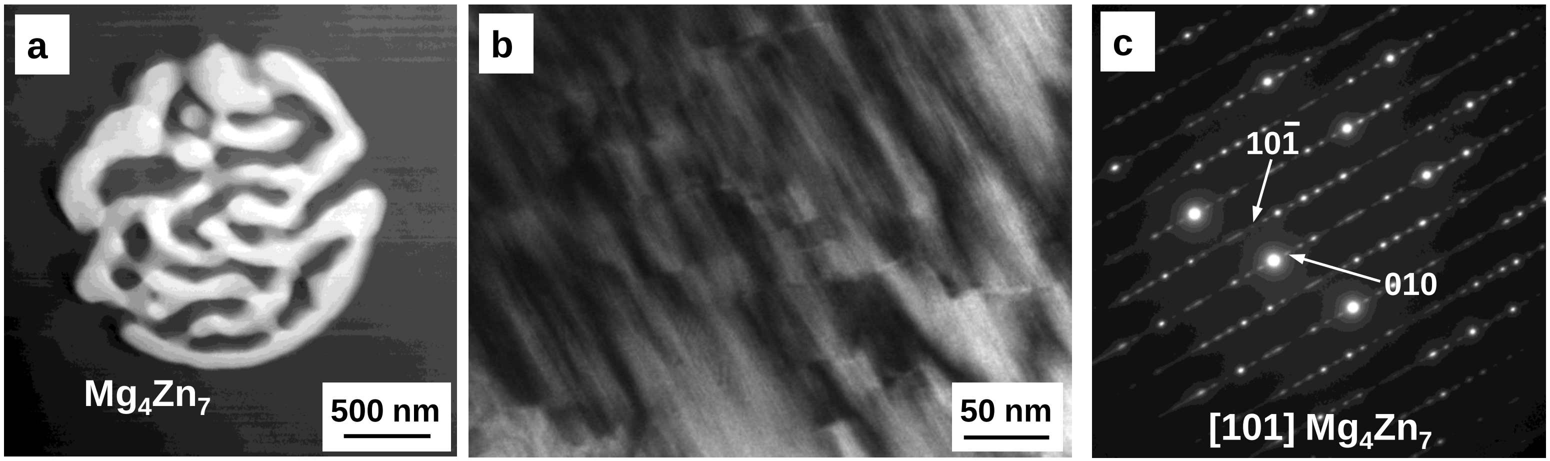
Lattice parameters increase with increasing Ca content

Calcium addition causes the formation of ternary $Ca_2Mg_6Zn_3$ phase

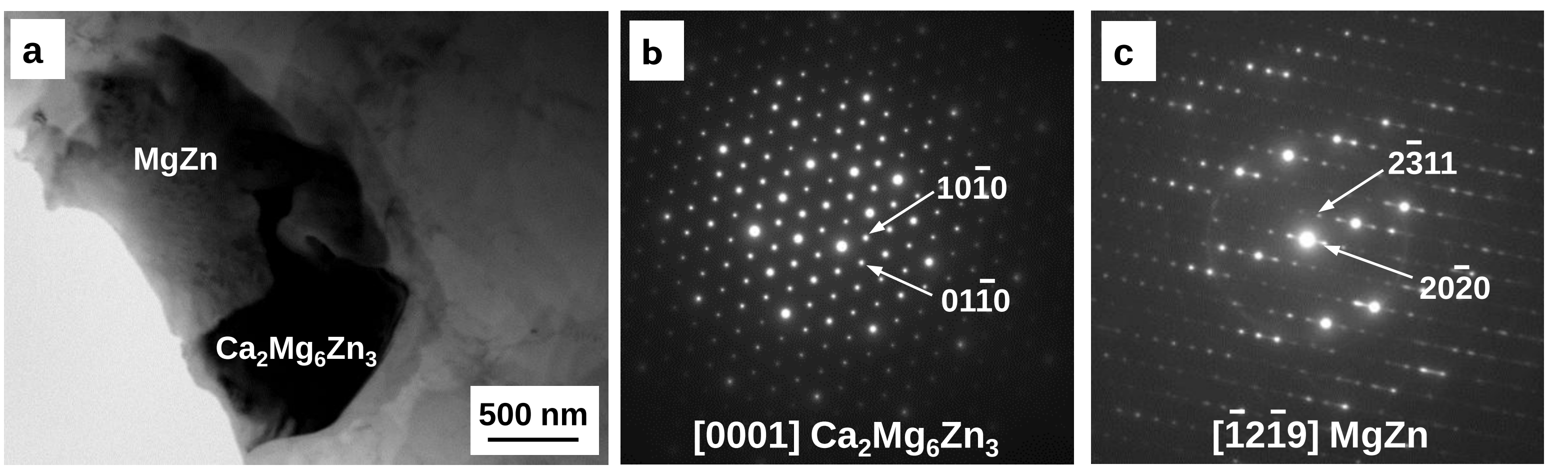
Tab. 2 Crystallographic orientation of the phases in the Mg-Zn-Ca system obtained with XRD

Phase	Pearson symbol	Space group	Lattice parameters (Å)	
			a, b	c
Mg	hP2	*P6₃/mmc* (194)	3.199	5.154
$Ca_2Mg_6Zn_3$	hP36	*P6₃/mmc* (194)	9.725 for **Mg-3Zn-0.5Ca** to 9.912 for **Mg-3Zn-1.3Ca**	10.148 for **Mg-3Zn-0.5Ca** to 10.352 for **Mg-3Zn-1.3Ca**

Results: TEM, examples

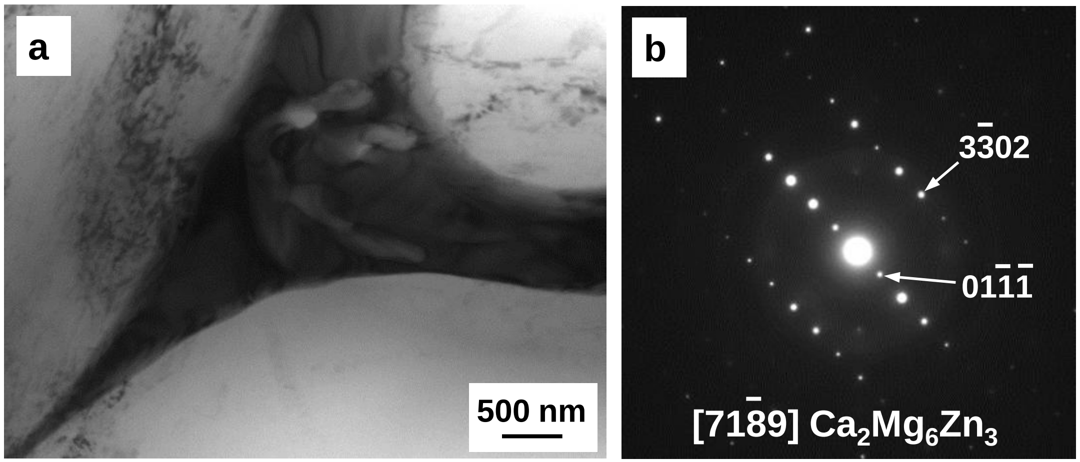


Mg-3Zn; a) STEM-HAADF image of globular particle of Mg_4Zn_7 phase; b) TEM bright field of the particle shown in (a); and c) corresponding SAD pattern



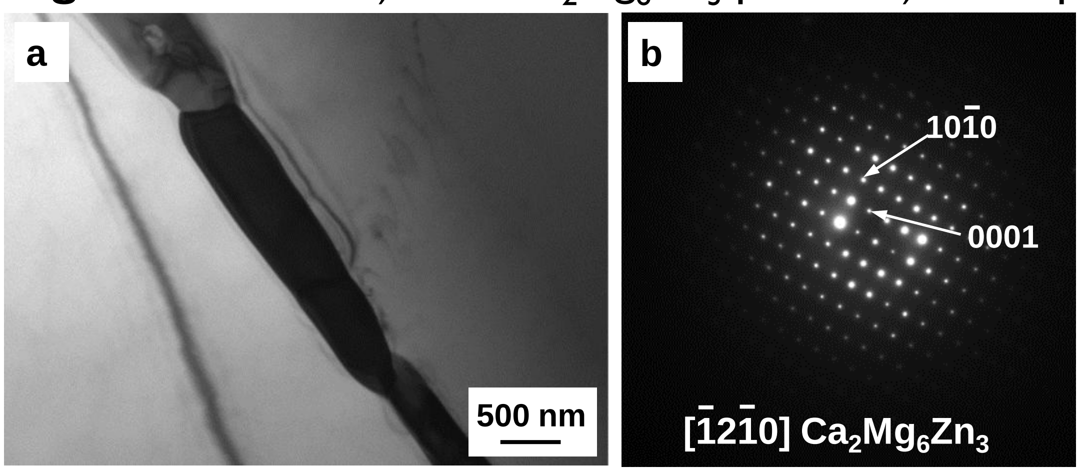
Mg-3Zn-0.2Ca; a) TEM bright field of precipitations of MgZn and $Ca_2Mg_6Zn_3$phases and (b, c) SAD patterns of respecive phases

Results: TEM, examples



- $Ca_2Mg_6Zn_3$ phase has been found in calcium containing alloys
- In the Mg-3Zn-0.2Ca wt.% sample, apart from the ternary phase, the Mg-Zn phase has been identified
- Mg_4Zn_7 phase has been identified in reference Mg-3Zn wt.% alloy,

Mg-3Zn-0.5Ca; a)BF, of $Ca_2Mg_6Zn_3$ phase; b) corresponding SAD pattern

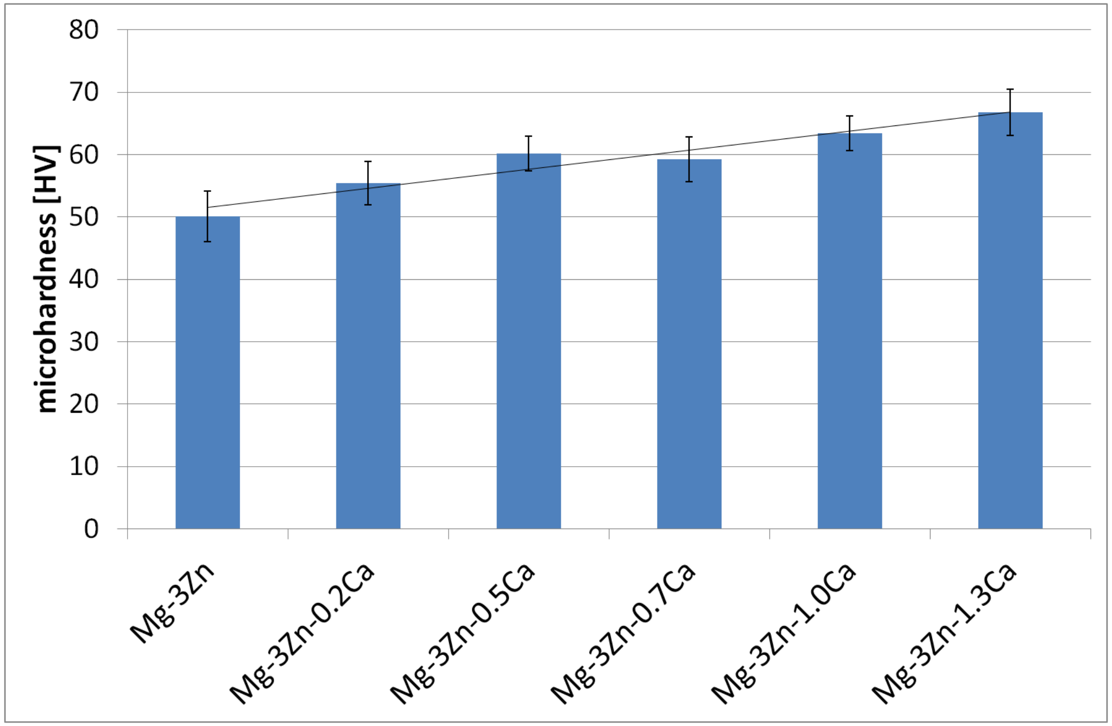


Tab. 3 Composition of $Ca_2Mg_6Zn_3$ phase in investigated alloys

Alloy	Composition (at. %)		
	Mg	Zn	Ca
Mg-3Zn-0.2Ca	31.8	54.1	14.1
Mg-3Zn-0.5Ca	51.4	34.5	14.1
Mg-3Zn-0.7Ca	53.4	31.7	14.8
Mg-3Zn-1.0Ca	59.7	25.8	14.5
Mg-3Zn-1.3Ca	62.0	22.8	15.2

Mg-3Zn-1.3Ca; a)BF, $Ca_2Mg_6Zn_3$ phase; b) corresponding SAD diffraction

Results: Microhardness



Microhardness of Ca containing alloys increases to about 67 HV compared to 50 HV for Mg-3Zn wt.% alloy due to the formation of $Ca_2Mg_6Zn_3$

CSM Instrument Vickers microhardness tester with an indenter load of 1 N (102 g) and a loading time of 30s has been used and ten separate indentations for each sample has been found. Standard deviation bars are given with linear trend line

Summary

- All alloys revealed dendritic microstructure of α(Mg) and secondary phases distributed in interdendritic spacings and within the dendrities
- The Mg_4Zn_7 was identified as a main intermetallic phase in Mg-Zn alloy
- Ca additions cause the formation of $Ca_2Mg_6Zn_3$ hexagonal phase ($Ca_3Mg_xZn_{15-x;}$ IM1)
- The content of Mg in the phase varies in the range from ~36 at.% for Mg-3Zn-0.2Ca to ~65 at.% for Mg-3Zn-1.3Ca, what indicates increase of the lattice parameters
- The microhardness of the Ca containing alloys increase to about 67 HV compared to the 50 HV for Mg-Zn alloy

Long time goal and plans for the nearest future

Our aim:

Investigation of the relationship between the composition, microstructure, corrosion and mechanical properties

Plans for the nearest future:

- ambient and artificial age-hardening
- corrosion rate measurments (EIS electrochemical impedance spectroscopy, weight changes measurments)

Thank you for your attention