Precipitation Effects in Mg-Zn-Y Alloys Strengthened by Quasicrystalline Phase

M. Vlcek[1], J. Cizek[1], F. Lukac[1], O. Melikhova[1], I. Prochazka[1], M. Vlach[1], I. Stulikova[1], B. Smola[1] and A. Jäger[2]

[1]Faculty of Mathematics and Physics, Charles University in Prague, V Holešovičkách 2, CZ-180 00, Praha 8, Czech Republic
[2]Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, CZ-182 21 Praha 8, Czech Republic

Quasicrystals

They exhibit a unique combination of physical properties:

- High strength, hardness and brittleness due to low density of dislocations and their low mobility
- Low surface energy
- Low adhesivity and high abrasion resistance
- Highly isotropic elastic properties
- High corrosion resistance

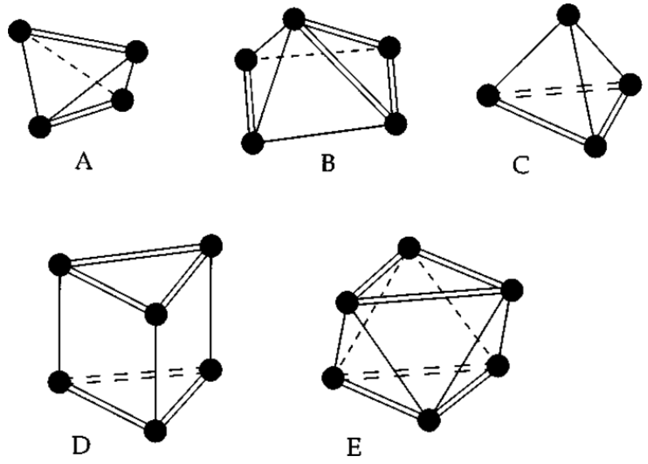
Most of discovered quasicrystalline materials were prepared as single phase materials. However recently quasicrystalline precipitates in Mg-Zn-Y alloys were observed [Yi et. al., Mat. Sci. Eng. A 300 (2001)].

Motivation: Unique structure of these precipitates could lead to improvement of mechanical properties of magnesium alloys.

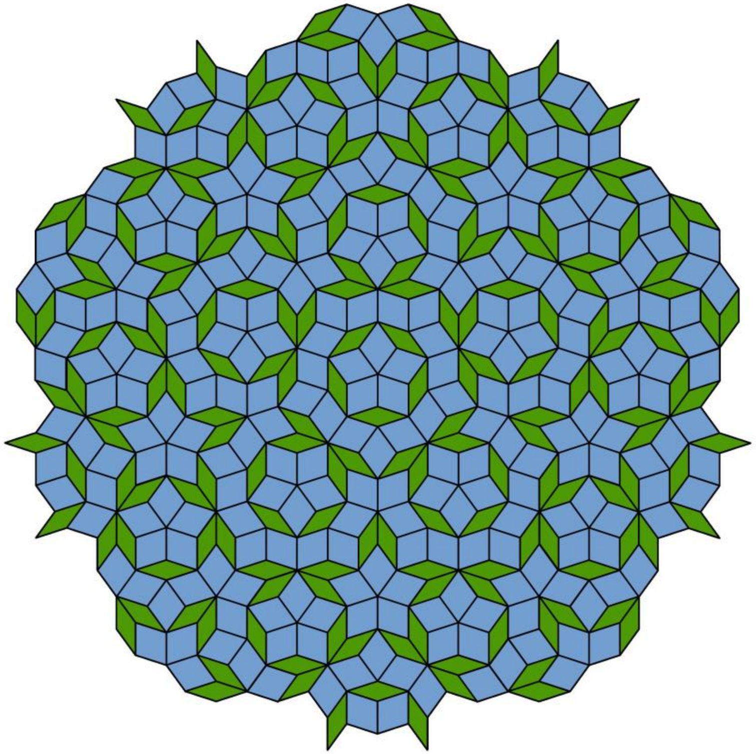
Quasicrystals

Periodic crystals ⟶ only 2,3,4 and 6-fold rotational symmetries

Multiple units ⟶ tiling with 'forbidden' rotational symmetry but without translational symmetry



Units of 3D icosahedral tiling



Penrose tiling

Samples

Samples of studied were prepared by squeeze casting. Composition table of Mg-Zn-Y-based alloys in wt.%:

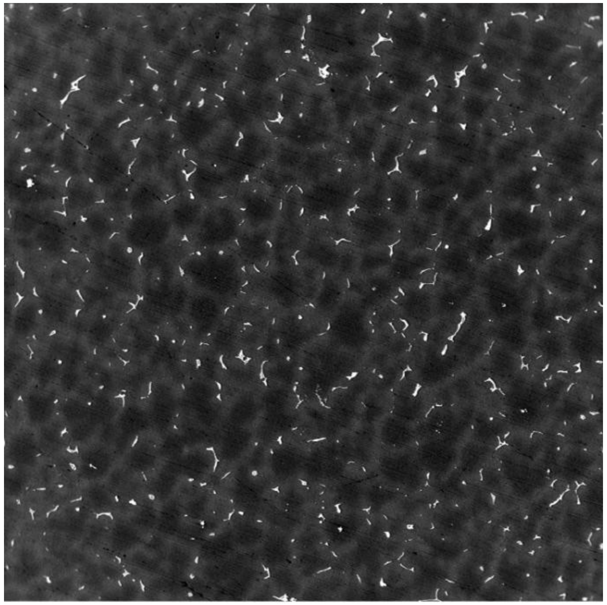
	Zn	Y	Nd	Zr	Gd	Mg
WE43	-	2.95	2.48	0.30	0.15	balance
WE43+11Zn	10.90	1.80	0.73	0.28	0.12	balance
WE43+14Zn	13.80	3.06	1.04	0.29	0.10	balance
WE43+26Zn	25.82	3.02	1.16	0.27	0.17	balance

Composition of Mg-Zn-Al-based alloys in wt.%:

	Zn	Al	Ca	Mg
Mg5Zn3Al	5.3	3.2	0.1	balance
Mg12Zn3Al	11.9	3.1	-	balance

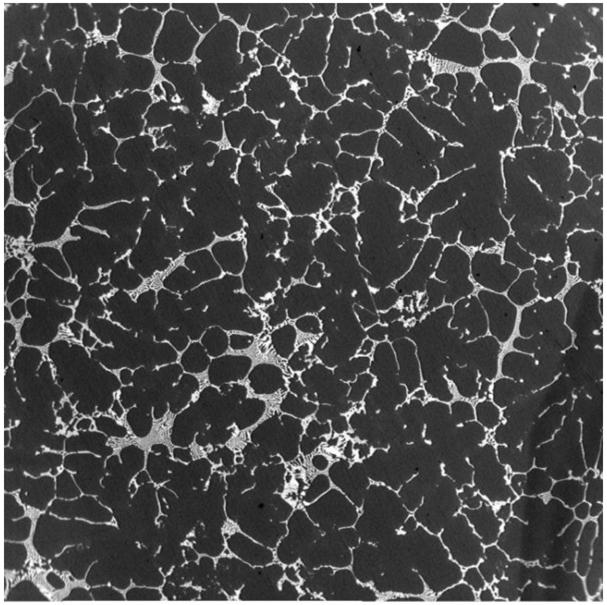
Scanning electron microscopy

SEM images of as cast alloys in backscattered electrons



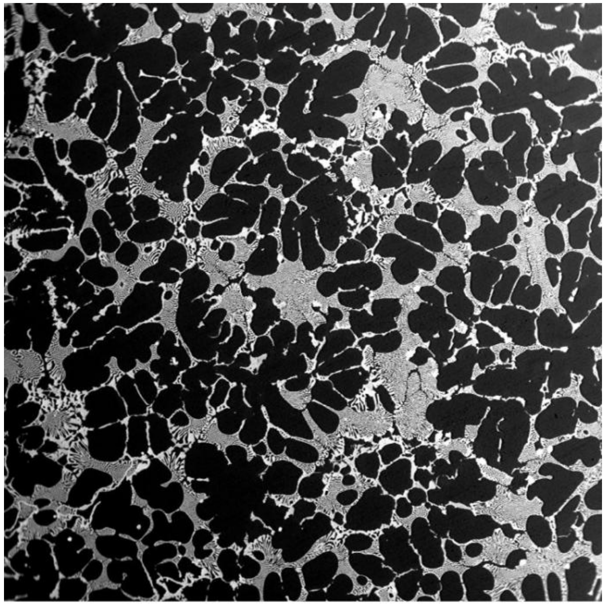
170 µm

WE43



250 µm

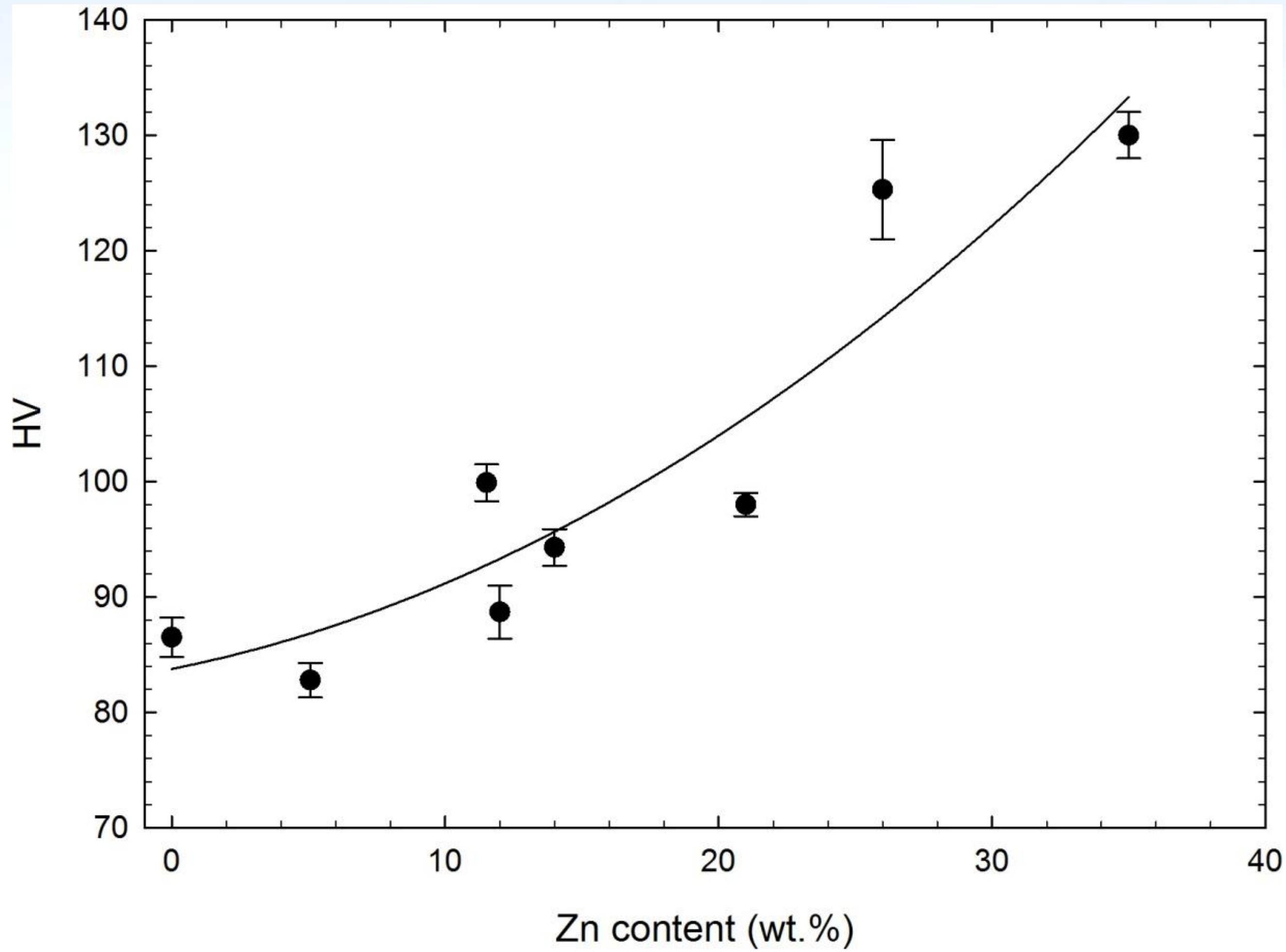
WE43+14Zn



210 µm

WE43+26Zn

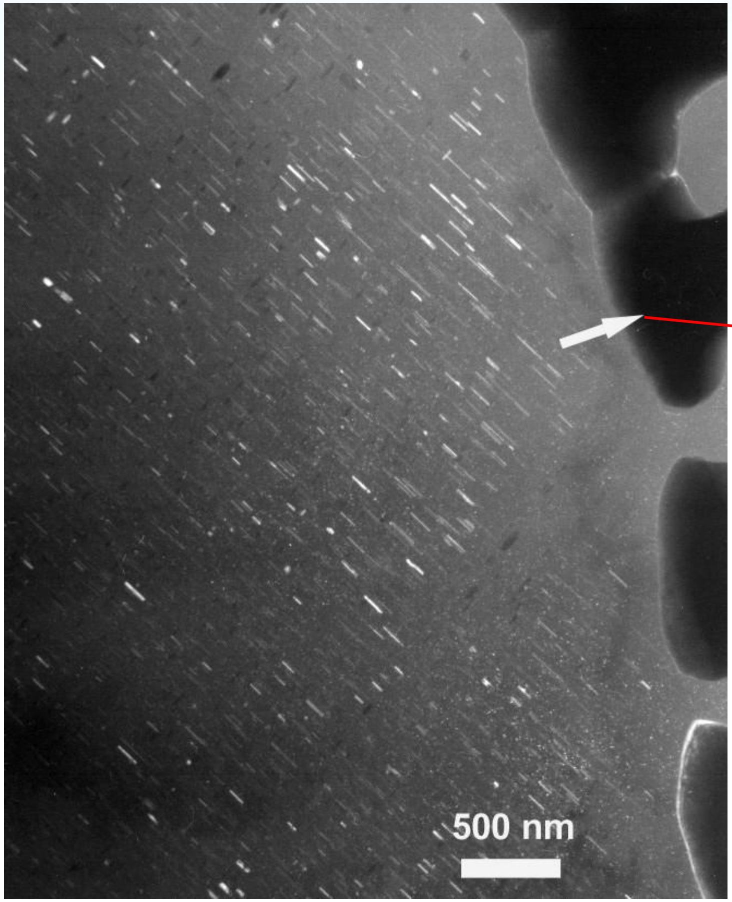
Microhardness of as cast alloys



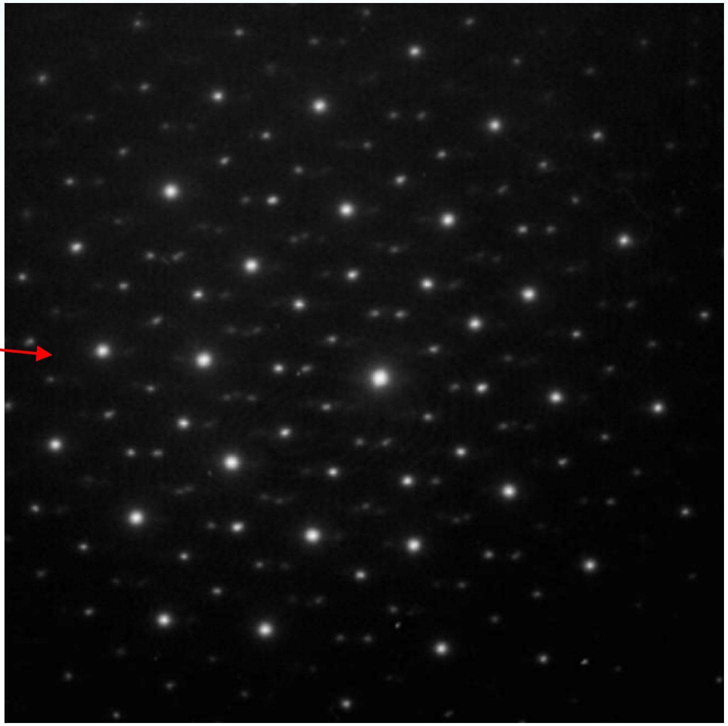
Correlation of hardness and zinc content of studied alloys
Hardness of alloys significantly increases with increasing zinc content

Transmission electron microscopy

As cast WE43+26Zn alloy



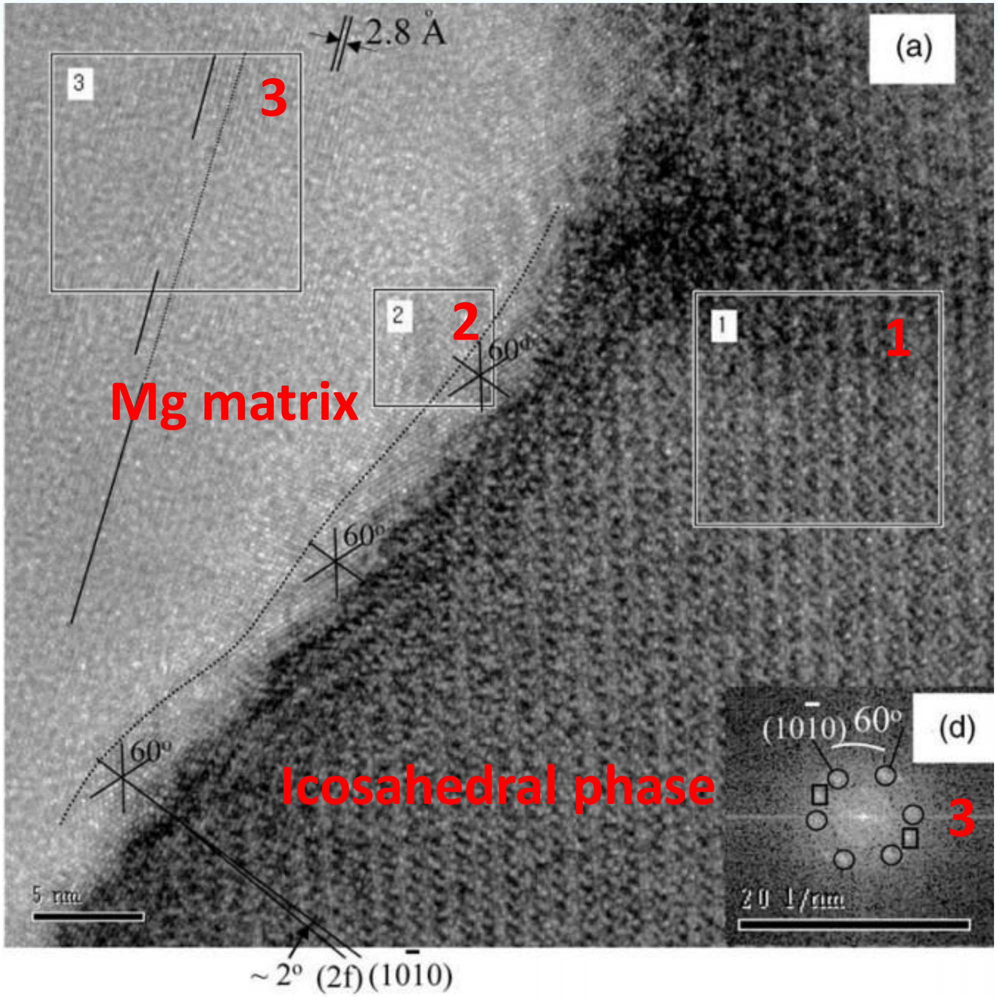
Bright field – large particles of eutectic and small rods in matrix

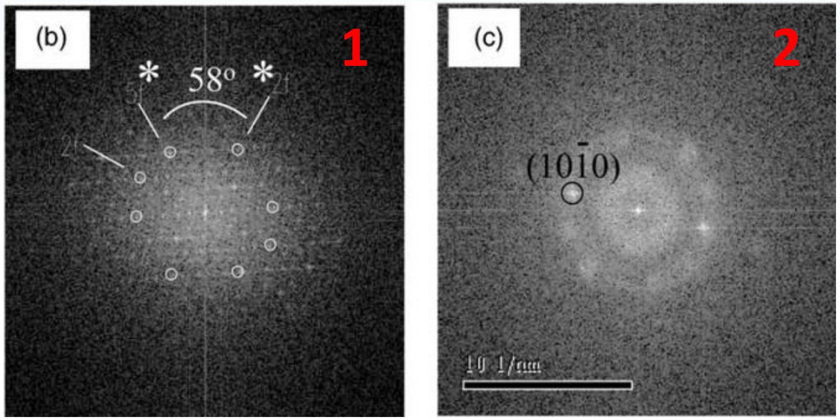


Electron diffraction – 10-fold symmetry of diffraction pattern confirms presence of icosahedral phase

High resolution transmission electron microscopy

Mg-2.4Y-10.6Zn alloy hot-rolled and annealed at 400 °C for 0.5 h





Stairs or ledges are present at the interface of the Mg matrix and icosahedral phase due to their incommensurability

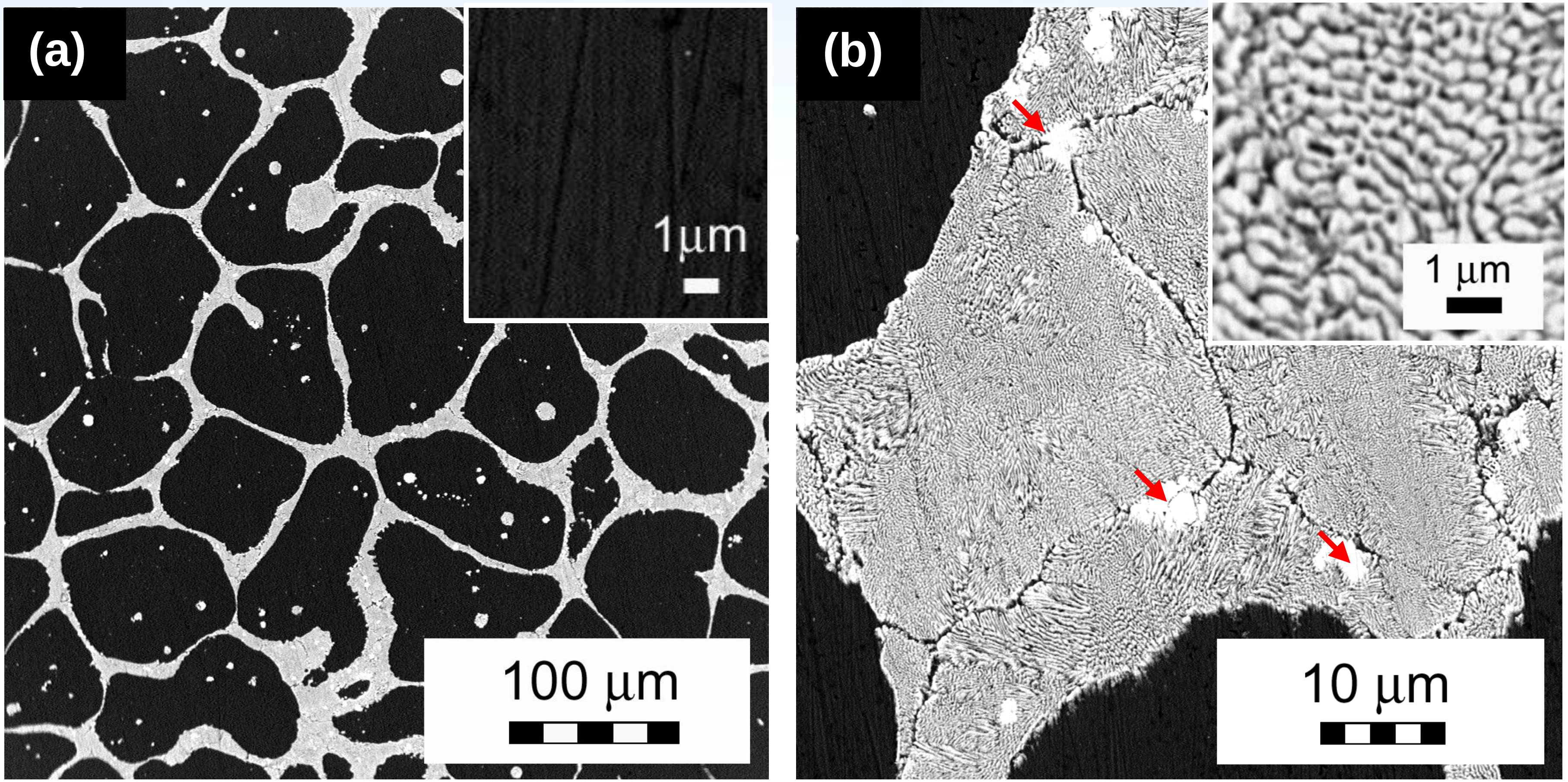
D.H. Bae, S.H. Kim, D.H. Kim, W. T. Kim, *Acta Materialia* **50** (2002) 2343.

Positron lifetime spectroscopy

Description	State	τ_1 (ps)	I_1(%)	τ_2 (ps)	I_2(%)
WE43	as-cast	223.9(3)	100	-	-
WE43+26Zn	as-cast	192(4)	56(3)	302(4)	44(3)
WE43+14Zn	as-cast	187(2)	58(2)	302(3)	42(2)
WE43+11Zn	as-cast	201(2)	67(3)	296(5)	33(3)
Mg5Zn3Al	as-cast	219(1)	96(1)	290(10)	4(1)
Mg12Zn3Al	as-cast	217.3(5)	93.9(5)	300(10)	6.1(5)

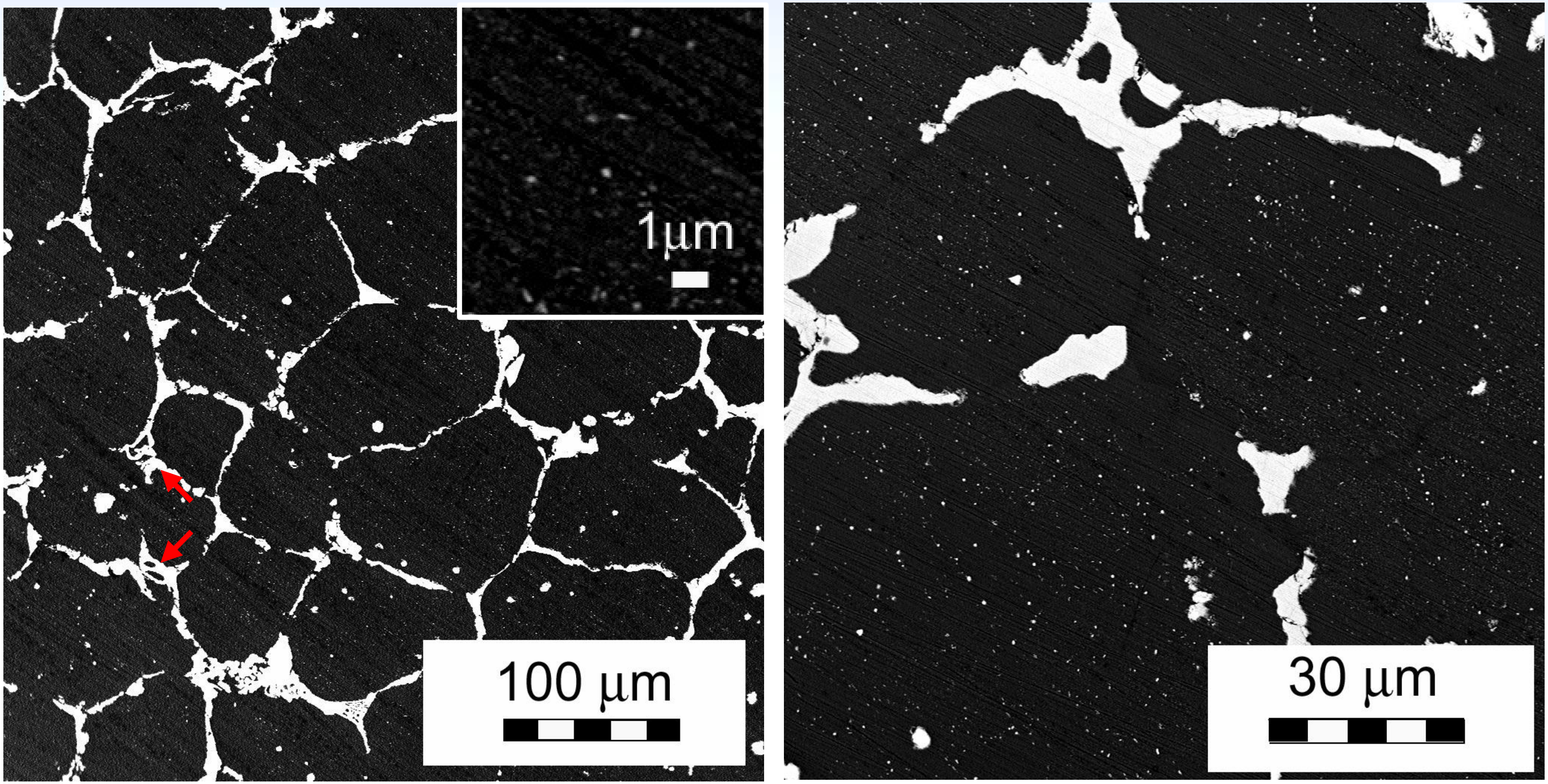
- All studied alloys containing quasicrystalline phase exhibit second component with positron lifetime ~300 ps
- Misfit defects in alloys containing semicoherent or incoherent precipitates usually exhibit second component with positron lifetime ~260 ps [Hruska et. al., Acta Phys. Pol. A **125** (2014) 718]
- Therefore, defects associated with quasicrystalline phase are larger than those commonly associated with non-quasicrystalline precipitates

Scanning electron microscopy



WE43+14Zn alloy annealed 500 °C/1 h and quenched
Red arrows indicate few particles of W-phase ($Mg_3Zn_3Y_2$), remaining part of grain boundary phase is formed by I-phase (Mg_3Zn_6Y)

Scanning electron microscopy



WE43+14Zn alloy annealed 500 °C/1 h and slowly cooled

Red arrows indicate few particles of W-phase ($Mg_3Zn_3Y_2$), remaining part of grain boundary phase is formed by I-phase (Mg_3Zn_6Y)

Scanning electron microscopy

Results of SEM measurements of WE43+14Zn alloy:

Sample	*D* (µm)	λ (µm)	f_{GBP} (%)	$f_{I\text{-}phase}$ (%)	F (%)
as-cast	44(5)	1-2	12.6(2)	33(5)	10.6
500°C/1h slowly cooled	102(5)	5-10	9.7(5)	81(4)	2.7
500°C/1h quenched	98(5)	0.2-0.4	8.5(5)	96(3)	6.6

D – the mean grain size

λ – the spacing of lamellas in eutectic

f_{GBP} – the volume fraction of GBP

$f_{I\text{-}phase}$ – the proportion of I-phase in GBP (the proportion of W-phase is the complement to 100%)

F – fraction of positrons trapped at defects

Annealing at 500 °C for 1 hour significantly increases volume fraction of I-phase in grain boundary phase

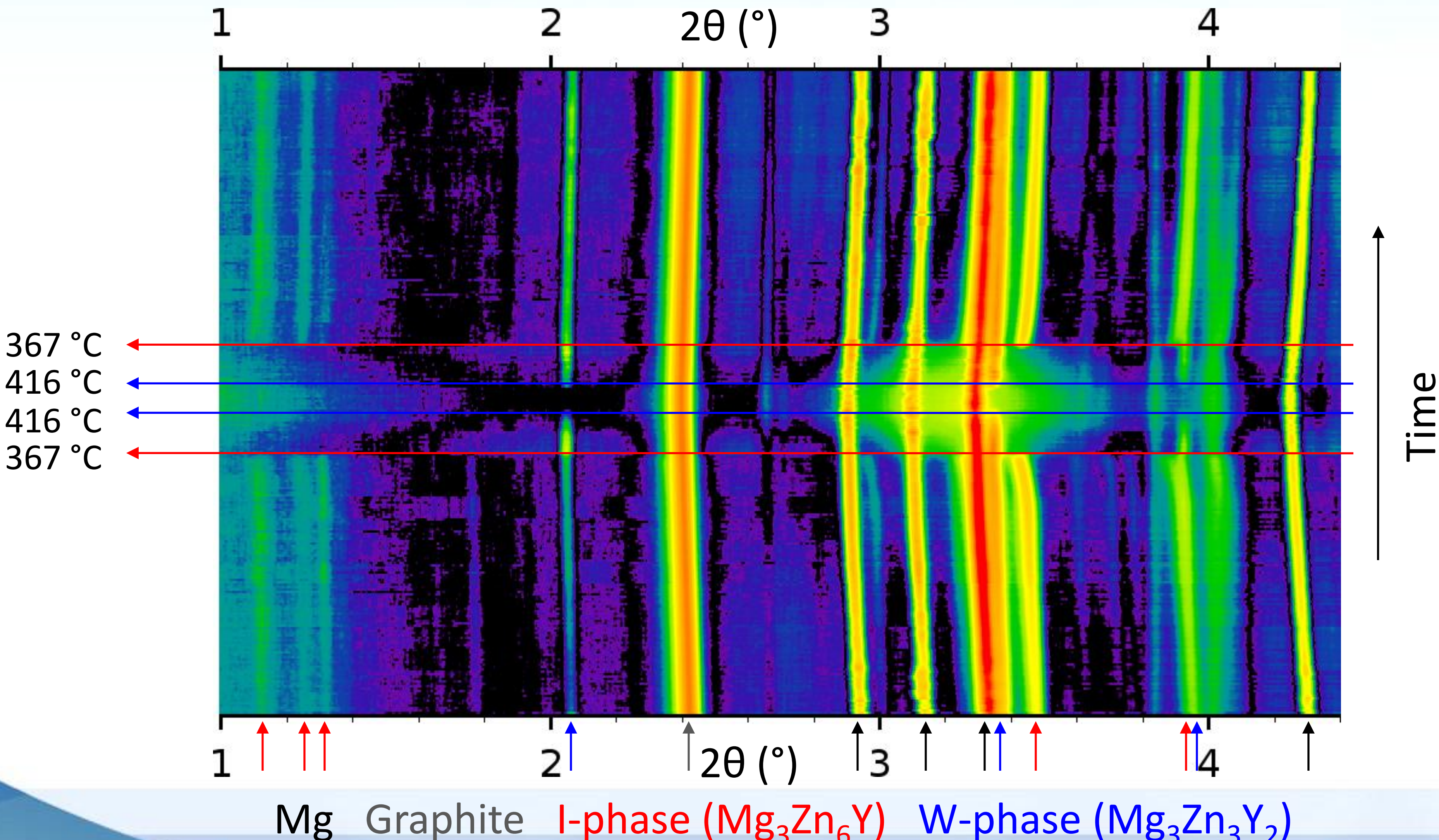
Positron lifetime spectroscopy

Sample	State	τ_1 (ps)	I_1(%)	τ_2 (ps)	I_2(%)	F(%)
WE43+11Zn	as-cast	201(2)	67(3)	296(5)	33(3)	10.6
WE43+11Zn	500^{o}C/1h Q	212(5)	73(9)	280(10)	27(9)	6.6
WE43+11Zn	500^{o}C/1h SC	218(2)	89(1)	290(10)	11(1)	2.7

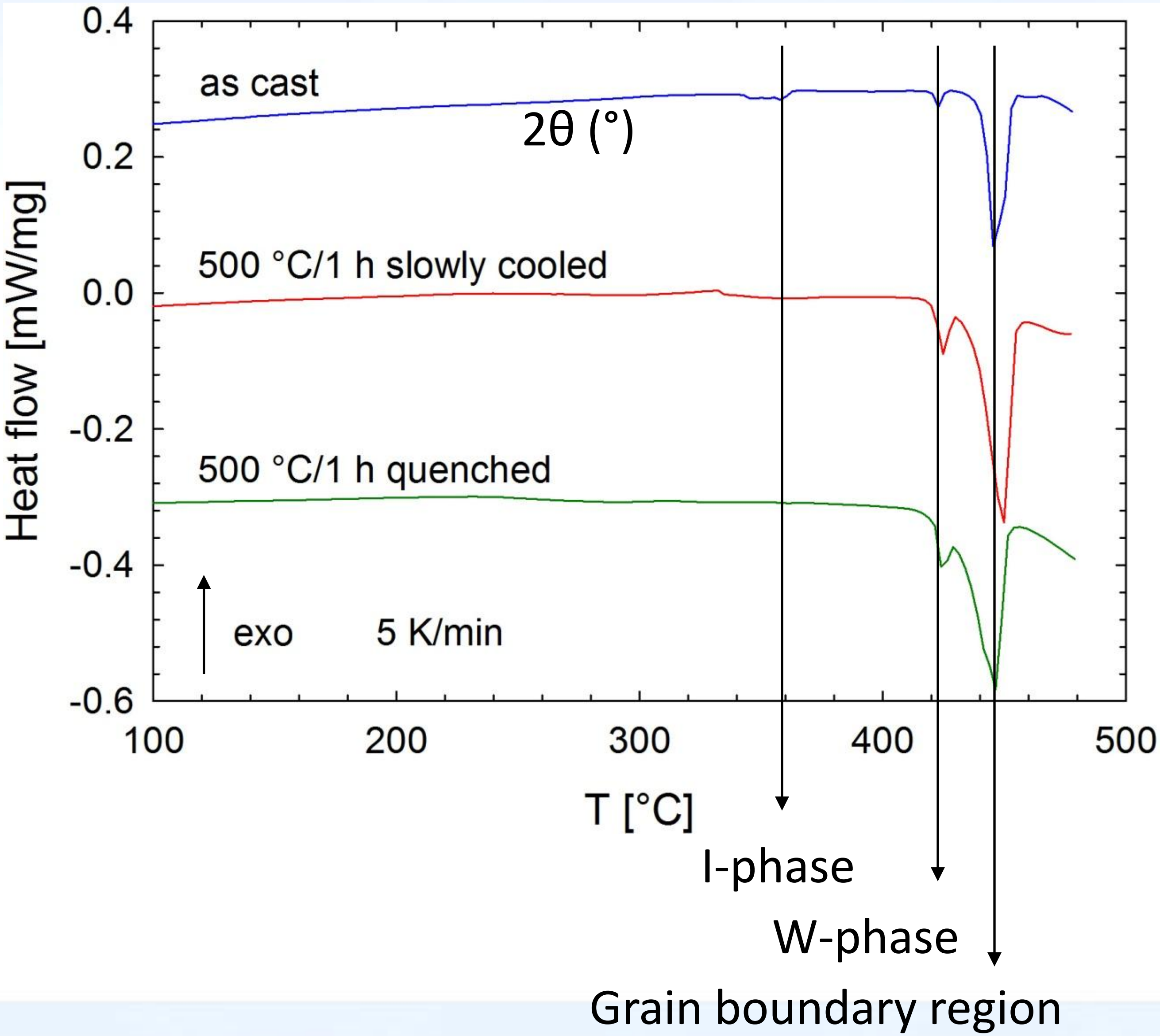
- Density of defects decreases after annealing at 500 °C even though volume fraction of I-phase in GBP increased
- However, average concentration of Y and Zn in Mg matrix decreases during annealing
- Although volume fraction of I-phase in GBP increases, numerical density of small precipitates in Mg matrix decreases after annealing
- These small precipitates dominates the contribution to second component in positron lifetime spectrum, therefore decrease in defect density occurred after annealing

In situ XRD during heat treatment

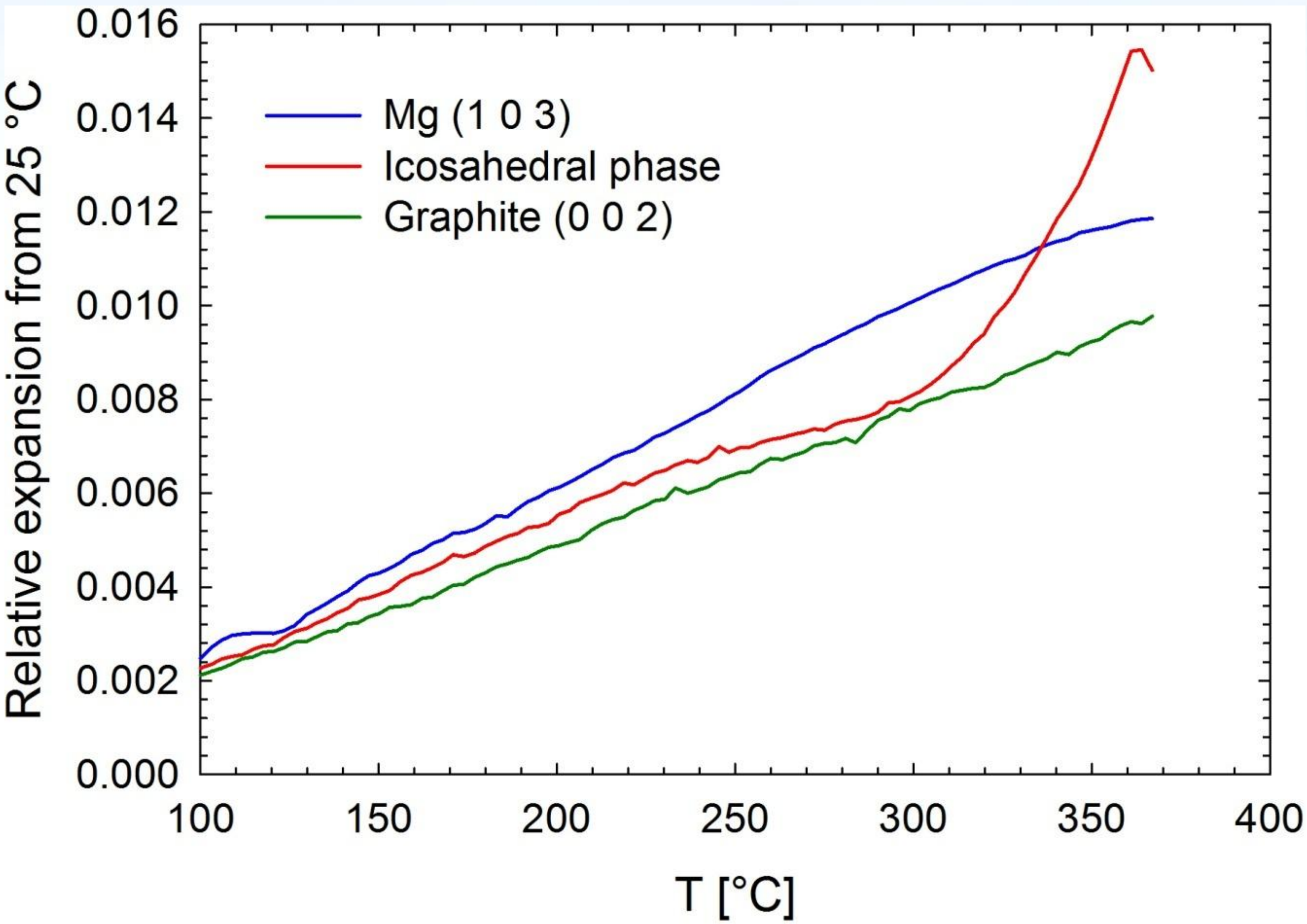
- Linear heating from room temperature to 425 °C and cool down back to room temperature. Heating/cooling rate 5 K/min. λ = 0.142 Å



Differential scanning calorimetry – WE43+14Zn



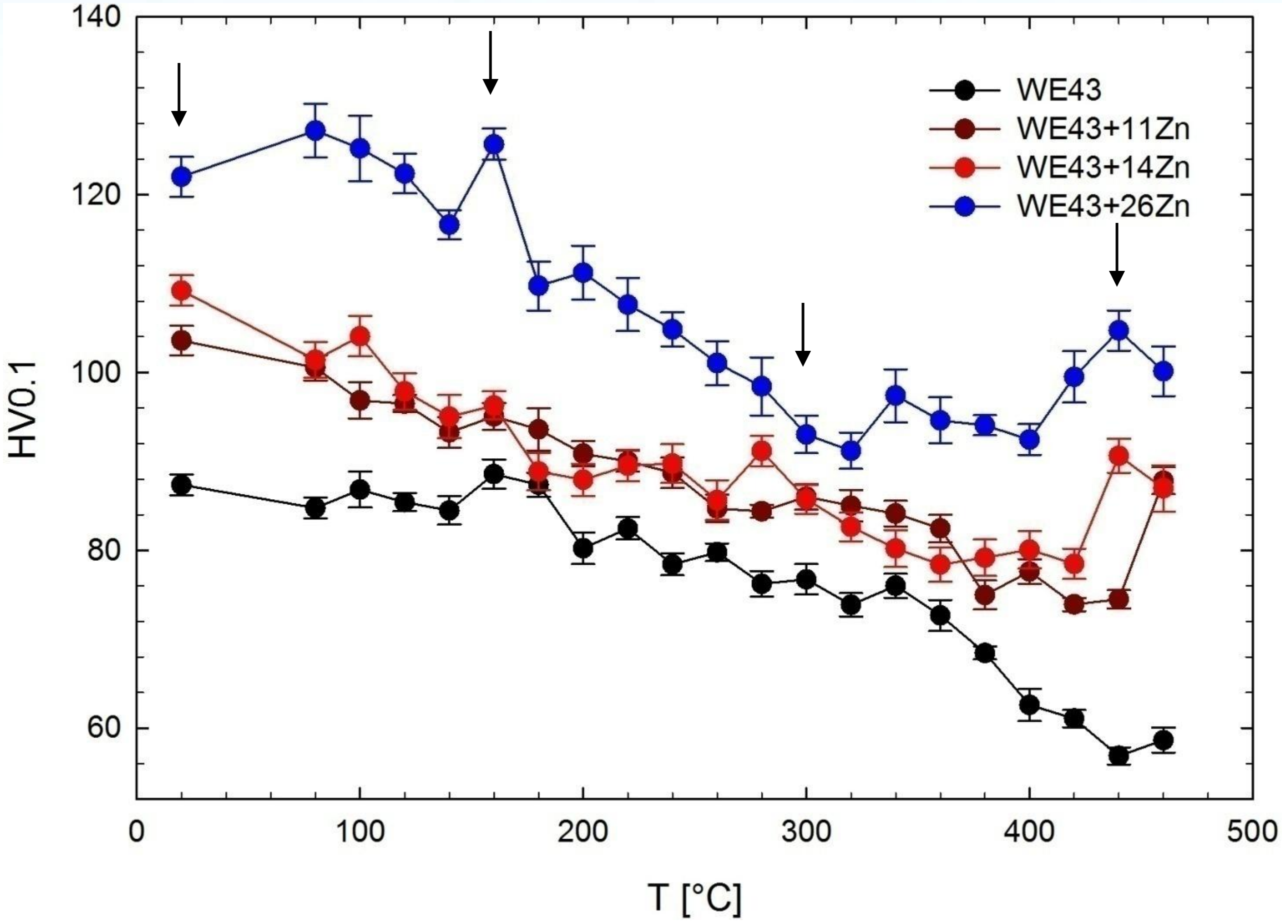
In situ XRD during heat treatment



- Coefficient of thermal expansion of I-phase significantly changes at ~310 °C
- Sign of structural change of I-phase?

Microhardness

Development of hardness during isochronal annealing with step 20 K/20 min



Positron lifetime measurements were done at selected temperatures

Positron lifetime spectroscopy

Results of LT measurements during isochronal annealing with step 20 K/20 min

Sample	State	τ_1 (ps)	I_1(%)	τ_2 (ps)	I_2(%)
WE43+11Zn	as-cast	201(2)	67(3)	296(5)	33(3)
WE43+11Zn	160^{o}C	180(10)	48(4)	278(9)	52(4)
WE43+11Zn	300^{o}C	203(9)	70(5)	298(7)	30(5)
WE43+11Zn	440^{o}C	210(10)	75(5)	300(10)	25(5)

- Intensity of second component increases and lifetime of the second component slightly decreases after annealing at 160 °C
- Positron trapping at defects with lifetime of ~260 ps associated with precipitates was observed in binary Mg-Zn alloy after annealing at 220 °C [Hruska et. al., Acta Phys. Pol. A **125** (2014) 718]
- These two components cannot be separated due to limited experimental resolution for sample annealed at 160 °C
- Instead, one component with average lifetime of 278(9) ps is observed

Conclusions

- Vacancy-like defects associated with interface between icosahedral phase and Mg matrix were observed
- Density of defects decreases after annealing at 500 °C due to decrease of numerical density of rod-like precipitates in Mg matrix and grain growth
- Nonlinear increase of thermal expansion of I-phase was observed above 310 °C, which indicates some structural change in the I-phase
- Temperatures of phase transformations occurring in WE43+14Zn alloy were determined by in situ XRD during linear heating and also by DSC