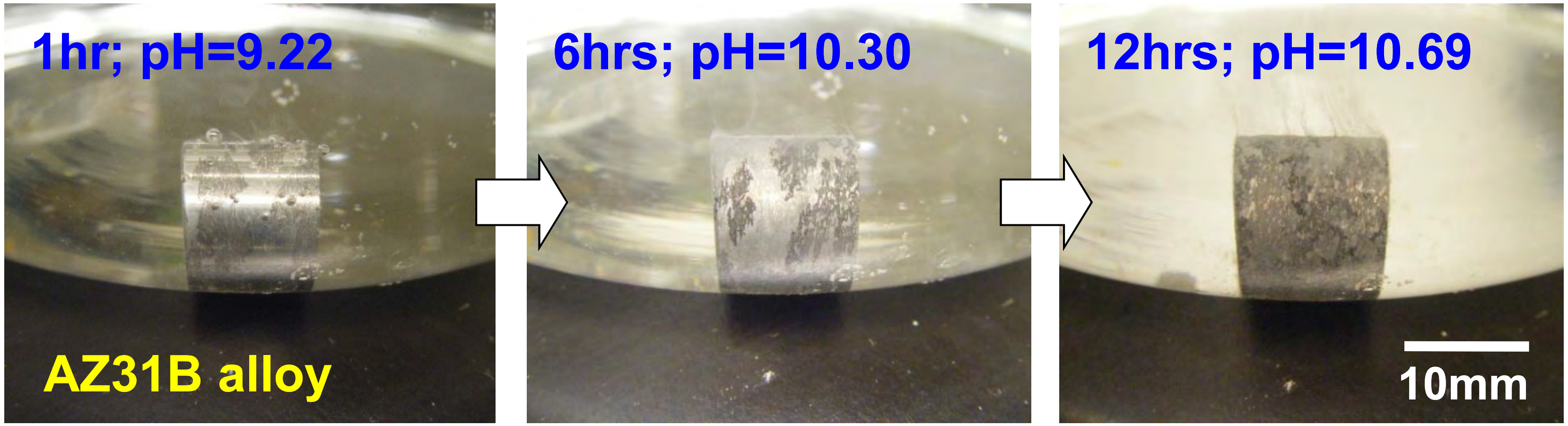
SKPFM Quantitative Evaluation of Initial Galvanic Corrosion Phenomenon of Magnesium Alloys

Background – Corrosion phenomenon of Mg alloy

- **Standard electrode potential of pure metal elements**

Metal	Mg	Al	Zn	Fe	Ni	Cu	Ag	Au
Standard electrode potential (V)	-2.36	-1.66	-0.76	-0.44	-0.23	0.34	0.80	1.40

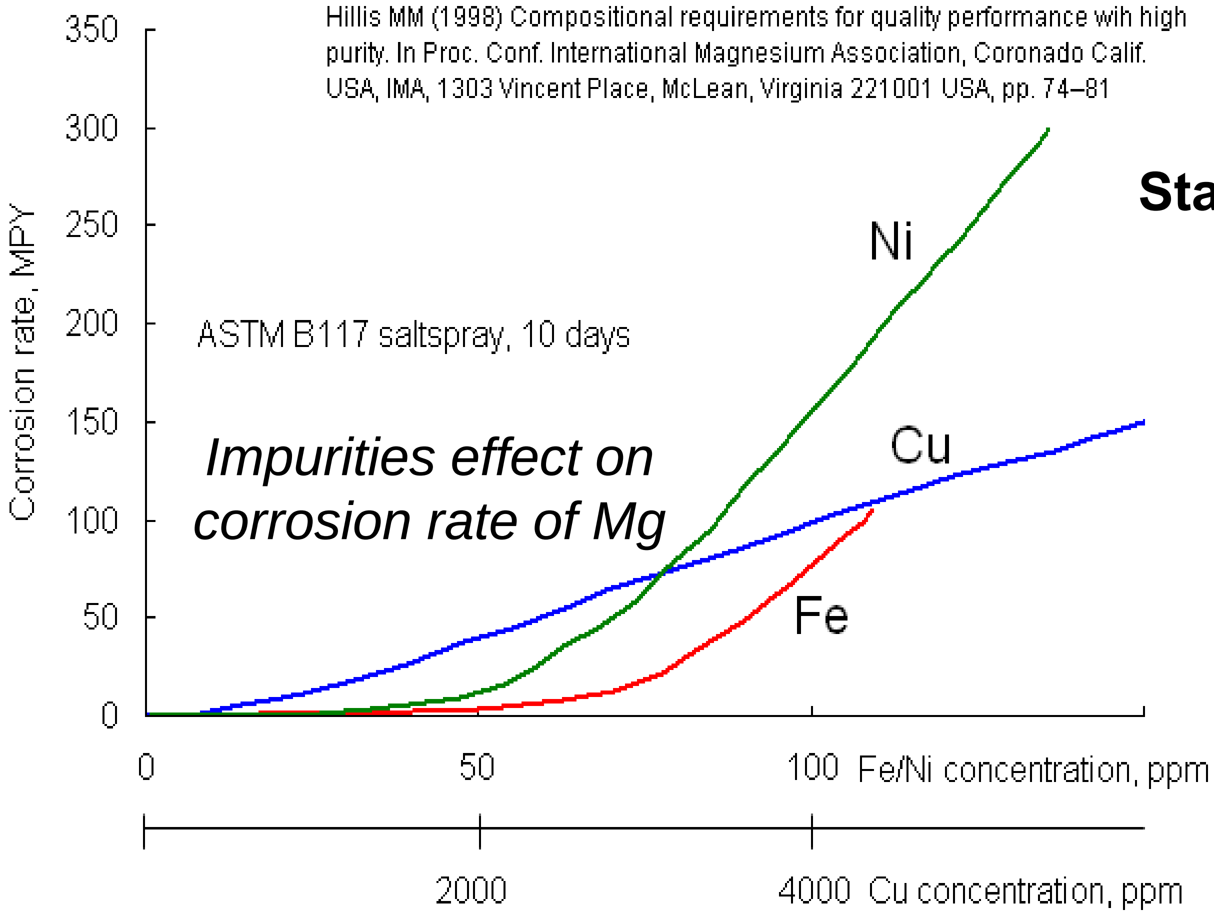
- **Salt water immersion test at 35C (NaCl concentration; 3%)**



$$Mg \rightarrow Mg^{2+} + 2e^-, \quad 2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$$

Effect of metal impurities on corrosion phenomenon

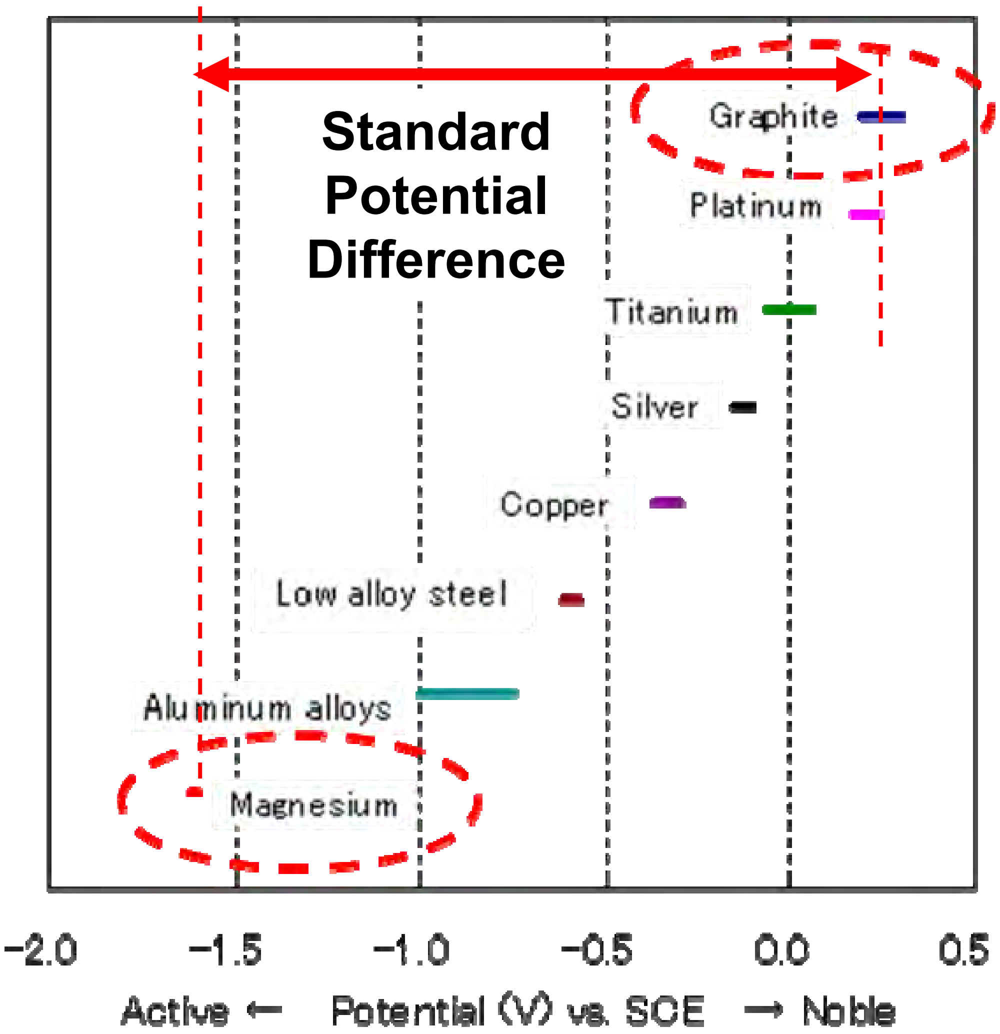
- **Standard potential difference causing corrosion of magnesium**



Standard potential

Mg	**-2.36 V**
Fe	**-0.44 V**
Ni	**-0.23 V**
Cu	**+0.34 V**

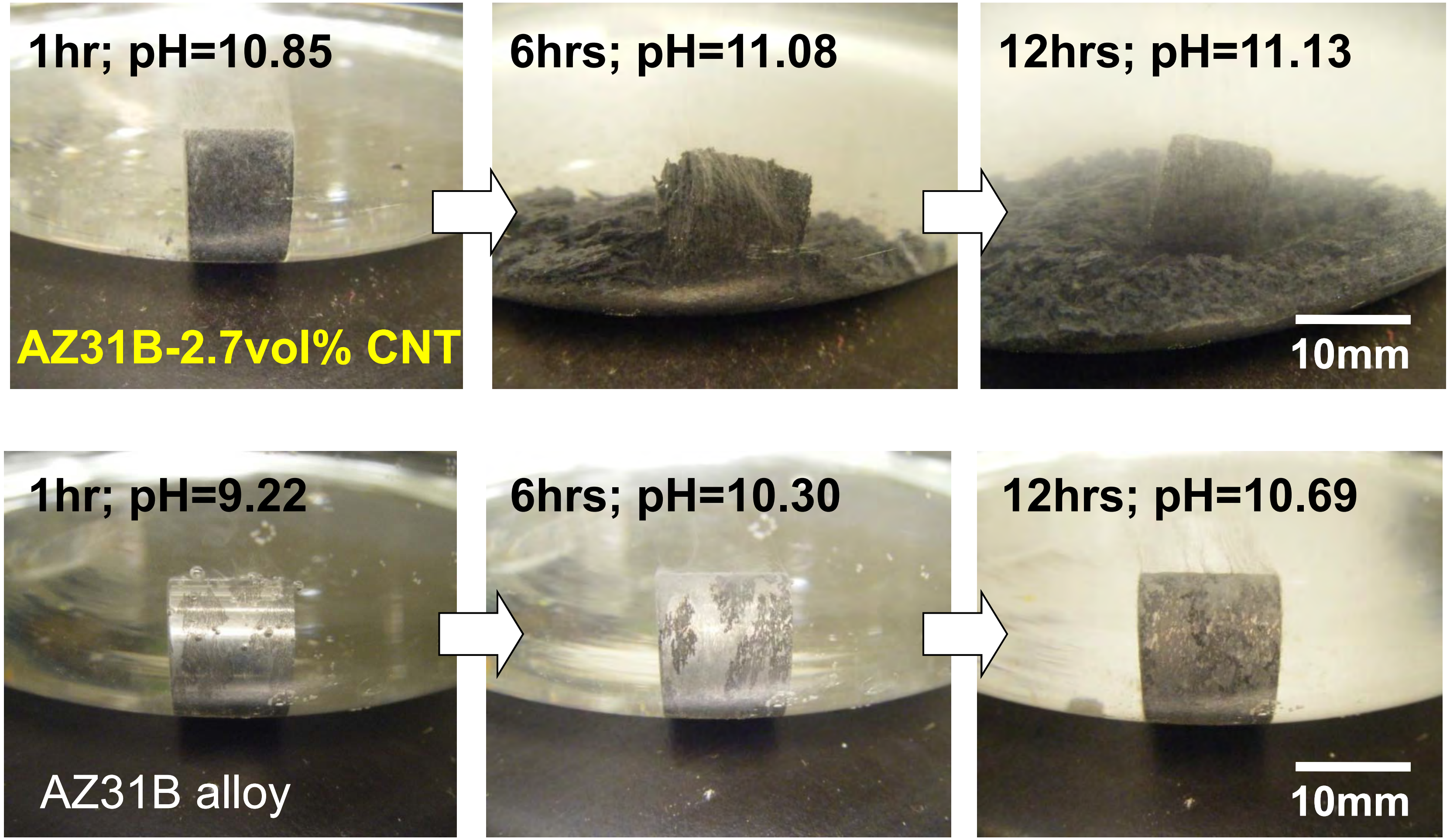
Graphite accelerates corrosion phenomenon?



D. A. Jones, Principles and prevention of corrosion, 2nd ed., Prentice Hall, Englewood Cliffs, 1996.

Graphite accelerates corrosion phenomenon?

- Salt water immersion test at 35C (NaCl concentration; 3%)



Objectives

- Investigation of initial galvanic corrosion phenomenon due to local cell

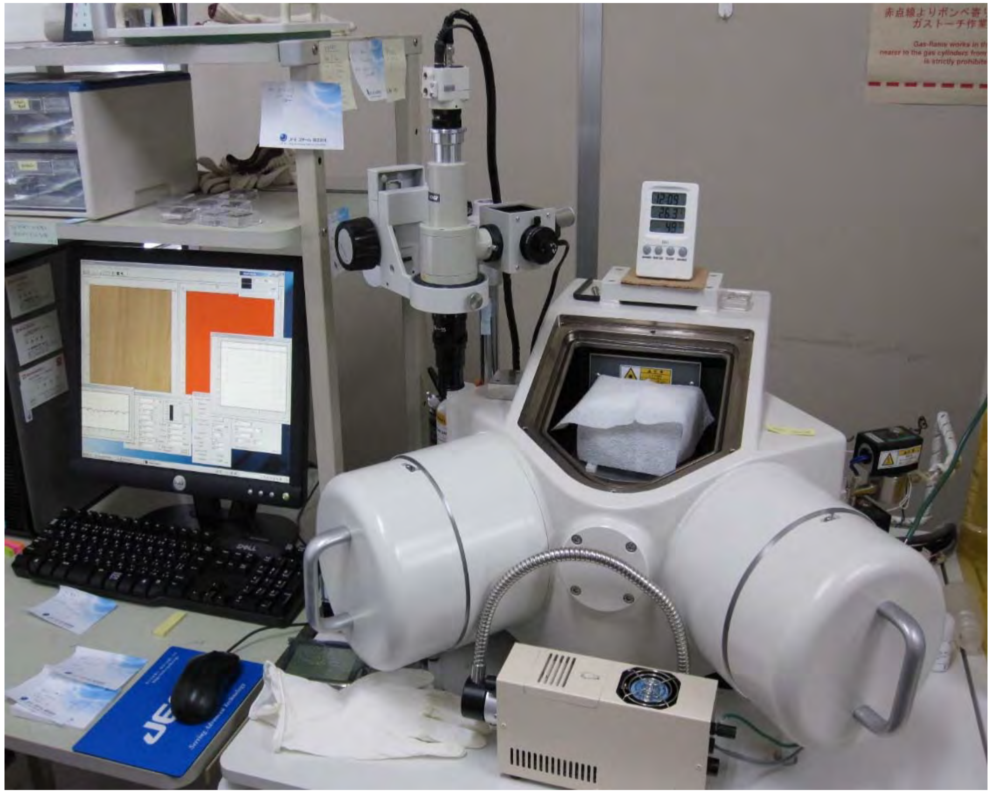
  -Potential difference at interface between α-Mg and dispersoids
  by Scanning Kelvin Prove Force Microscope (SKPFM)

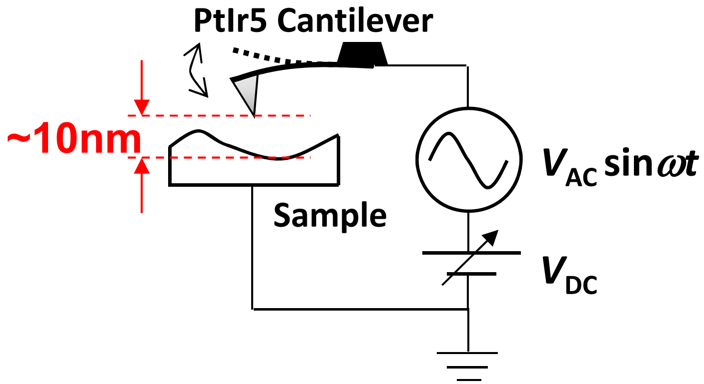
  -Formation of interlayer to decrease potential difference

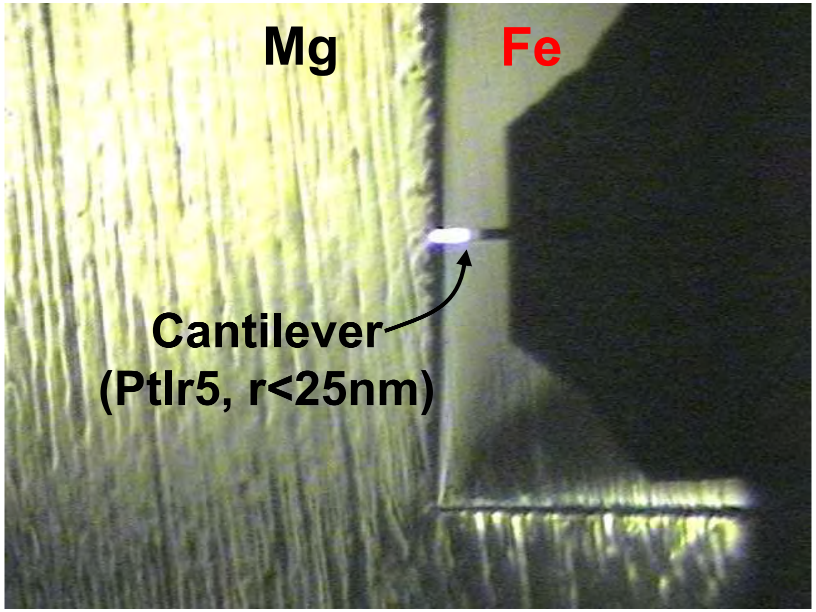
  -Observation of corrosion phenomenon by salt water immersion test

SKPFM analysis of surface potential difference (SPD) at interface

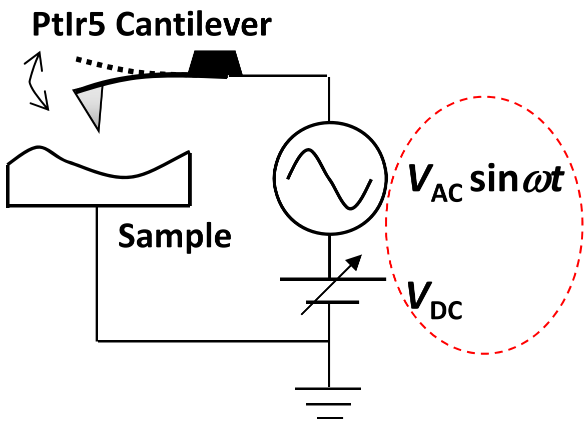
SKPFM measurement system
with atmosphere control chamber







Principle of SKPFM system for SPD measurement



Cantilever close to specimen surface;

→ Fermi level difference equivalent to zero

Contact potential difference (V_{CPD});

$$V_{CPD} = V_{SP} = \left(\phi_{PtIr5} - \phi_{sample}\right)/e \qquad (1)$$

$\mathbf{V_{SP} \rightarrow F_{AF} + F_{ESF}}$ (F_{AF}; Atomic force, F_{ESF}; Electrostatic force)

Electrostatic force (F_{ESF});

$$F_{ESF} = \frac{1}{2}\frac{\partial C}{\partial z}V_{CPD}^2 \quad \text{(C; Electrostatic capacity, z; Distance)} \qquad (2)$$

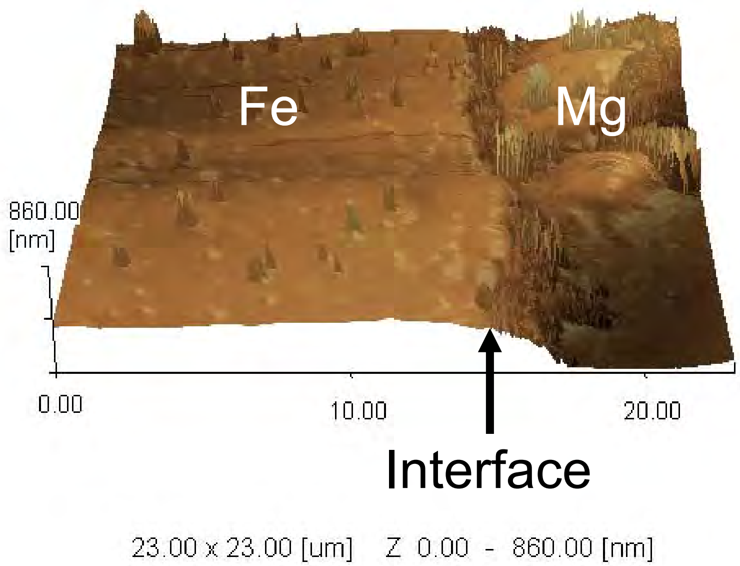
$$V = V_{DC} + V_{AC}\sin\omega t \rightarrow \mathbf{V_{DC} = V_{CPD}} \Rightarrow V_{CPD} = V - V_{AC}\sin\omega t$$

$$F_{ESF} = \frac{1}{2}\frac{\partial C}{\partial z}\left\{\left(V_{DC} - V_{CPD}\right)^2 + \frac{1}{2}V_{AC}{}^2 + 2\left(V_{DC} - V_{CPD}\right)V_{AC}\sin\omega t - \frac{V_{AC}{}^2}{2}\cos 2\omega t\right\}$$

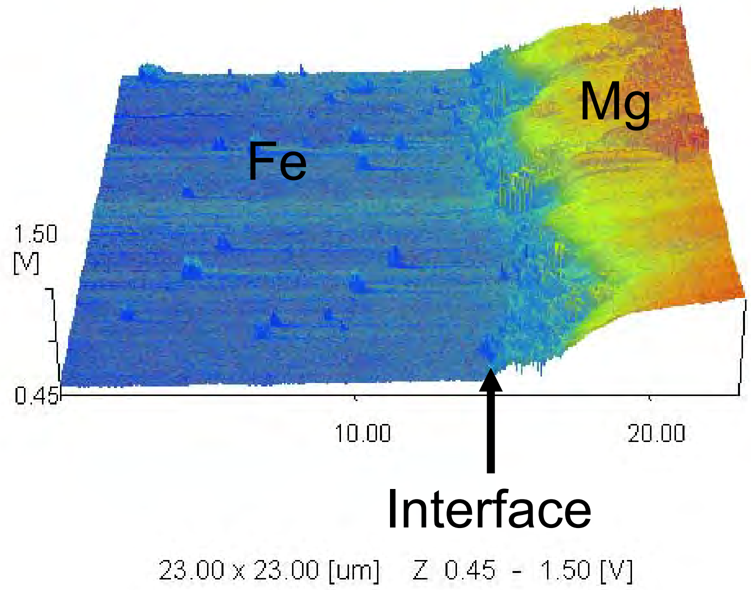
R. Takei, H. Fukuda, H. Imai, J. Umeda, K. Kondoh, Corrosion Phenomenon Evaluation of Mg Alloys using Surface Potential Difference Measured by SKPFM, Magnesium Technology, (2010), 169-172.

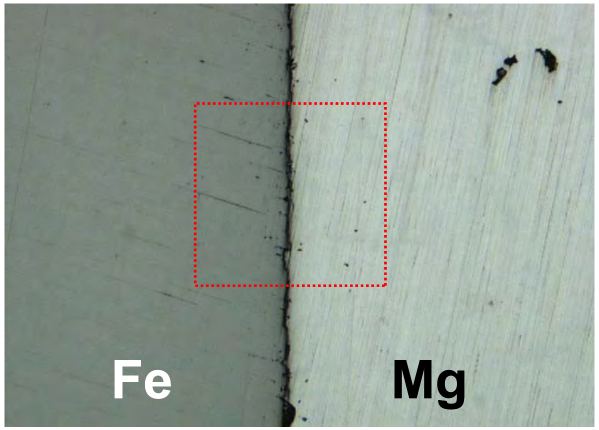
AFM and KFM analysis at pure Mg/Fe interface

Surface morphology (AFM)

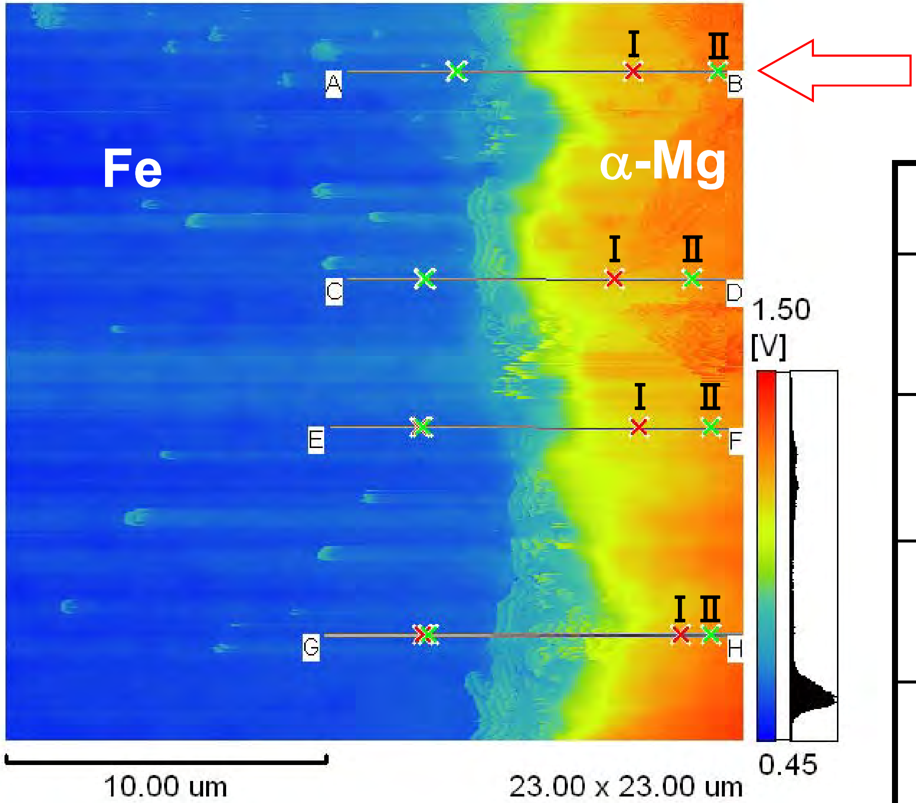


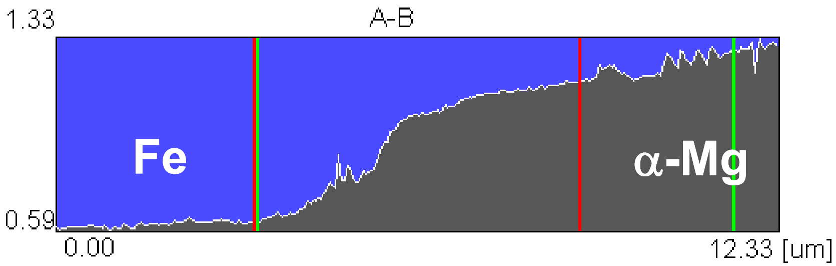
Surface potential mapping (KFM)





AFM and KFM analysis at pure Mg/Fe interface





Measurement point		V_{SPD} (V)
A - B	I (red)	0.54
	II (green)	0.66
C - D	I (red)	0.55
	II (green)	0.61
E - F	I (red)	0.53
	II (green)	0.61
G - H	I (red)	0.62
	II (green)	0.67

Max. 0.67V
Min. 0.53V

Preliminary experimental results – Effect of surface oxide film on SP

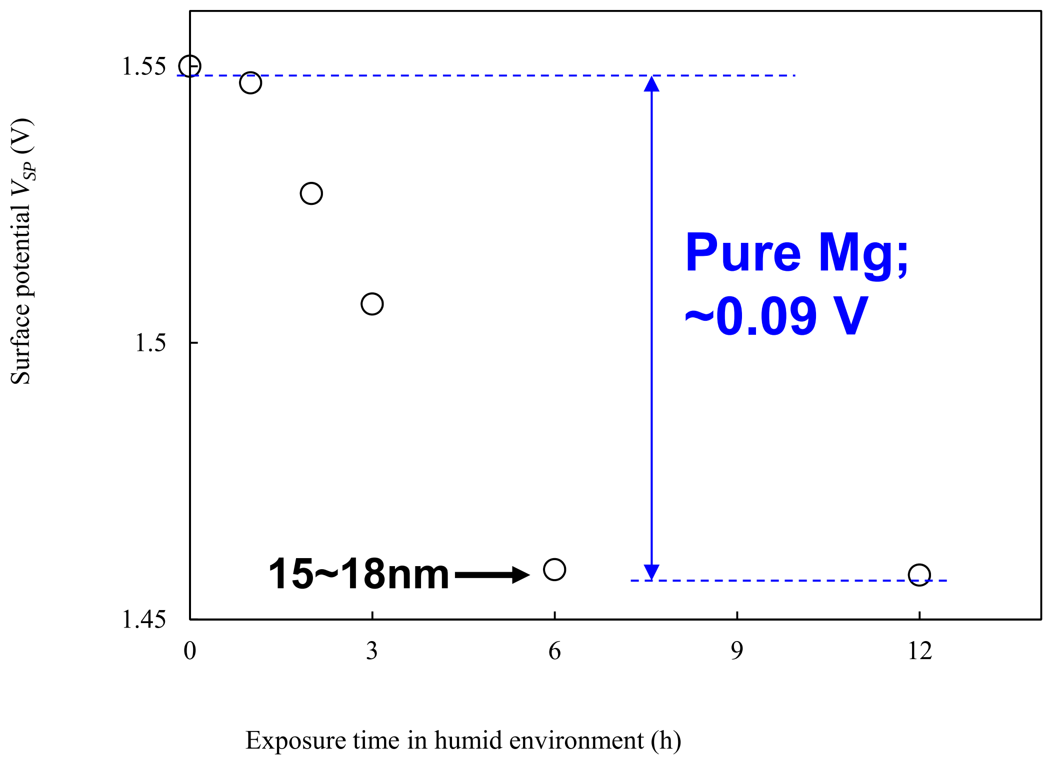
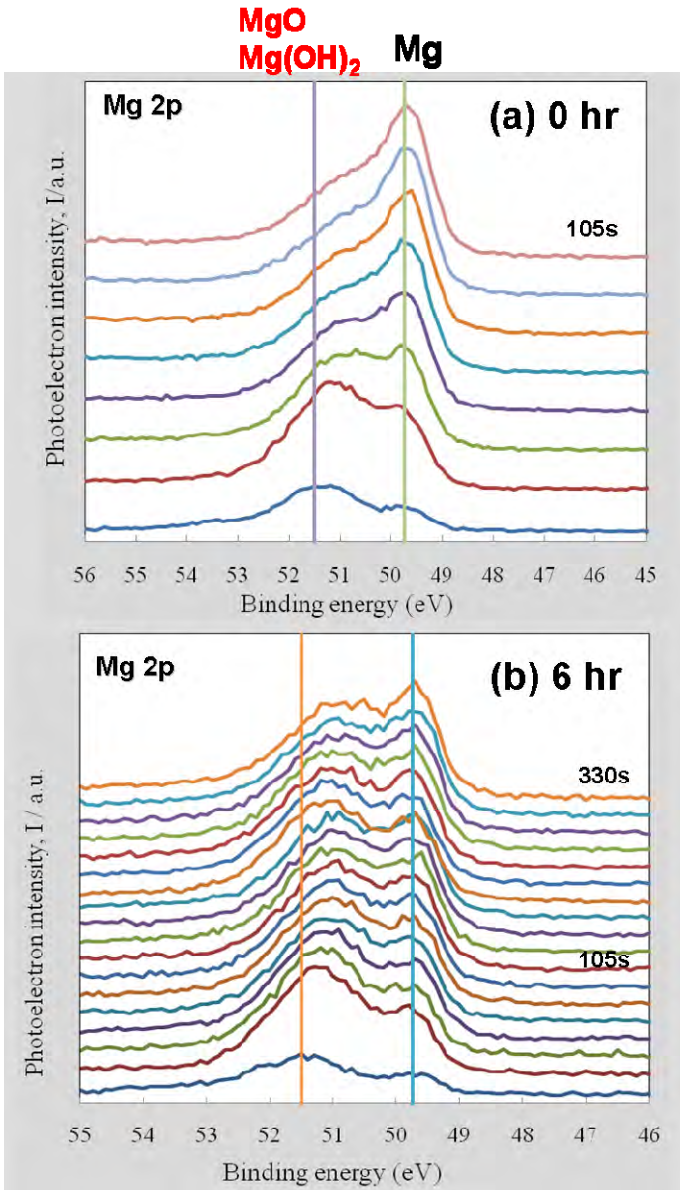
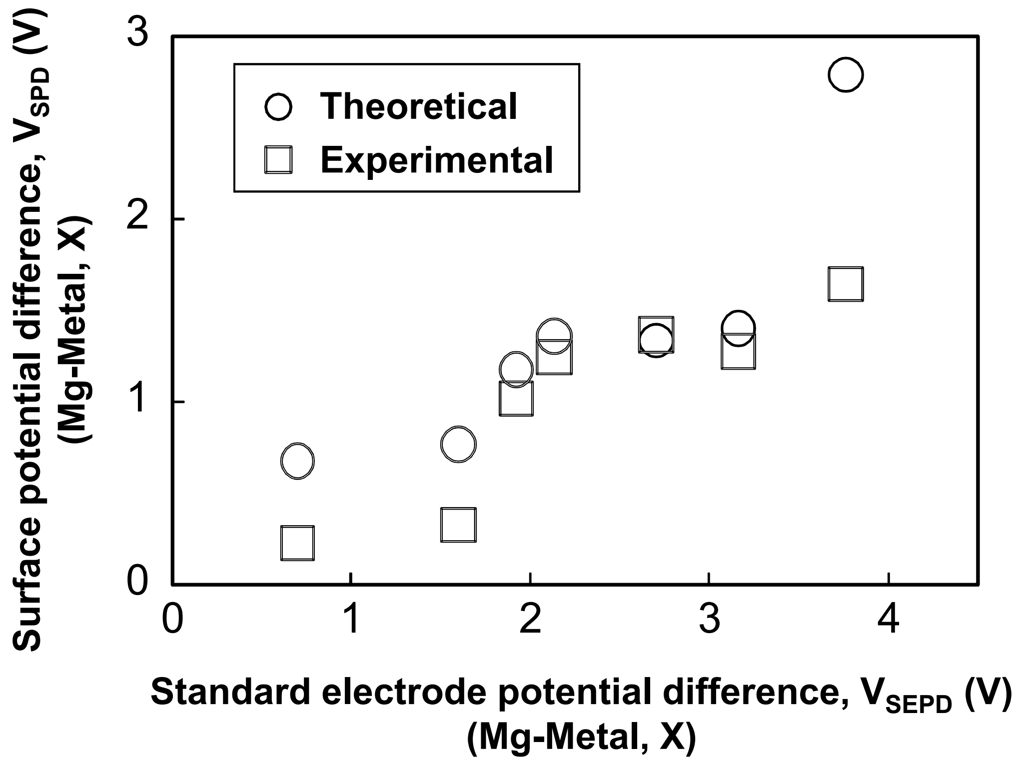


Fig. Surface potential of pure Mg plate dependence on exposure time in humid condition (~60%RH). MgO surface thin film effective in decrease of surface potential due to their higher work function than pure Mg.

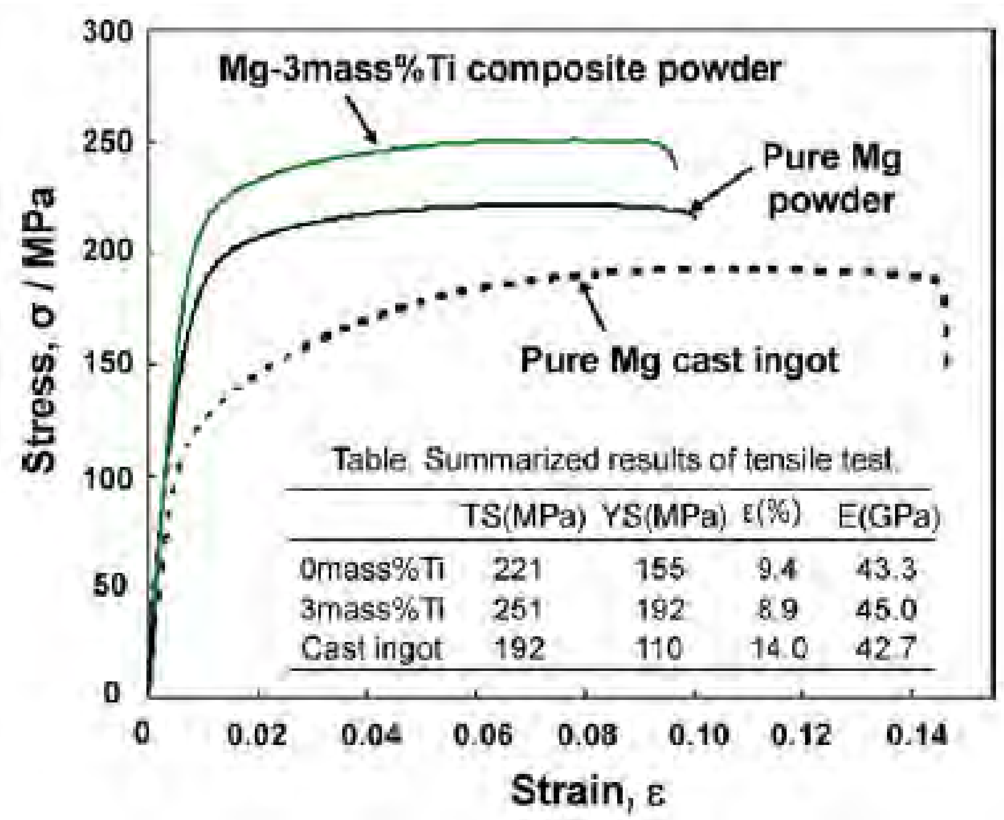


Preliminary experimental results – Reliability of SPD measurement



Exposure time (h)	Temperature in chamber (C)	Relative humidity (%RH)
12	30 ± 1	60 ± 1

Experimental – Ti particle reinforced Mg composite



	TS(MPa)	YS(MPa)	ε(%)	E(GPa)
0mass%Ti	221	155	9.4	43.3
3mass%Ti	251	192	8.9	45.0
Cast ingot	192	110	14.0	42.7

1) K. Kondoh at al, Acta Materialia, 58 (2010) 606-614.
2) J. Umeda at al, Materials Chemistry and Physics, 123 (2010) 649-657.

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Wettability of pure Ti by molten pure Mg droplets

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Abstract

The wetting behavior of molten pure Mg droplets on pure Ti substrate, a crucial phenomenon in the design of Mg matrix composites reinforced with Ti particles, was investigated by the sessile drop method. The contact angle was measured in high-purity argon (99.999%) at 1073 K. In particular, the effects of two important parameters on the contact angle were evaluated: Mg evaporation during the wetting test; and surface oxide film of the substrate. The calculation method to estimate the modified contact angle involved taking the morphological changes of the droplet outline due to the evaporation into consideration. By changing the thickness of the surface oxide films on the Ti substrate, it was possible to examine the wettability and the chemical reactions at the interface between the solidified Mg drop and the substrate were investigated by scanning electron microscopy–energy dispersive X-ray spectrometry analysis. At the initial wetting stage, a large contact angle with 95–110° was obtained, which depended on the reduction of TiO_2 surface films by Mg droplets. When the molten Mg contacts an area of pure Ti after reduction, the contact angle suddenly decreased. The equilibrium value at the stable state strongly depended on the surface roughness of the Ti plate.

Keywords: Pure magnesium; Titanium; Contact angle; Young's equation; Evaporation

Materials Chemistry and Physics 123 (2010) 649–657
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Microstructural and mechanical properties of titanium particulate reinforced magnesium composite materials

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ABSTRACT

Pure titanium (Ti) particulate reinforced pure magnesium (Mg) composite materials were fabricated via powder metallurgy route, and their microstructural and mechanical properties were evaluated. When using the elemental mixture of pure Mg and pure Ti powders and consolidating them by solid-state sintering process, no significant increase in tensile strength of the composites was obtained, because of poor bonding strength at the interface between α-Mg matrix and Ti particles. In particular, coarse magnesium oxide (MgO) particles of about 100 nm were formed via thermite reaction between TiO_2 surface films of Ti particles and Mg raw powders and resulted in preventing the improvement of the mechanical properties of the composite material. On the other hand, when using the atomized pure Mg composite powders reinforced with Ti particulates, their extruded composite material showed obviously improved tensile strength and good elongation, compared to the extruded pure Mg powder material including no Ti particle. The obvious improvement in the tensile strength was due to the restriction of dislocation movement by Ti reinforcements under applied tensile load.

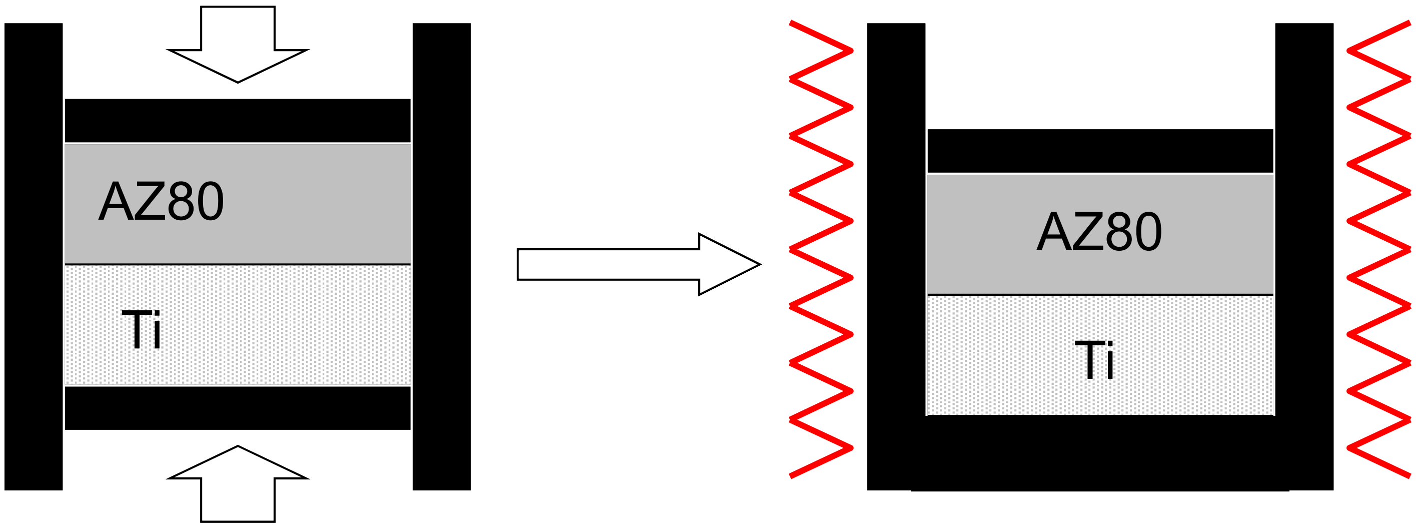
Experimental – Preparation of AZ80/Ti bonded materials

(1) Solid-state bonding by SPS

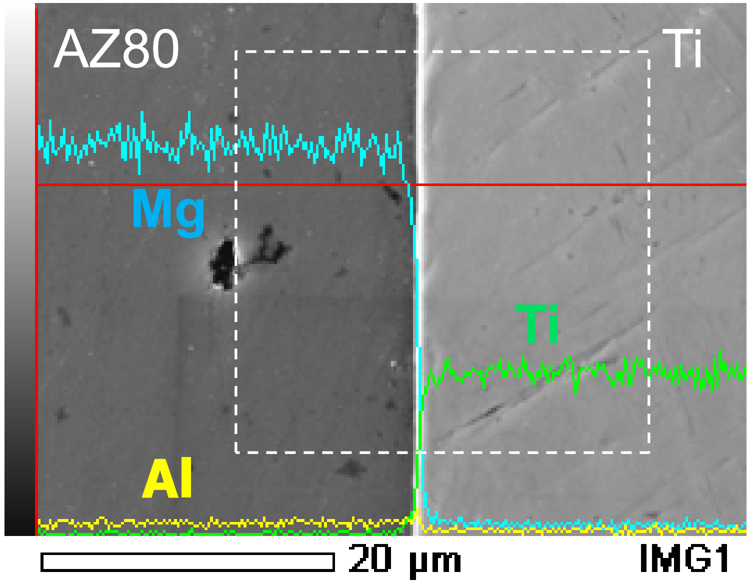
T= 400C for 1.8ks
P=40MPa

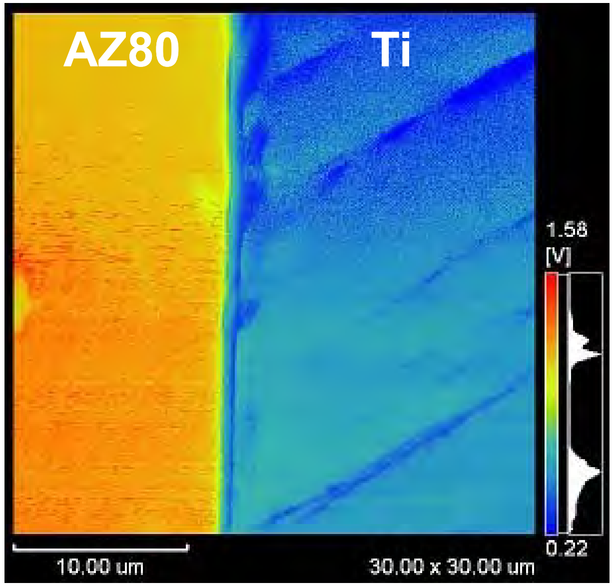
(2) Liquid-state bonding by melting

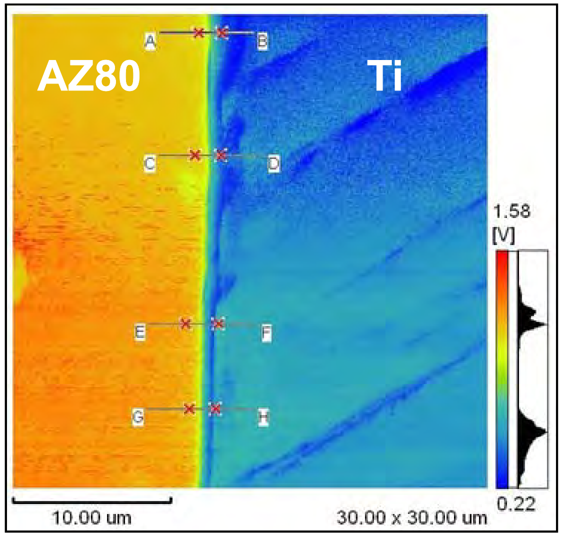
T= 800C for 1.8ks
(Ar gas atmosphere)

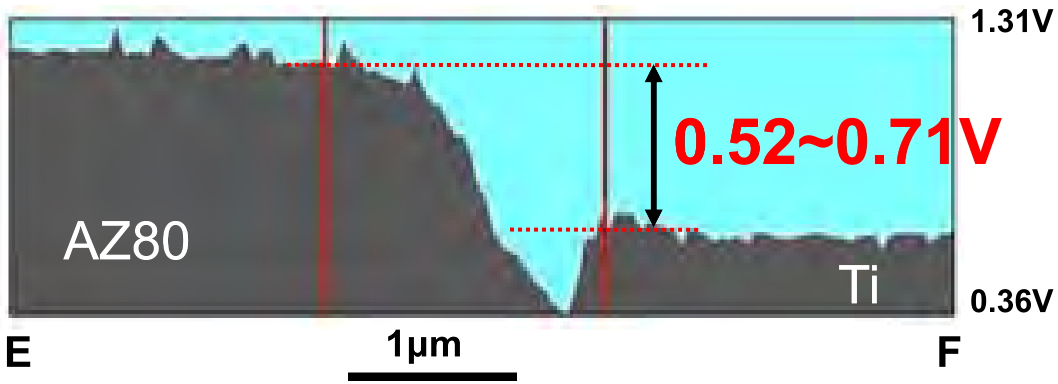


Results – EDS & KFM analysis on AZ80/Ti specimen (solid-state bonded)







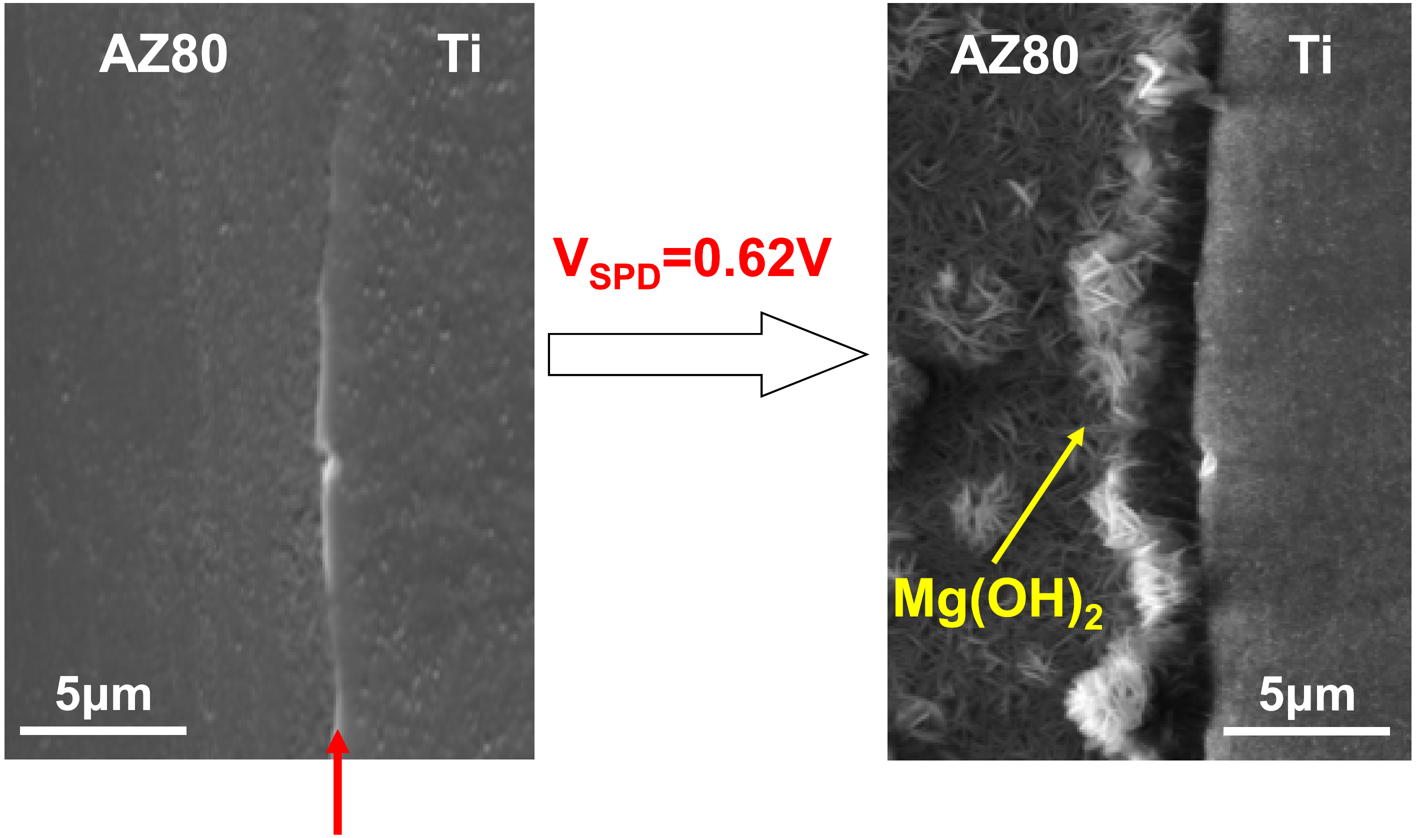


Results – Immersion test of AZ80/Ti specimens (solid-state bonded)

<u>Salt water immersion test</u> ($Mg + 2H_2O \rightarrow$ **$Mg(OH)_2$** $+ H_2$)

Solution; 5wt% NaCl (30C), Soaking time; 10.8 ks

(a) **Before** immersion test (b) **After** immersion test



Results – Interlayer formation at AZ80/Ti interface (liquid-state bonded)

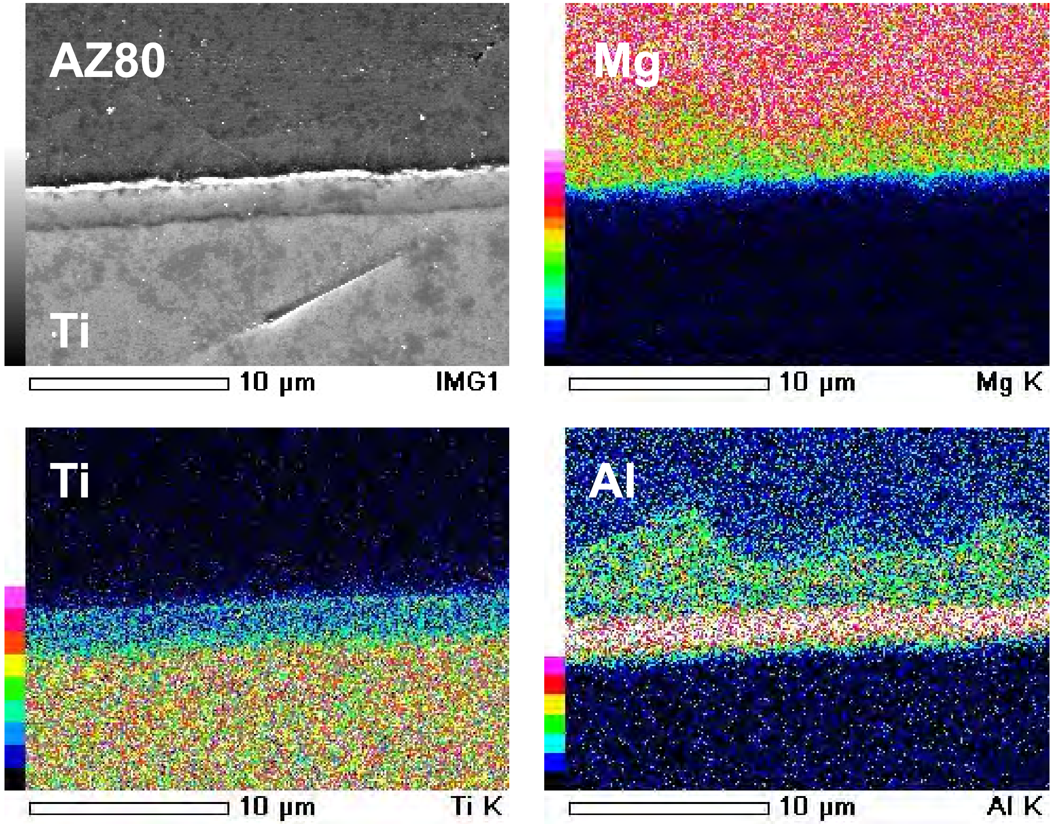
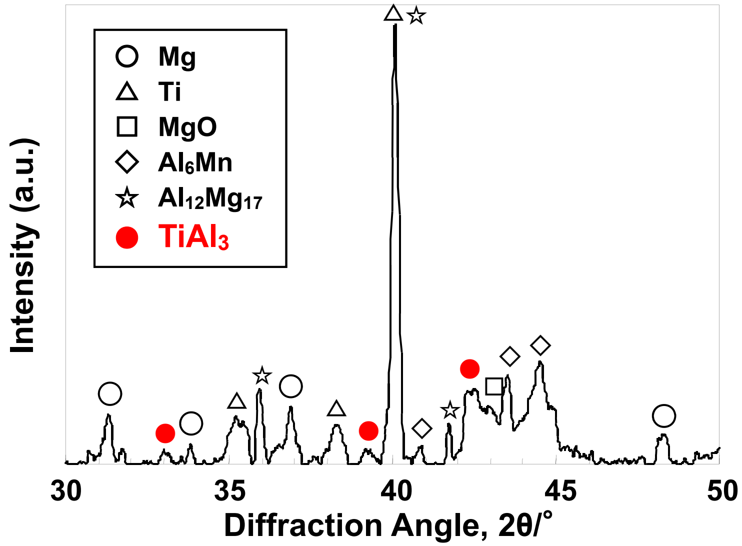


Fig. SEM-EDS analysis on interface between AZ80 and pure Ti plate after wettability test (T=973K for t=2.1ks).



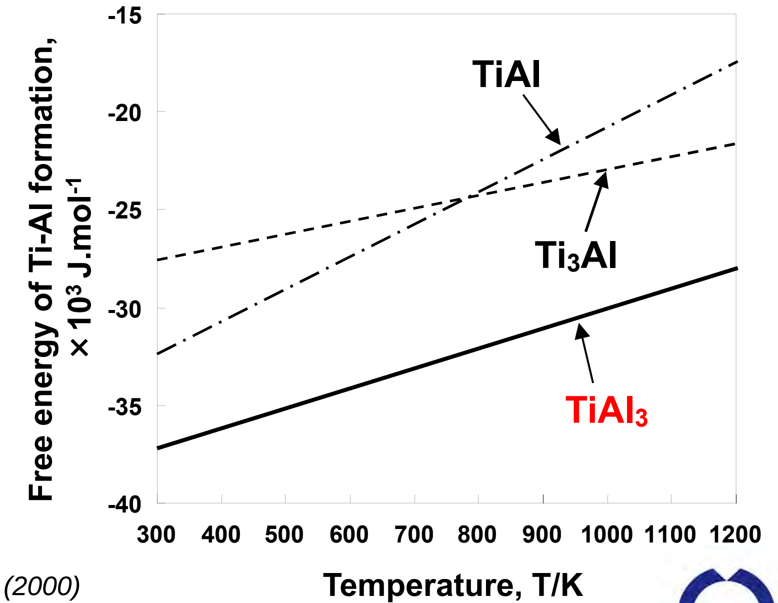
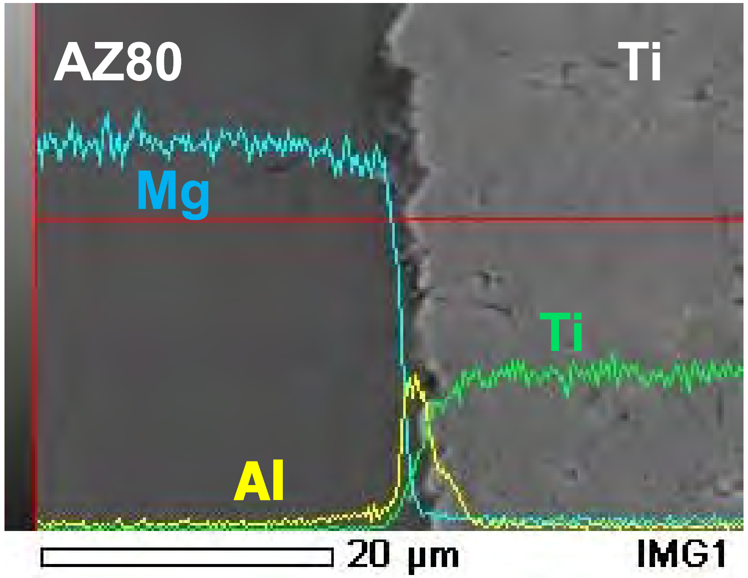
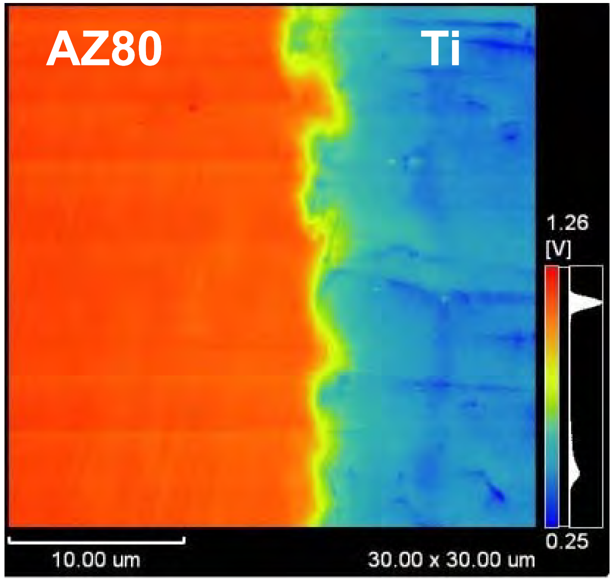


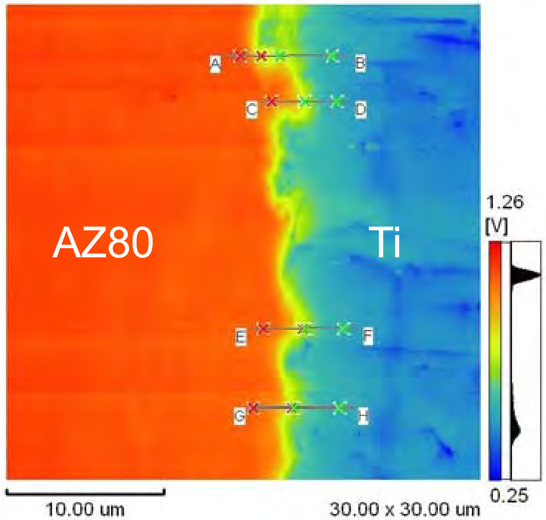
Fig. XRD pattern of interface between AZ80 solidified droplet and Ti plate after wettability test (t=2.1ks), and free energy of formation of various Ti–Al intermetallic compounds [1].

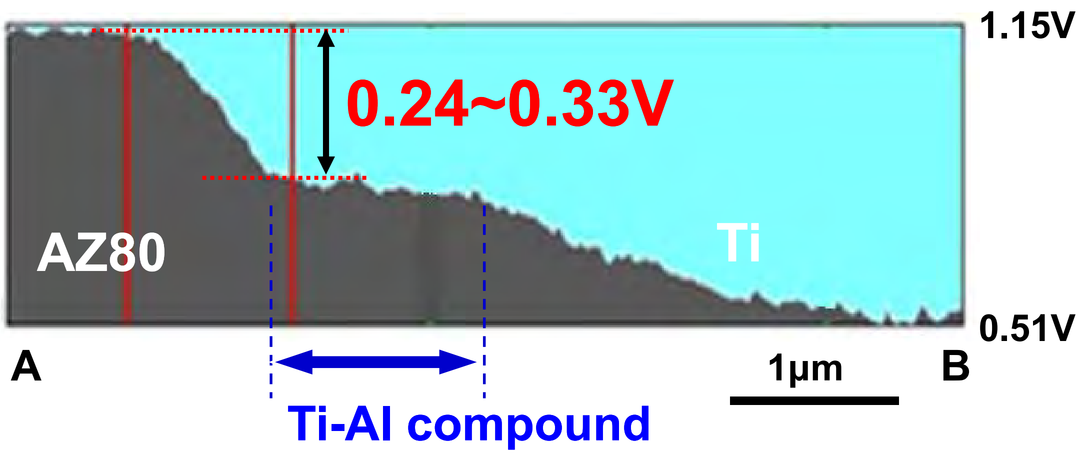
[1] *J.H.Westbrook, R.L.Fleischer: Intermetallic Compounds, JOHNWILEY & SONS (2000)*

Results – EDS & KFM analysis on AZ80/Ti specimen (liquid-state bonded)







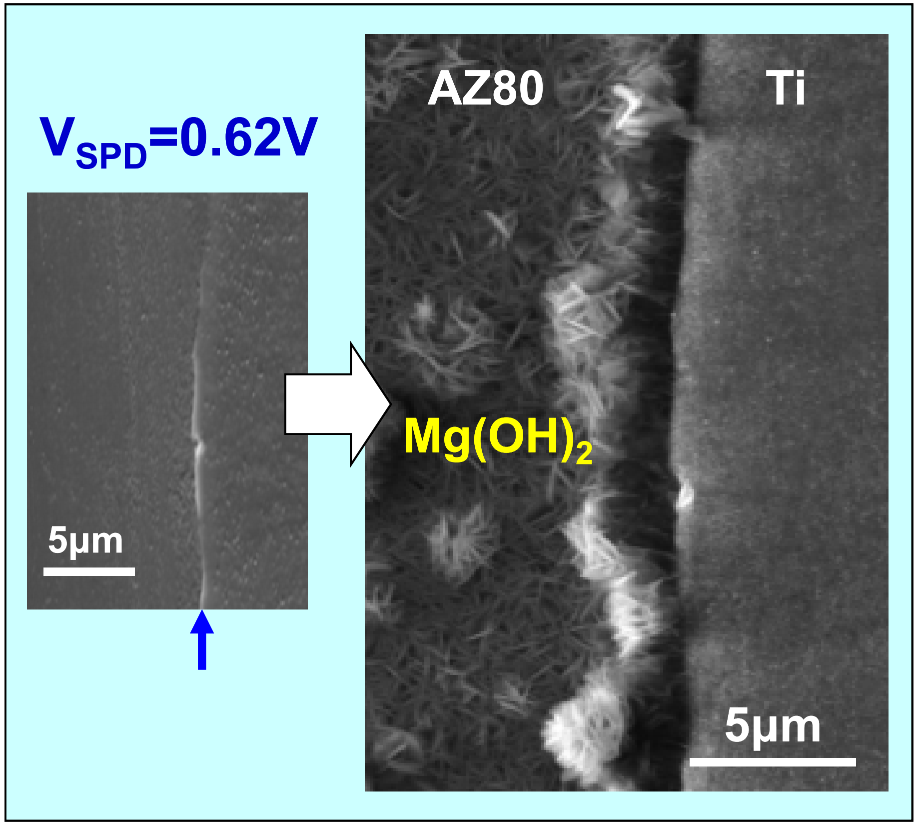


Results – Immersion test of AZ80/Ti bonded materials

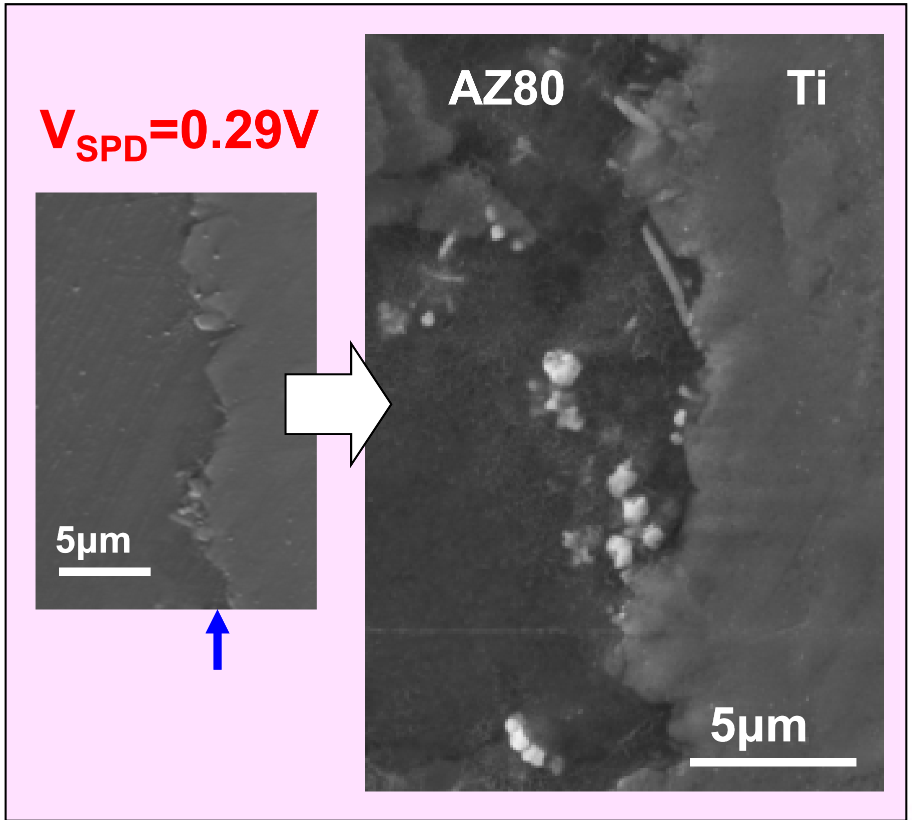
<u>Salt water immersion test</u> ($Mg + 2H_2O \rightarrow$ **$Mg(OH)_2$** $+ H_2$)

Solution; 5wt% NaCl (30C), Soaking time; 10.8 ks

Solid-state bonded (without interlayer)

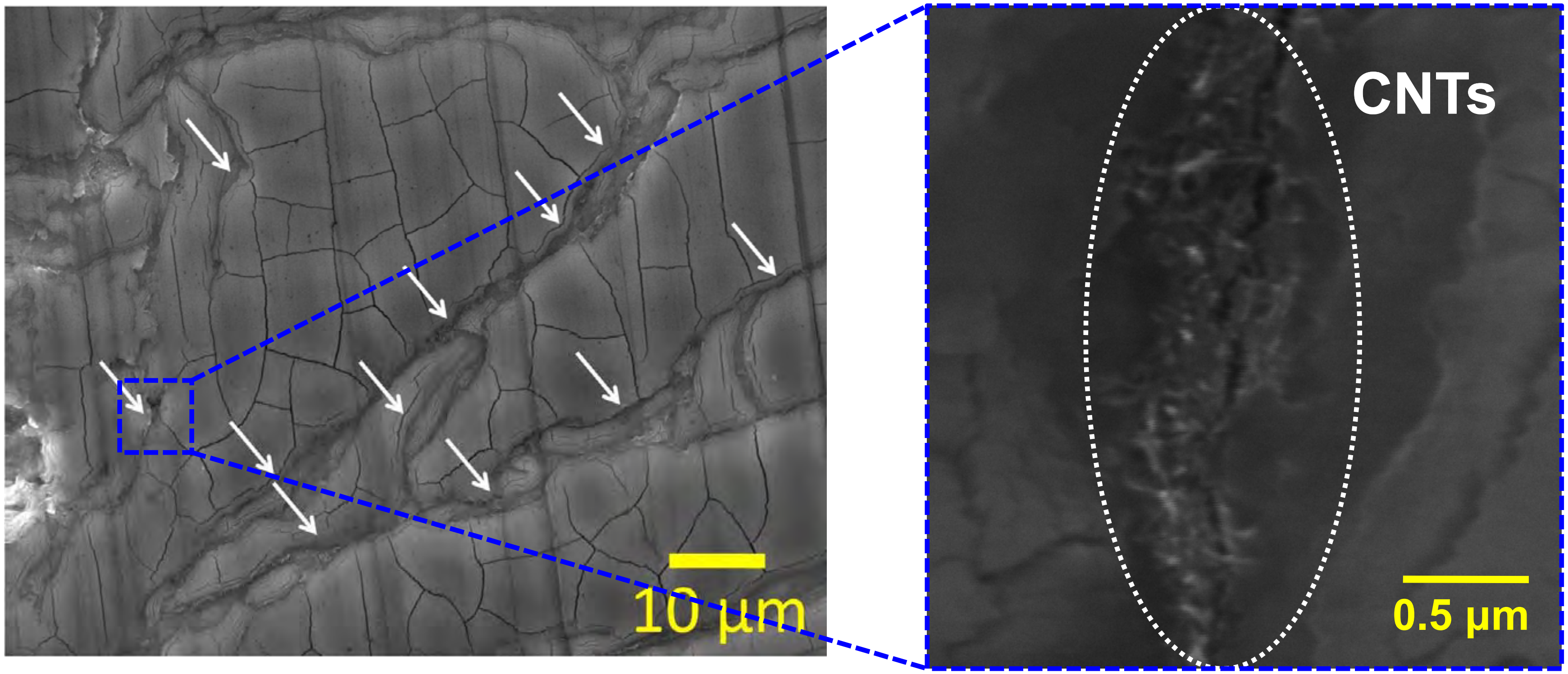


Liquid-state bonded (with $TiAl_3$ layer)



Background – Galvanic corrosion phenomenon at CNT/AZ31B interface

MWCNTs reinforced AZ31B sintered composite (CNT; 2.66vol.%)



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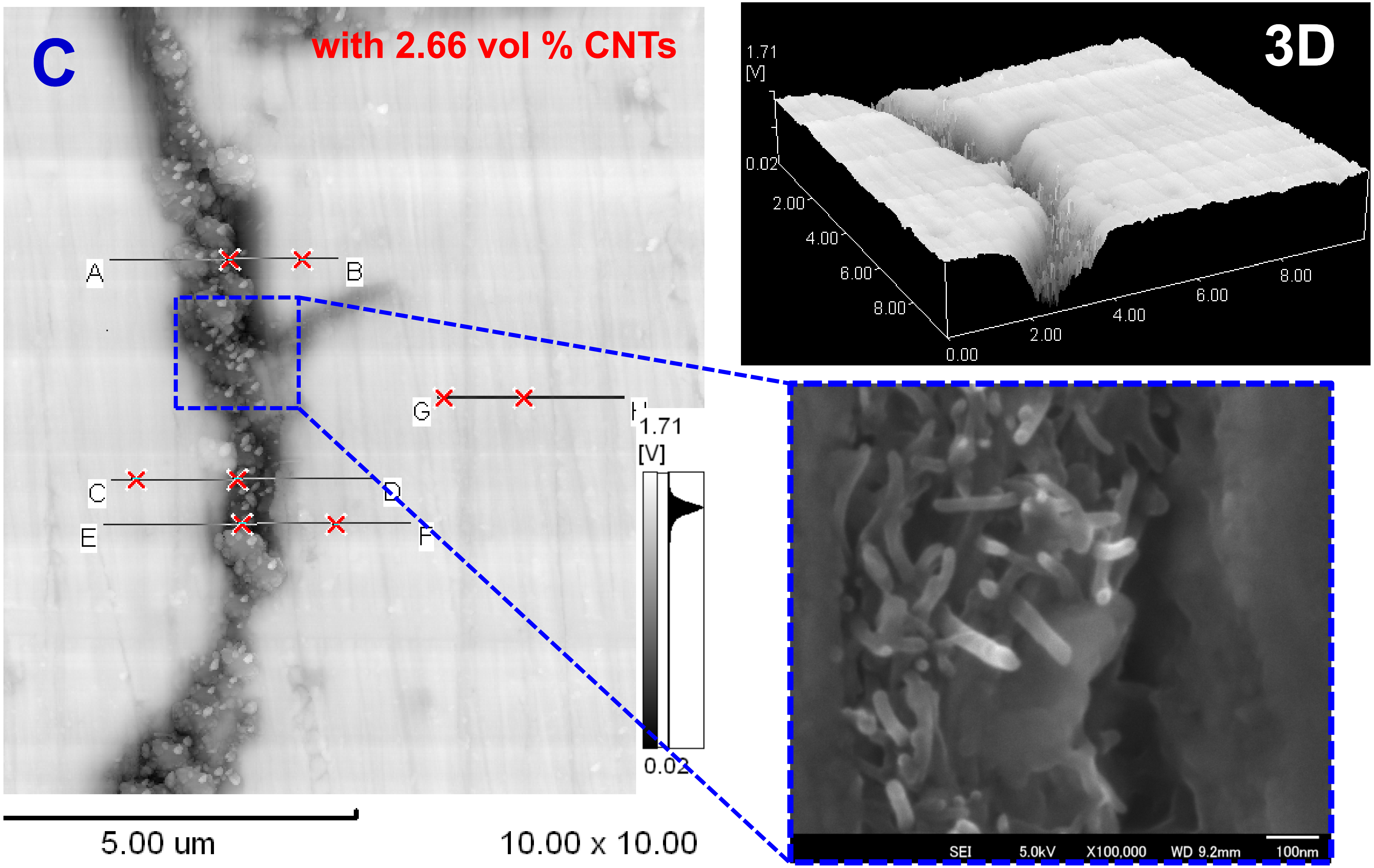
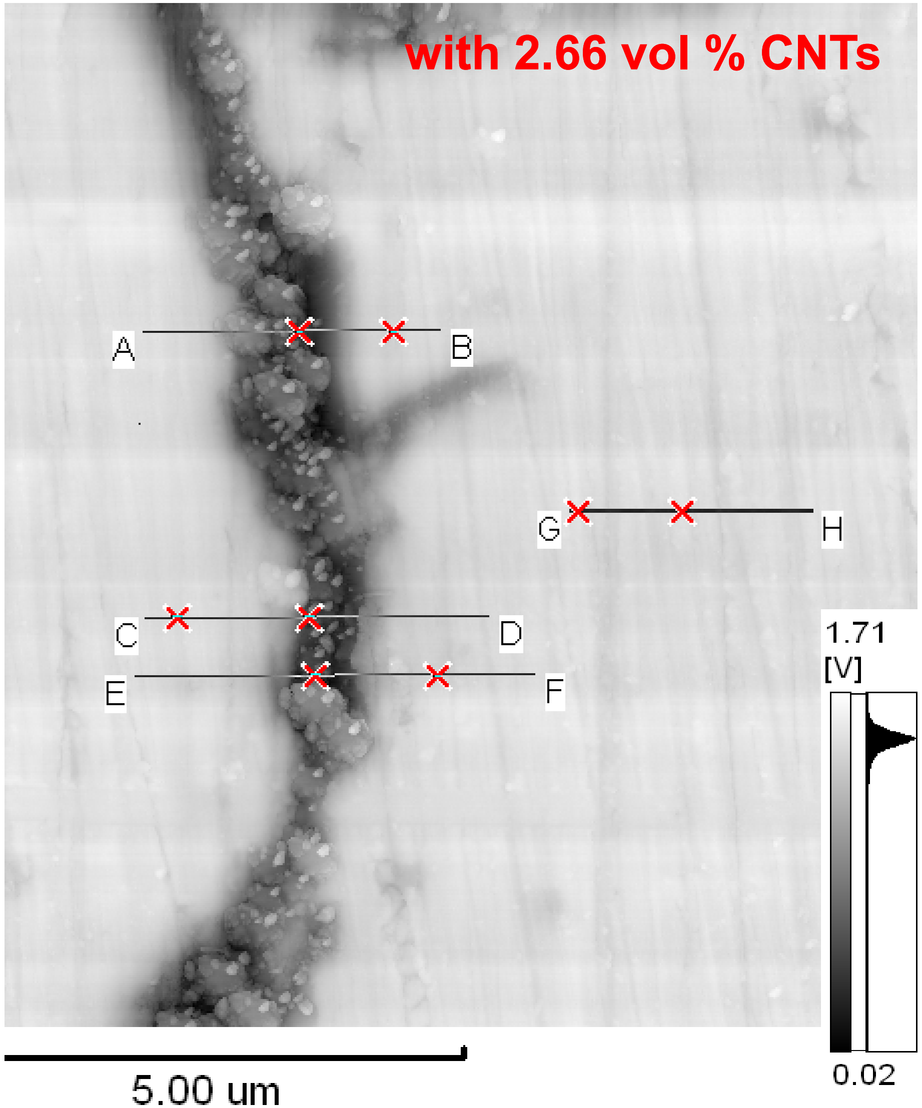


H. Fukuda, J.A. Szpunar, K. Kondoh, R. Chromik, Corrosion Science, 52 (2010) 3917-3923.

Surface potential difference effective on Galvanic corrosion



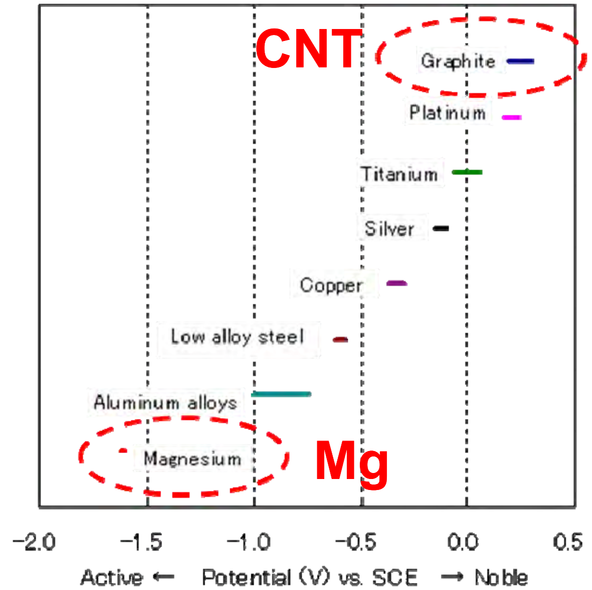
Potential difference

A-B 1.06 V
C-D 1.09 V
E-F 1.14 V
} **CNT-matrix**

G-H 0.01 V (matrix)

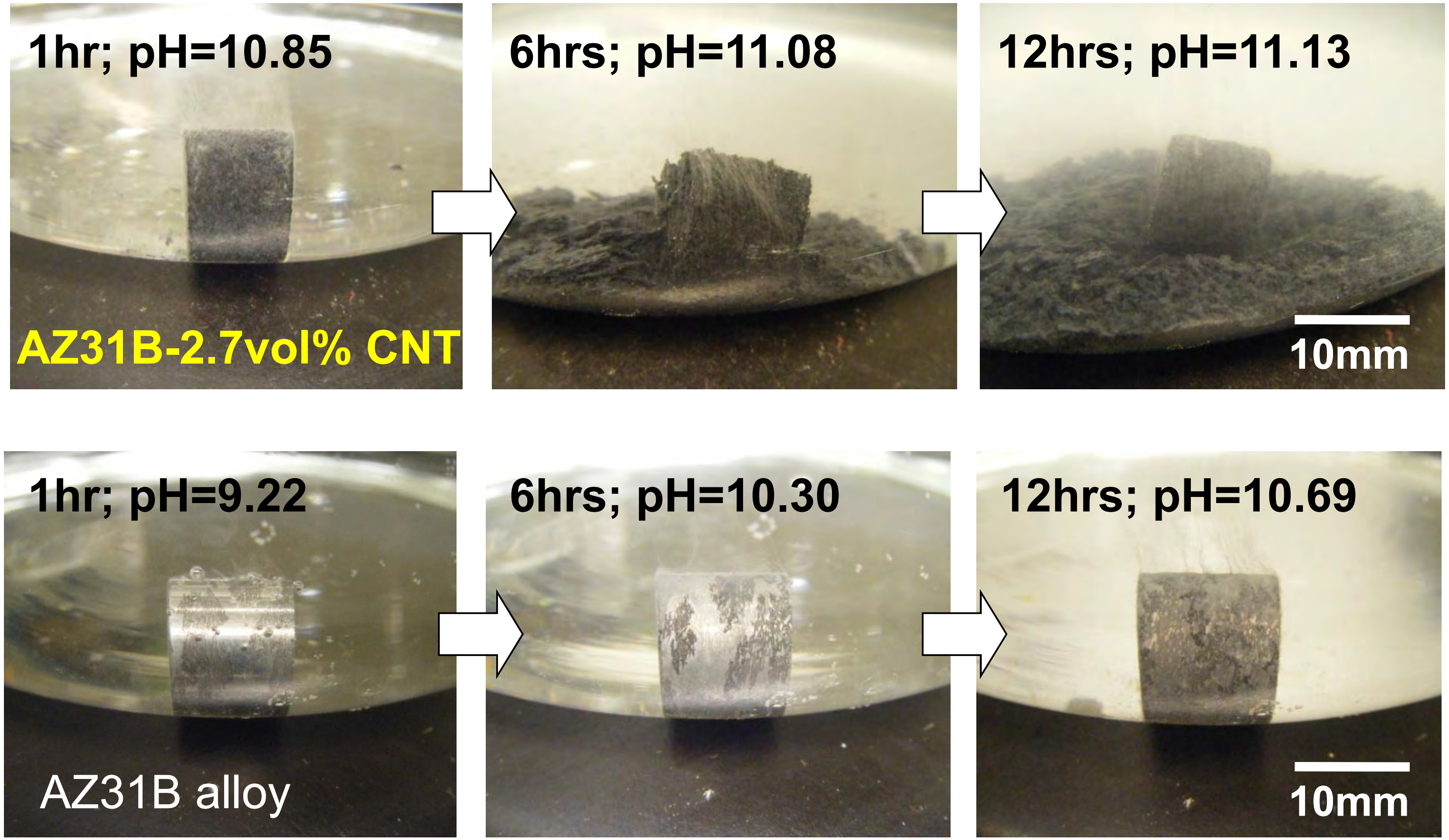
Mg-**Fe** **~0.8 V**

Mg-Mg_2**Cu** **~0.68 V**

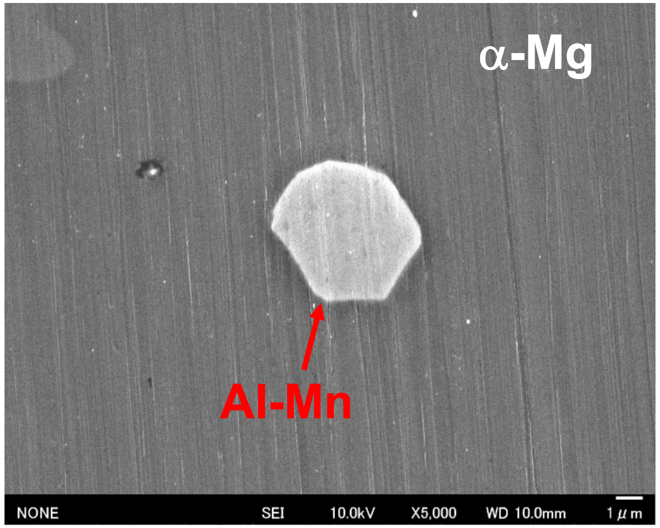


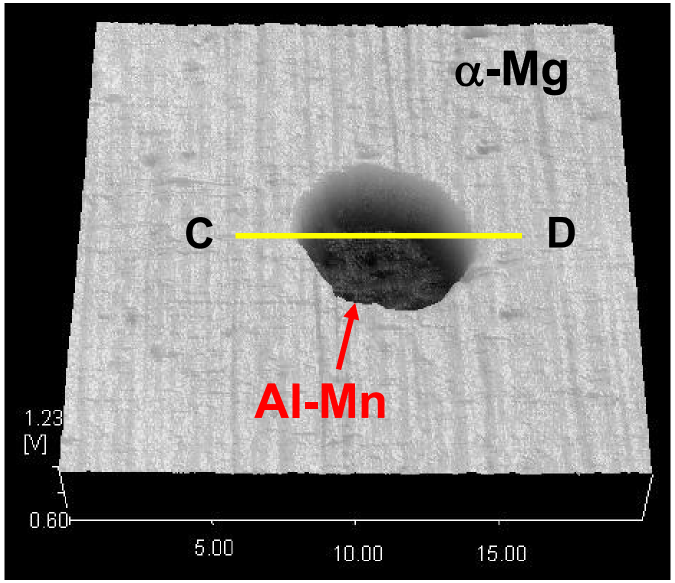
Graphite accelerates corrosion phenomenon

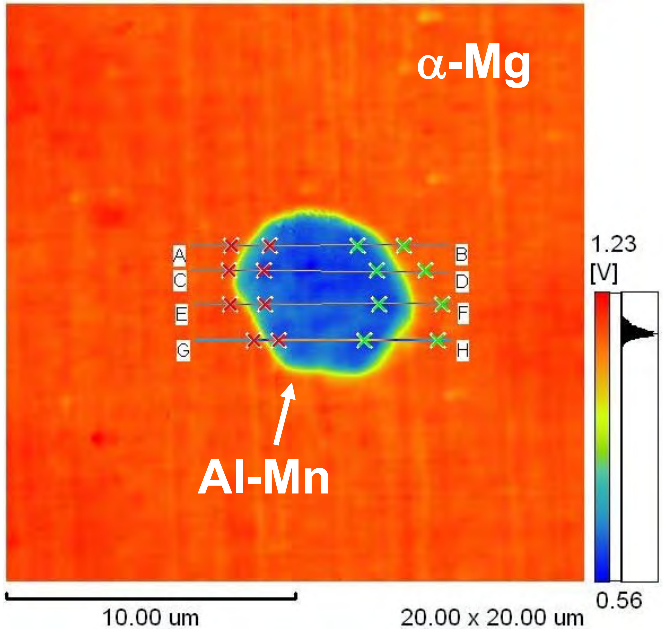
- Salt water immersion test at 35C (NaCl concentration; 3%)

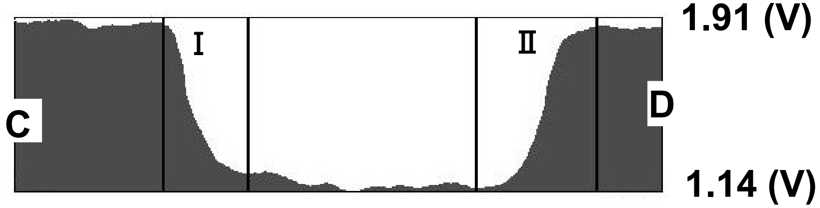


Results and Discussion – Al-Mn intermetallic of AZ91B alloy





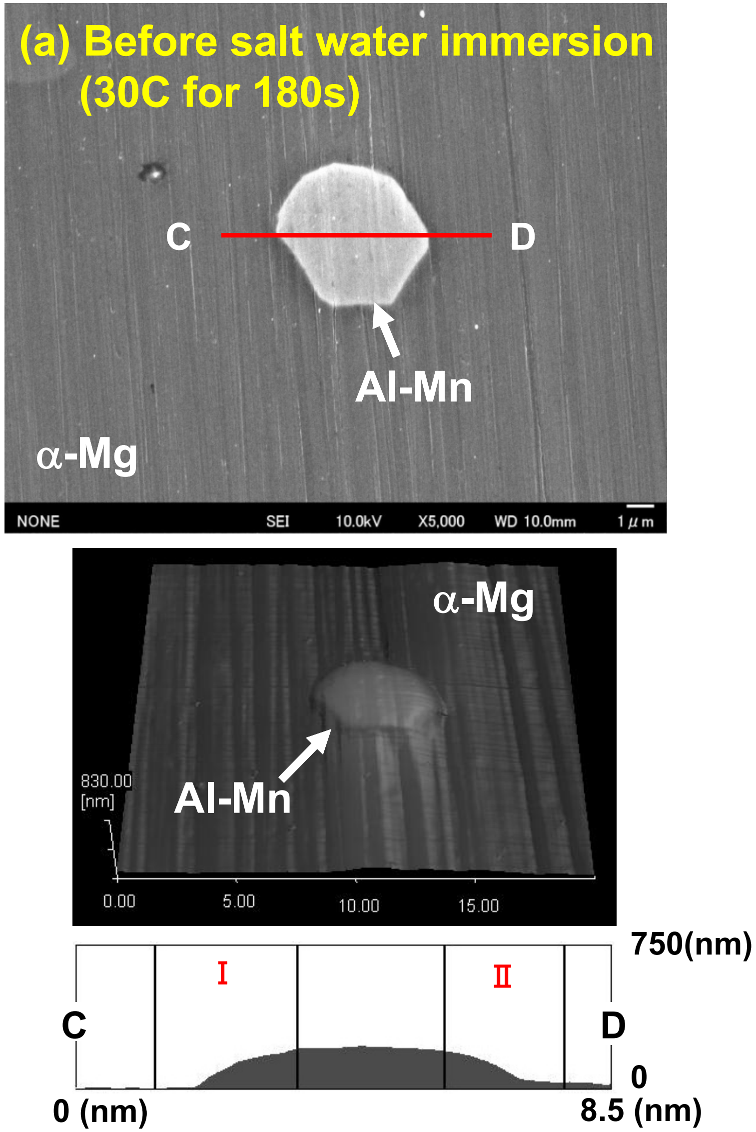


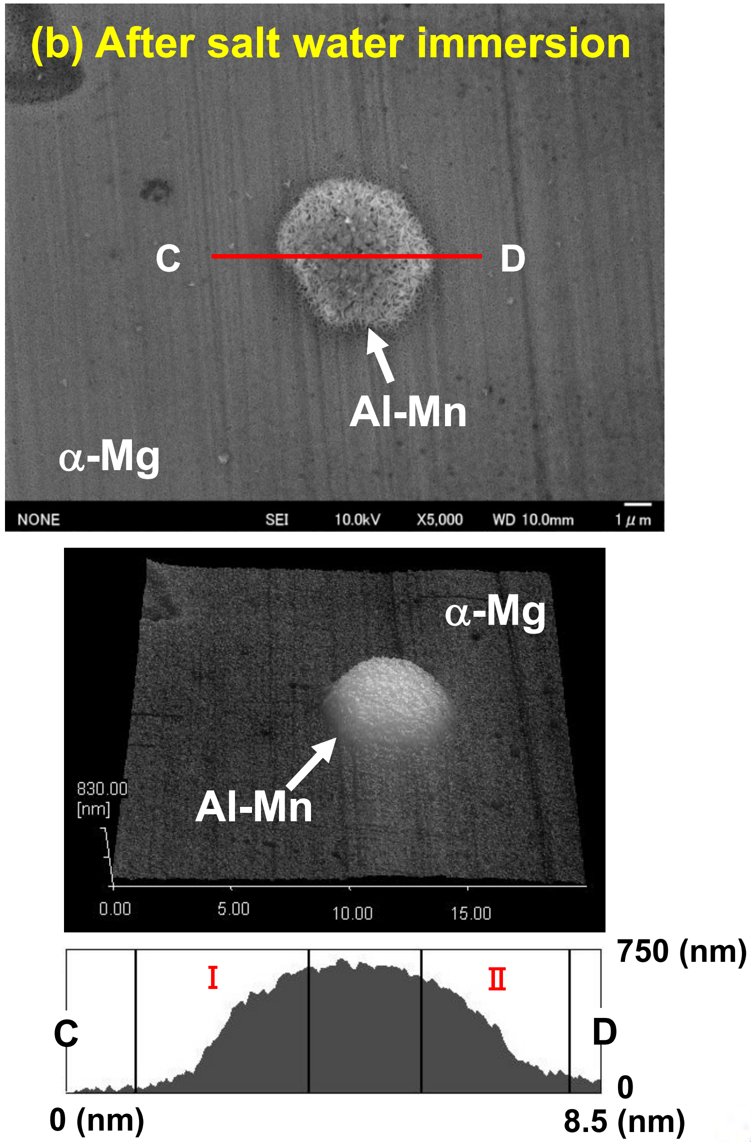


Surface potential difference, V_{SPD} (V)

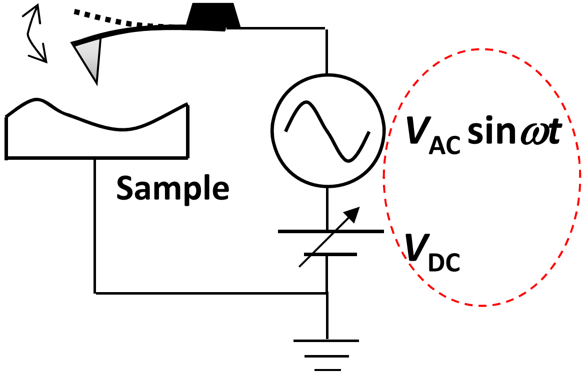
Point	A-B	C-D	E-F	G-H
(red line)	-0.46	-0.53	-0.46	-0.45
(green line)	-0.50	-0.50	-0.53	-0.53

Results and Discussion – Immersion test around Al-Mn of AZ91B alloy

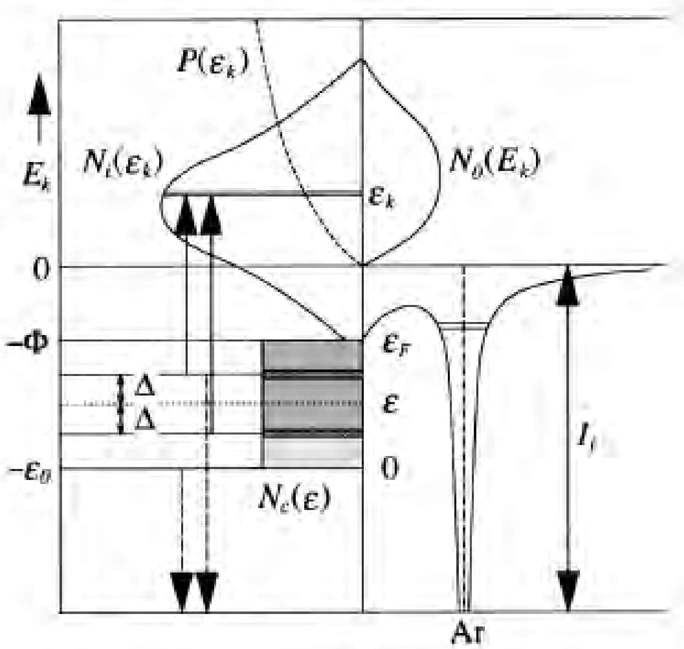




Work function – Fermi potential relation for Galvanic control



Appl. Phys. Lett., Vol. 76, No. 23, 5 June 2000



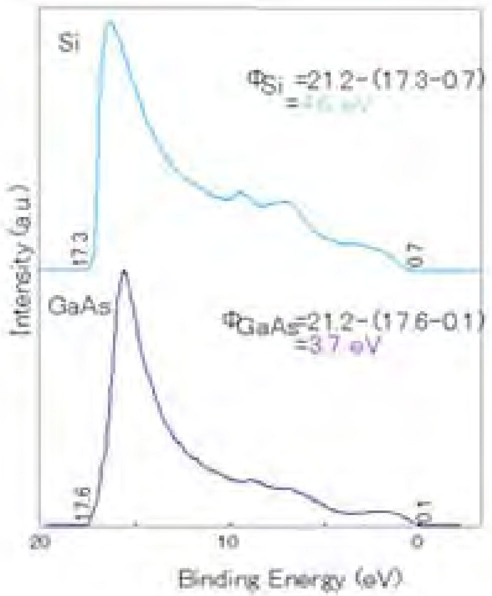
Cantilever close to specimen surface;

→ Fermi level difference equivalent to zero

Contact potential difference (V_{CPD});

$$V_{CPD} = V_{SP} = \left(\phi_{PtIr5} - \phi_{sample}\right)/e \qquad (1)$$

Work function measured by UPS



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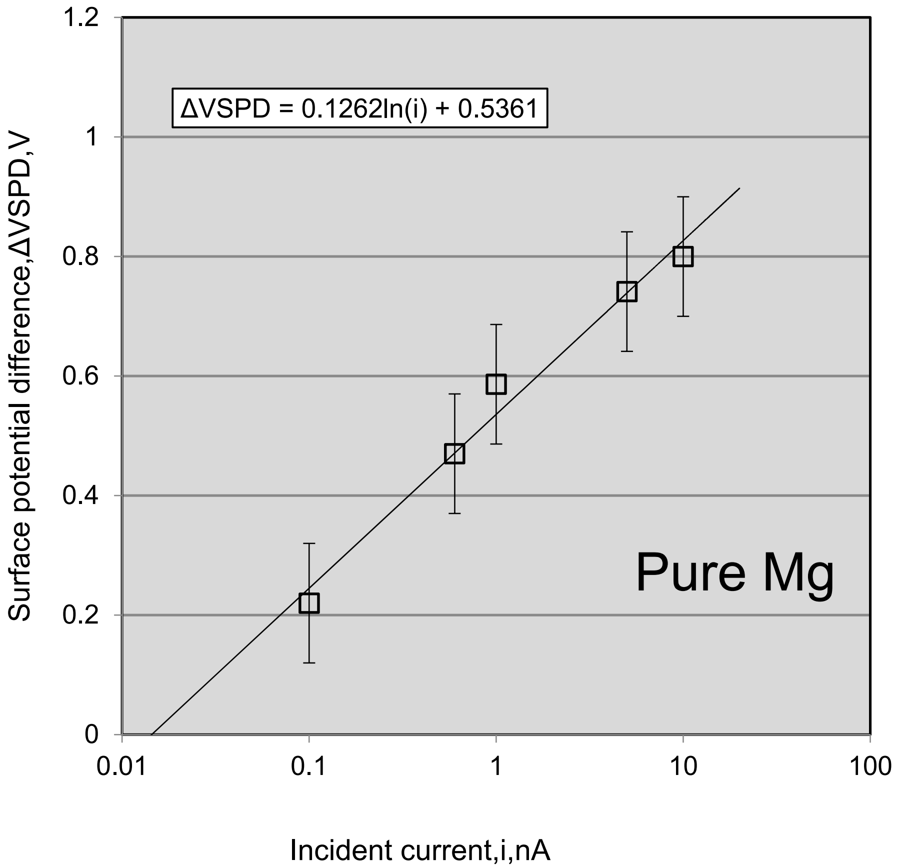

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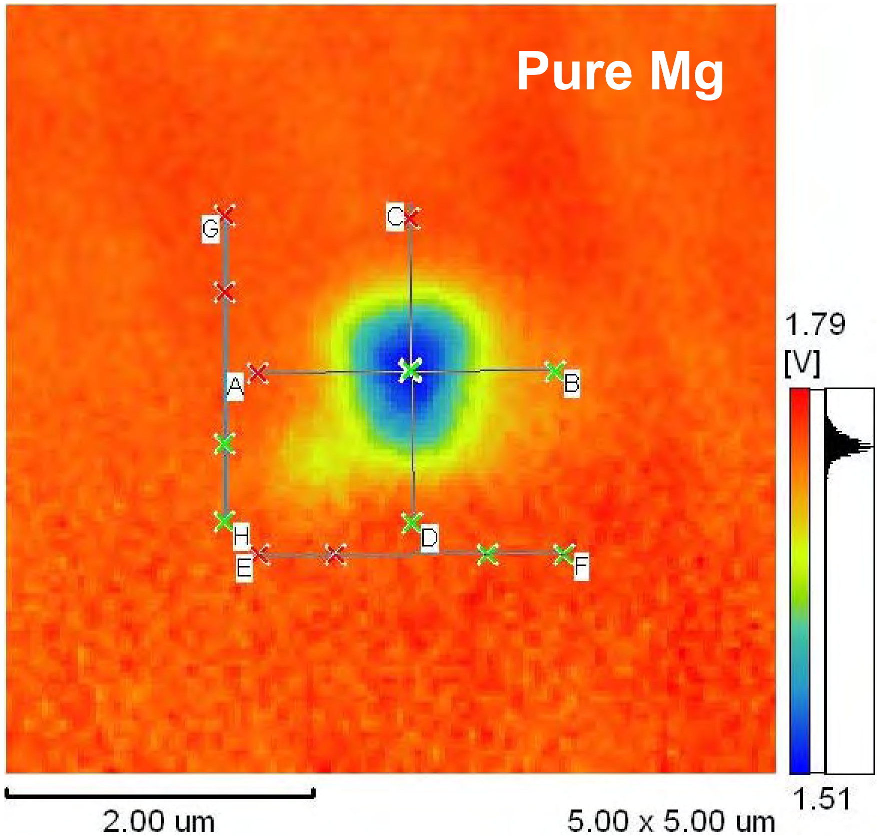
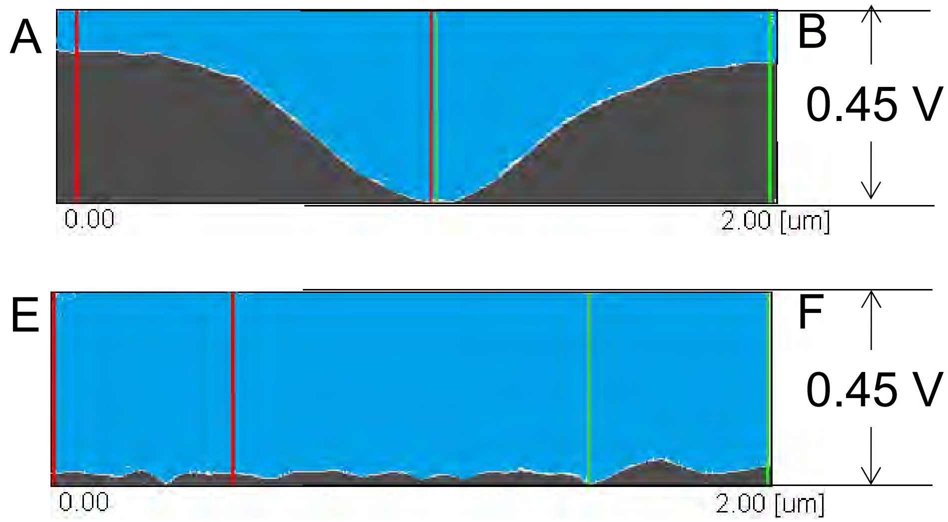
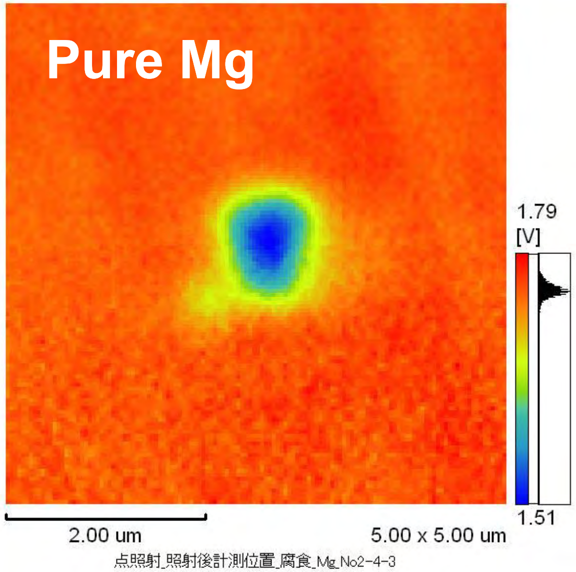




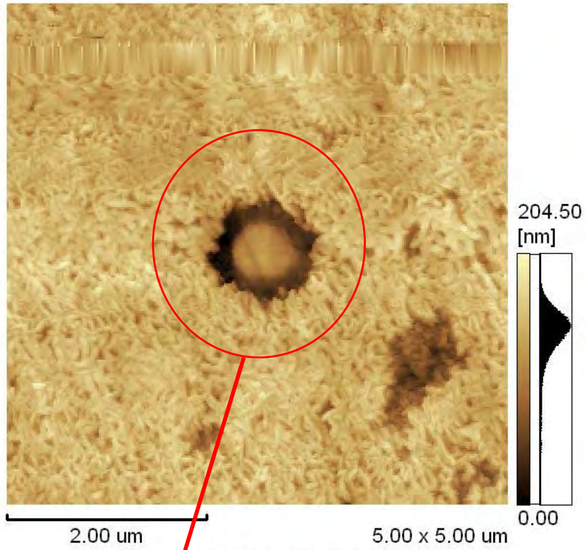
Surface potential difference (V)

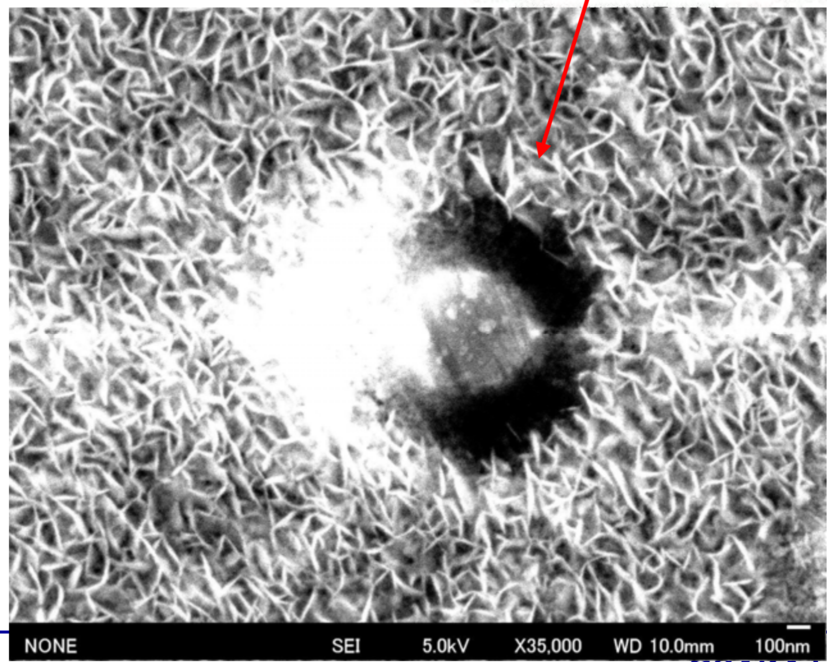
Point	A-B	C-D	E-F	G-H
red line	-0.23	-0.24	+0.00	+0.00
green line	-0.22	-0.24	-0.03	+0.01

Work function – Fermi potential relation for Galvanic control



5%NaCl solution (30C)
Soaked for 180s



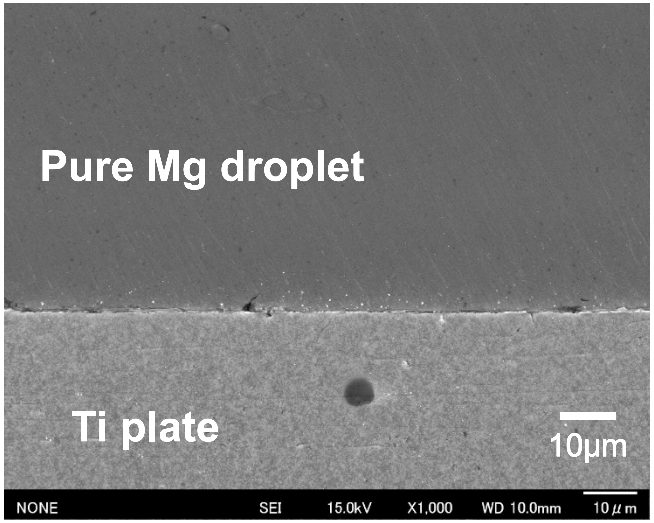


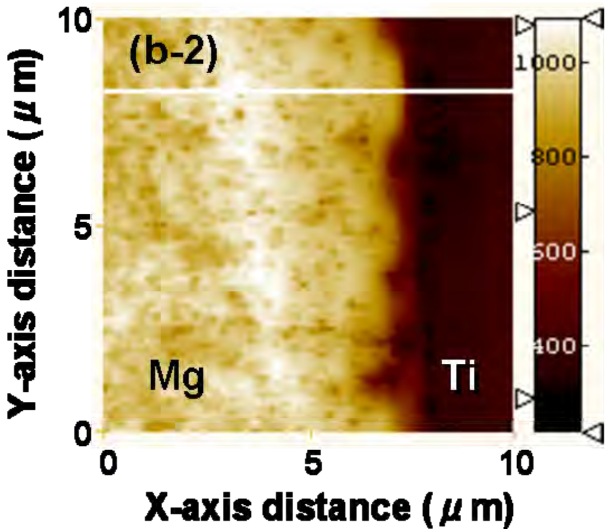
SKPFM analysis at pure Mg/Ti interface

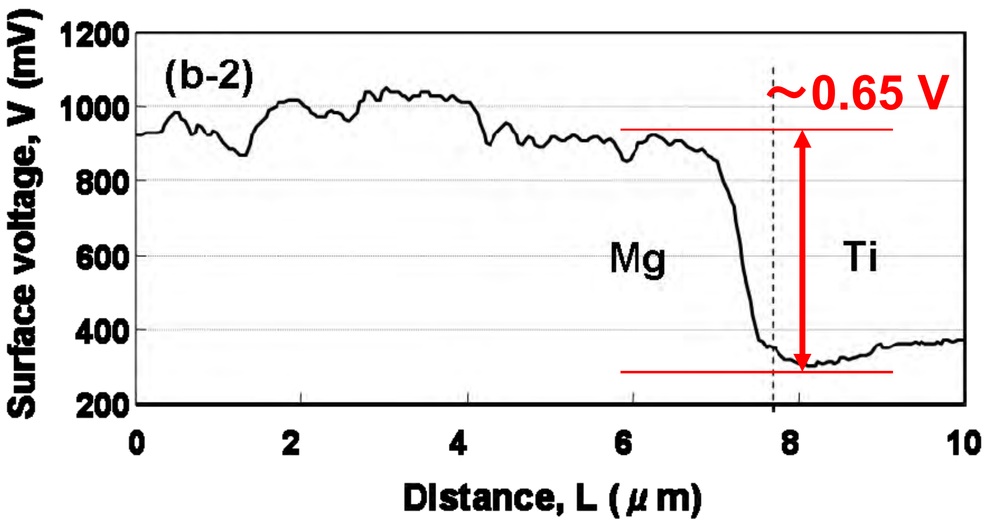
$Mg^{2+} + 2e^{-} \rightarrow Mg$ (SEP=-2.36V)

$Ti^{2+} + 2e^{-} \rightarrow Ti$ (SEP=-1.63V)

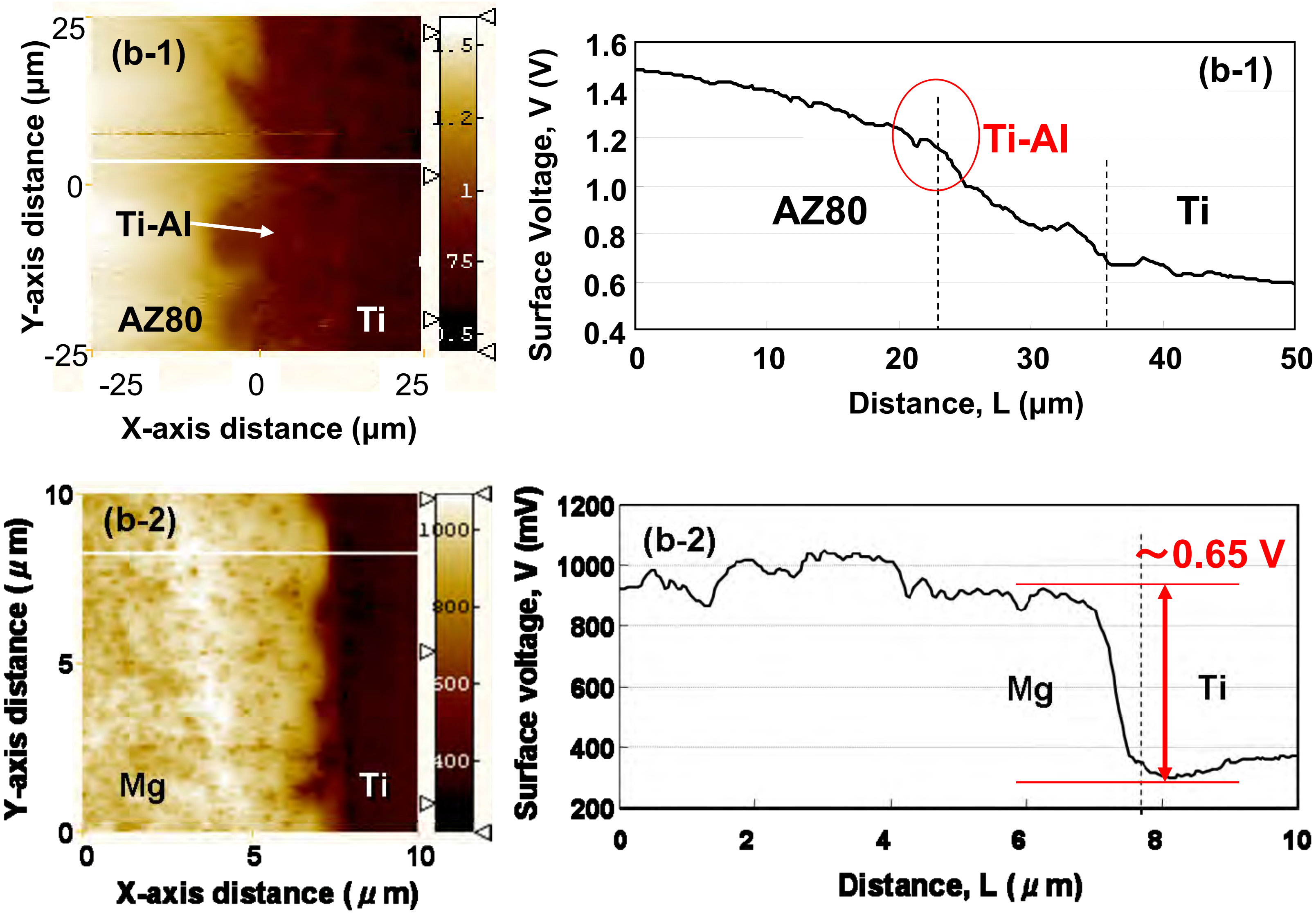
V_{SEPD} = 0.73V at Mg/Ti







SKPFM analysis (wettability test specimen)



Summaries

SKPFM Quantitative Evaluation of Initial Galvanic Corrosion Phenomenon of Magnesium Alloys

SKPFM system has been established to quantitatively evaluate corrosion resistance at the interface between dispersoids and α-Mg by using Δ*VSPD* measurements. The correlation between Δ*VSPD* and galvanic corrosion behavior was investigated by SKPFM and SEM observation. The results obtained in the present study were summarized as follows:

• Surface potential of low SEP metal was generally high. Δ*VSPD* also had positive correlation with Δ*VSEP*, theoretically and experimentally. Therefore, galvanic corrosion can be evaluated using Δ*VSPD* at the interface between dispersoids and α-Mg.

• Mg-Ti interface caused galvanic corrosion due to large Δ*VSPD* of 0.52~0.71V. The formation of $TiAl_3$ interlayer was effective in reducing Δ*VSPD* (0.24~0.33V), and resulted in prevention of corrosion phenomenon of Mg-Ti bonded specimen.