Nano-structure investigation of HCM12A oxide layer

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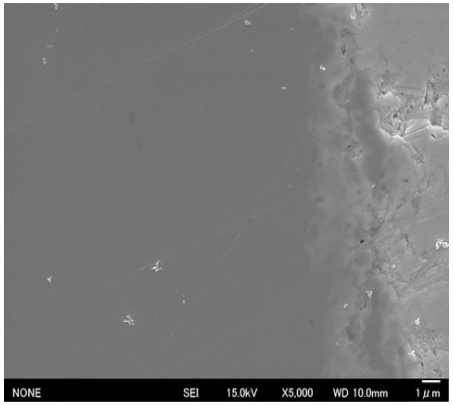
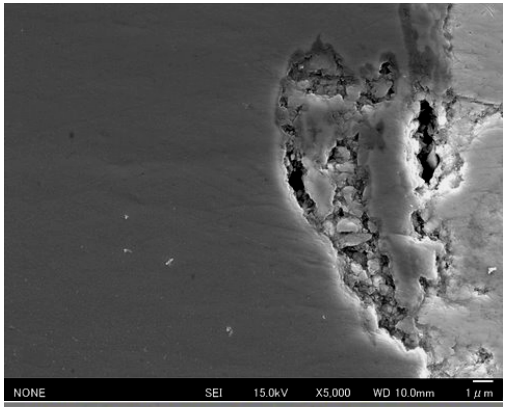
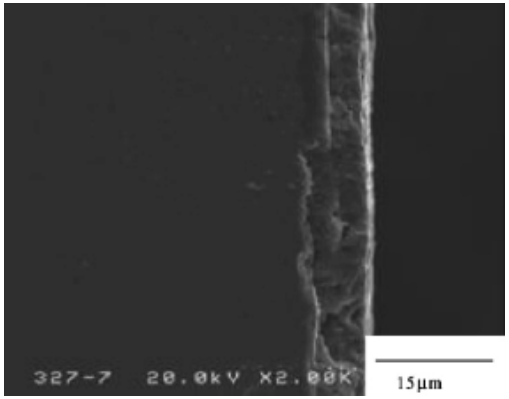
LBE materials performance
Material & Specimen
scanning probe microscopy
Results & Discussion
Summary

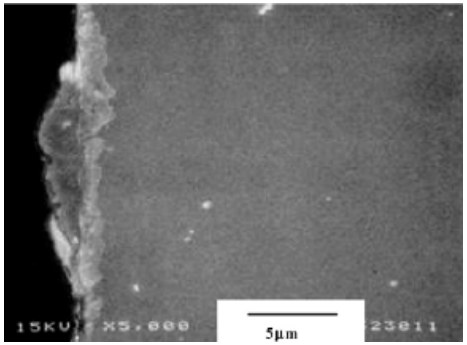
LBE materials performance

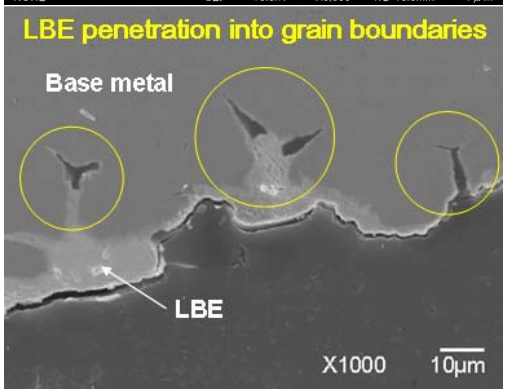
- A method of using materials such as F/M and austenitic stainless steels in LBE is to keep an oxide layer on the surface of the base metal in contact with LBE.

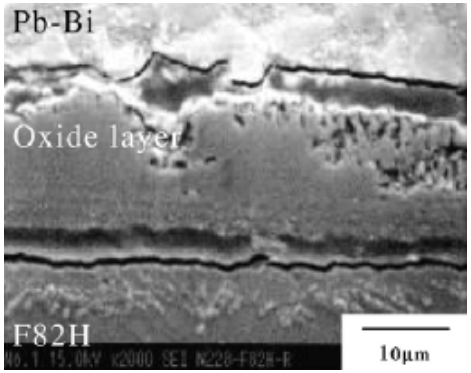












LBE materials performance

- An alternative is to add anticorrosion elements such as Al, which leads to a protective oxide that guards base metals on the surface, or to coat the surface by the elements.
- The oxide scale on the F/M steel is not a simple structure but consists of duplex layers; magnetite Fe_3O_4 near the LBE side and spinel $(FeCr)_3O_4$ near the base metal basically. The original surface exits at the interface between the magnetite and spinel.
- An early question was how the oxide layers on the surface of the base metal grew.

- The oxidation reaction needs a path, which formation is achieved by the dissociative/perforative growth in the magnetite.
- The path allows a quick diffusion of oxygen to the FM/spinel interface. Oxygen cannot diffuse in the oxide lattice because its rate is insufficient for Fe–Cr spinel formation.
- Quick oxygen diffusion could be possible along the grain boundaries or a short cut path.
- A function of surface potential and phase delay mode measurements in scanning probe microscope is adopted to the research on HCM12A oxide layer.

HCM12A

- Procured from Sumitomo Metal Industries, Ltd.
  - ✓ with composition,

Table 1 Chemical composition of HCM12A (mass%).

Fe	Cr	Si	Mn	Mo	C	Cu	W	Ni	V
Bal.	10.64	0.3	0.61	0.37	0.14	0.84	1.94	0.32	0.19

- One of the third-generation 12Cr ferritic steels
  - ✓ with tempered martensite, which was originally developed for heavy section components such as headers and steam pipes for use at temperatures up to 620°C and pressures up to 34MPa, and applicable to the usage in the core cladding.

Specimen preparation (1)

- The same material with the previously reported
  - ✓A stability of oxide layers formed in LBE on HCM12A to external loading, IWSMT-9.

- Samples are cut from the specimen holder tube with o.d. 48mm and t. 3mm, which was used under the condition:

Table 2
The condition of temperature and oxygen concentration in LBE during the operation.

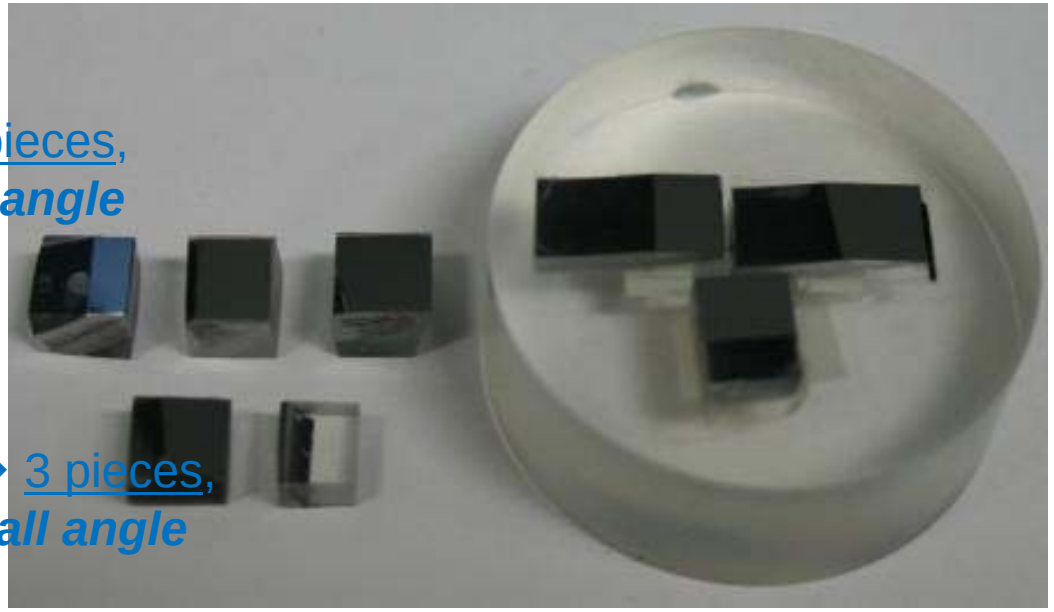
Time (h)	Temperature (°C)	Oxygen concentration (wt.%)
0–1000	450	5×10^{-6}–5×10^{-5}
1000–2000	500	2×10^{-5}–5×10^{-5}
2000–5000	450	1×10^{-5}–5×10^{-5}
5000–5500	450	5×10^{-6}–5×10^{-5}

Specimen preparation (2)

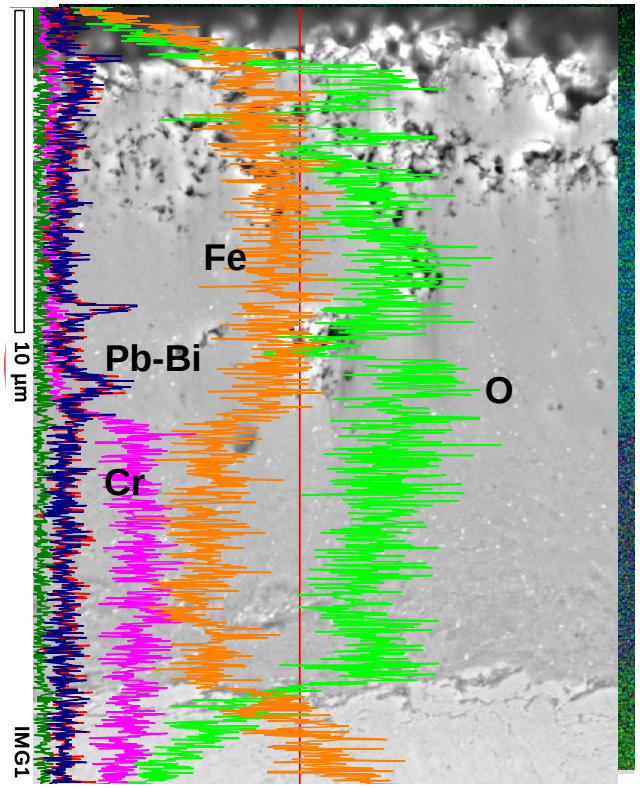
- Pieces are cut from big ring, polished to enlarge oxide layer from 15 to max. 100 μm, and finalized by 0.25μm diamond paste.

Big Ring → 5 pieces,
incline, small angle

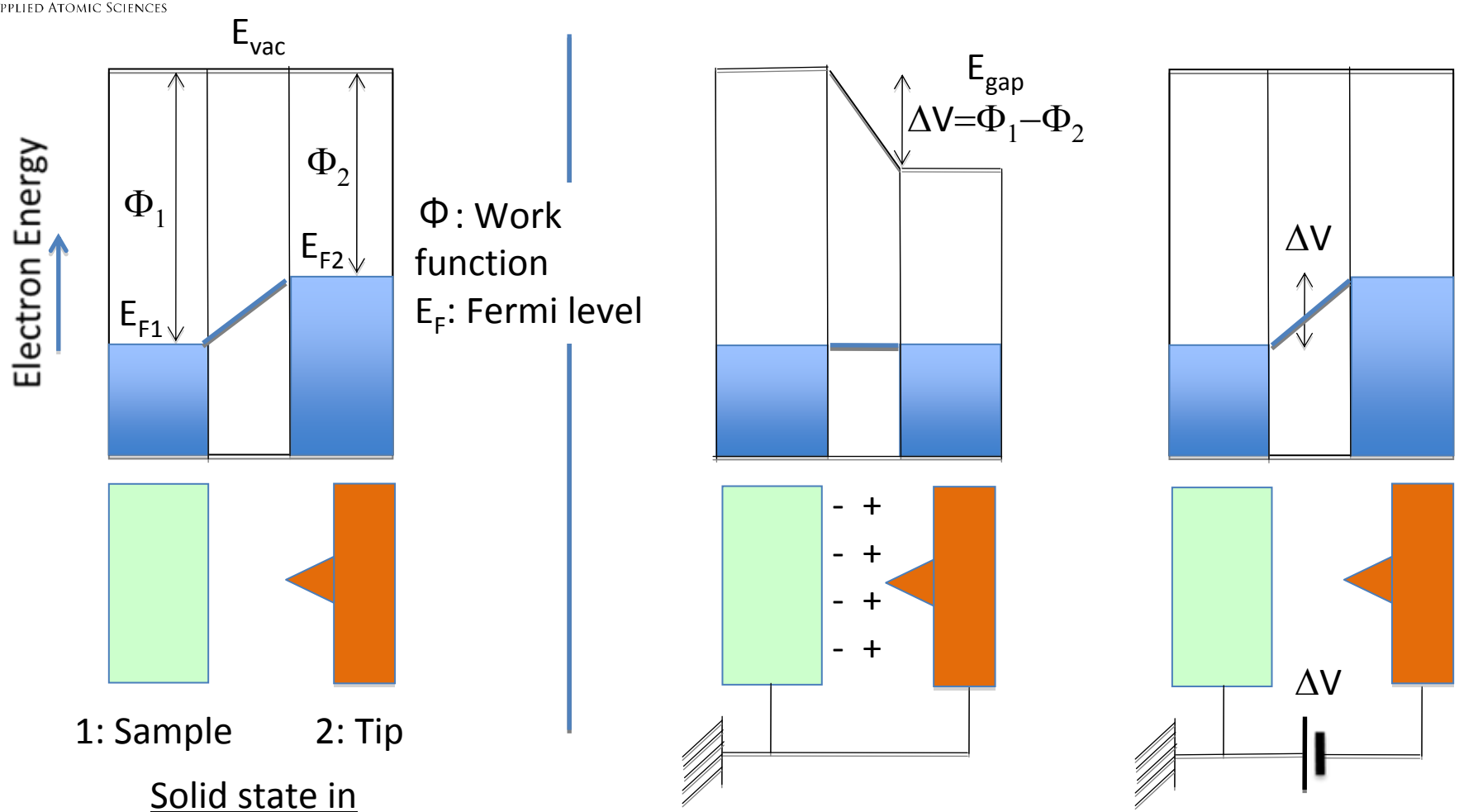
Small Ring → 3 pieces,
incline, small angle



FE-SEM / JEOL-7000



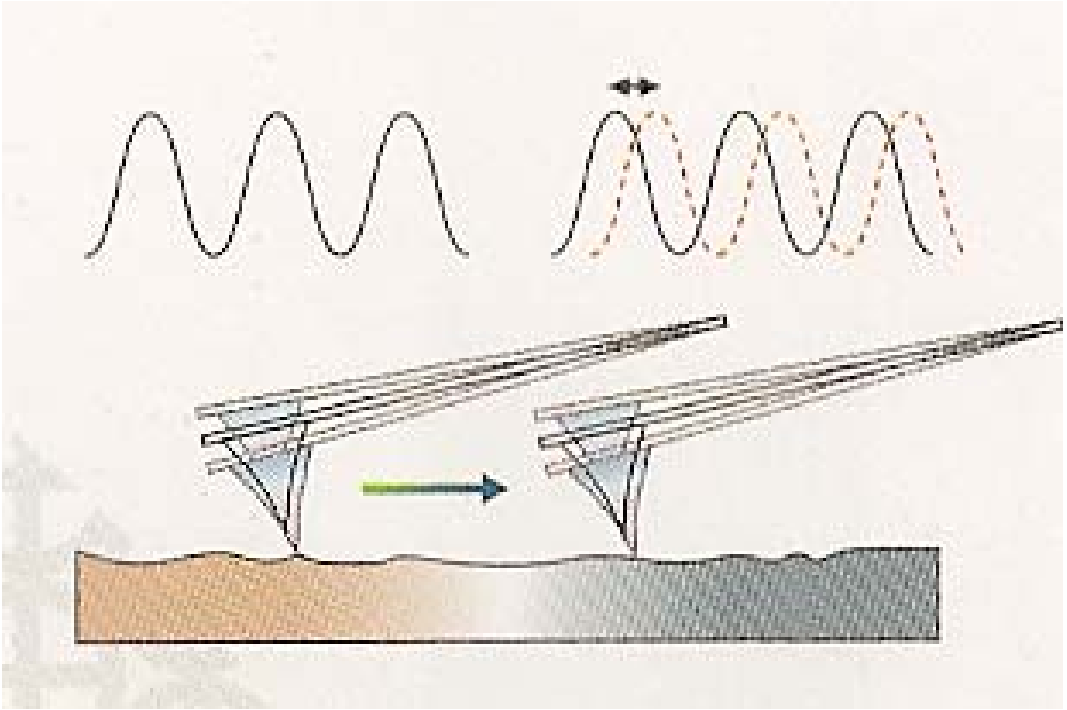
Surface potential measurement in scanning probe microscopy



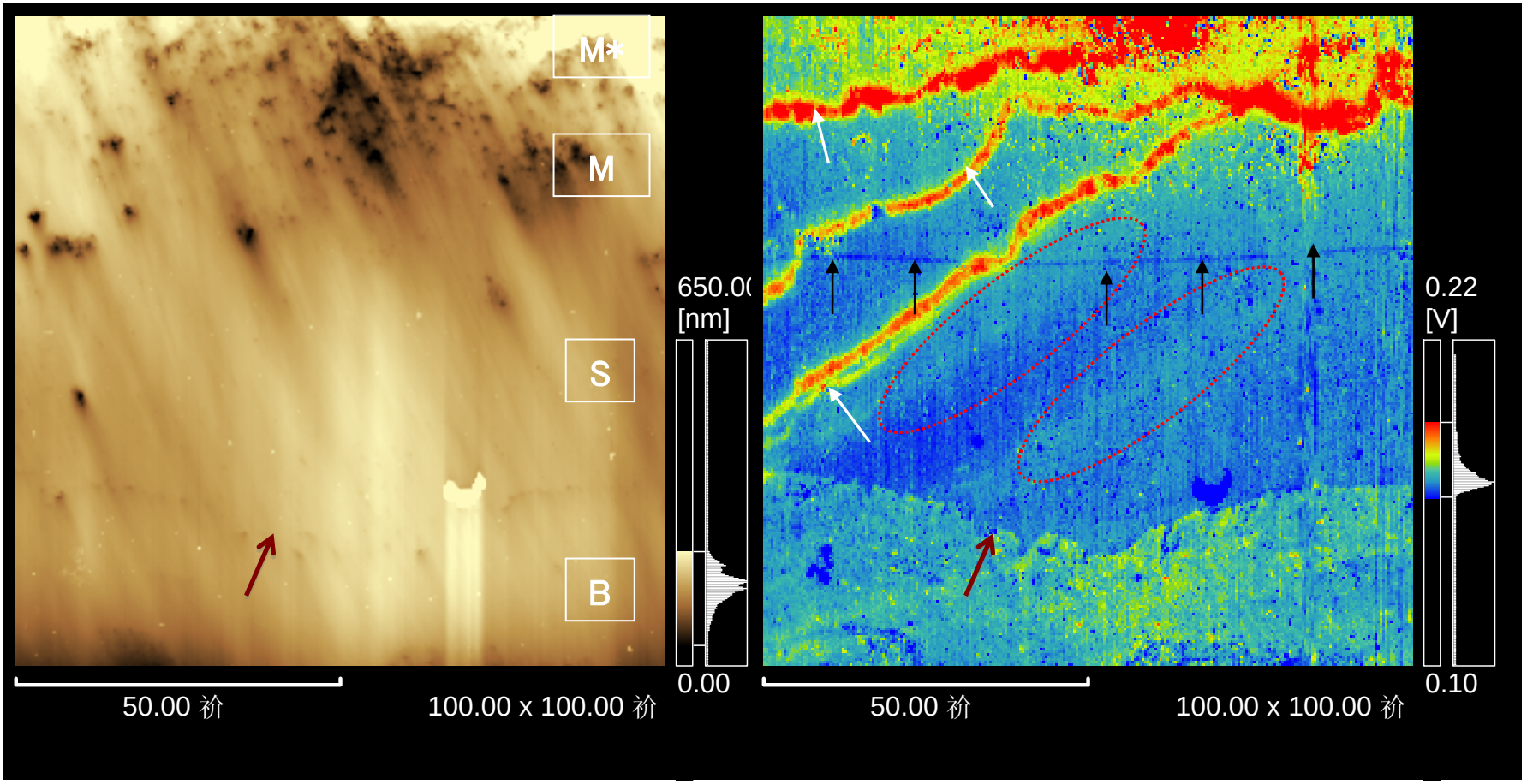
1: Sample 2: Tip

Solid state in semiconductor

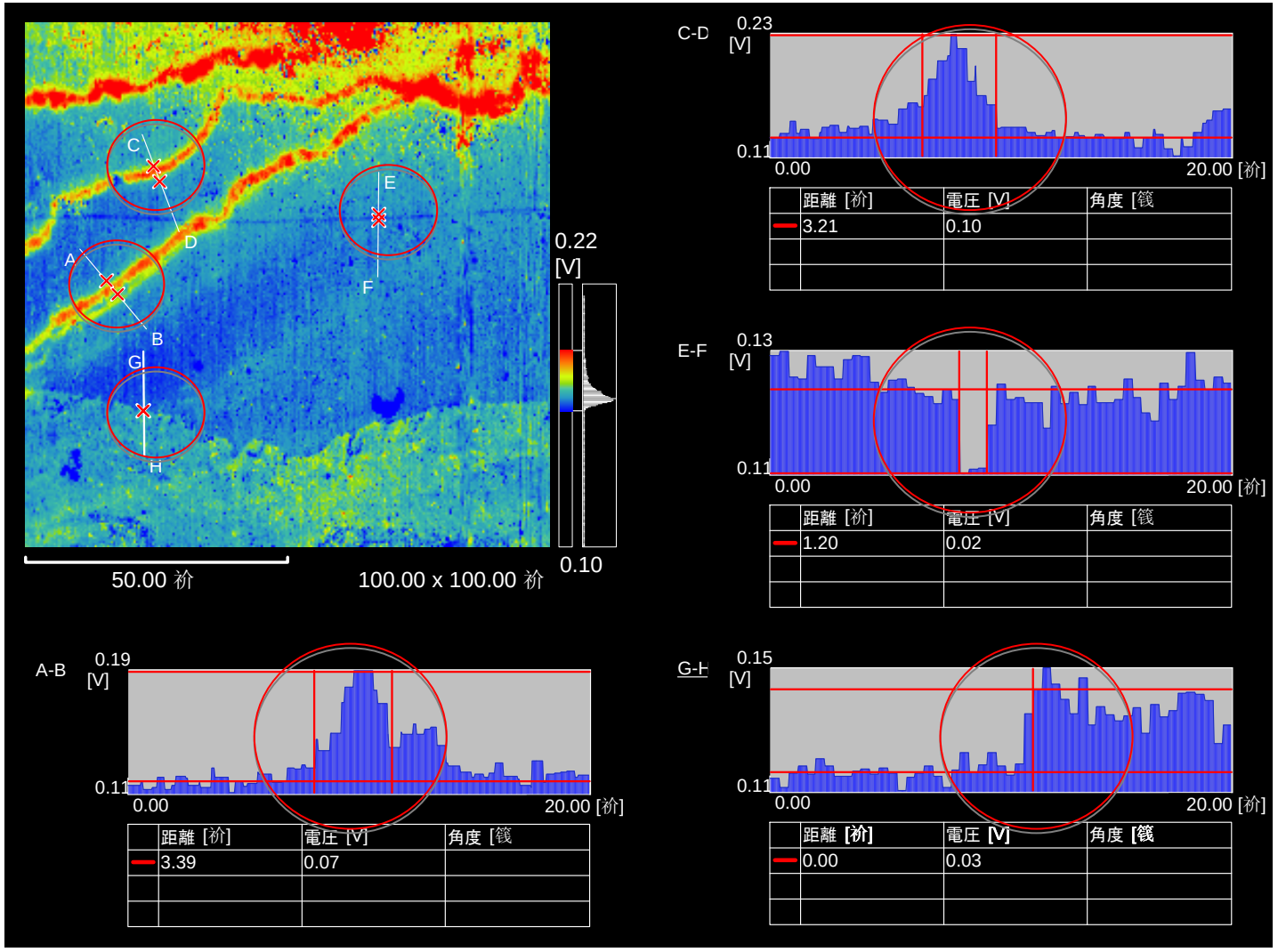
Surface delay phase measurement in scanning probe microscopy



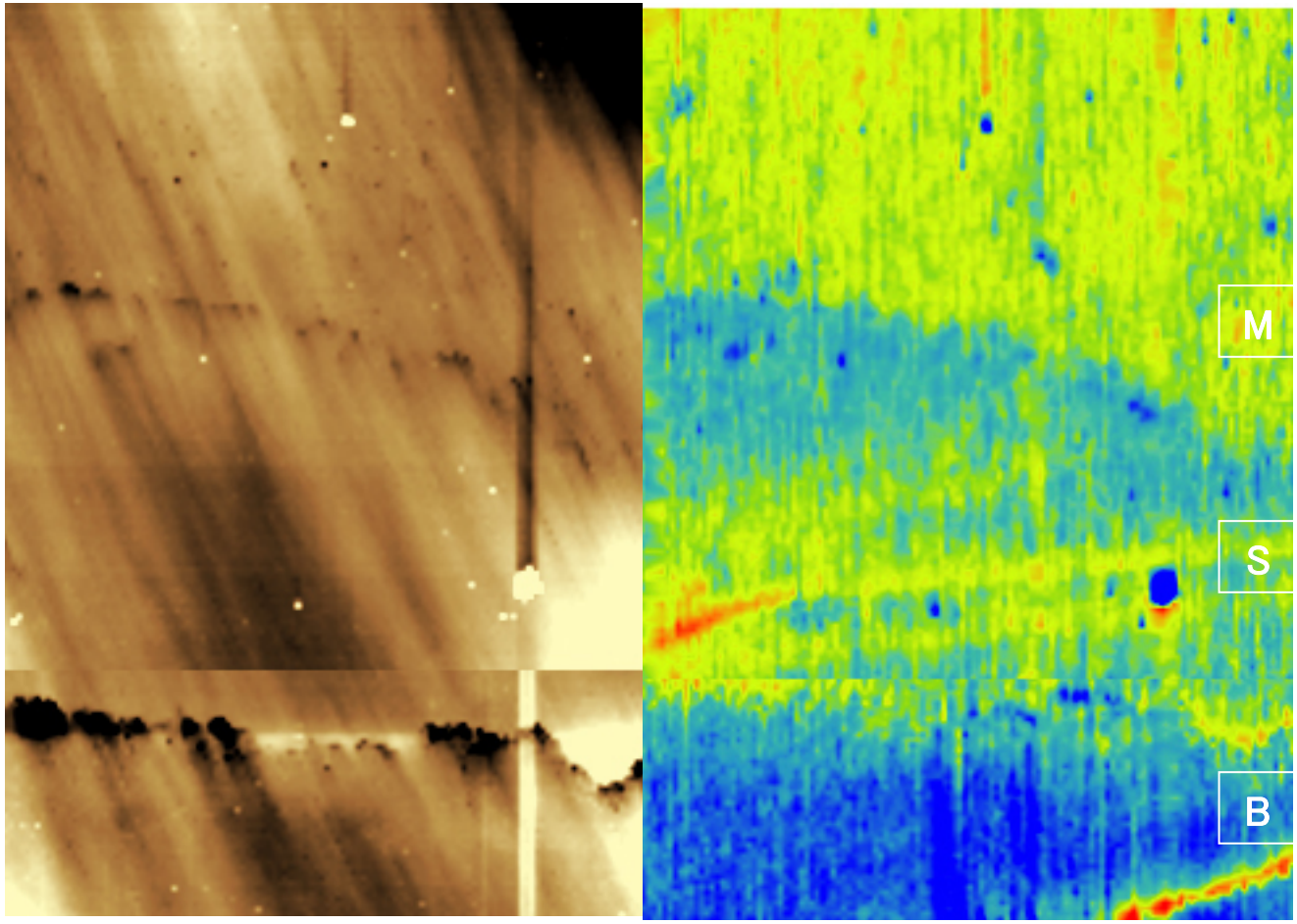
Height profile (L) and surface potential (R)
SPM-9600 / example 1



Local potential



Height profile (L) and surface potential (R) – example 2



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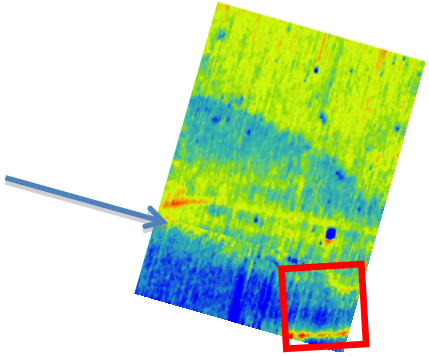

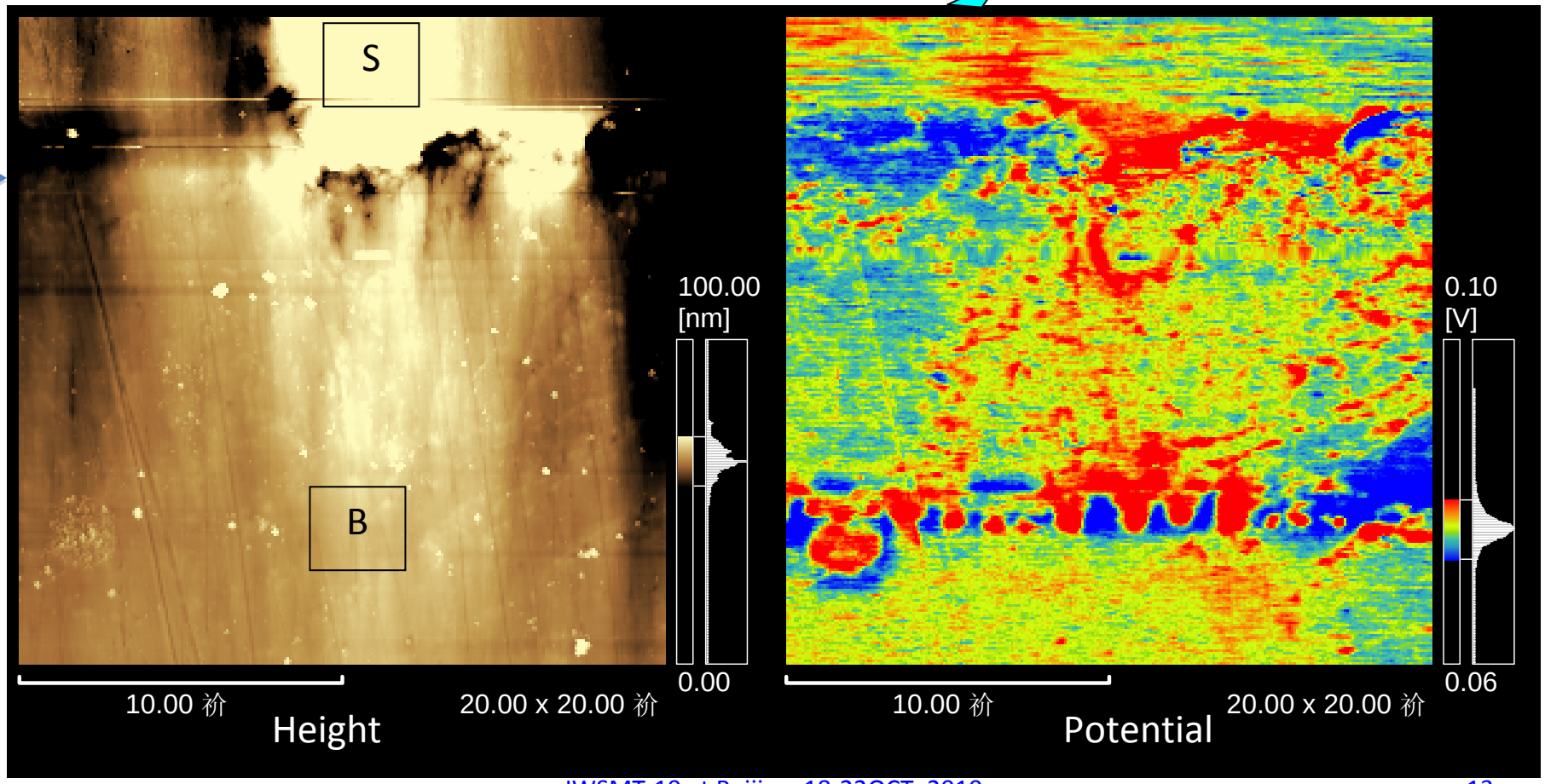

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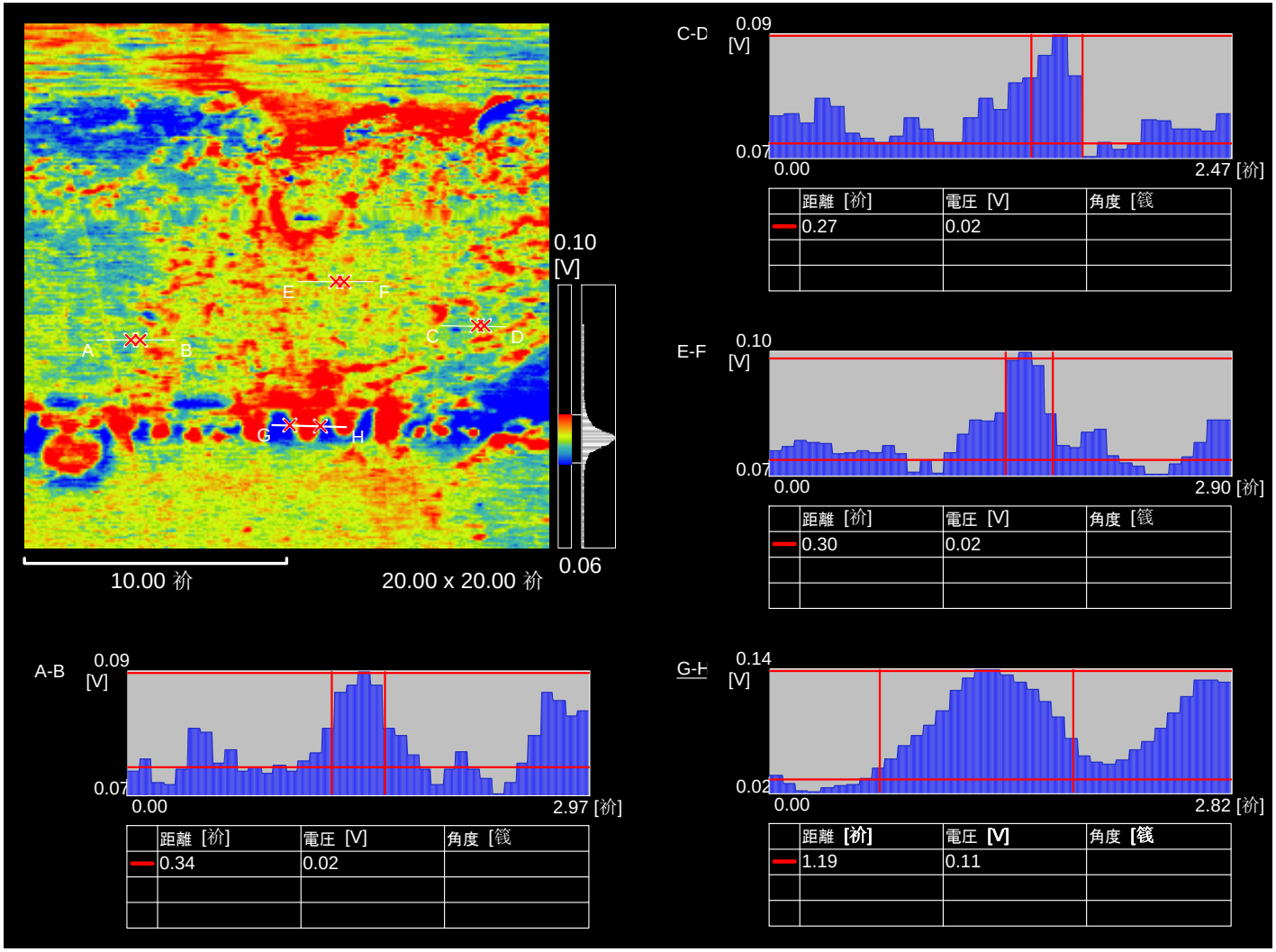
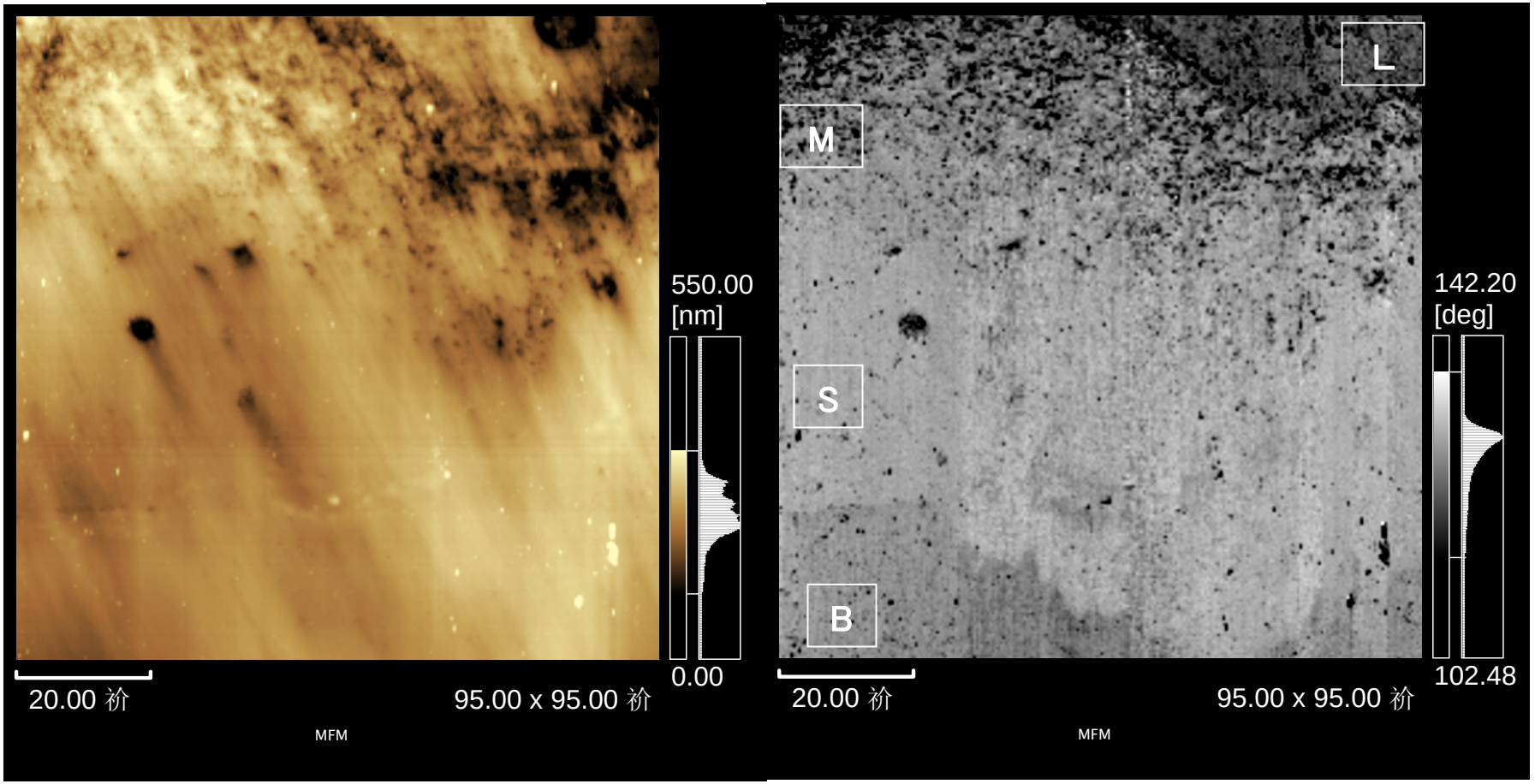
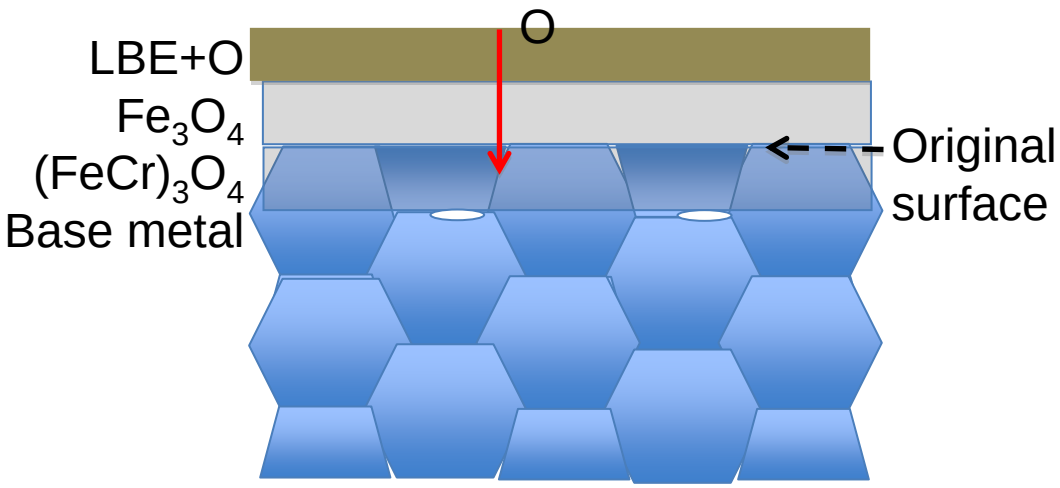


Delayed phase between surface and magnetized probe tip



Small black dots: noise

?


O
LBE+O
Fe_3O_4
$(FeCr)_3O_4$
Base metal
Original surface

Conclusions

- Scanning probe microscope with a function of surface potential and phase delay mode measurements was adopted to investigate the oxide layer of HCM12A.
- Surface potential measurement reveals the boundary between $(Fe,Cr)_3O_4$ and Fe_3O_4.
- A facet-type structure was shown in the base metal near the spinel layor.
- In the phase delay mode, magnetized probe scanned by sinusoidal wave reacts to the sample surface. Spinel layer is not homogenious. So the Fe-Cr structure is likely to be related.

Acknowledgement

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Thanks for your attention!