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中国核动力研究设计院
Nuclear Power Institute Of China

Zircaloy cladding with Cr-coating: diffusion-reaction mechanism and structural degradation in extreme temperatures

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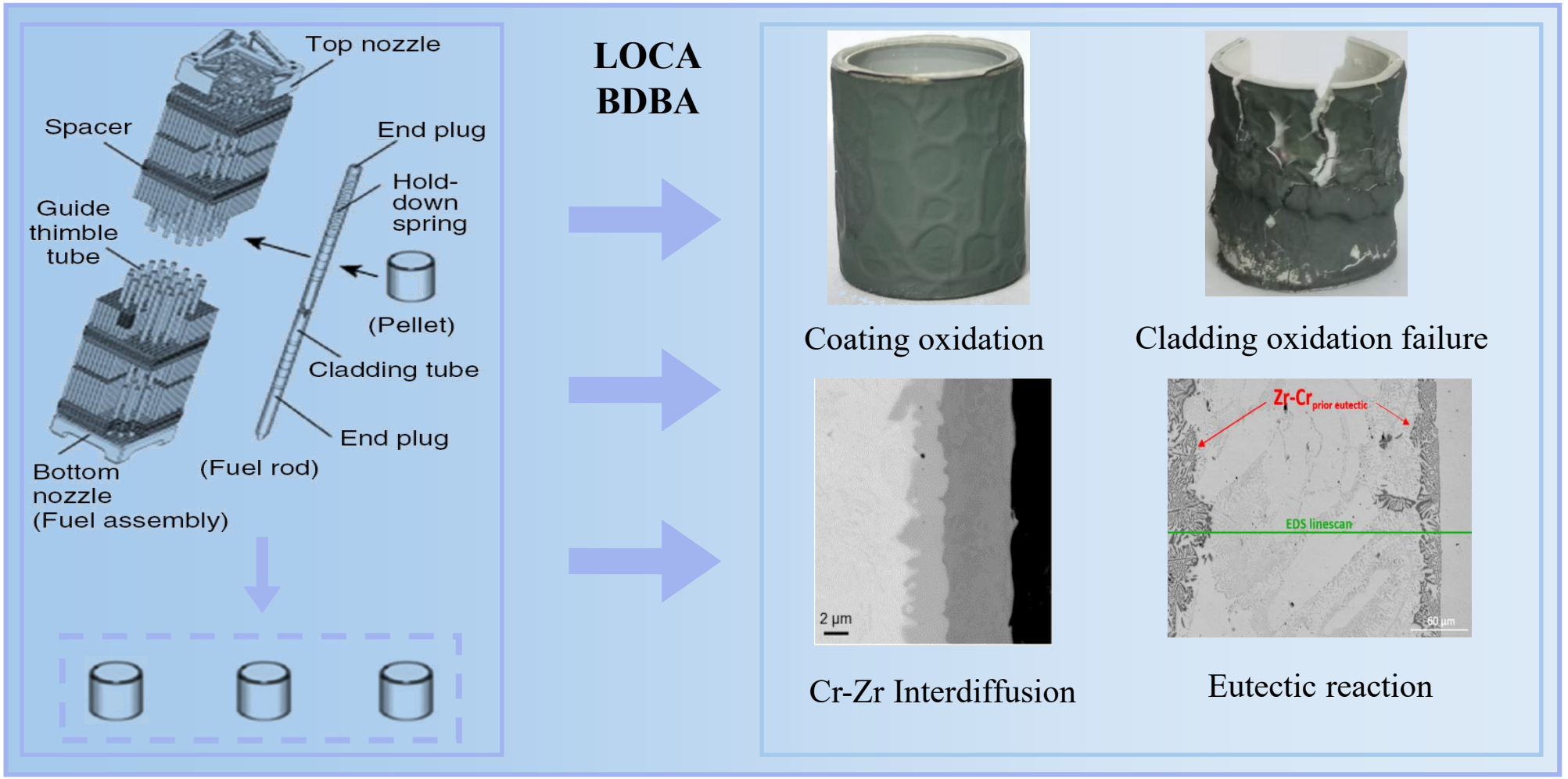
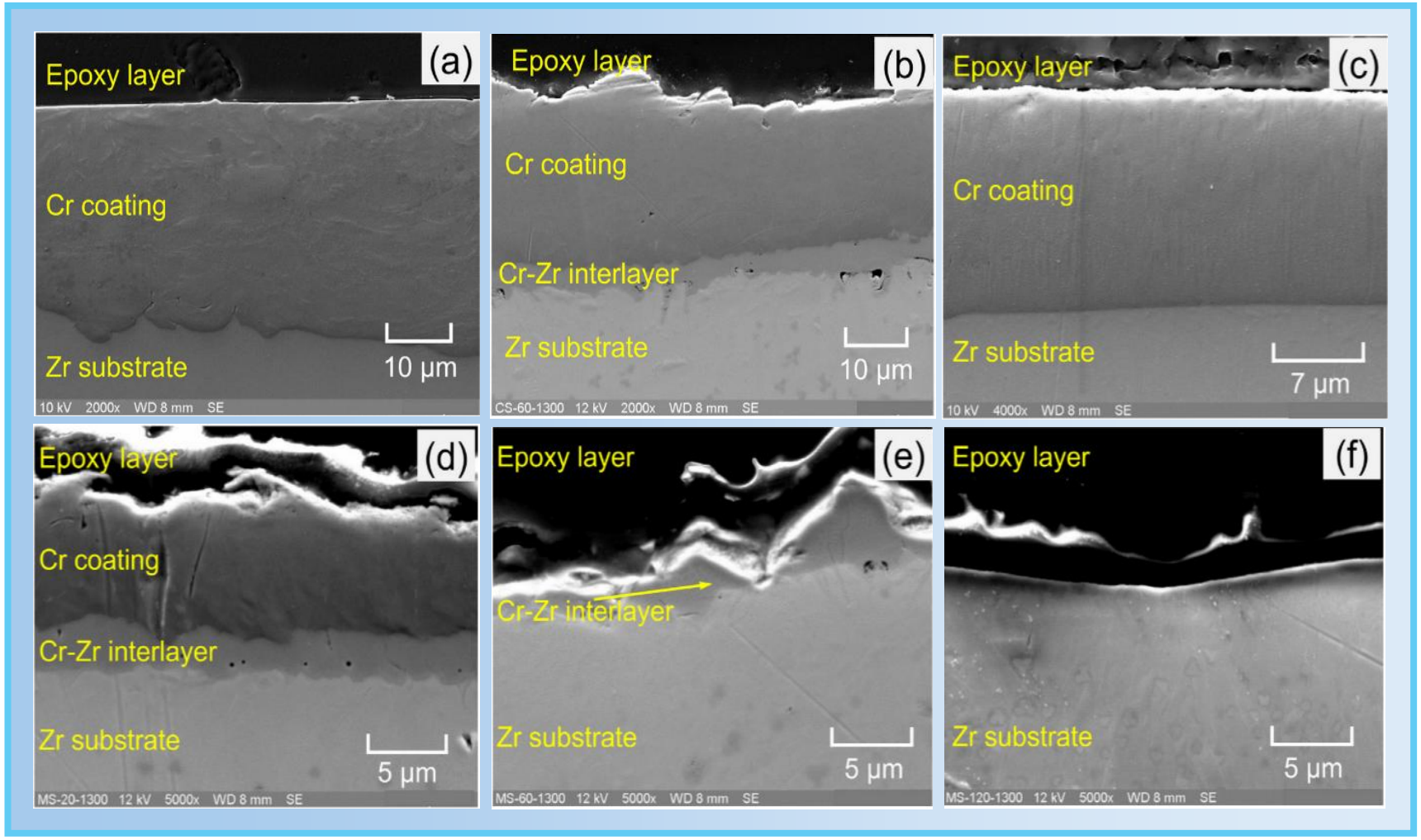
01 Background

1.1 Background



▸▸ 1.2 Research Status of Cr-Zr Interdiffusion

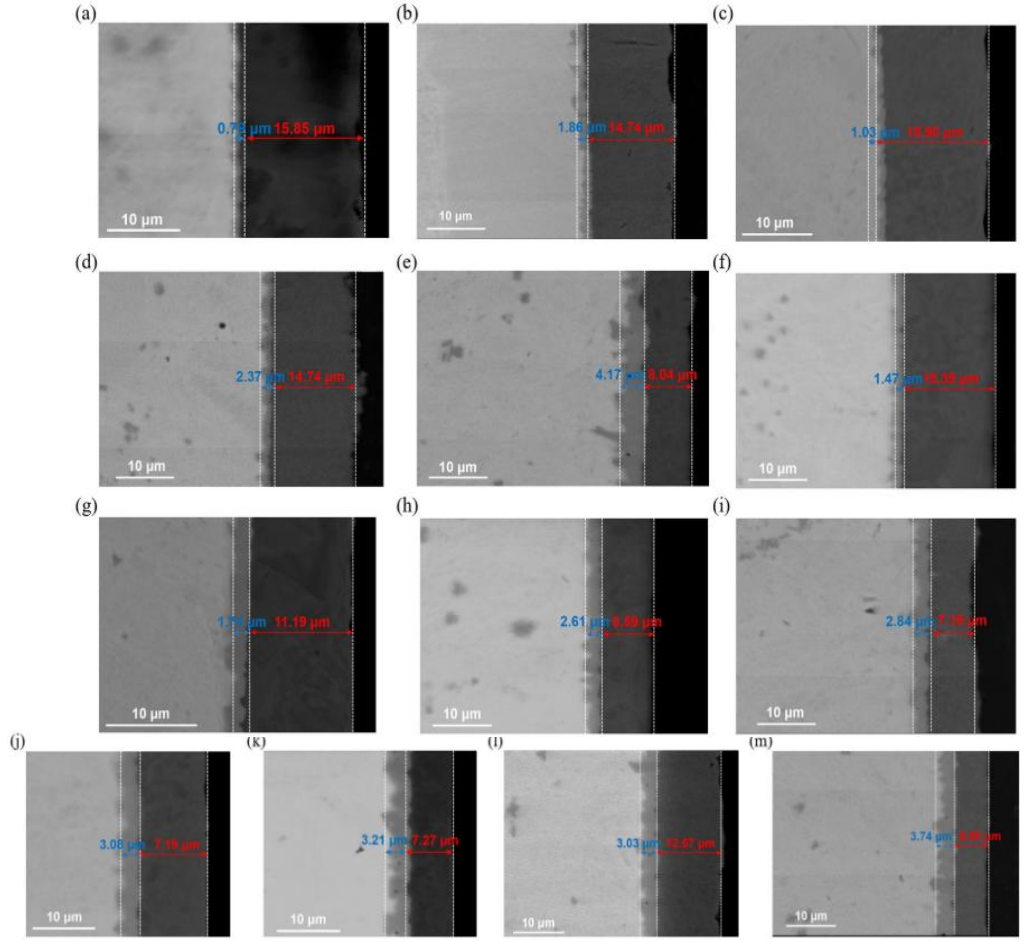


SEM images of Cr-coated zirconium alloy samples exposed at 1300°C for different durations:

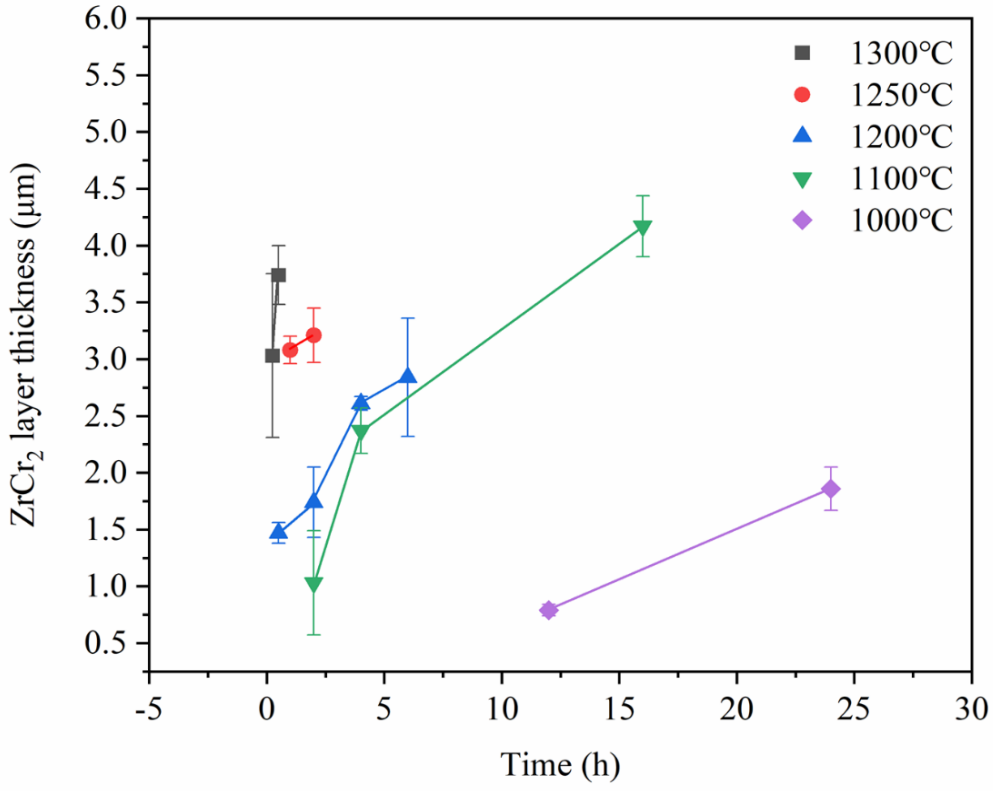
(a) As-received CS sample, (b) 1300°C,60min, (c) As-received MS sample, (d) 1300°C,20min (e) 1300°C,60min (f) 1300°C,120min

Yang et al., Jour. Nucl. Mater. (2021)

▸▸ 1.3 Research Status of Cr-Zr Interdiffusion



Measured BE-SEM image of each specimen and average Cr and $ZrCr_2$ layer thicknesses; (annealed temperature, annealed time):
(a) 1000 ℃, 12 h. (b) 1000℃, 24 h. (c) 1100 ℃, 4 h. (d) 1100 ℃, 6 h. (e) 1100 ℃, 16 h. (f) 1200 ℃, 0.5 h. (g) 1200 ℃, 2 h. (h) 1200 ℃, 4 h. (i) 1200 ℃, 6 h. (j) 1250 ℃, 1 h. (k) 1250 ℃, 2 h.(l) 1300 ℃, 0.25 h. (m) 1300 ℃, 0.75 h.



Measurement of $ZrCr_2$ Layer Thickness under Different Temperatures and Time Conditions.

Kim et al., Surf. Coat. Tech. (2023)

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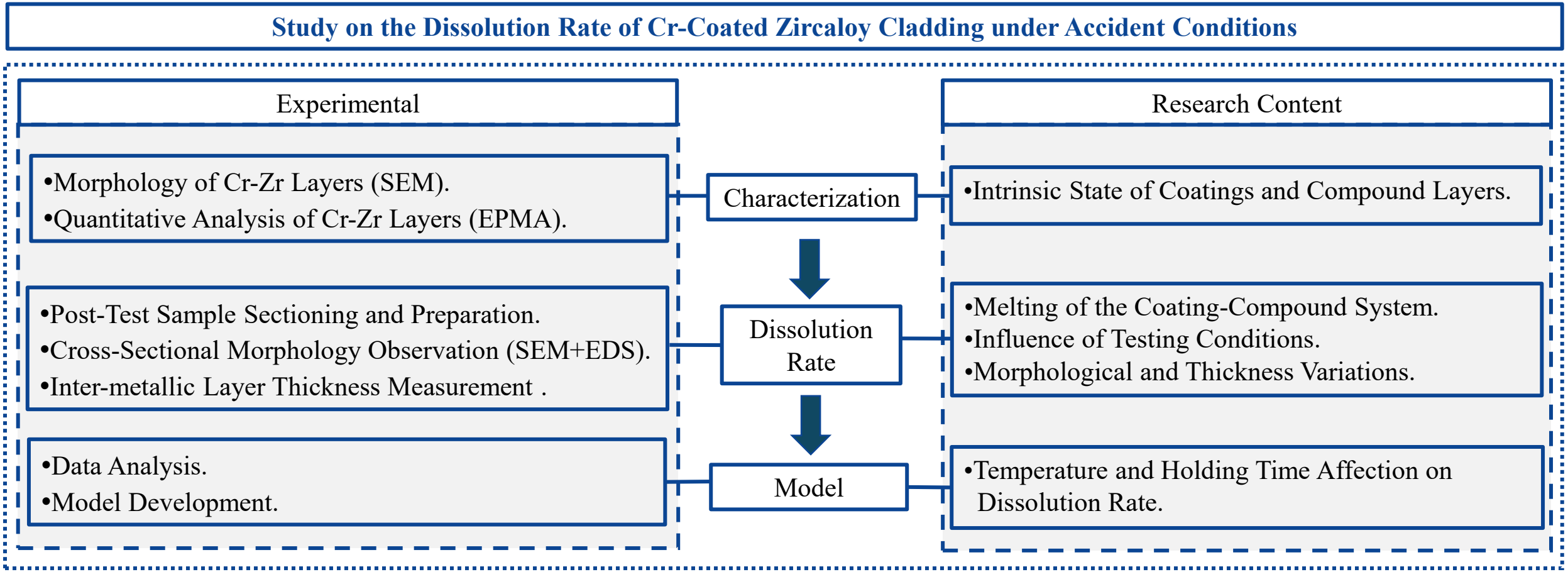
02 Experiments

▸▸ 2.1 Methods


Study on the Dissolution Rate of Cr-Coated Zircaloy Cladding under Accident Conditions
Experimental
•Morphology of Cr-Zr Layers (SEM).
•Quantitative Analysis of Cr-Zr Layers (EPMA).
•Post-Test Sample Sectioning and Preparation.
•Cross-Sectional Morphology Observation (SEM+EDS).
•Inter-metallic Layer Thickness Measurement .
•Data Analysis.
•Model Development.
Characterization
Dissolution Rate
Model
Research Content
•Intrinsic State of Coatings and Compound Layers.
•Melting of the Coating-Compound System.
•Influence of Testing Conditions.
•Morphological and Thickness Variations.
•Temperature and Holding Time Affection on Dissolution Rate.

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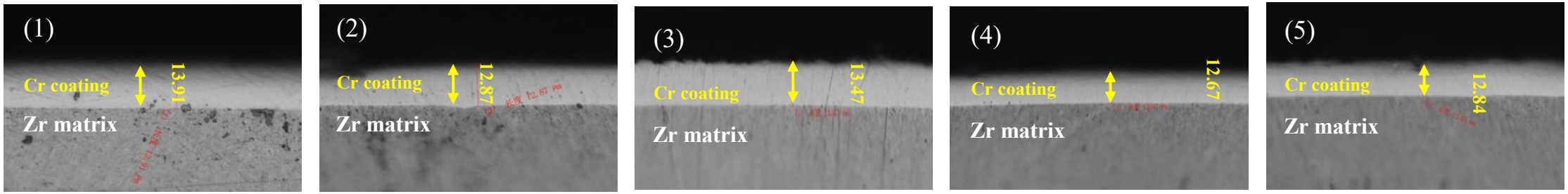
03 Diffusion Process and Results

3.1 Progress — Thickness Assessment of Cr Coating

Assessment of Cr Coating Uniformity



As-received tube

Specimen IDs 1–5

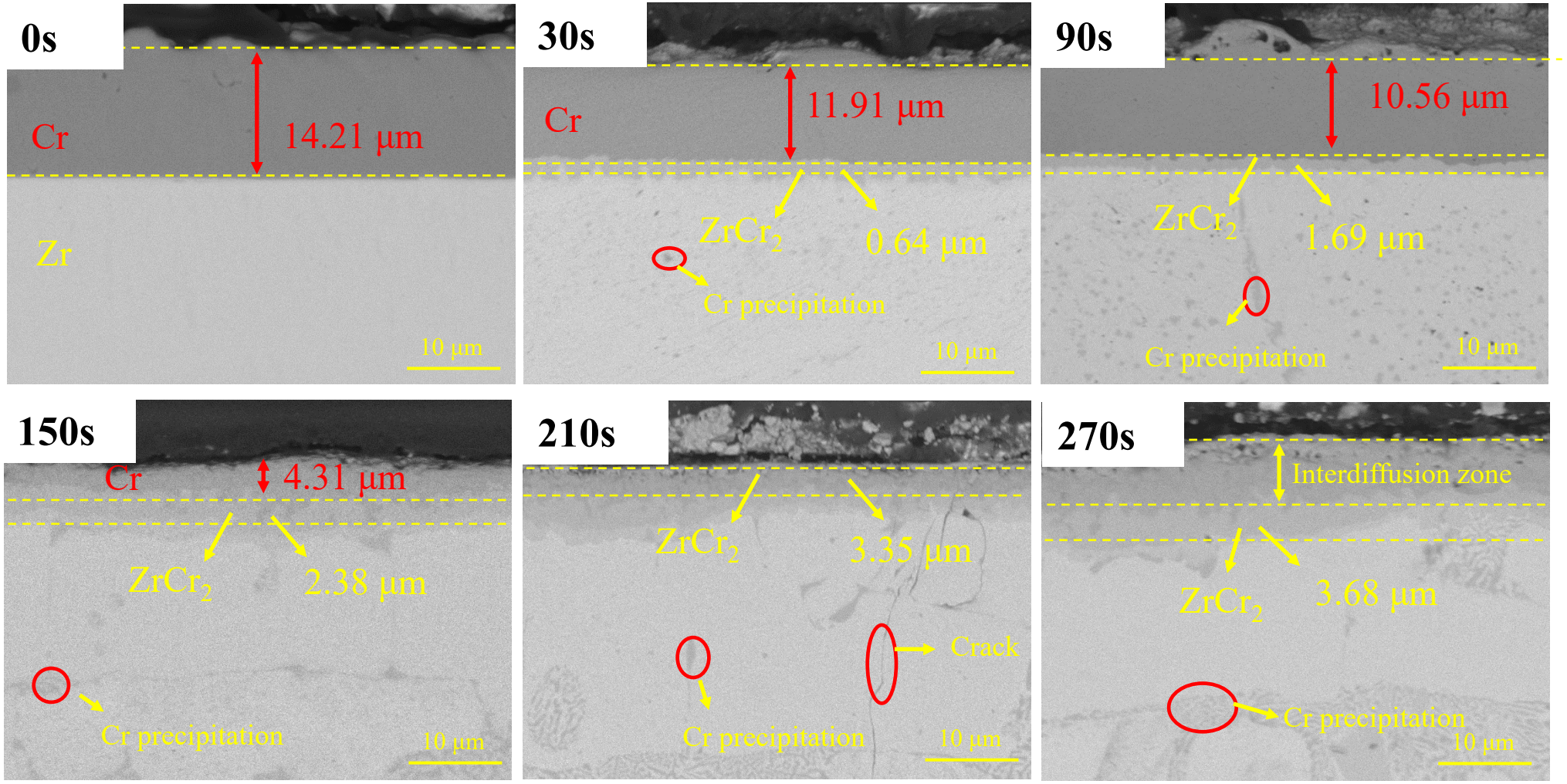
One specimen was taken every 20 cm.

Specimen ID	1	2	3	4	5
Thickness(μm)	13.9	12.8	13.4	12.6	12.8
	14.5	13.7	14.1	13.5	12.7
	12.8	14.8	12.6	11.9	11.4

The Cr coating on cladding tubes is 12–16 μm thick, largely defect-free and compliant with test requirements.

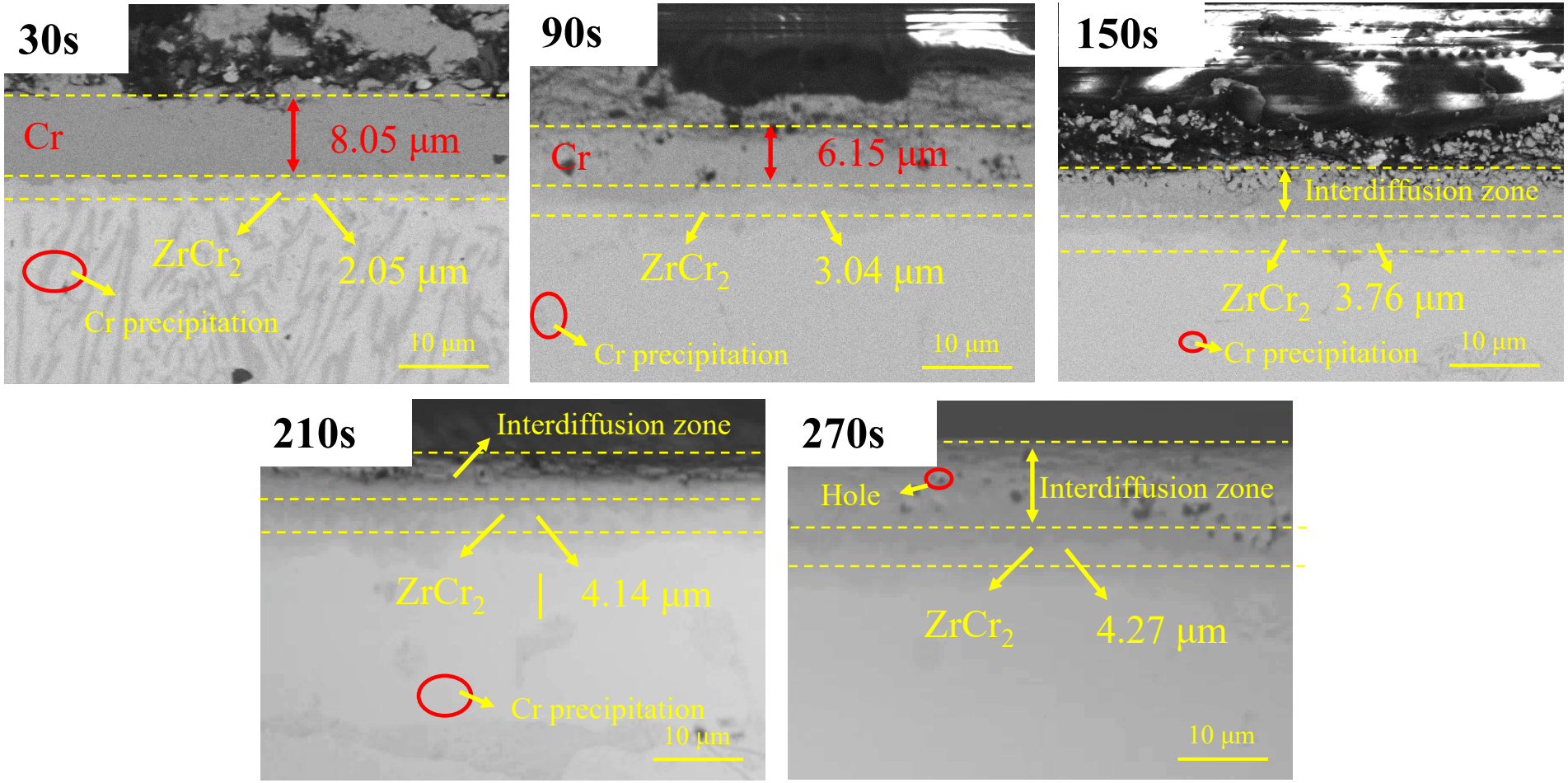
▶▶ 3.2 Kinetics at 1350 °C (Isothermal Hold)

SEM



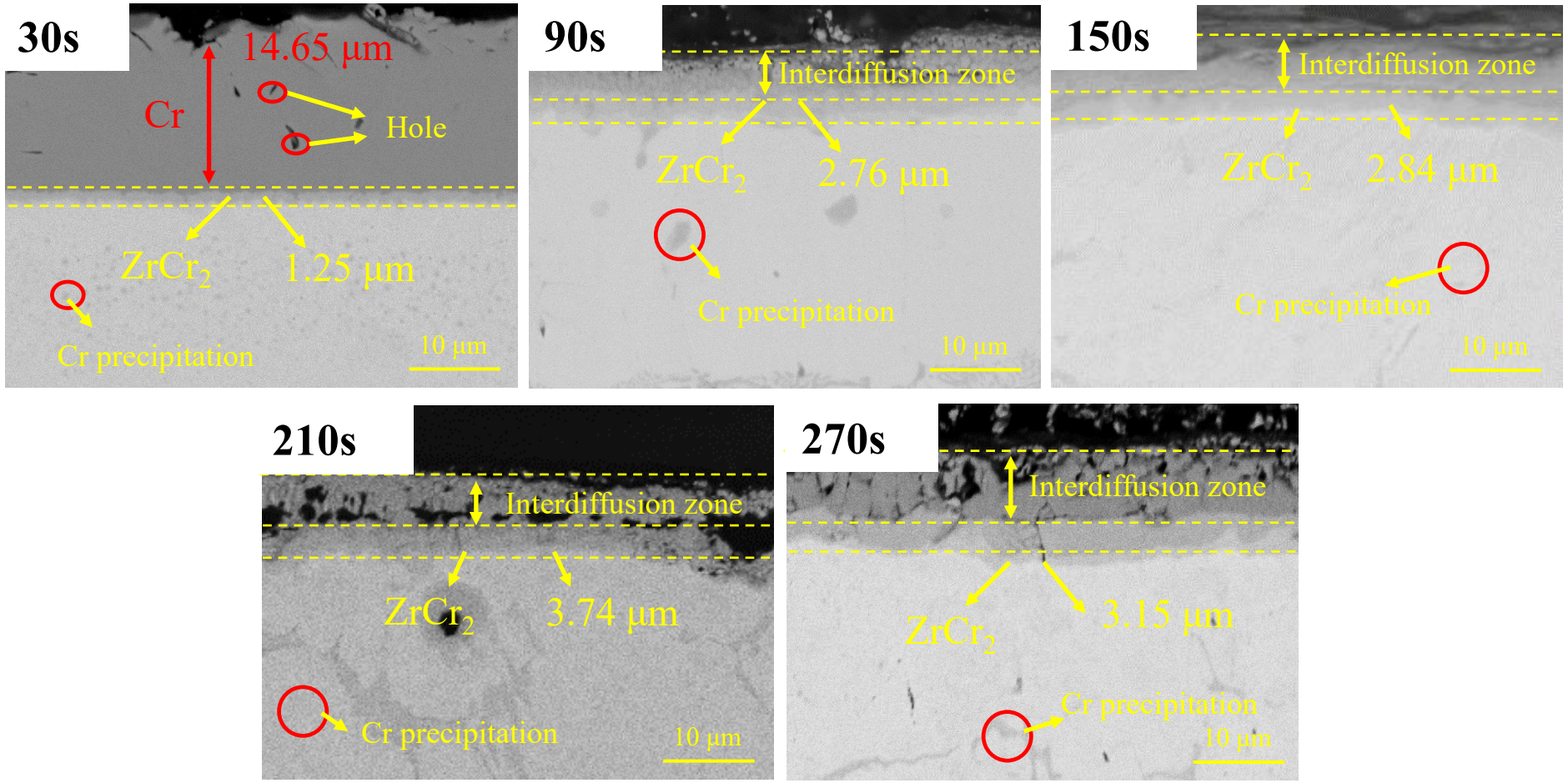
▶▶ 3.3 Kinetics at 1400 °C (Isothermal Hold)

SEM



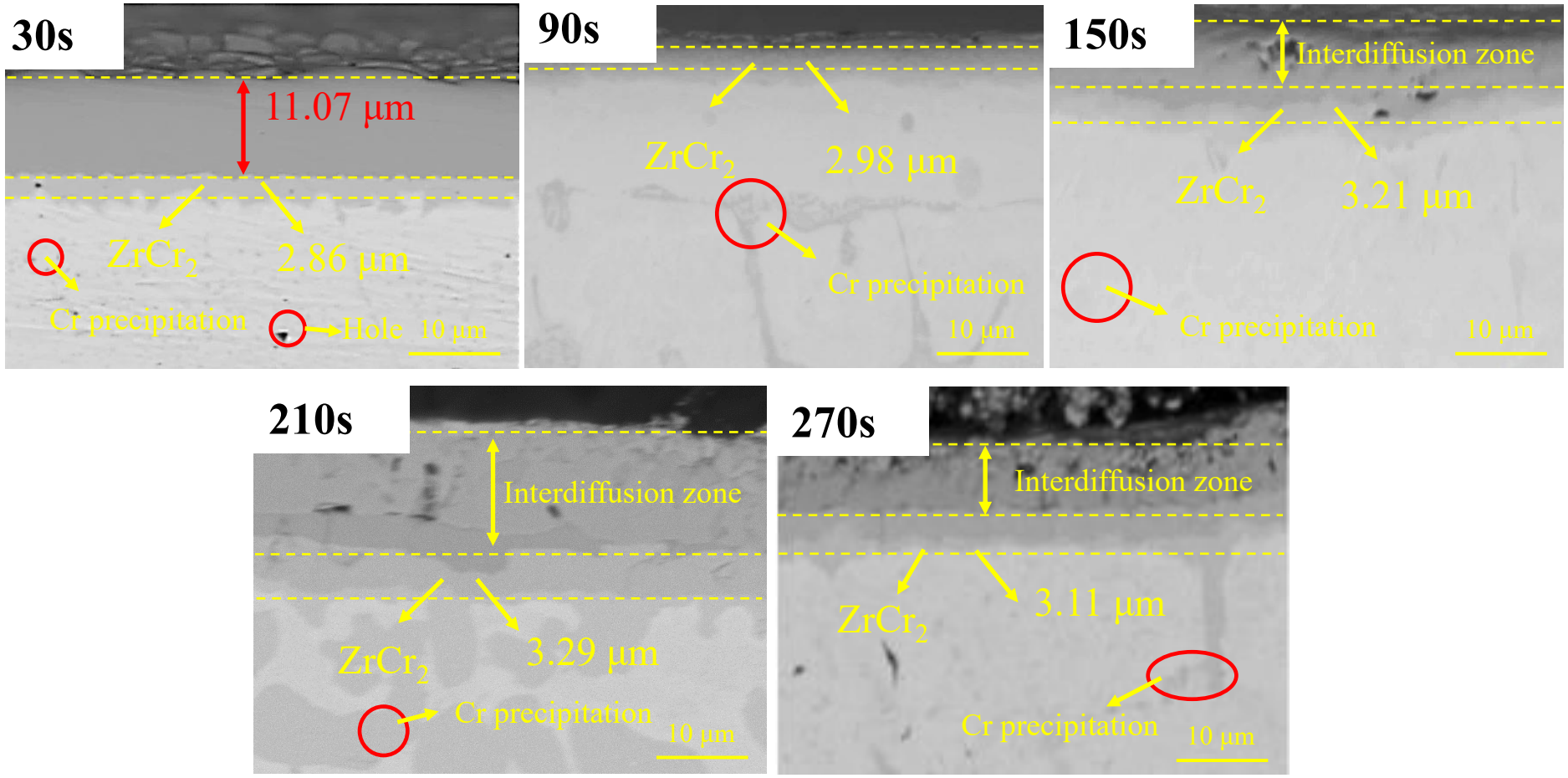
3.4 Kinetics at 1425 °C (Isothermal Hold)

SEM



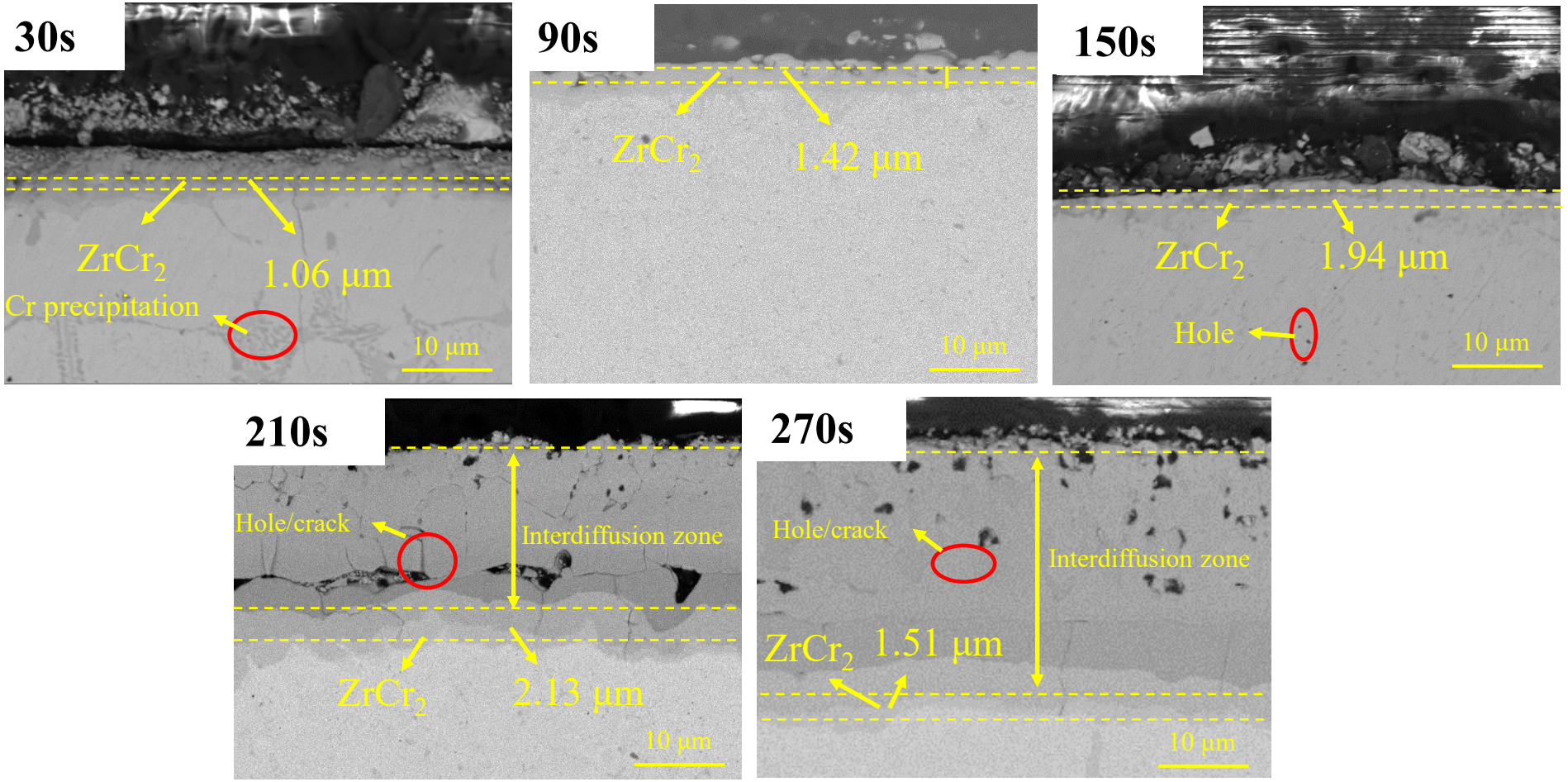
▶▶ 3.5 Kinetics at 1450 °C (Isothermal Hold)

SEM



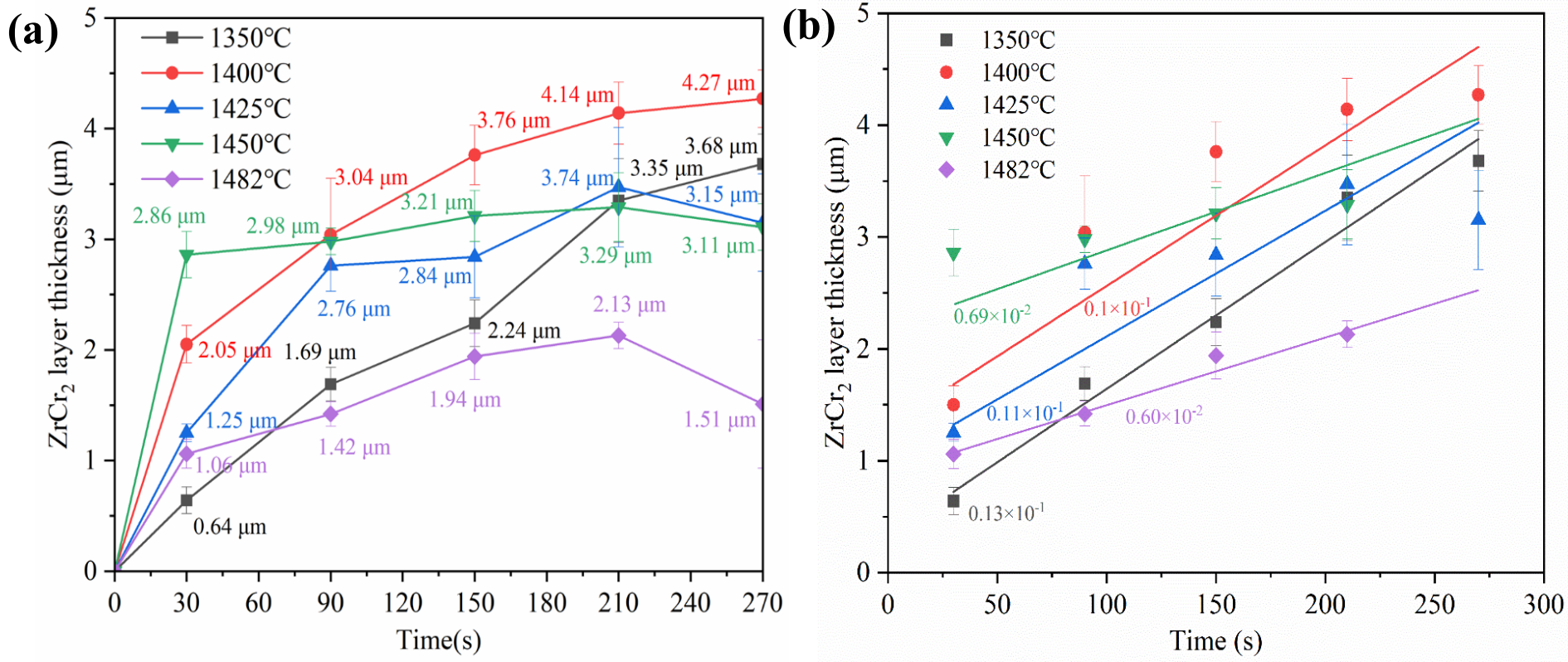
3.6 Kinetics at 1482 °C (Isothermal Hold)

SEM



3.7 Overall Diffusion Evolution in Extreme Temperatures

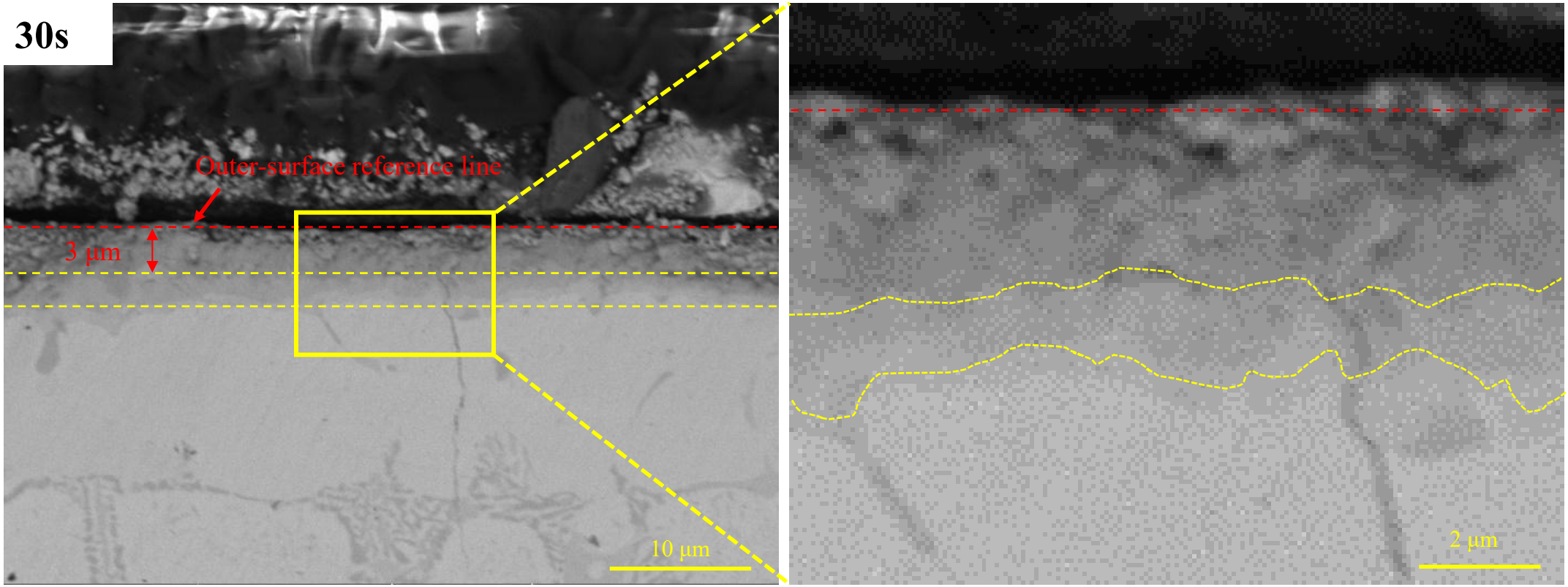
Kinetics of Cr Coating Evolution



$ZrCr_2$ layer thickness of Cr-coated Zr alloy cladding at different temperatures and holding times: (a) Evolution curves; (b) Fitted evolution curves

▶▶ 3.8 Depthwise Migration of the Diffusion Layer at 1482 °C

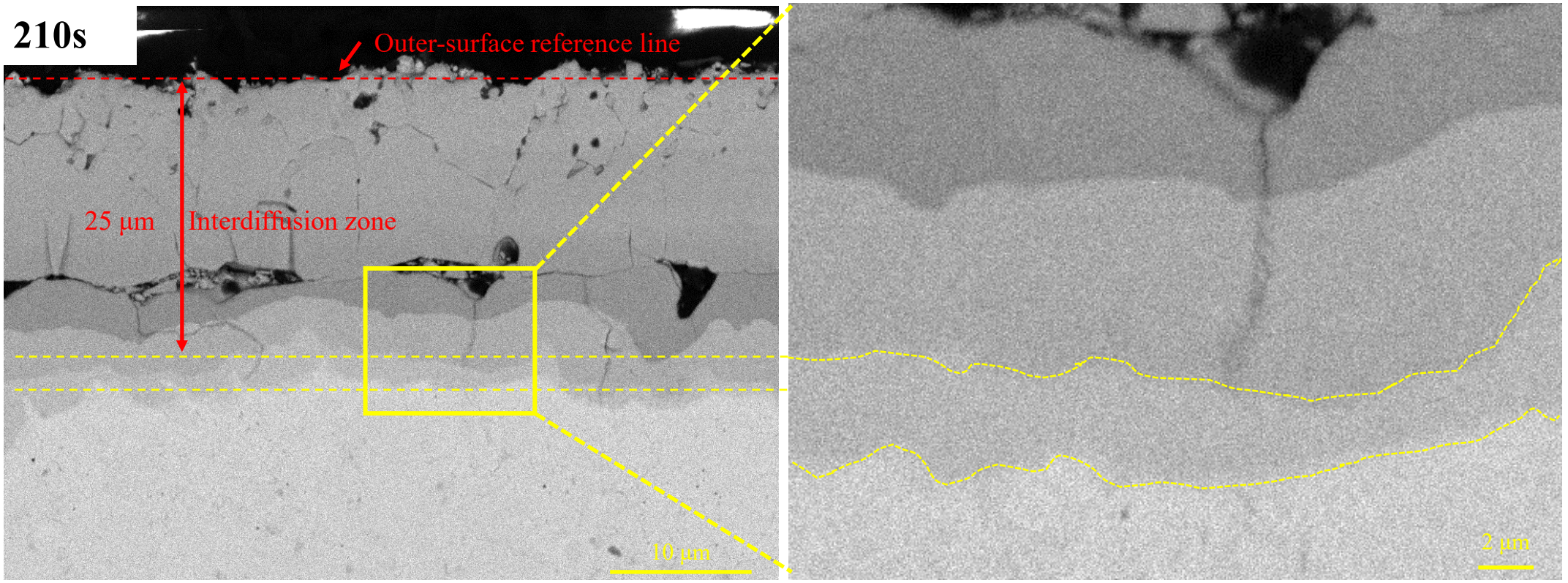
Migration of the $ZrCr_2$ layer



After holding for more than 30 s, the depth of the $ZrCr_2$ layer reached ~3 μm.

▶▶ 3.9 Depthwise Migration of the Diffusion Layer at 1482 °C

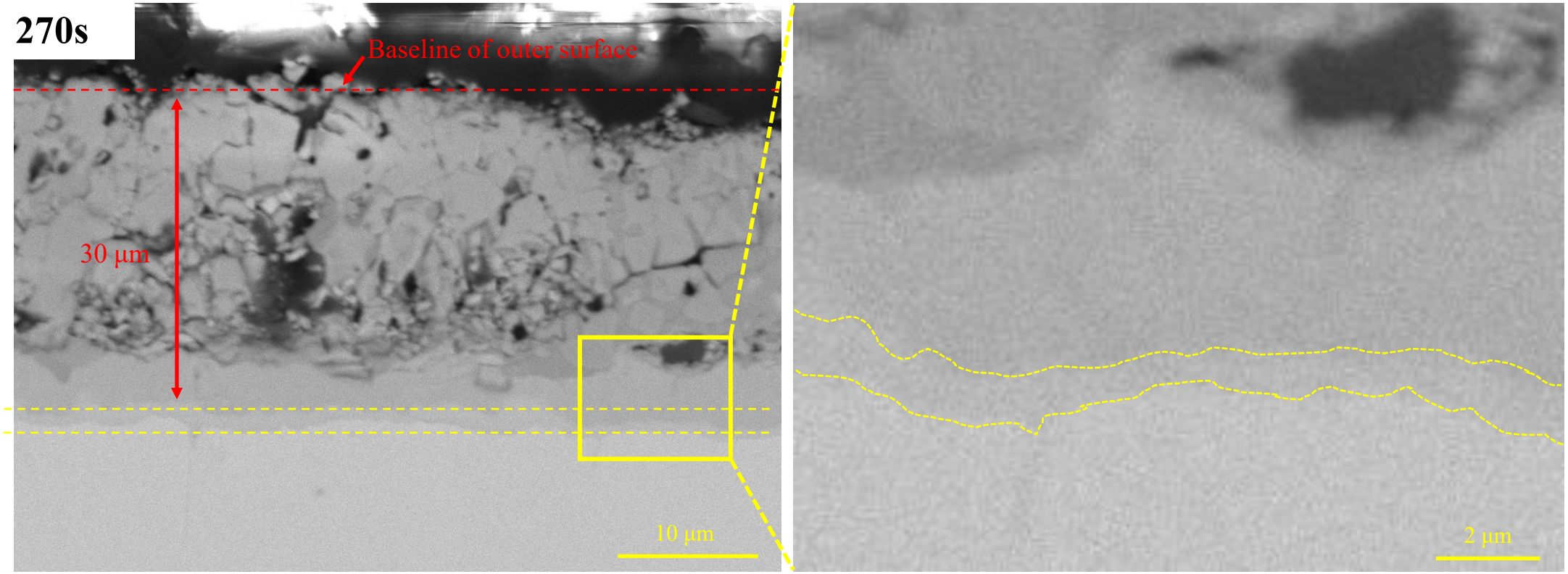
Migration of the $ZrCr_2$ layer



After holding for more than 210 s, the depth of the $ZrCr_2$ layer reached ~25 μm.

▶▶ 3.10 Depthwise Migration of the Diffusion Layer at 1482 °C

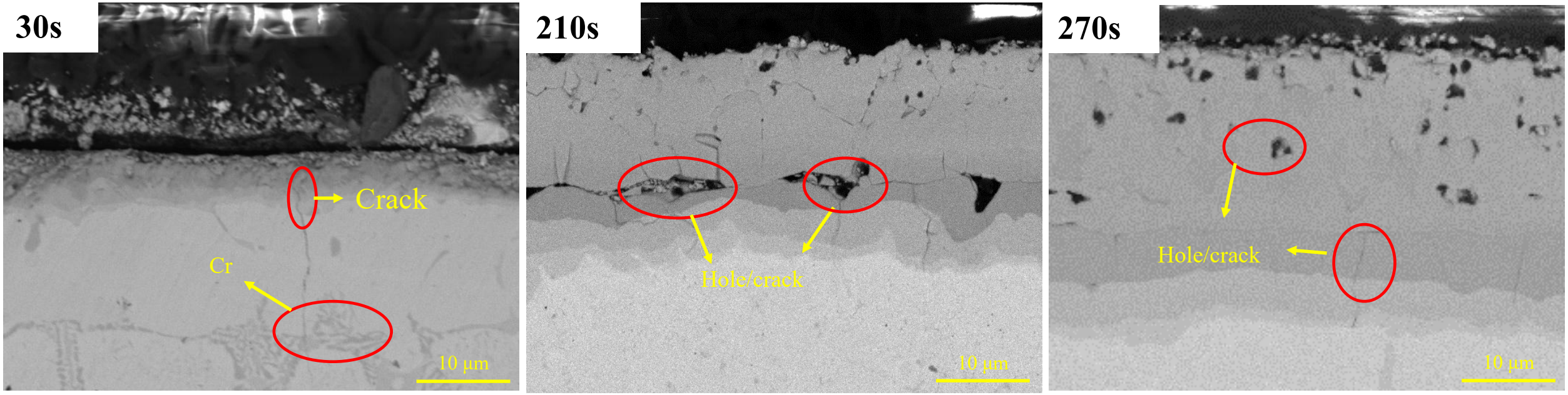
Migration of the $ZrCr_2$ layer



The $ZrCr_2$ layer progressively migrated inward with time; after holding at 1482 °C for 210 s, the penetration depth exceeded 25 μm.

▶▶ 3.11 Defect Evolution near the $ZrCr_2$ Layer (1482 °C)

Evolution of defects



Cracks and holes that form near the $ZrCr_2$ layer progressively propagate toward the substrate, with the size and quantity increasing.

3.12 Phase-Field Modeling

Total free-energy density

$$\mathcal{F}[c, \boldsymbol{\eta}] = \sum_{p\in\{B,H,L\}} h(\eta_p) G^p(T,c) + \frac{\kappa_c}{2}|\nabla c|^2 + \sum_p \left(\frac{\kappa_\eta}{2}|\nabla\eta_p|^2 + W g(\eta_p)\right) + \omega \sum_{p\neq q} \eta_p^2 \eta_q^2 .$$

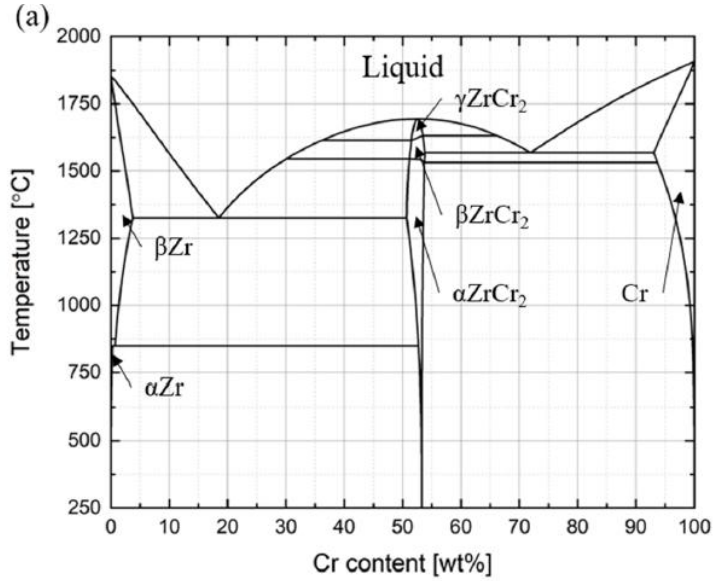
Governing equations

$$\frac{\partial c}{\partial t} = \nabla\cdot(M\nabla\mu_{tot}), \mu_{tot} = \mu_{loc} - \kappa_c\nabla^2 c.$$

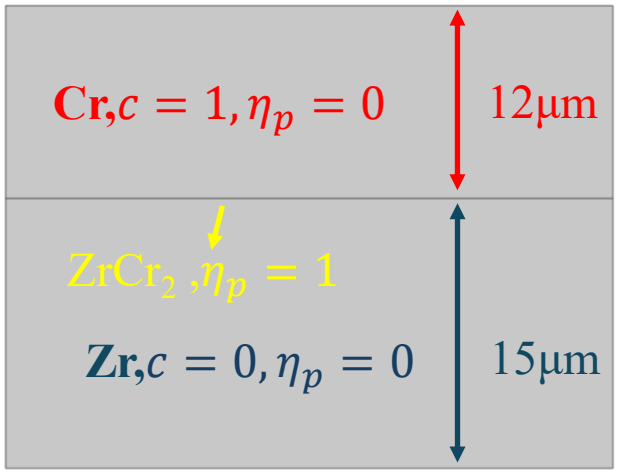
$$\frac{\partial \eta_p}{\partial t} = -L_\eta \frac{\delta\mathcal{F}}{\delta\eta_p}$$

Functional derivative with respect to $\boldsymbol{\eta_p}$

$$\frac{\delta\mathcal{F}}{\delta\eta_p} = -\kappa_\eta\nabla^2\eta_p + W g'(\eta_p) + \frac{h'(\eta_p)}{H}(G^p - \bar{F}) + 2\omega\eta_p \sum_{q\neq p}\eta_q^2$$

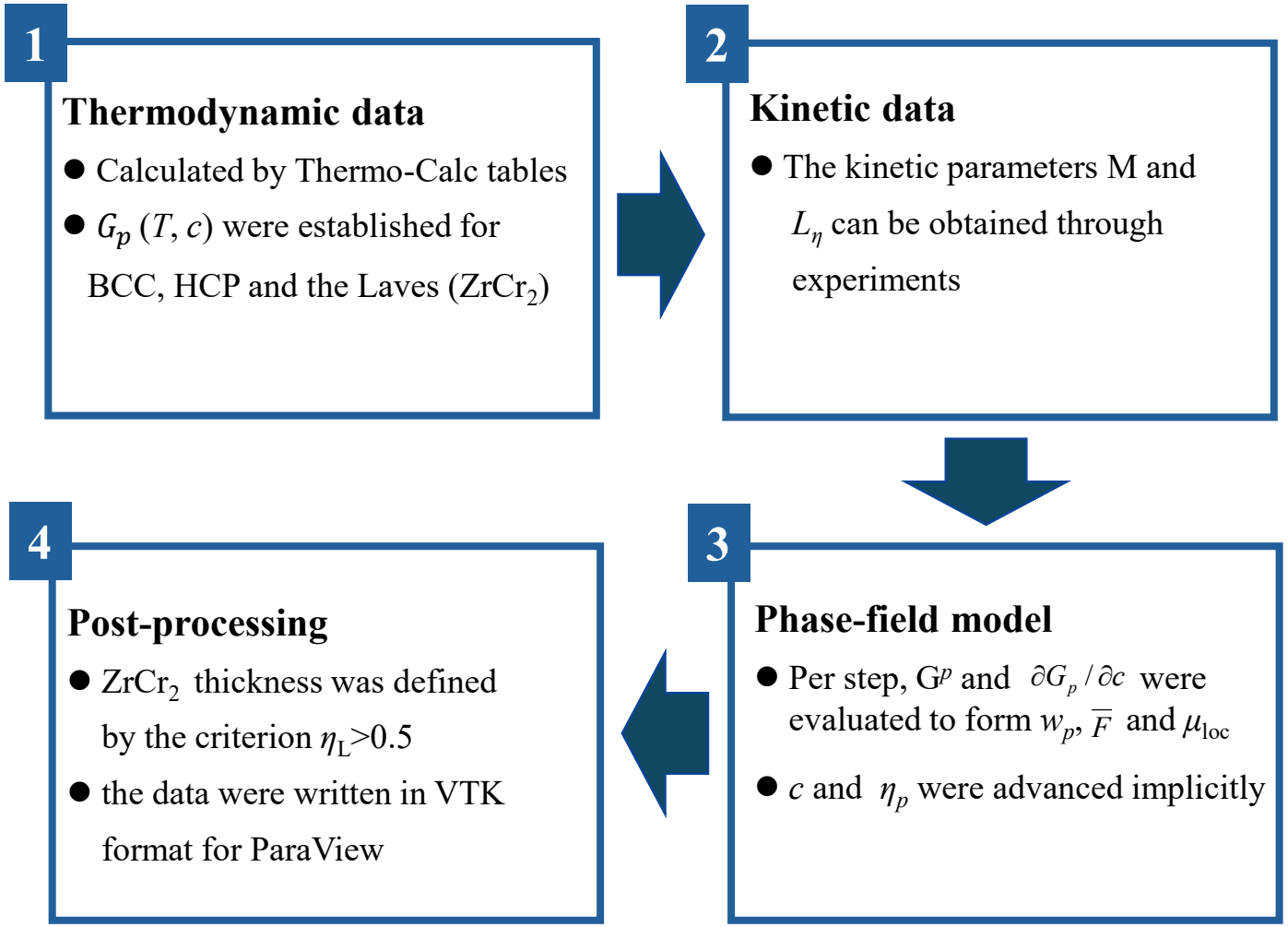


Zr–Cr binary phase diagram



Geometry settings

3.13 Computational Workflow and Variables

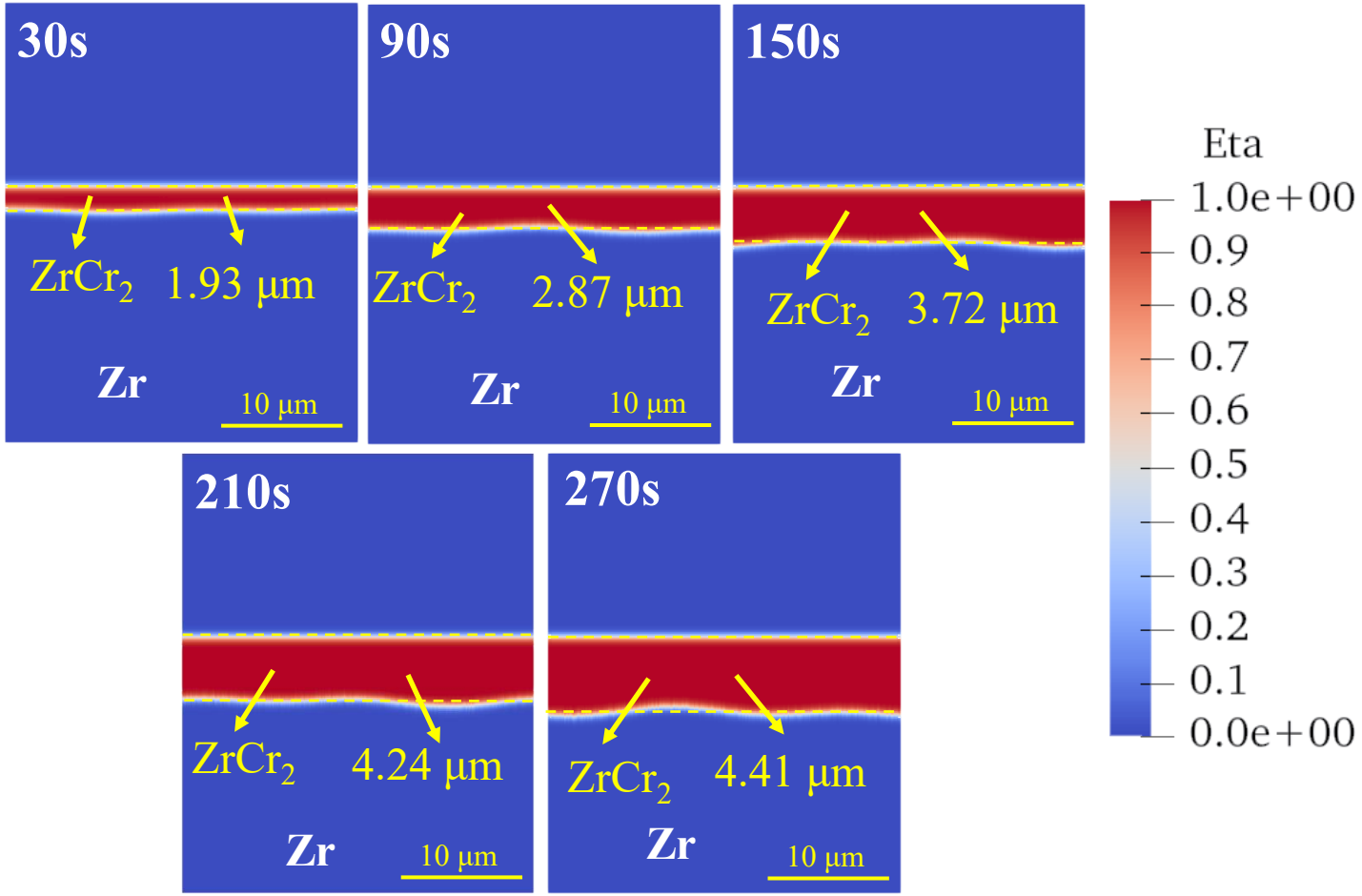


Computational workflow

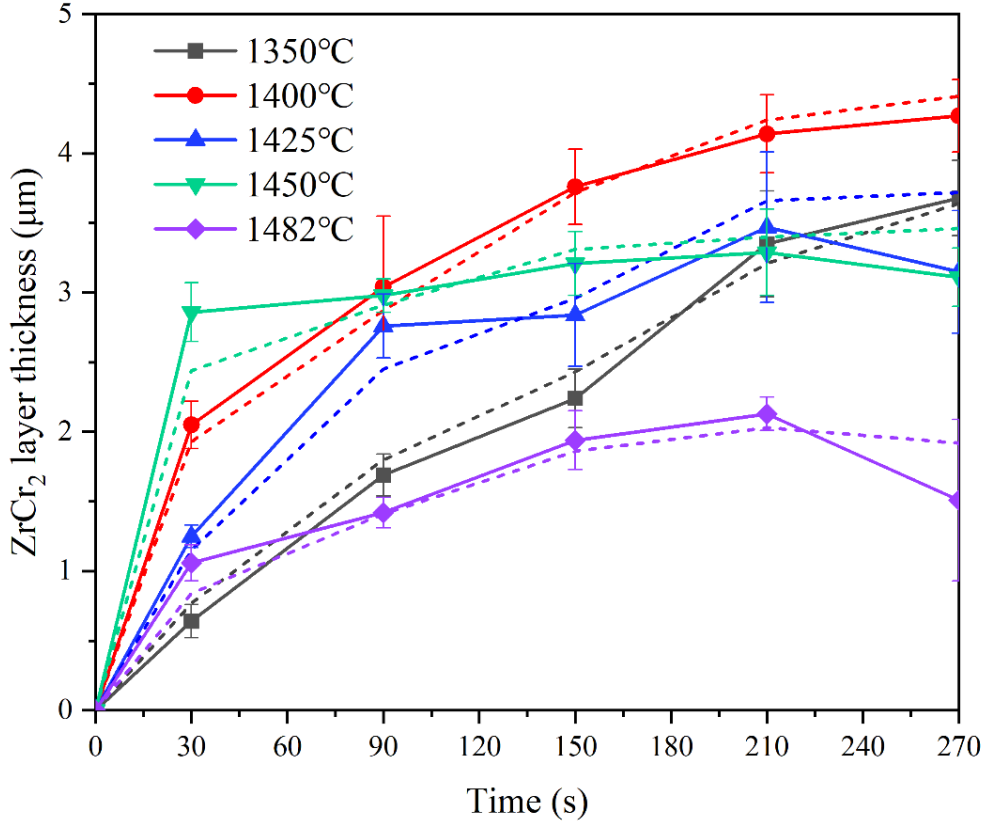
Variables and Symbols

Symbol	Meaning	Notes / Units
T	Absolute temperature	K
c	Chromium mole fraction	0~1
η, $G_p(T,c)$	Phase-field order parameter and molar Gibbs free energy	[0,1]; from Thermo-Calc tables; J·mol⁻¹
$\partial G_p/\partial c$	Compositional derivative of G_p	chemical potential; J·mol⁻¹
w_p	Normalized interpolation weight	$w_p = h(\eta_p)\sum_q h(\eta_q)$ with $h(\eta) = \eta^2(3-2\eta)$
$\bar{F}$	Mixture free energy density	$\bar{F} = \sum_p w_p G_p$
μ_{loc}, μ_{tot}	Local and total chemical potentials	$\mu_{loc} = \sum_p w_p \frac{\partial G_p}{\partial c}$; $\mu_{tot} = \mu_{loc} - \kappa_c \nabla^2 c$
M	Effective mobility (composition)	C-H kinetics parameter; $m^2 \cdot s/J$
k_c	Gradient-energy coefficient (composition)	$J \cdot m^2/mol$
W	Double-well barrier strength	from the Landau potential; J/m³
L_η	Kinetic coefficient for Allen–Cahn evolution	m³/(J·s)
ω	Control the interplay between order parameter	J/m³

3.13 Phase-Field Results and Validation



Simulated cross-sectional morphologies of Cr-coated Zircaloy cladding after isothermal holding at 1400 °C.
$M=1.0\times10^{-18}m^2\cdot s/J$, $L_\eta=5.0\times10^{-5}m^3/(J\cdot s)$



$ZrCr_2$ layer thickness in Cr-coated Zircaloy cladding : experimental data (solid lines) vs. phase-field simulations (dashed lines).

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04 Conclusion

▸▸ 4 Conclusion

1. Diffusion Kinetics of the Cr Coating

- **Under 1350°C–1482°C, 30s–270s, the $ZrCr_2$ layer thickness increases with temperature and holding time.**

  A transition from solid-state to melt-assisted diffusion kinetics occurs in the 1400~1450 °C.

- **The Cr coating disappeared at: 1350°C (210s), 1400°C (150s), 1425°C (90s), 1450°C (90s), 1482°C (30s).**

2. Migration of the $ZrCr_2$ Layer

- **At 1482°C and > 210s, the $ZrCr_2$ layer depth exceeds 25μm, cracks and pores appear near the $ZrCr_2$ layer.**

3. Phase-Field Simulation

- **The thickness growth of $ZrCr_2$ layer follows a parabolic law.**

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Thanks for your attention