ZCO-70: Nature of Coating Development and Substrate Microcracking during Hot Press Forming

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Project Objectives – αFe(Zn) Coatings

- **Focusing on αFe(Zn) solid solution coatings, we will examine the following:**
  - **microstructural development of αFe(Zn) coatings from GA and GI precursor materials → obtain thin, high Zn content, cathodically protective coatings**
  - **substrate properties: $\sigma_{UTS} \geq 1400$ MPa; %elong $\geq 5\%$**
    - **planar die quenching experiments**
  - **microcracking mechanism determination – U-channel die using different strain paths**
  - **cathodic protection potential of αFe(Zn) coatings versus conventional GI, GA and DHPF Al-Si coatings**

Project Timeline and Current Status

	07/14-12/14	01/15-06/15	07/15-12/15	01/16-06/16	07/16-12/16	01/17-06/17
Task 1a: Literature survey						
Task 1b: Solicitation and delivery of substrates from sponsors, including fabrication of lower B materials						
Task 1c: Microstructural development of αFe(Zn) coatings – on-going in light of new samples						
Task 1d: Planar die forming trials and characterization – apparatus constructed and testing to begin						
Task 2a: Design and fabrication of U-channel and planar forming dies – on-going due to continued issue with McMaster press commissioning						
Task 2b: U-channel forming trials, characterization and correlation to microcracking propagation – to be started in early 2016						
Task 3: Corrosion testing of αFe(Zn) DHPF panels						
Task 4: Phosphating, E-coating and corrosion testing of αFe(Zn) DHPF panels – to start in late 2016 contingent on granting of NSERC CRD						
GAP Meeting Reports						
Mid-term and Final Reports						

ZCO-70 – Current Status

- **Significant surface oxidation occurred for all coatings, annealing times and temperatures, leading to a surface covered with ZnO and Al_2O_3**
- **For all GA or GI samples annealed at 700^{o}C, the coating transformed to Γ-Fe_3Zn_{10} for all annealing times**
  - **indicates that the coating was 100% Γ-Fe_3Zn_{10} before going through the peritectic temperature, regardless of the starting coating**
- **There was no significant evaporation of Zn from the coating layer during annealing, likely due to the postulated mechanism of vapourisation being inhibited by the surface Al_2O_3**

ZCO-70 – Current Status

- **GA60 × 900°C coatings**
  - **all coatings transformed to αFe(Zn), with no residual liquid present for the annealing times explored**
  - **the αFe(Zn) coatings produced did not contain the 30at% Zn hypothesized to provide cathodic protection for the substrate – to be verified through corrosion testing**

ZCO-70 – Current Status

- **GI70 × 900°C coatings:**
  - **the coating transforms to αFe(Zn) and Zn(Fe)(l), with the liquid disappearing from the microstructures for annealing times of 180s +**
  - **additional annealing at 700^{o}C + 60s after annealing at 900^{o}C decreased the Γ-Fe_3Zn_{10} content and increased the Zn content of the αFe(Zn)**
  - **Zn content of the αFe(Zn) coatings decreased with increasing time at 900^{o}C**
  - **coatings contained greater than 30at% Zn αFe(Zn) for annealing times of less than 300s – cathodic protection potential possible (from literature)**

ZCO-70 – Current Status

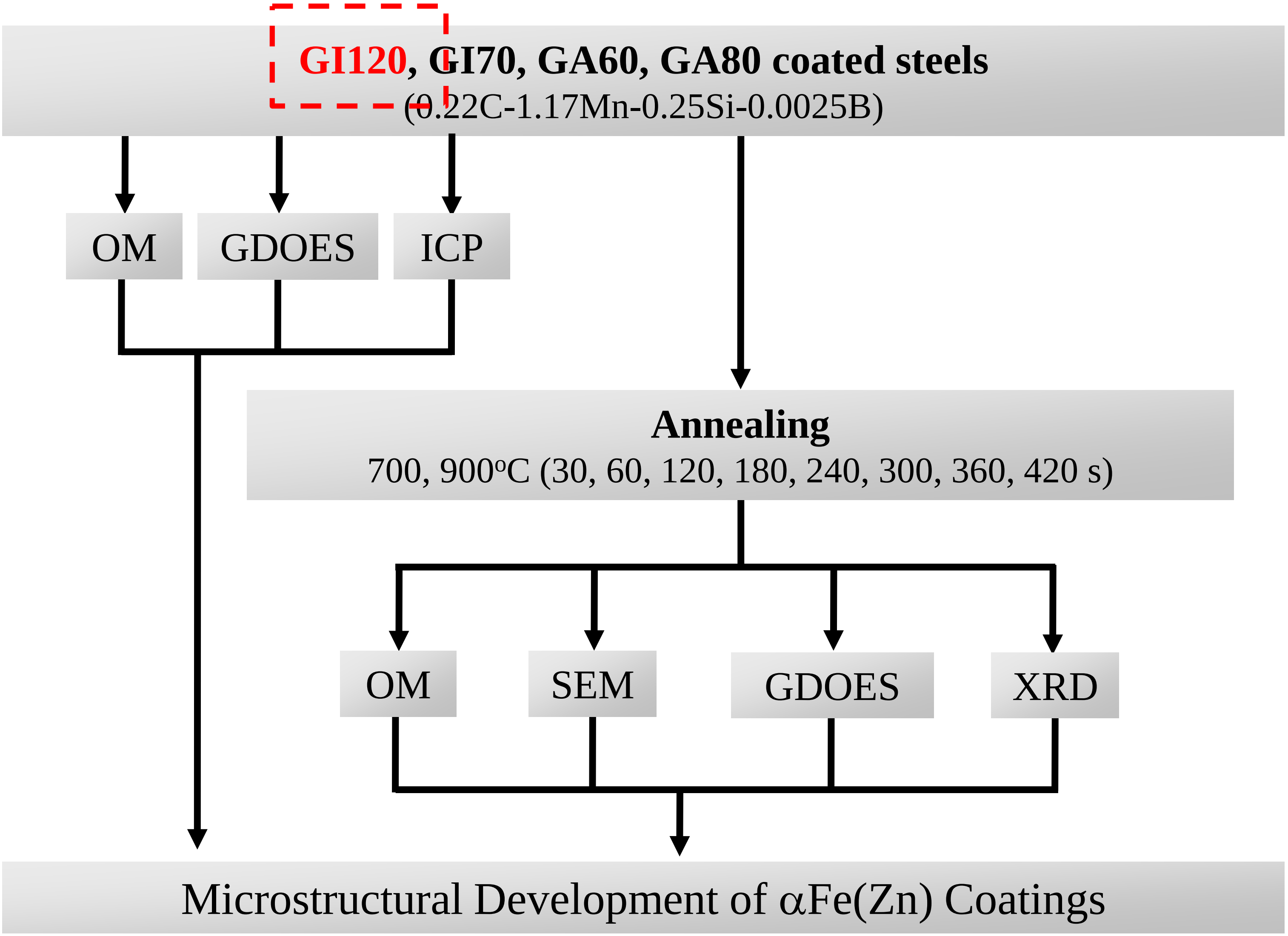
➢ GA80 × 900°C coatings

- all coatings transformed to αFe(Zn) + Zn(Fe)(l), with residual liquid present for annealing times of less than 300s
- Zn content of the αFe(Zn) coatings decreased with increasing time at 900^{o}C
- coatings contained greater than 30at% Zn in αFe(Zn) for annealing times of less than 300s – promising result from cathodic protection potential

➢ As hypothesised, coating weight seems to be a critical variable for Zn-coated PHS

- process window enlarges with increasing ctg. wt.?
- is there a critical volume fraction of residual liquid to avoid LME?

Experimental Flow Chart – Task 1



Experimental Materials

◎ Chemical composition of sample

Chemical composition (mass%)																				
C	Mn	Si	Cr	Mo	Nb	Ti	B	P	S	Ca	N	Al	Cu	Ni	V	Zr	W	Sn	Mg	Sb
0.221	1.169	0.252	0.179	0.0055	0.0016	0.0263	0.0025	0.0123	0.0026	0.0013	0.0064	0.0383	0.0385	0.0167	0.0060	0.0019	0.0022	0.0027	0.0002	0.0008

◎ Coating property

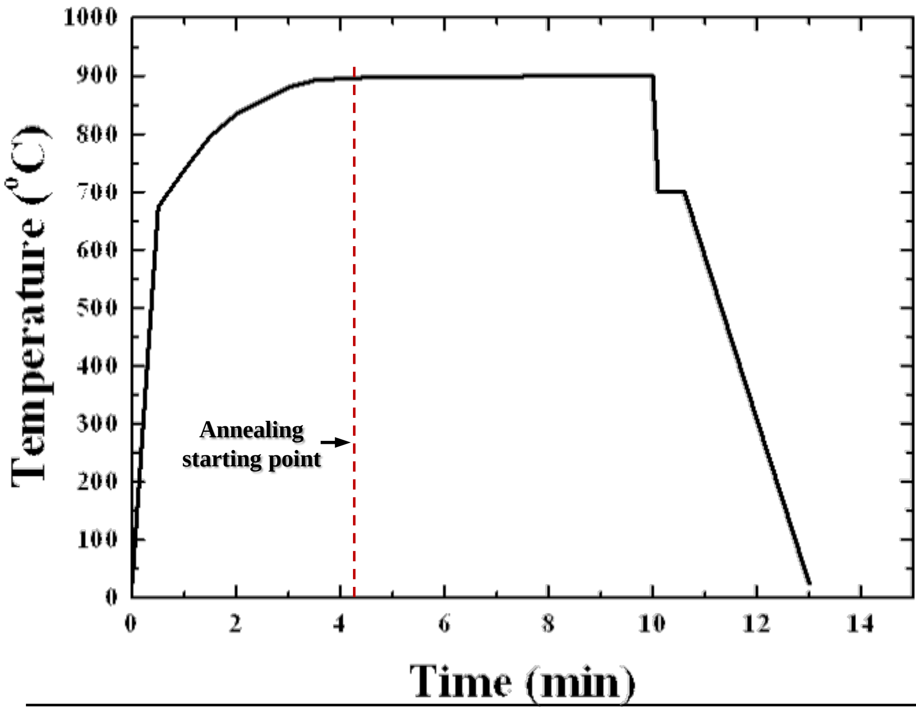
							Coating weight		Fe [mass%]	
ID	Length position	Width position	Surface	Coating weight (g/m^2/side)	Al (mass%)	Fe (mass%)	TST top (g/m^2/side)	TST bottom (g/m^2/side)	TST top (g/m^2/side)	TST bottom (g/m^2/side)
GI70	Tail	E1	top	76	0.49	0.34	73	73	0.35	0.37
			bottom	71	0.55	0.40				
		CTR	top	75	0.45	0.28				
			bottom	75	0.48	0.33				
		E2	top	68	0.56	0.42				
			bottom	74	0.53	0.39				
GI120							120	120		
GA60	Tail	E1	top	63	0.24	12.8	60.8	58.5	12.9	13.0
			bottom	60	0.26	13.0				
		CTR	top	61	0.26	12.7				
			bottom	58	0.27	13.0				
		E2	top	58	0.26	13.2				
			bottom	57	0.27	13.1				
GA80	Tail	E1	top	114	0.22	6.1	77.7	88.0	9.5	8.5
			bottom	60	0.28	10.2				
		CTR	top	79	0.25	9.6				
			bottom	84	0.25	9.2				
		E2	top	71	0.25	9.8				
			bottom	89	0.23	9				

Summary of Thermal Treatments

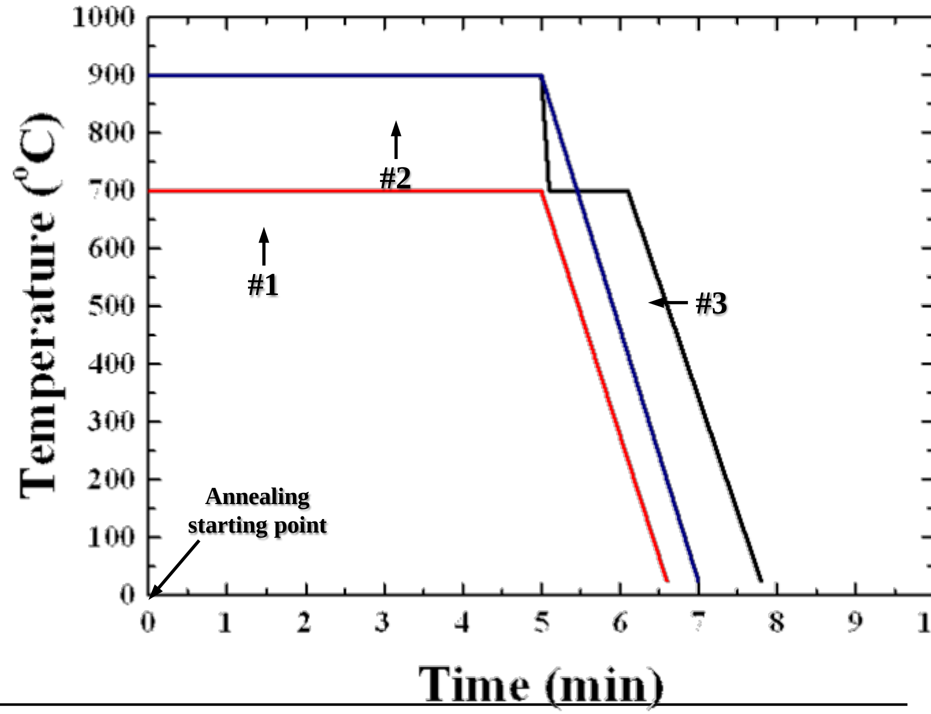
Annealing condition			
Sample	**Annealing temperature(°C)**	**Annealing time(s)**	**Heating type**
GI70 GI120	700	60, 180, 300	#1
	900	30, 60, 120, 180, 240, 300, 360, 420	#2
	900 (700°C + 60s)	30, 60, 120, 180, 240, 300	#3

Annealing condition			
Sample	**Annealing temperature(°C)**	**Annealing time(s)**	**Heating type**
GA60 GA80	700	60, 180, 300	#1
	900	60, 120, 180, 240, 300	#2

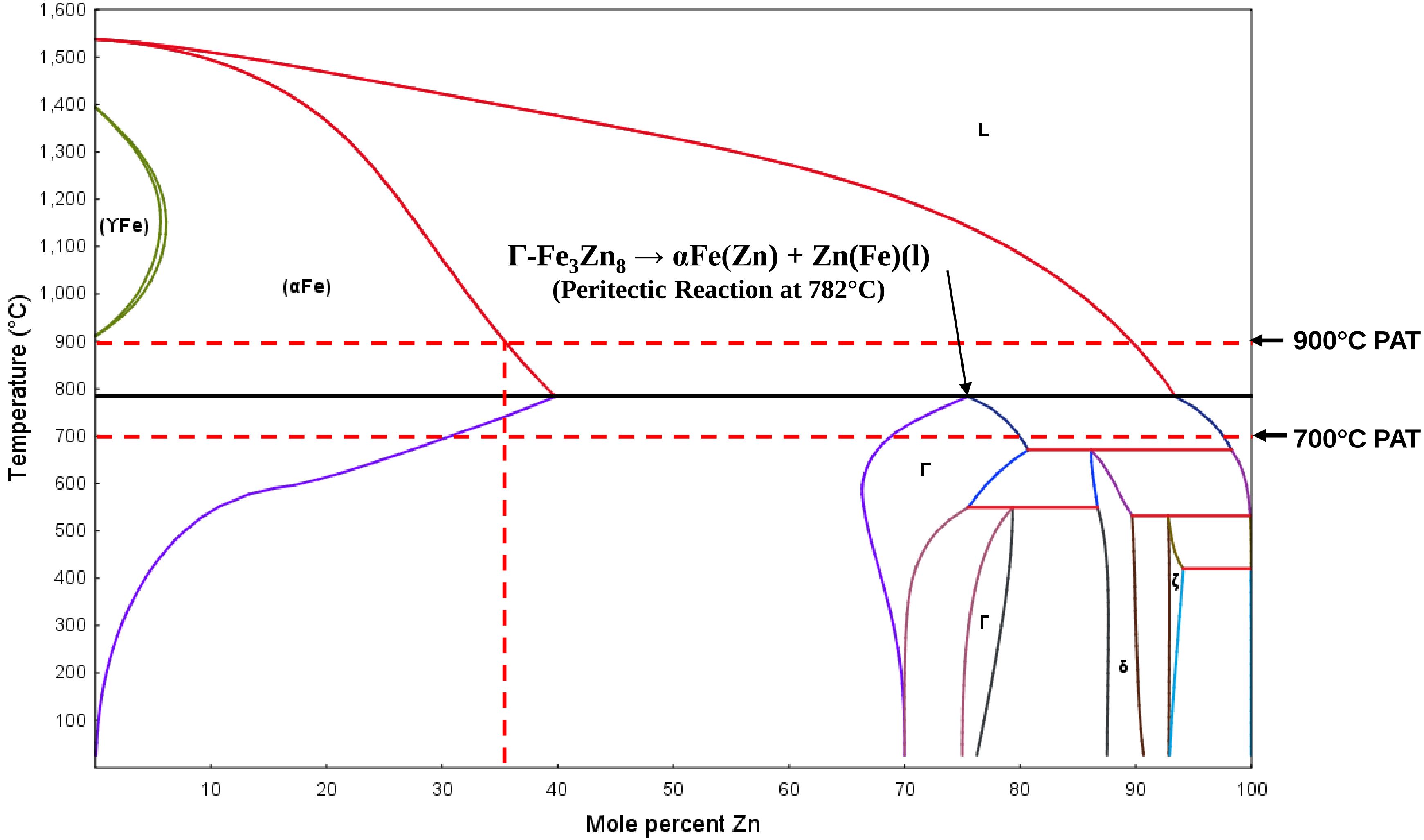
◎ Thermal cycle – Ambient heating



◎ Annealing cycles

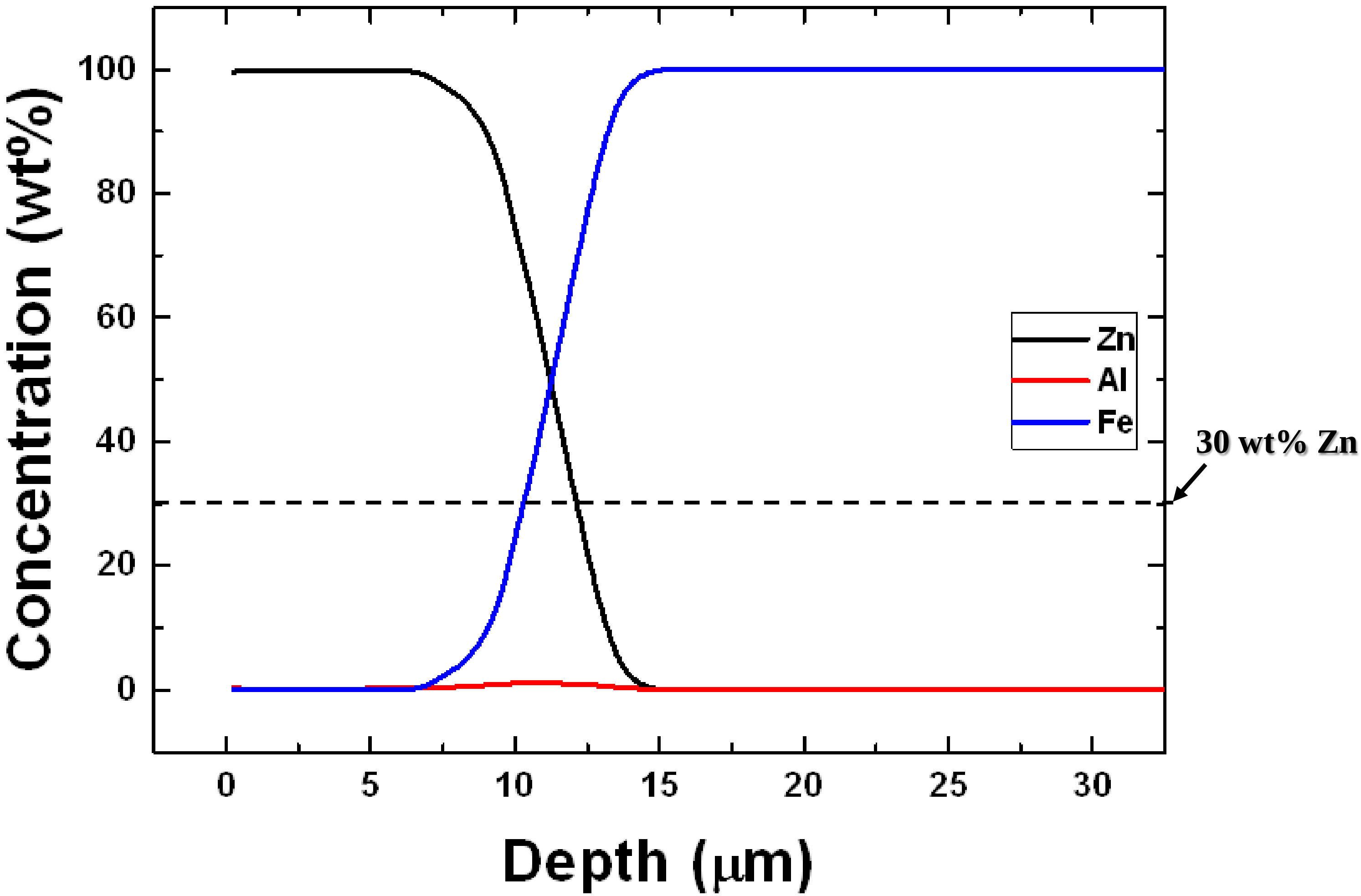


Fe-Zn Phase Diagram – 700°C and 900°C



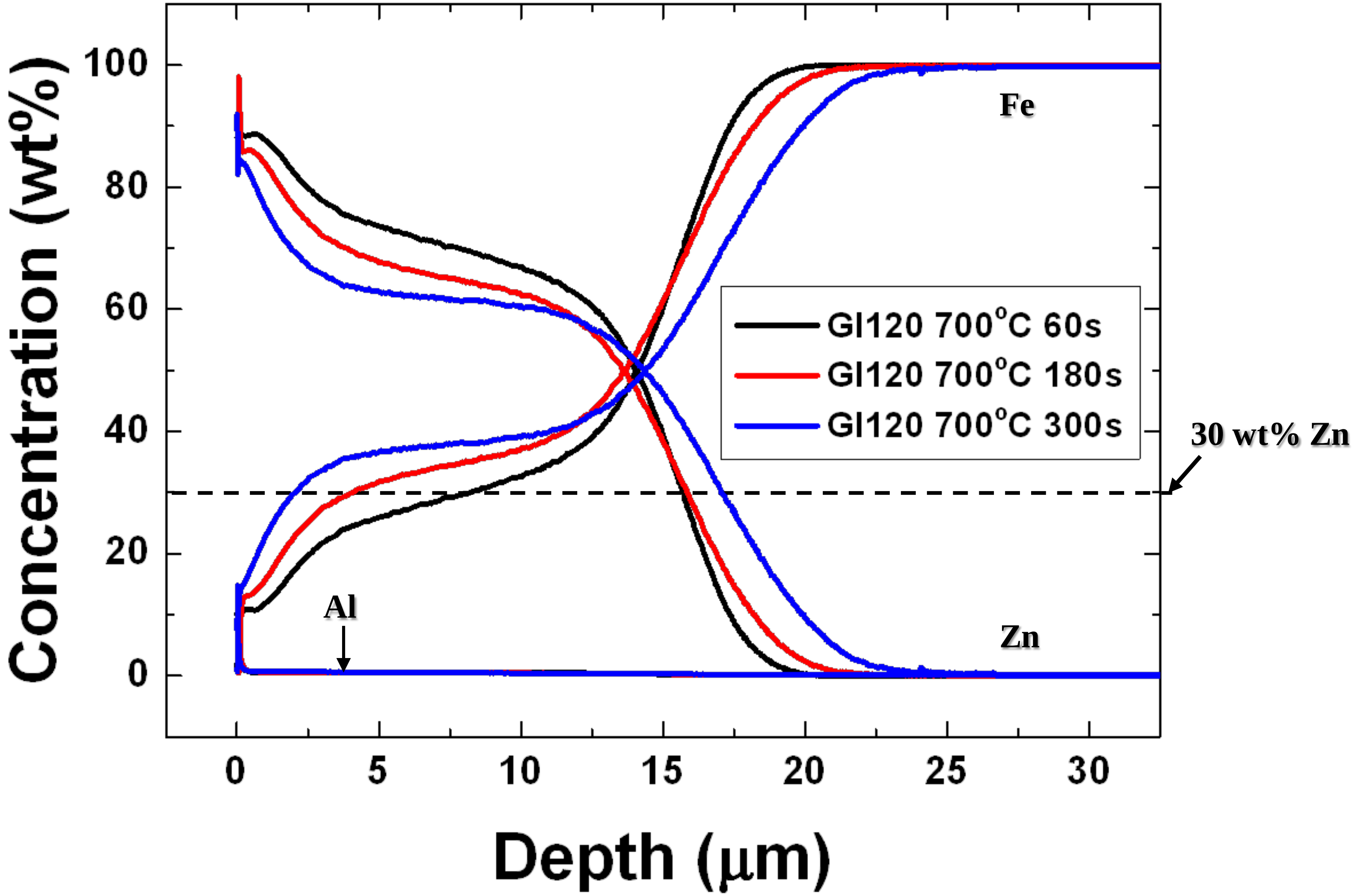
GDOES Depth Profiles – As-received GI120

GI120 as received



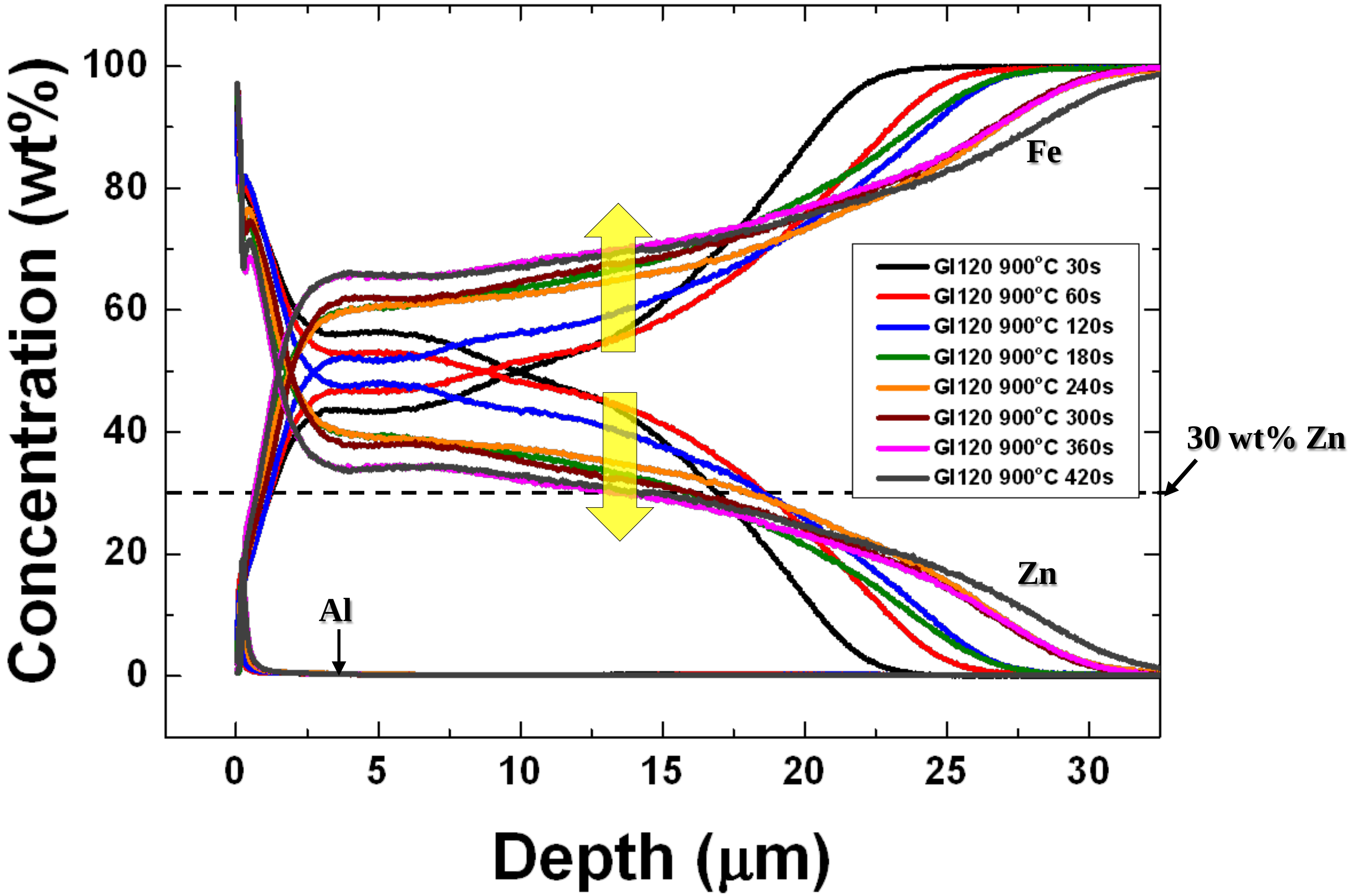
Coating Composition – GI120 at 700^{o}C vs. time

GI120 @ 700^{o}C PAT



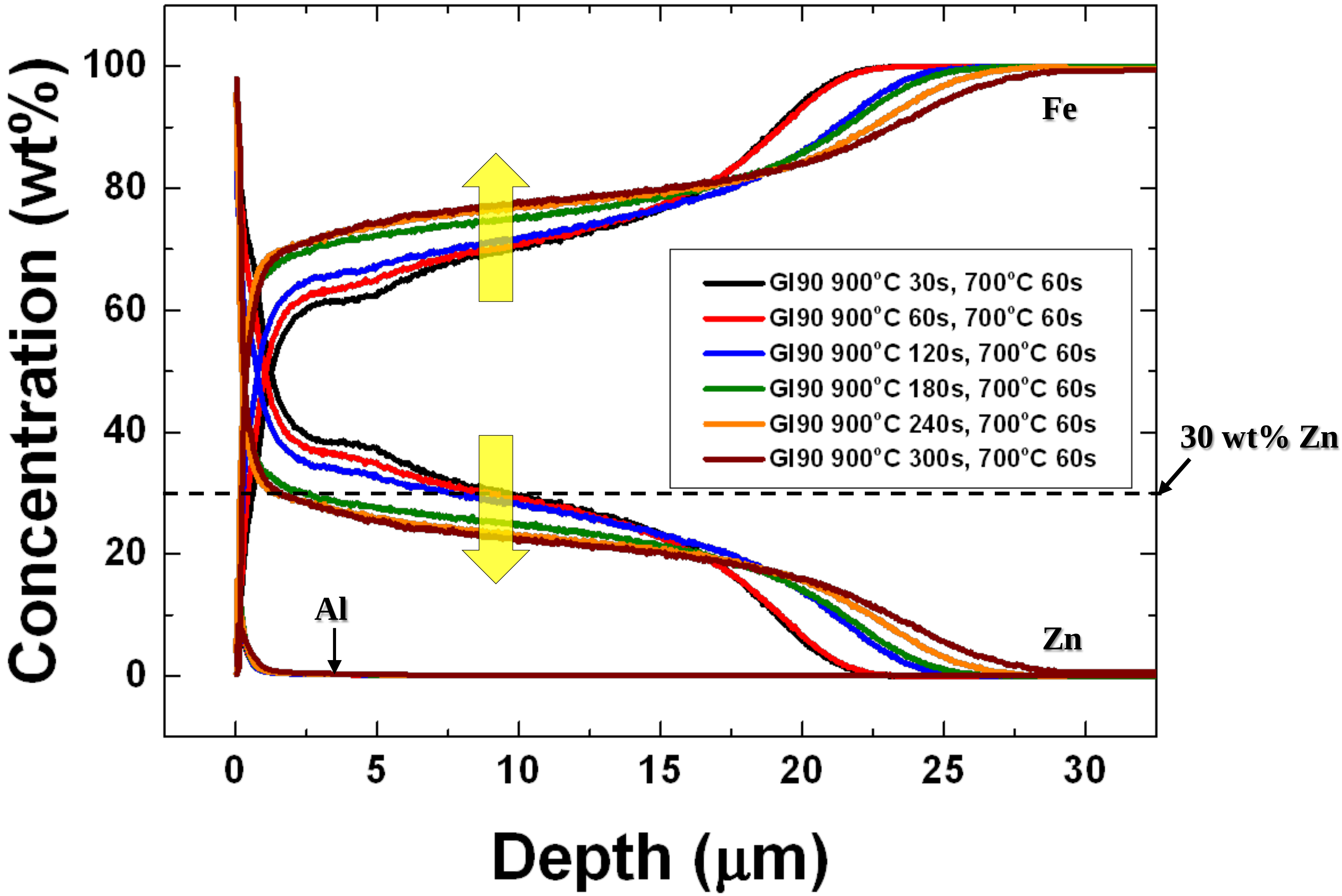
Coating Composition – GI120 at 900ºC vs. time

GI120 @ 900ºC PAT

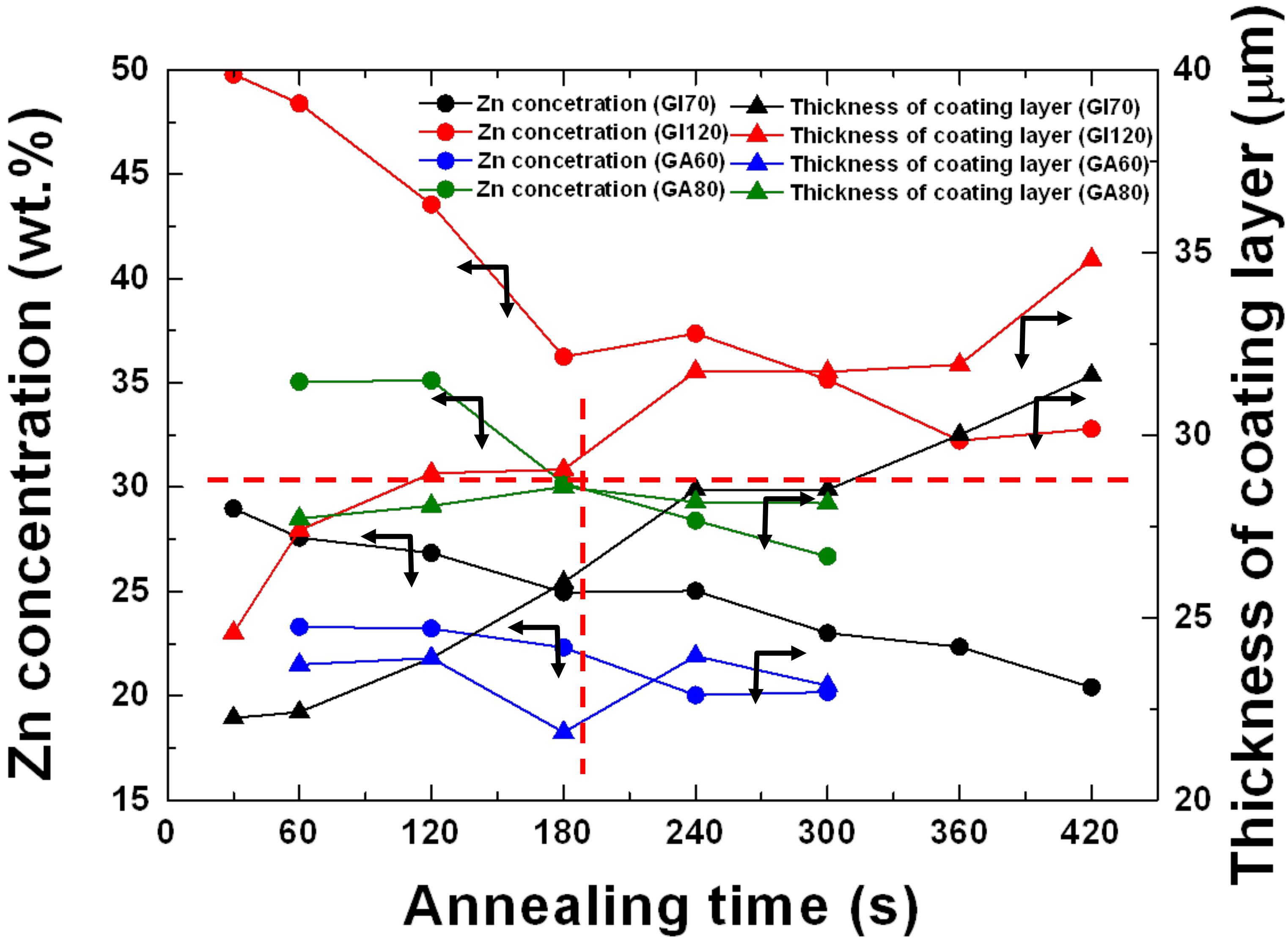


Coating Composition – GI120 at 900ºC + 700ºC vs. time

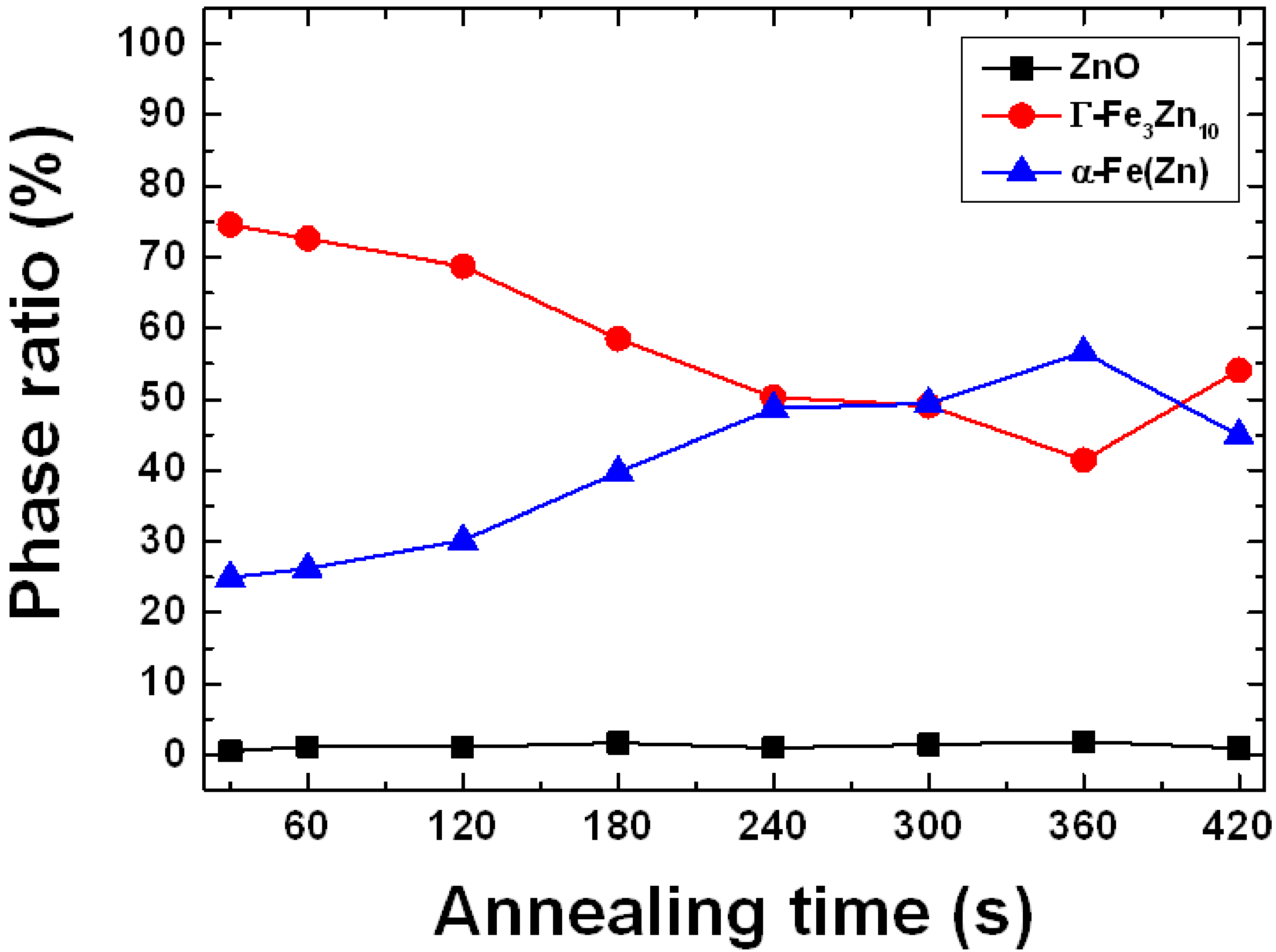
GI120 @ 900ºC PAT + 60s hold @ 700°C



Zn concentration at 10μm vs. thickness of the coating layer

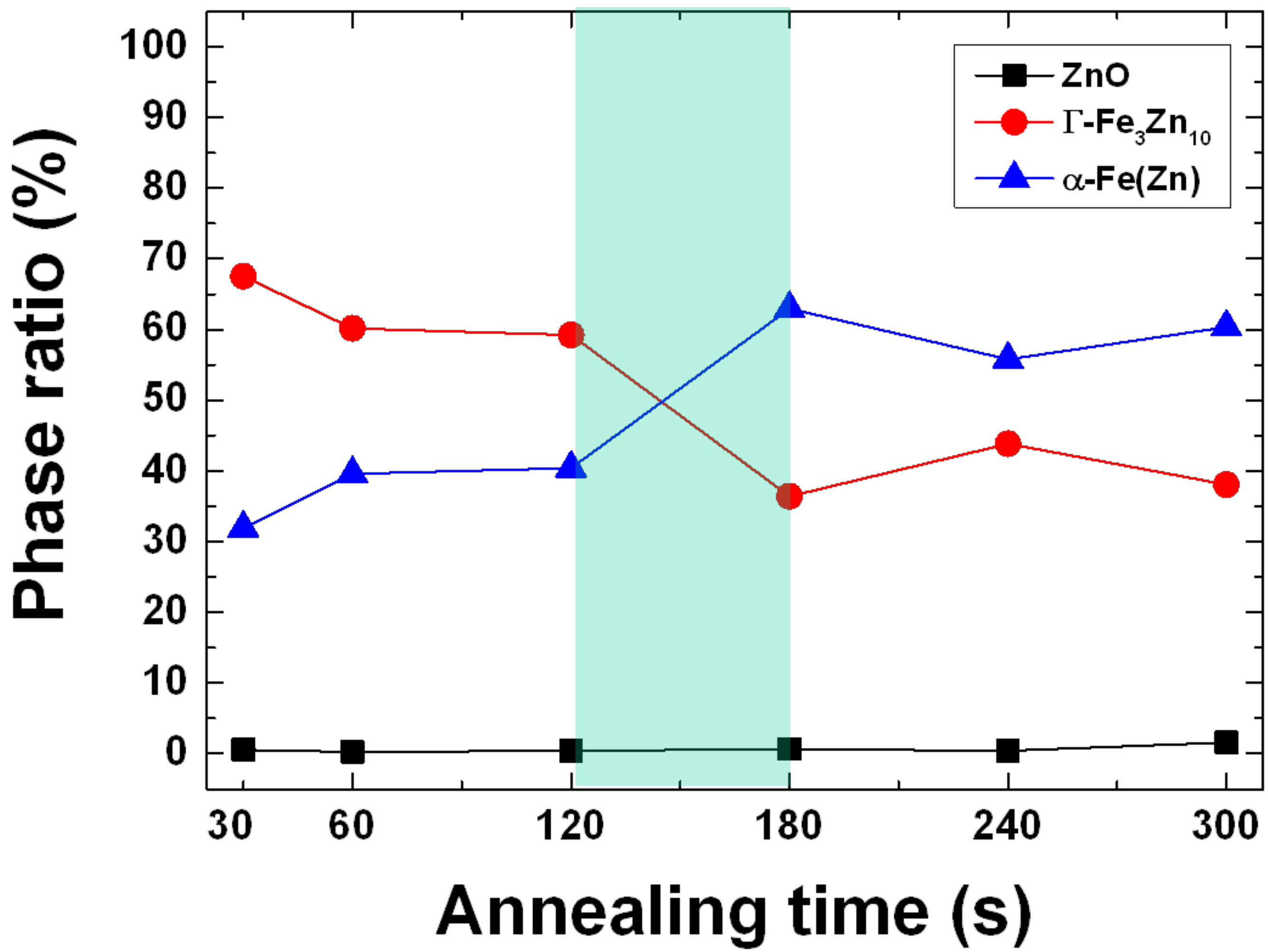


XRD Phase Analysis – GI120 at 900°C PAT



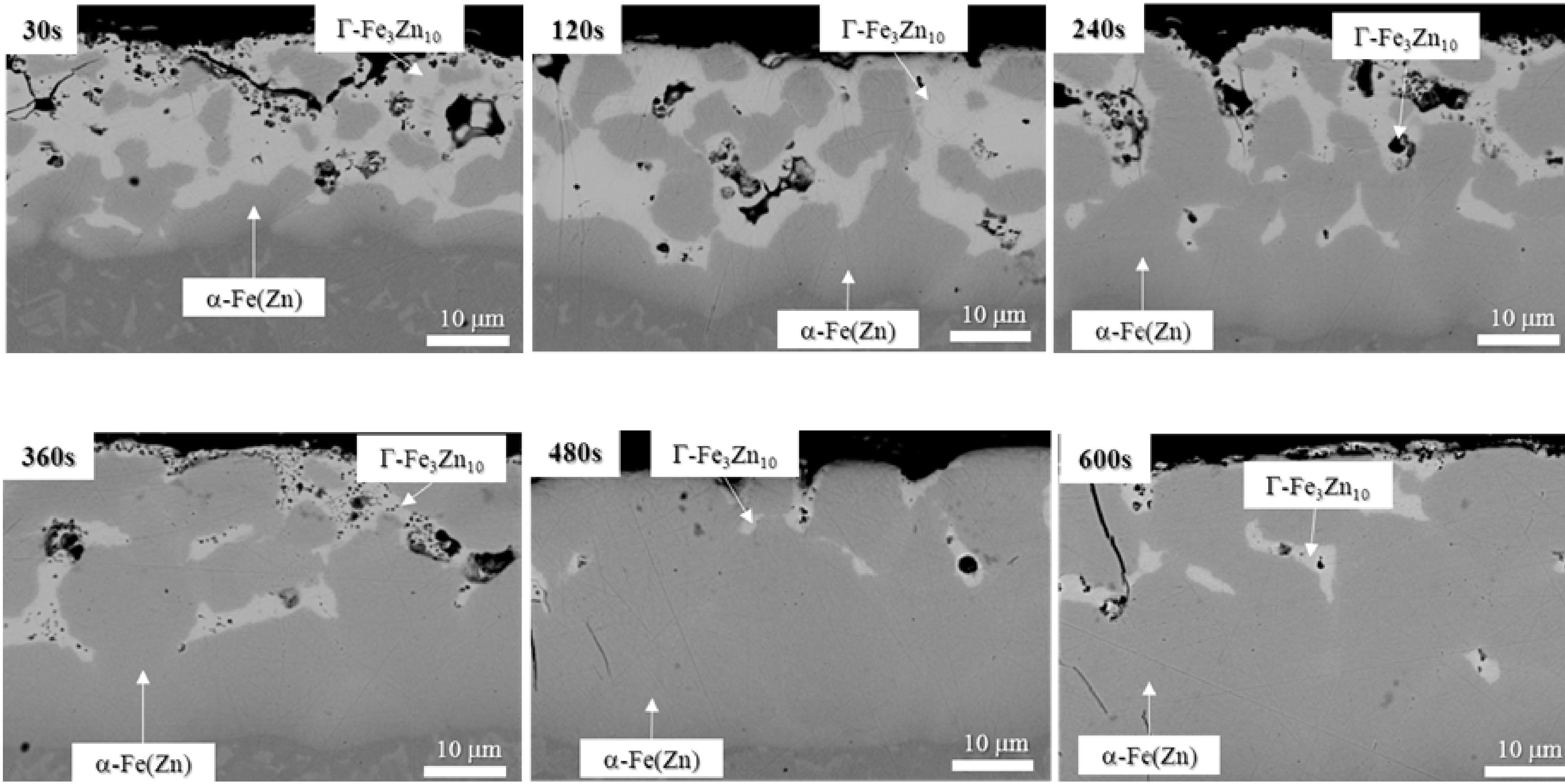
XRD Phase Analysis – GI120

GI120 @ 900ºC PAT + 60s hold @ 700°C



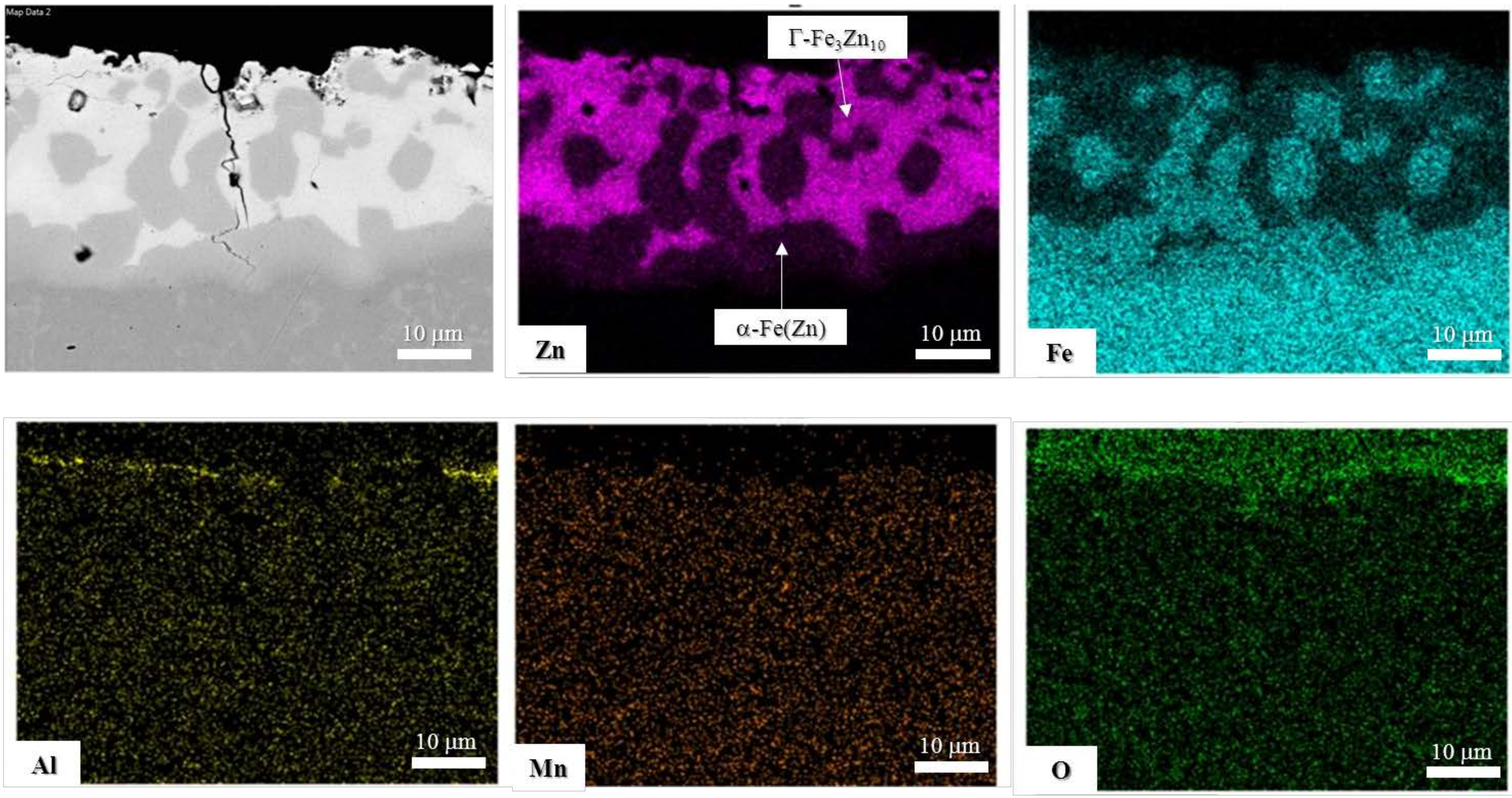
Microstructure vs. time – GI120 + 900ºC

GI120 annealed @ 900ºC



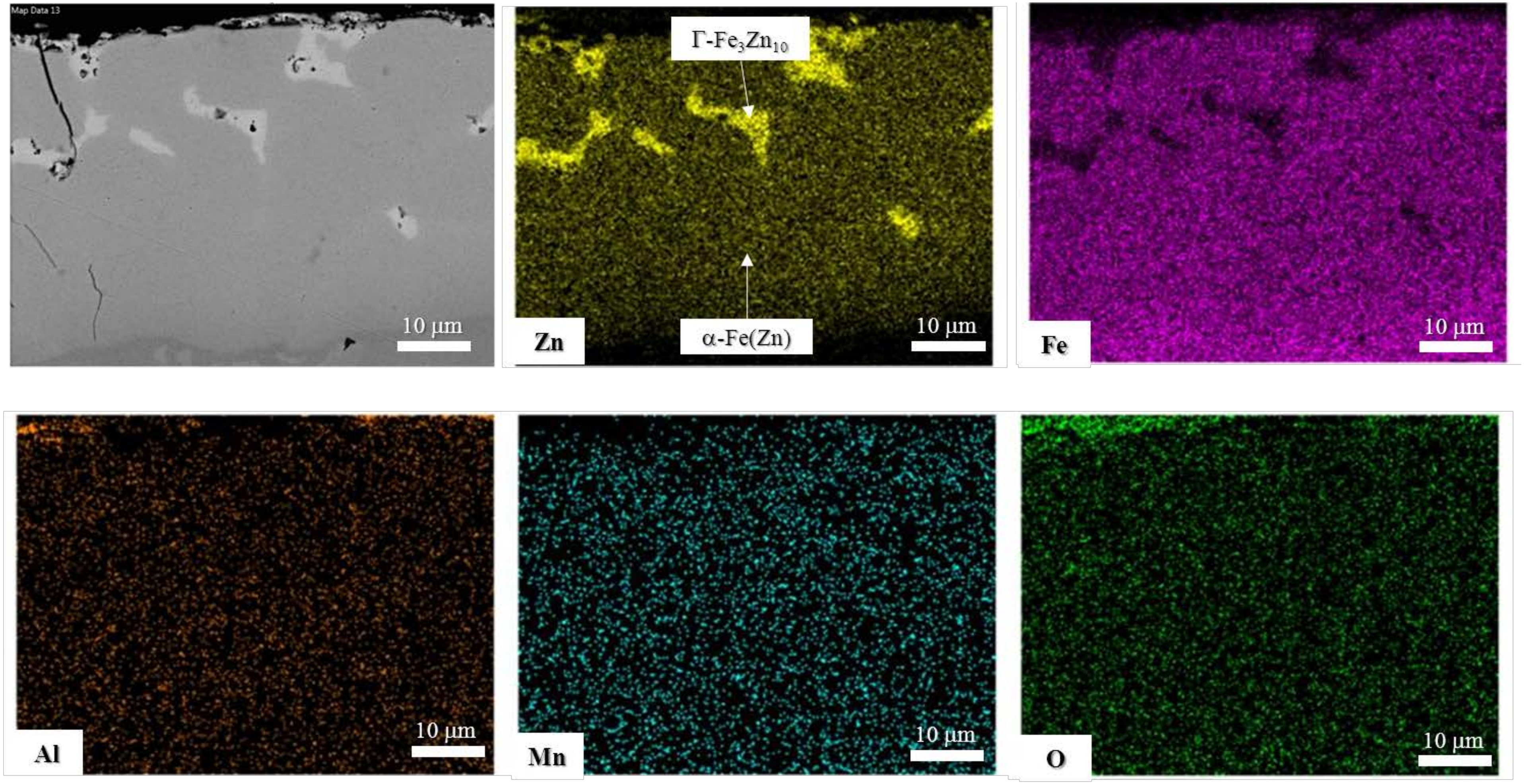
GI120 – 900ºC × 60s EDS maps

GI120 @ 900ºC PAT(60s)



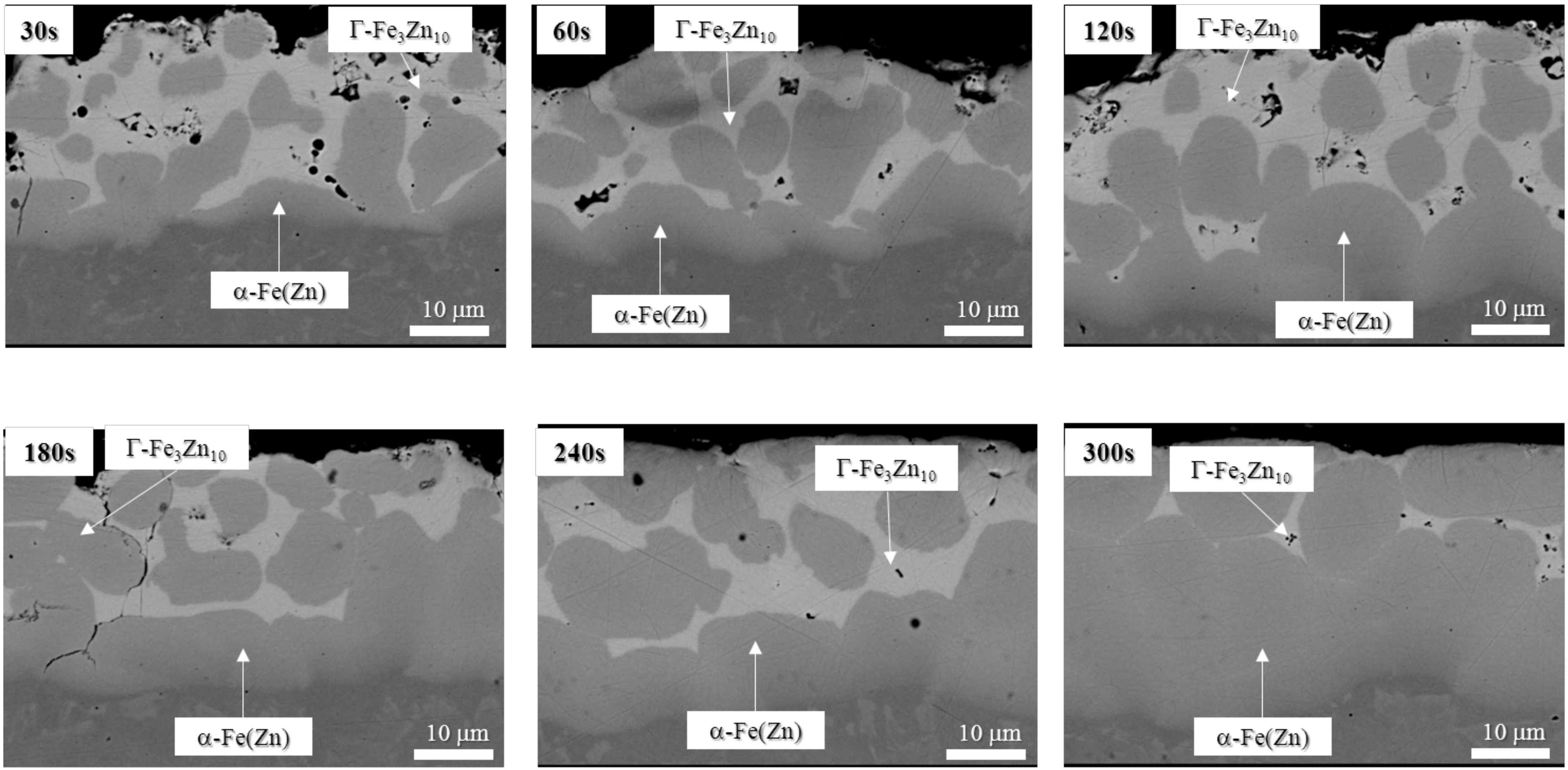
GI120 – 900ºC x 600s EDS maps

GI120 @ 900ºC PAT (600s)



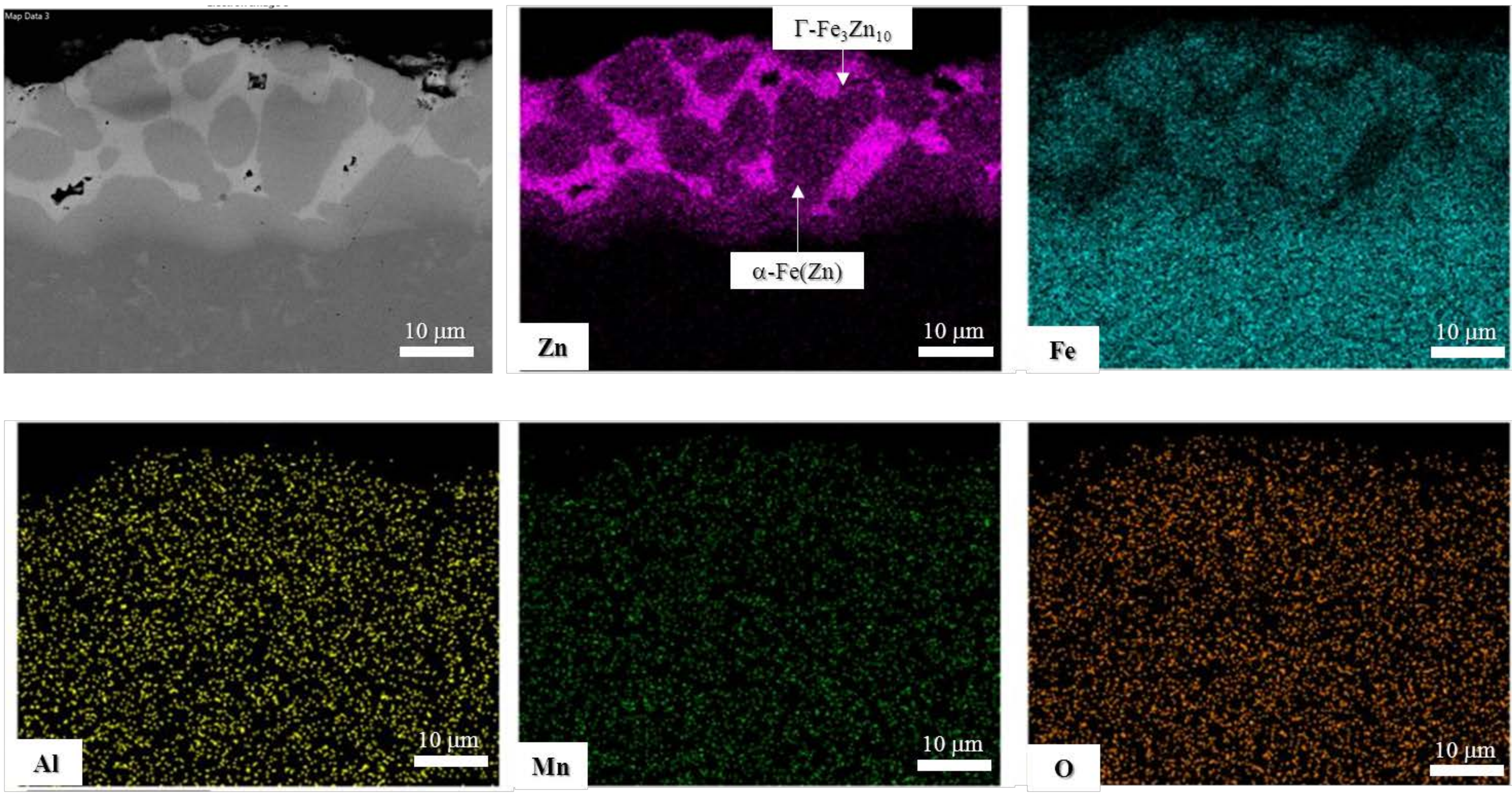
Microstructure vs. time – GI120 + 900ºC + 700ºC

GI120 @900ºC PAT + 700ºC (60s)



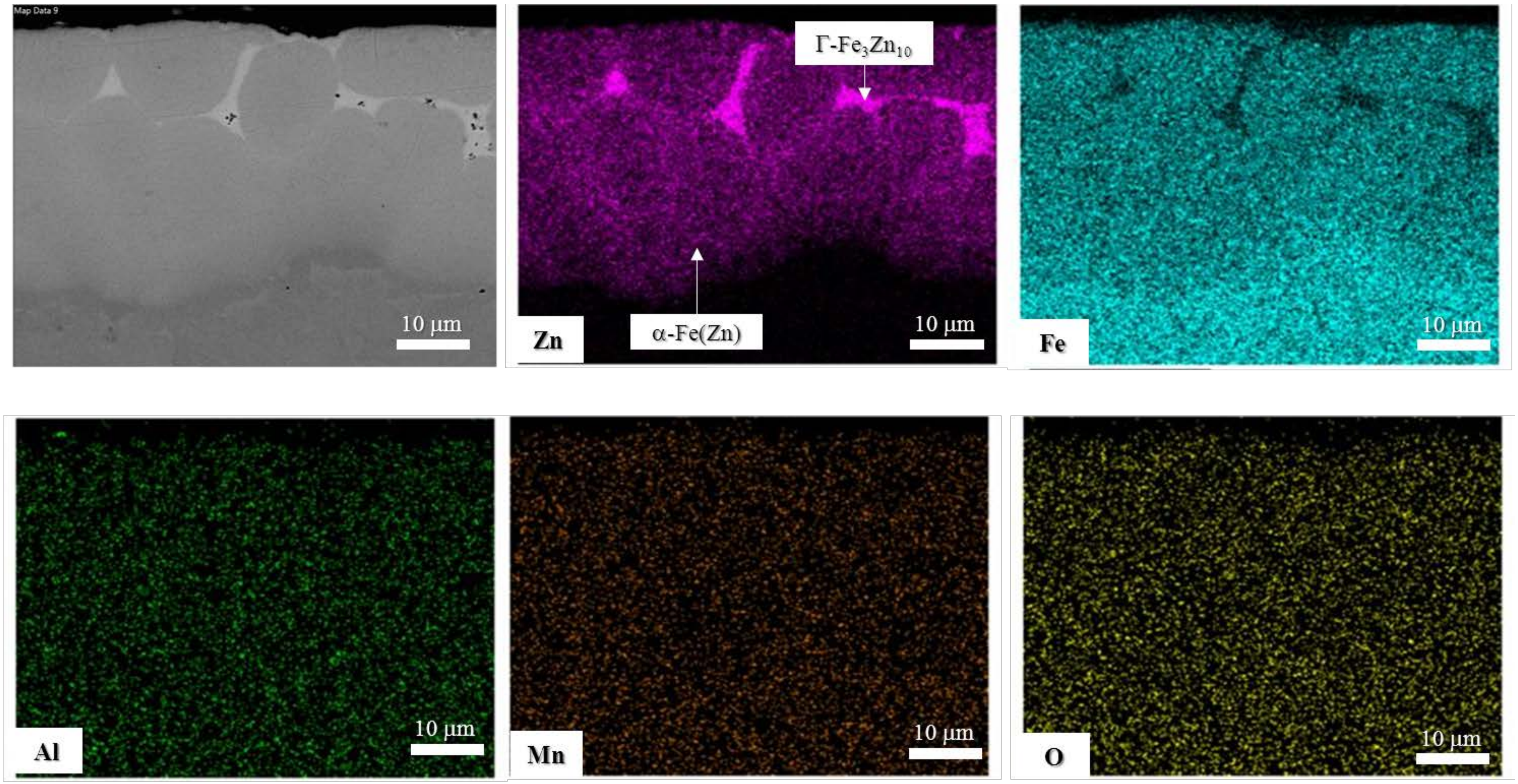
GI120 – 900ºC × 60s + 700ºC EDS maps

GI120 @ 900ºC PAT (60s) + 700ºC(60s)



GI120 – 900ºC × 300s + 700ºC EDS maps

GI120 @ 900ºC PAT (300s) + 700ºC (60s)



Task 1 – Summary for GI120 Coatings

➢ **GI120 × 900°C coatings:**

- **the coatings contained significant Zn(Fe)(l) for all annealing times**
- **Zn content of the αFe(Zn) coatings decreased with increasing time at 900°C**
- **additional annealing at 700°C + 60s after annealing at 900°C decreased the coating Γ-Fe_3Zn_{10} content and Zn content of the αFe(Zn) coating layer**
- **all coatings contained greater than 30wt% Zn in αFe(Zn)**

Experimental Flow Chart – Task 3

GI120, GI70, GA60, GA80 coated steels
(0.22C-1.17Mn-0.25Si-0.0025B)

↓

Annealing
900^{o}C (30, 60, 120, 180, 240, 300, 360, 420 s)

↓

Potentiodynamic polarization test
(3 wt% NaCl)

Cyclic corrosion test
(SAE J2334)

↓

SEM

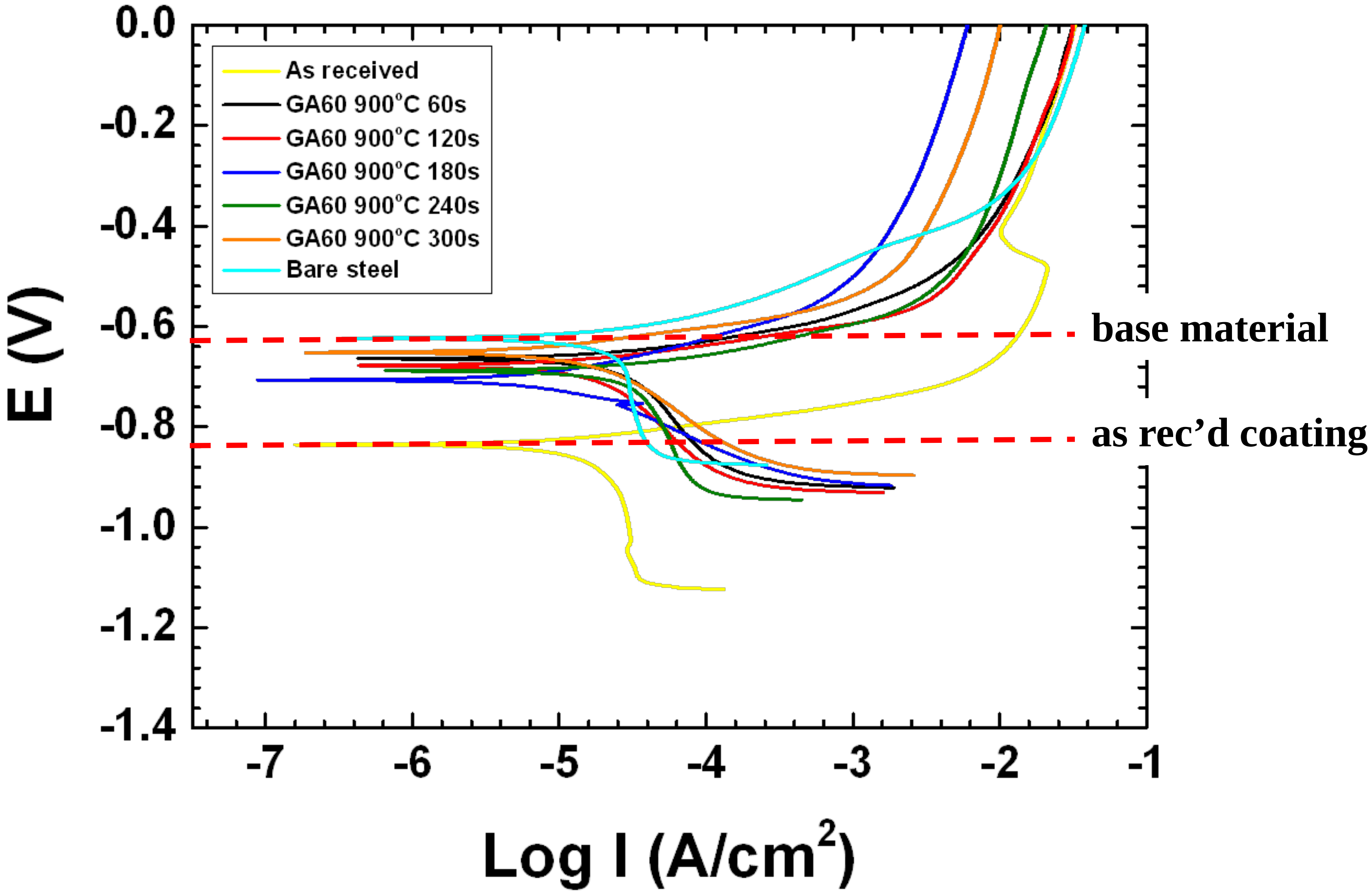
XRD

↓

Corrosion testing of αFe(Zn) DHPF panels

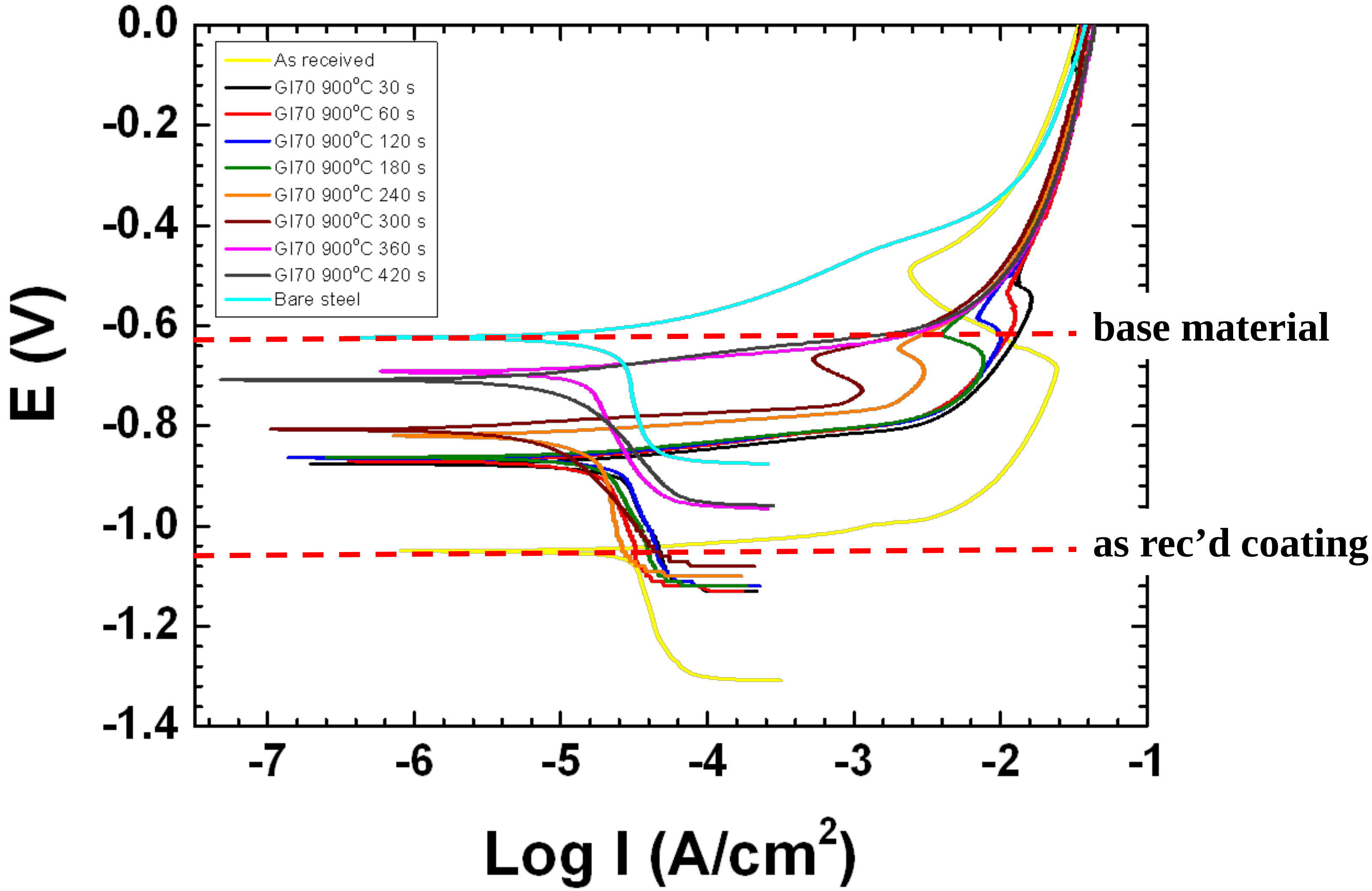
Potentiodynamic Polarization – GA60

GA60 @ 900°C PAT



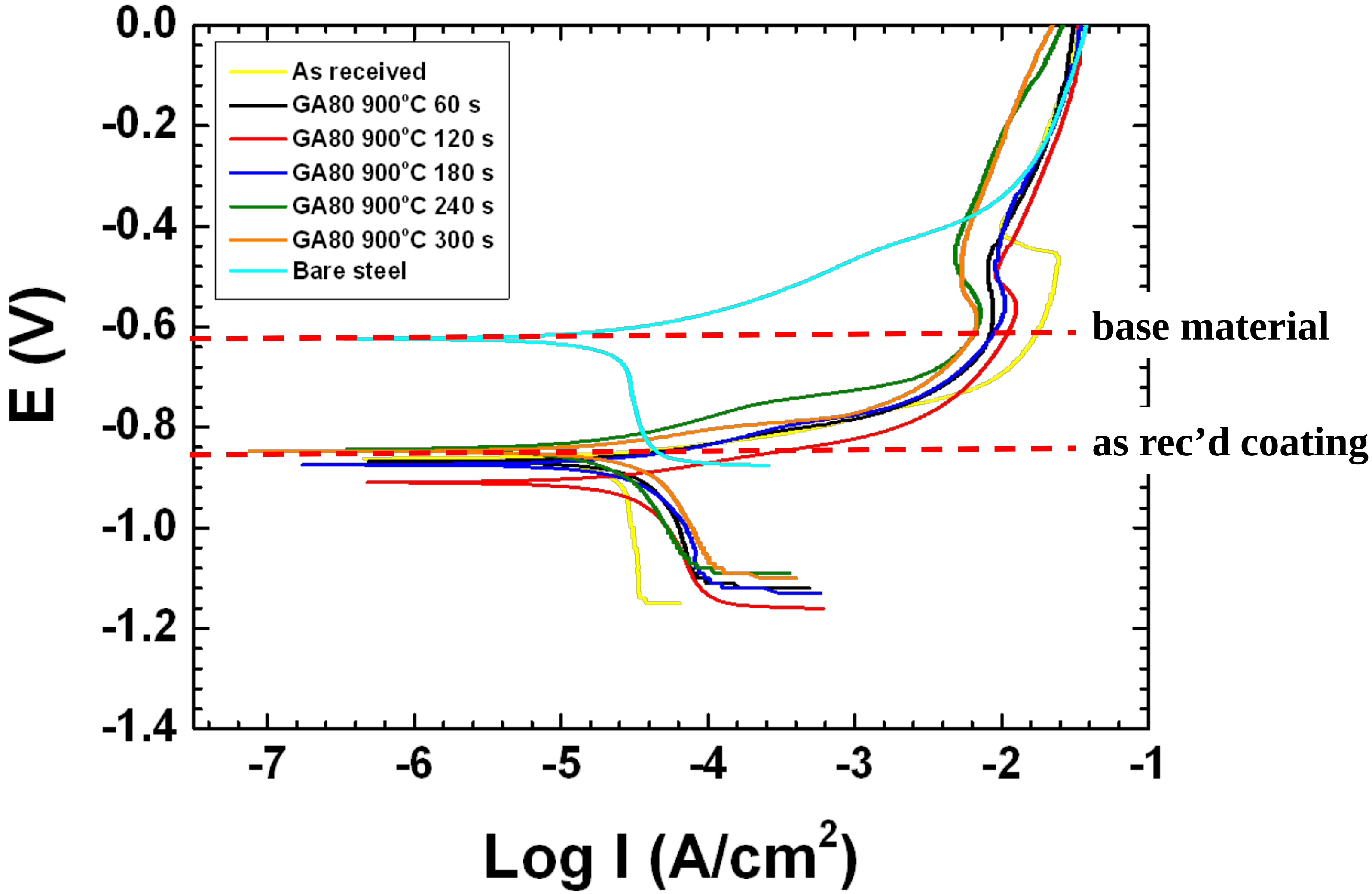
Potentiodynamic Polarization – GI70

GI70 @ 900°C PAT



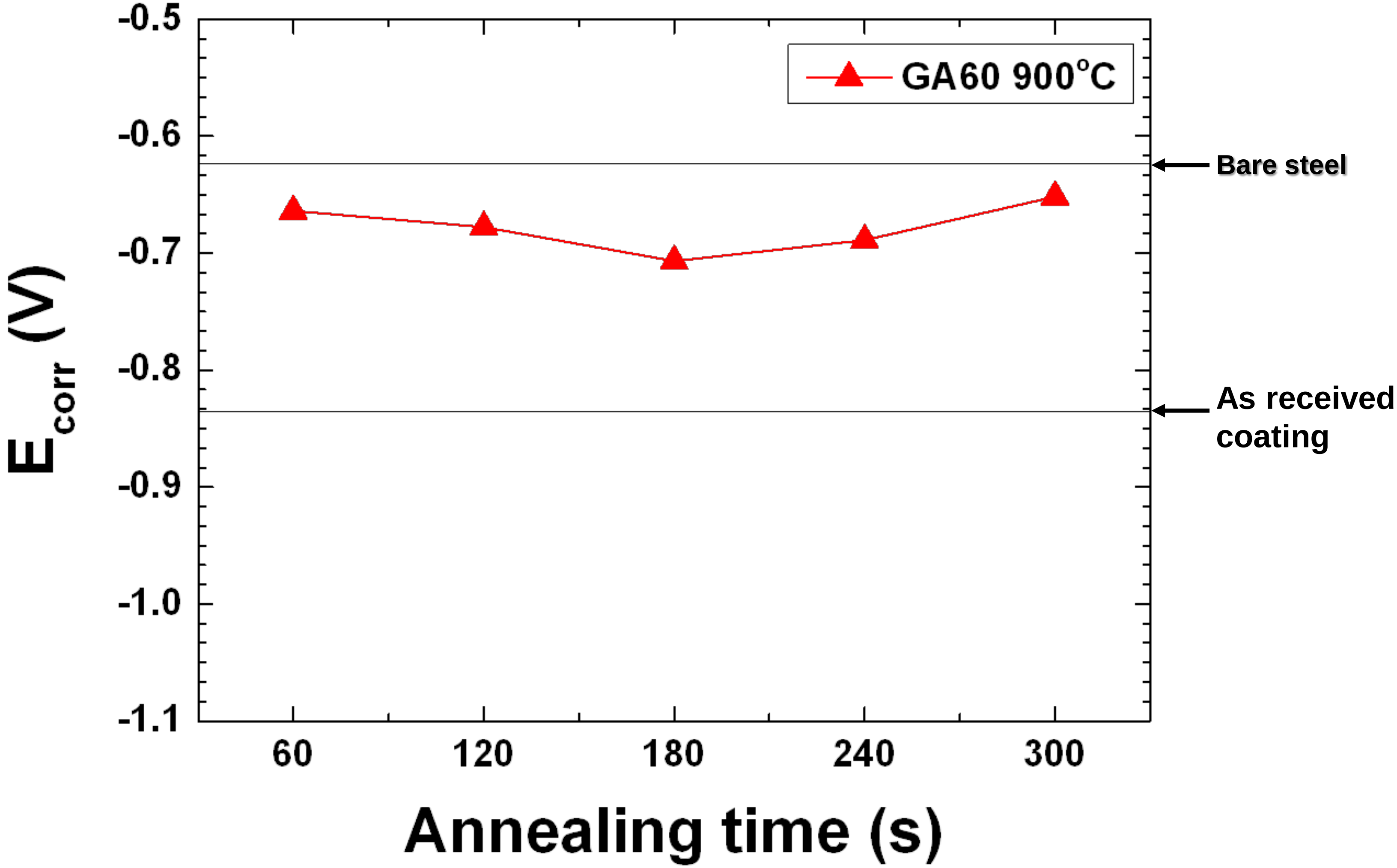
Potentiodynamic Polarization – GA80

GA80 @ 900°C PAT



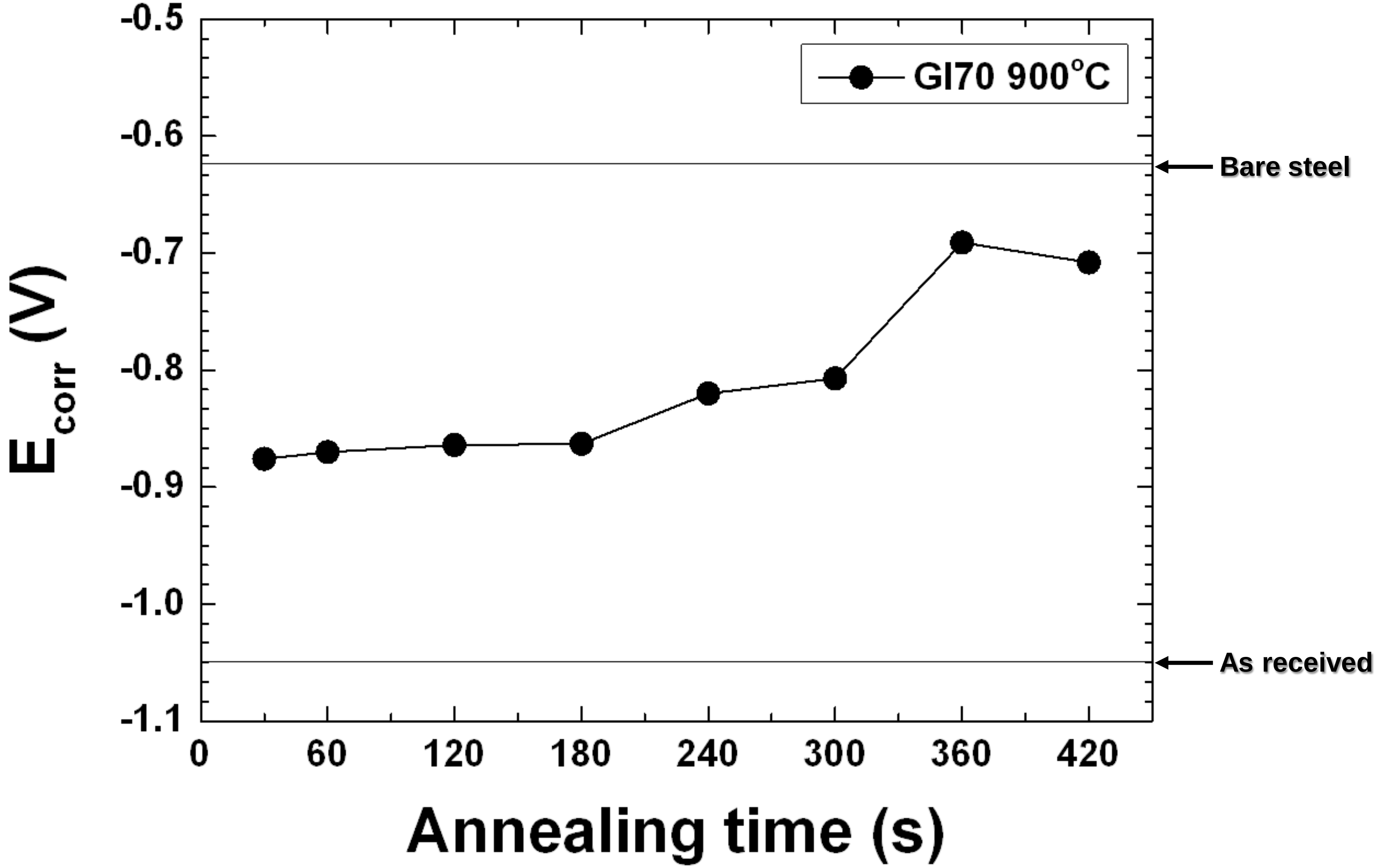
E_{corr} vs. Annealing Time – GA60

GA60 @ 900^{o}C PAT



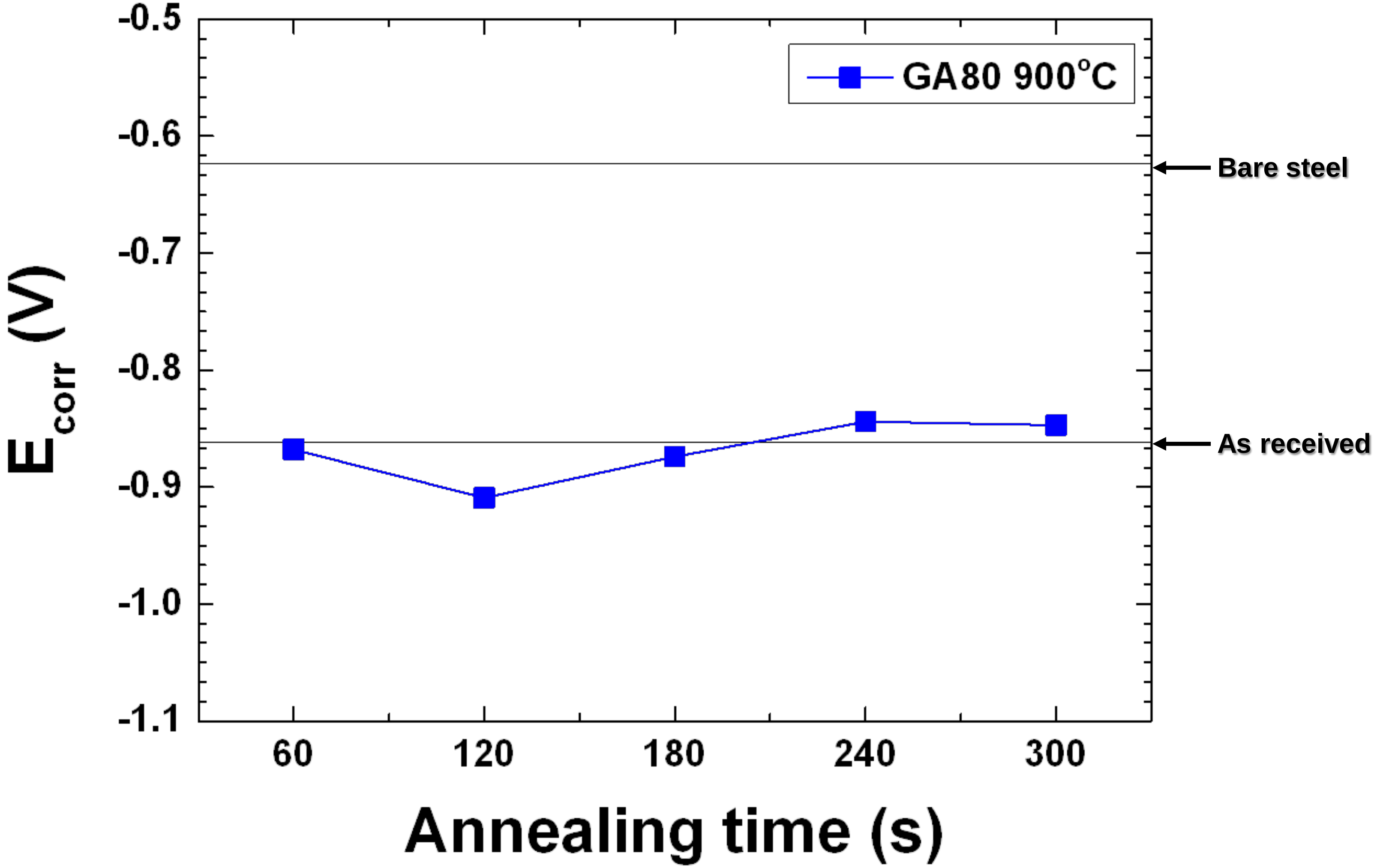
E_{corr} vs. Annealing Time – GI70

GI70 @ 900°C PAT



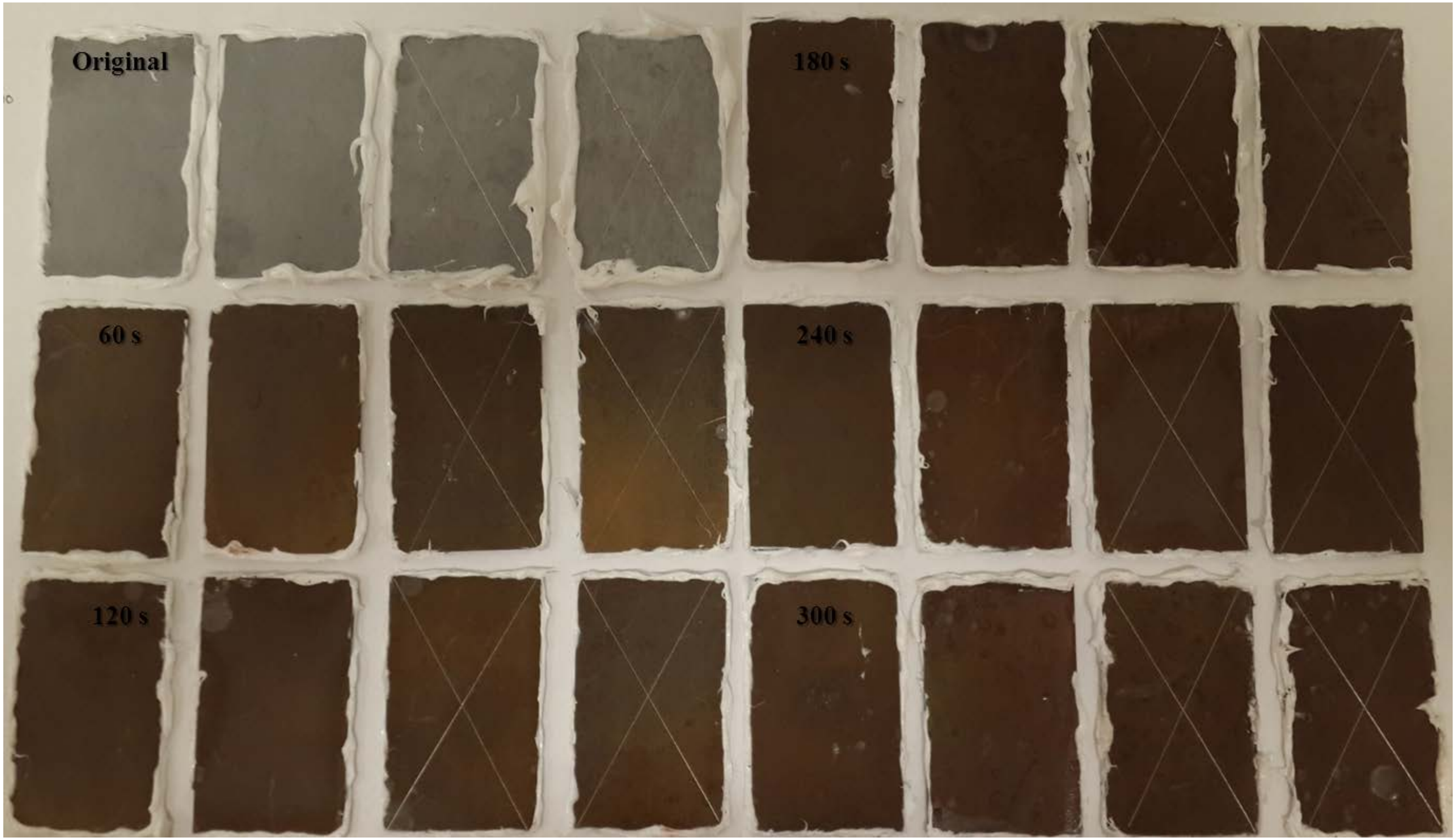
E_{corr} vs. time – GA80

GA80 @ 900°C PAT



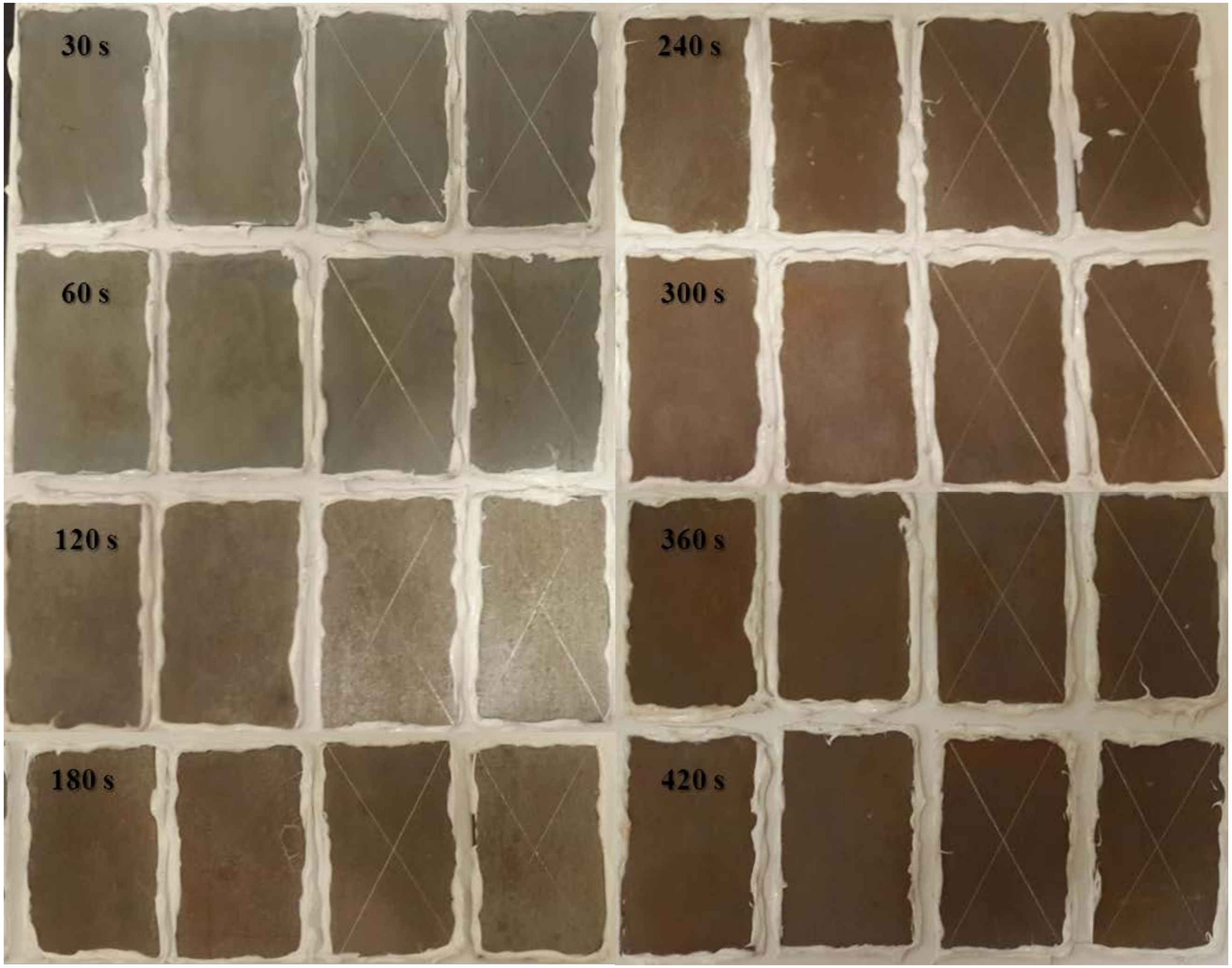
As-Annealed Surfaces – GA60

GA60 @ 900^{o}C PAT – week 0



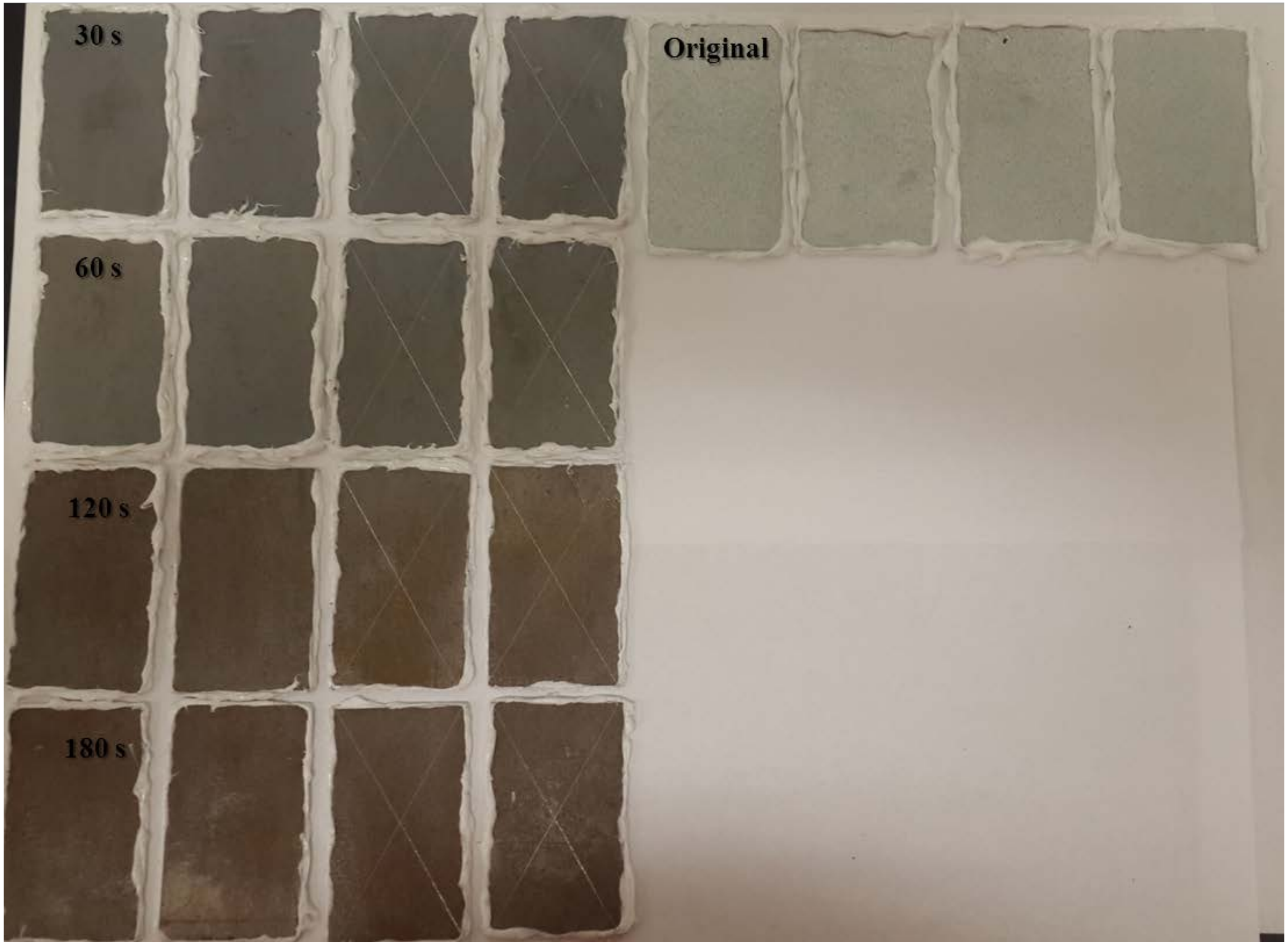
As-Annealed Sample Surfaces – GI70

GI70 @ 900^{o}C PAT – week 0



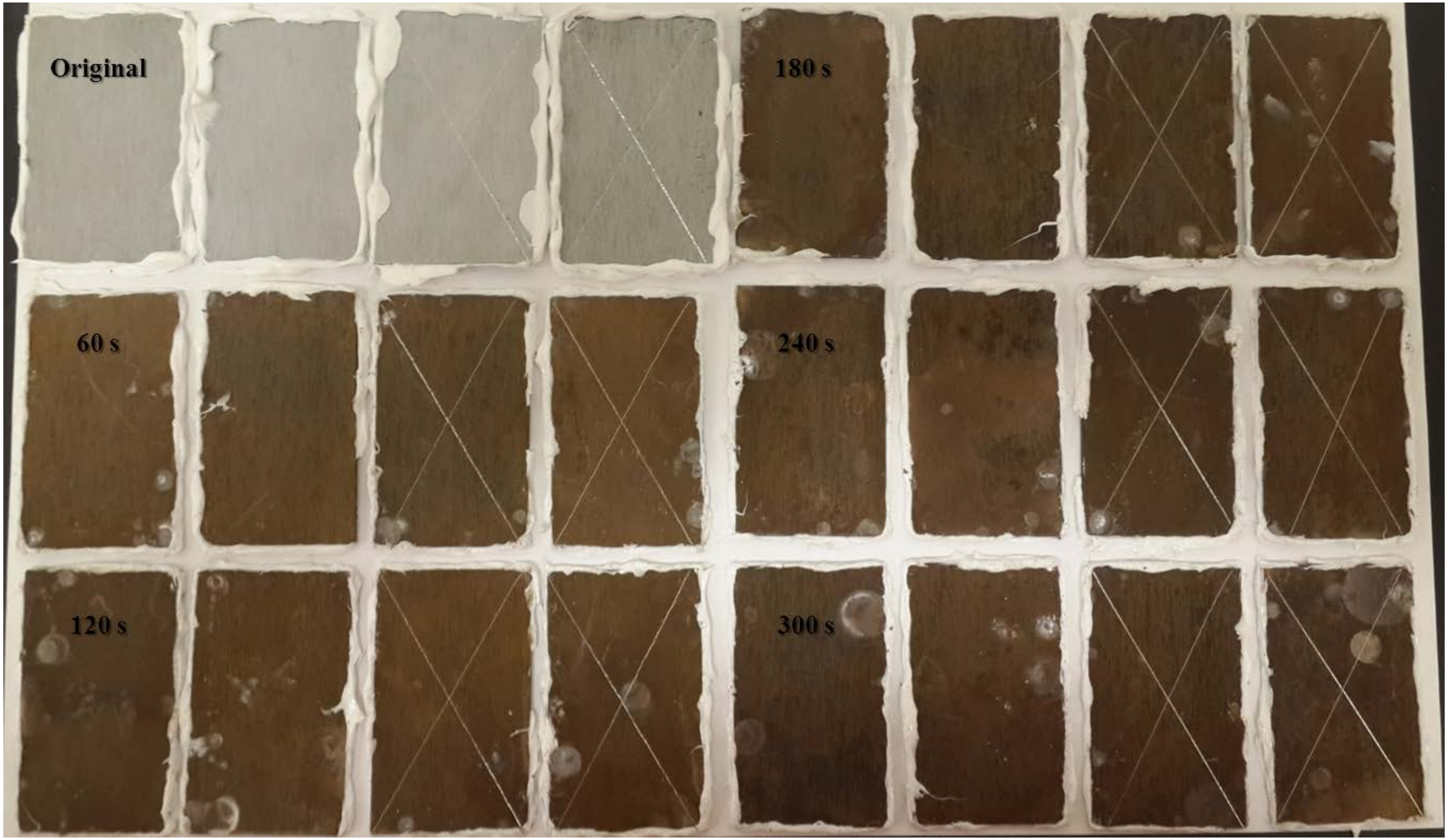
As-Annealed Sample Surfaces – GI70

GI70 @ 900ºC PAT + 60s hold @700ºC – week 0



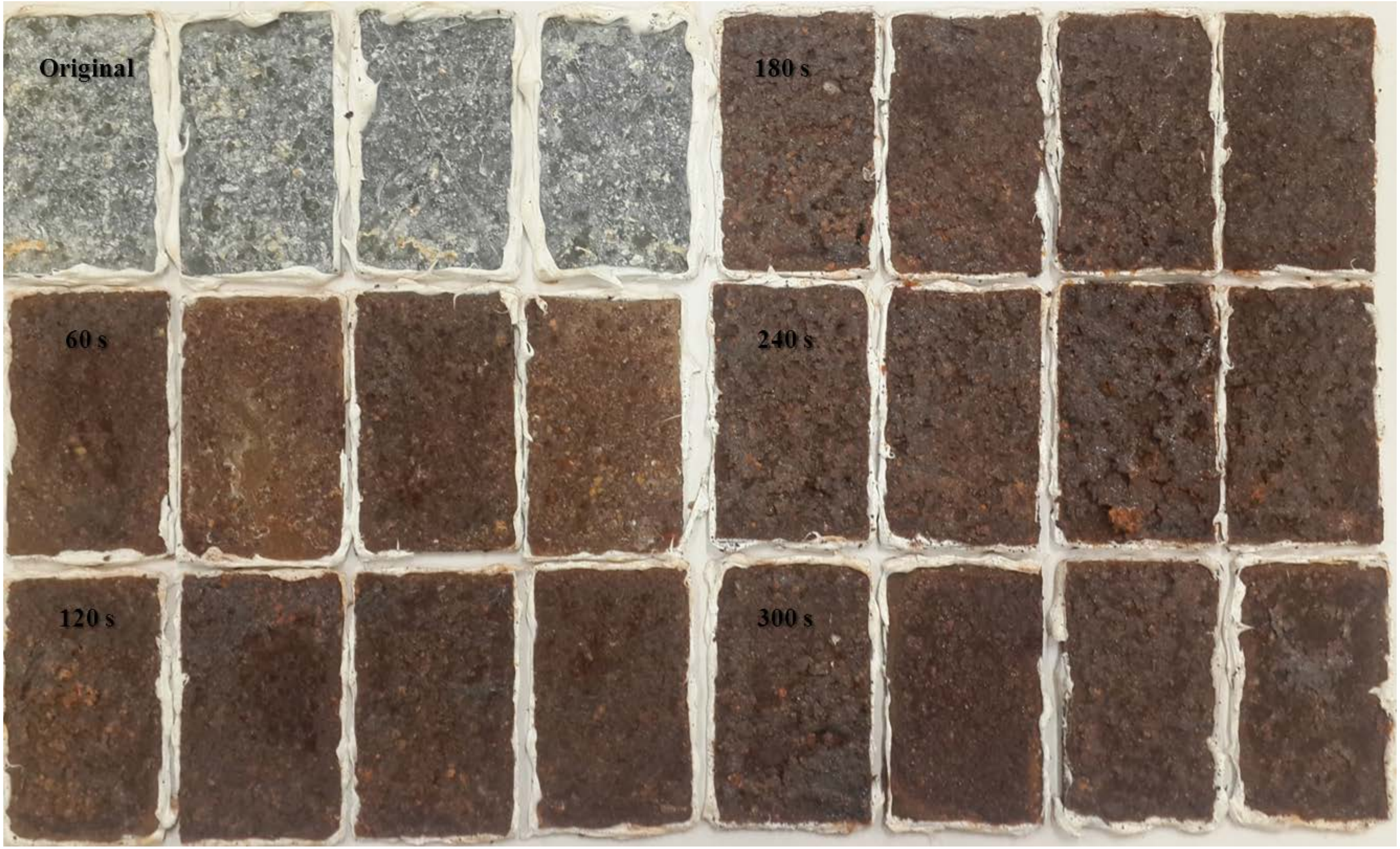
Sample Surfaces – GA80

GA80 @ 900^{o}C PAT – week 0



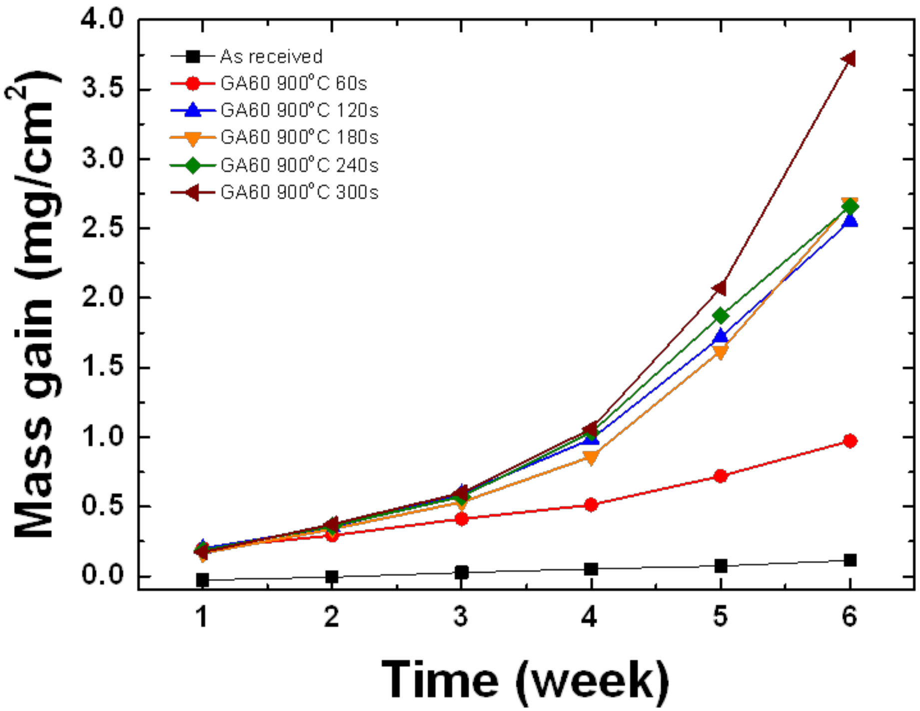
SAE J2334 Exposure Surfaces – GA60

GA60 annealed @ 900ºC – 6 week SAE J2334 Exposure

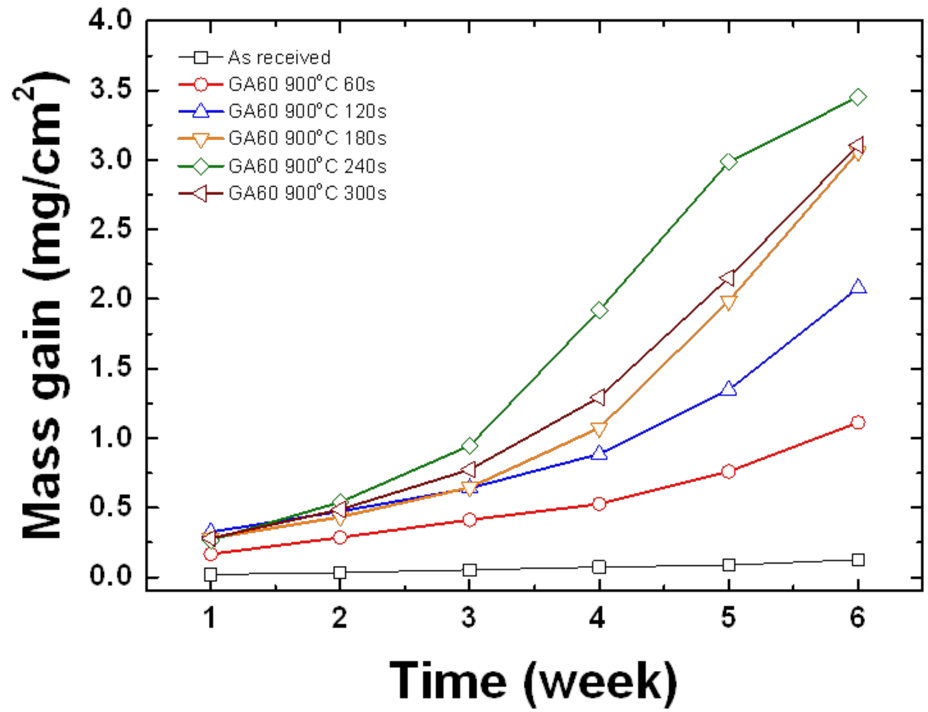


Weight Gain vs. Exposure time – GA60 (900°C)

GA60 Non-Scribed

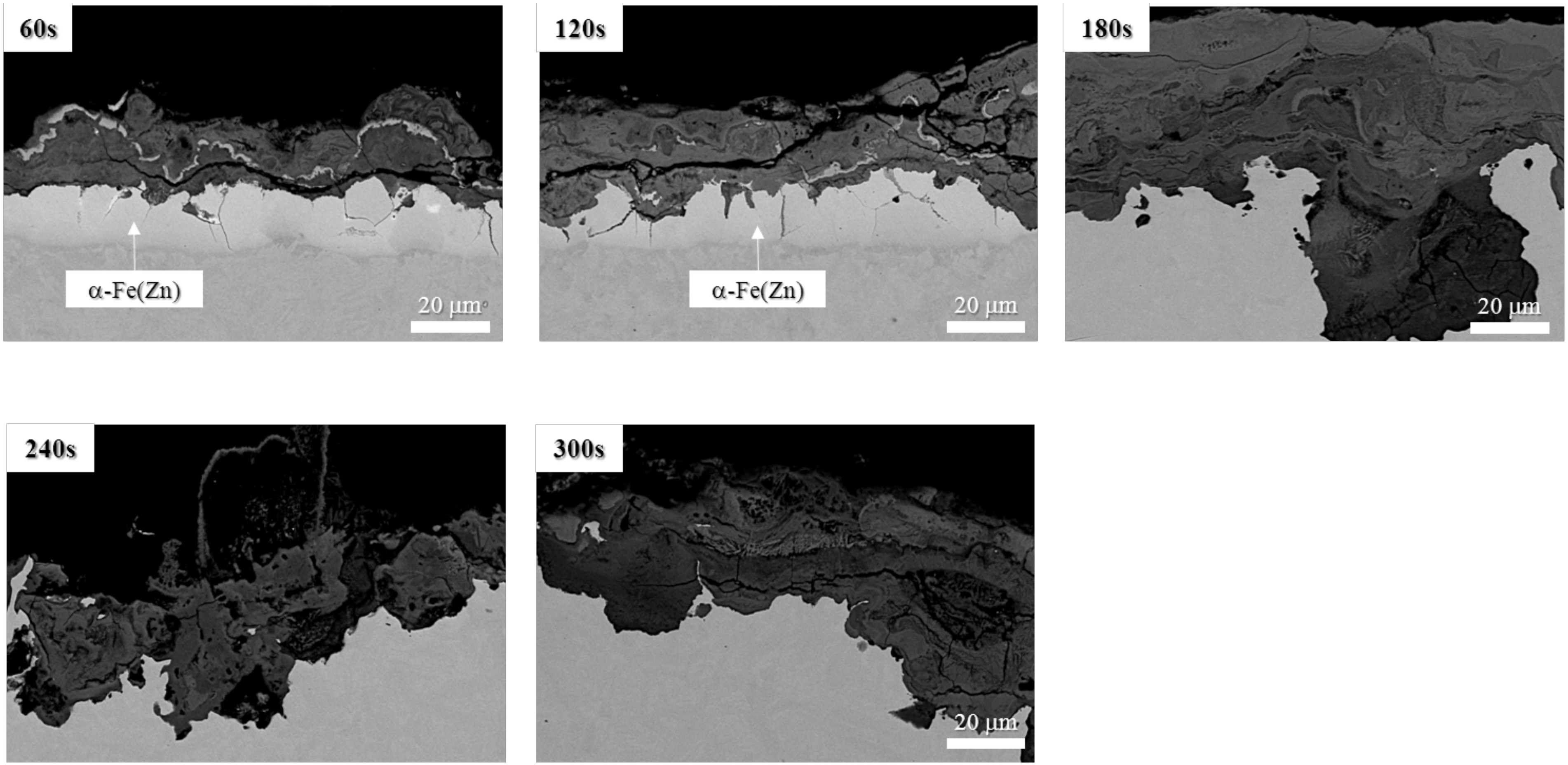


GA60 Scribed



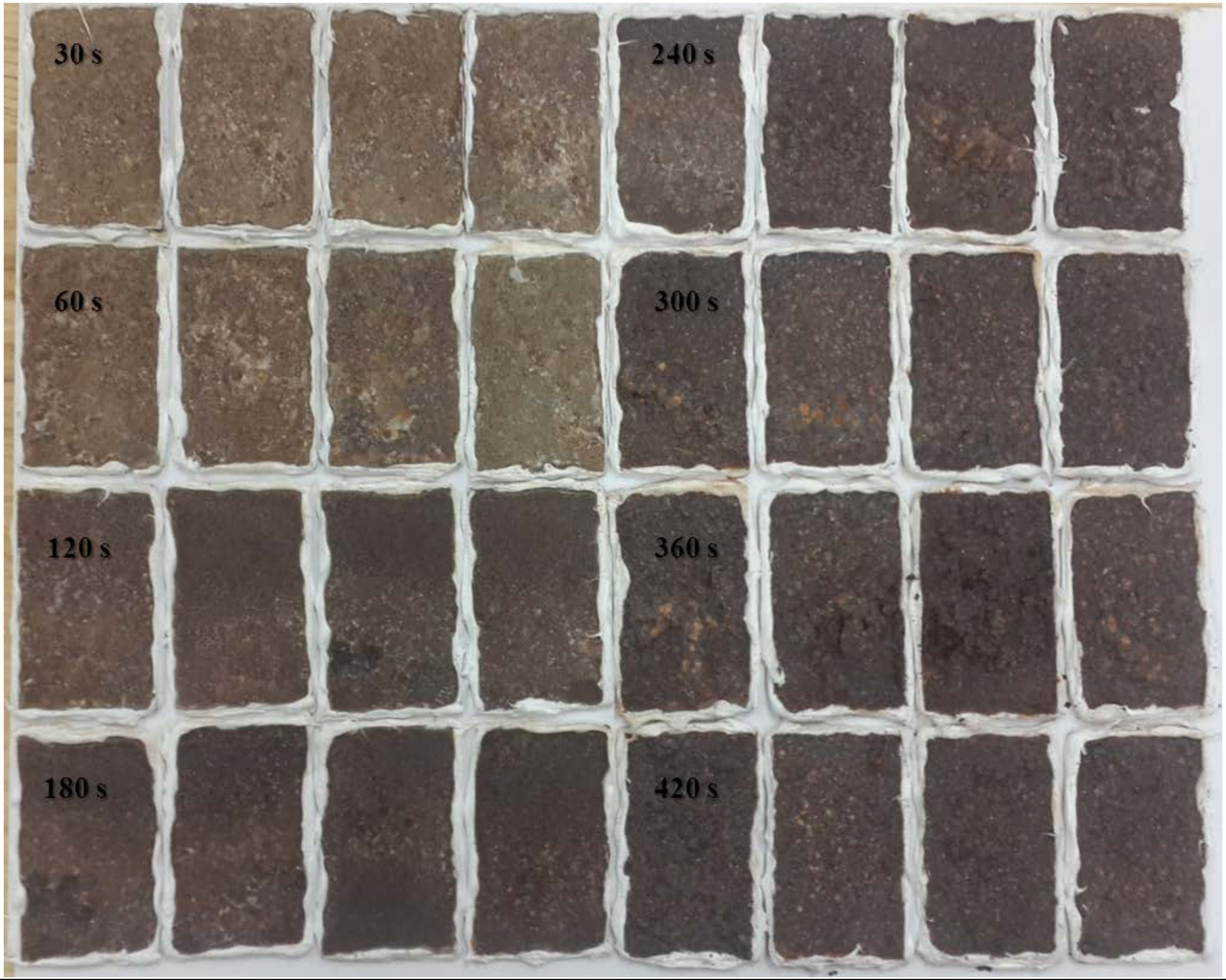
Coating Microstructure vs. Annealing Time – GA60

GA60 @ 900^{o}C PAT – 6week



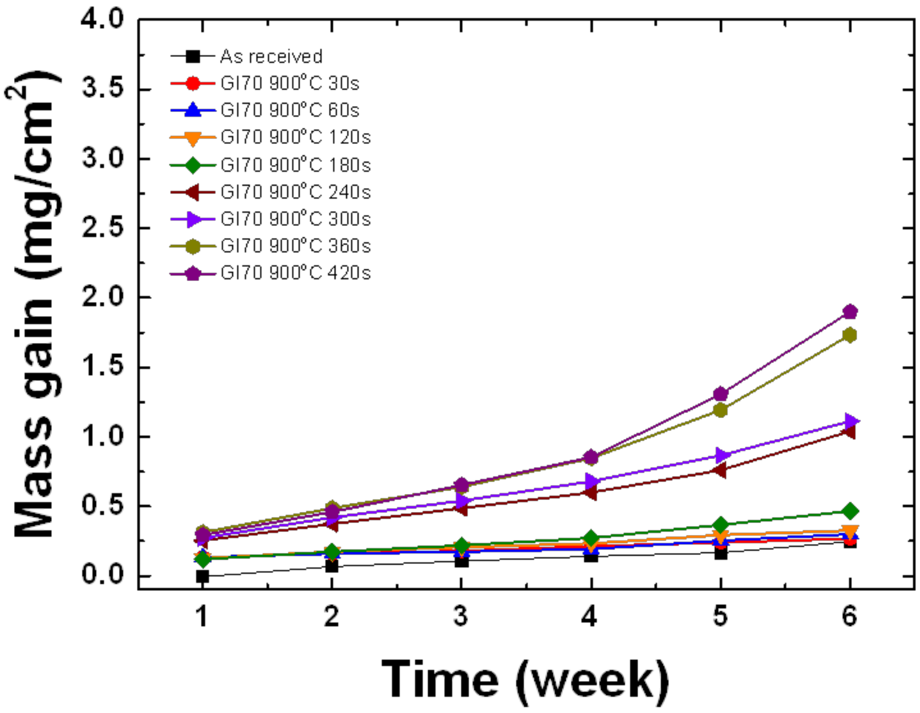
SAE J2334 Exposure Surfaces – GI70

GI70 @ 900^{o}C PAT – 6 week SAE J2334 Exposure

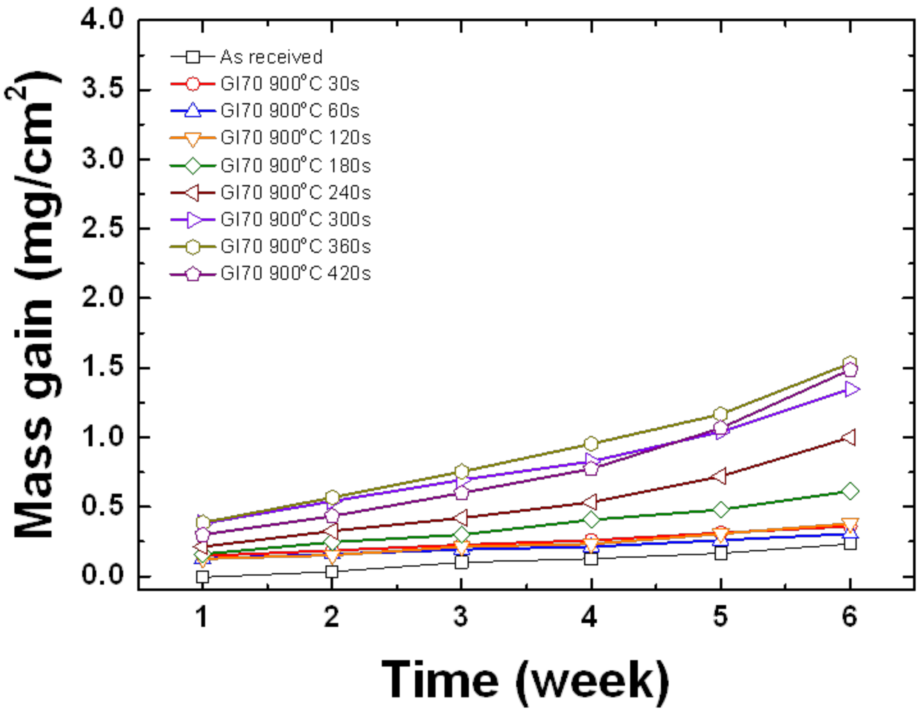


Weight Gain vs. Exposure Time – GI70 (900°C)

GI70 Non-Scribed

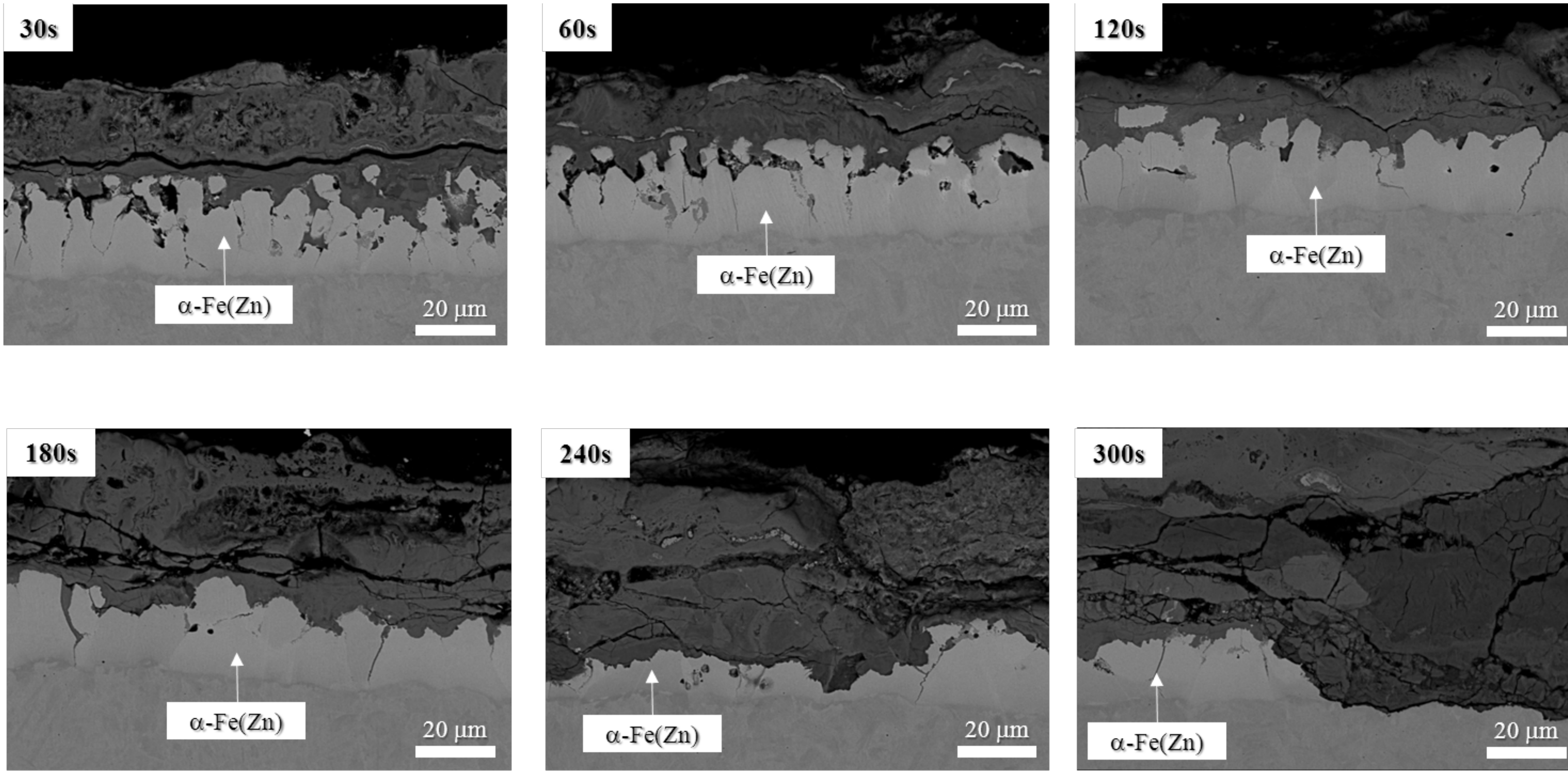


GI70 Scribed



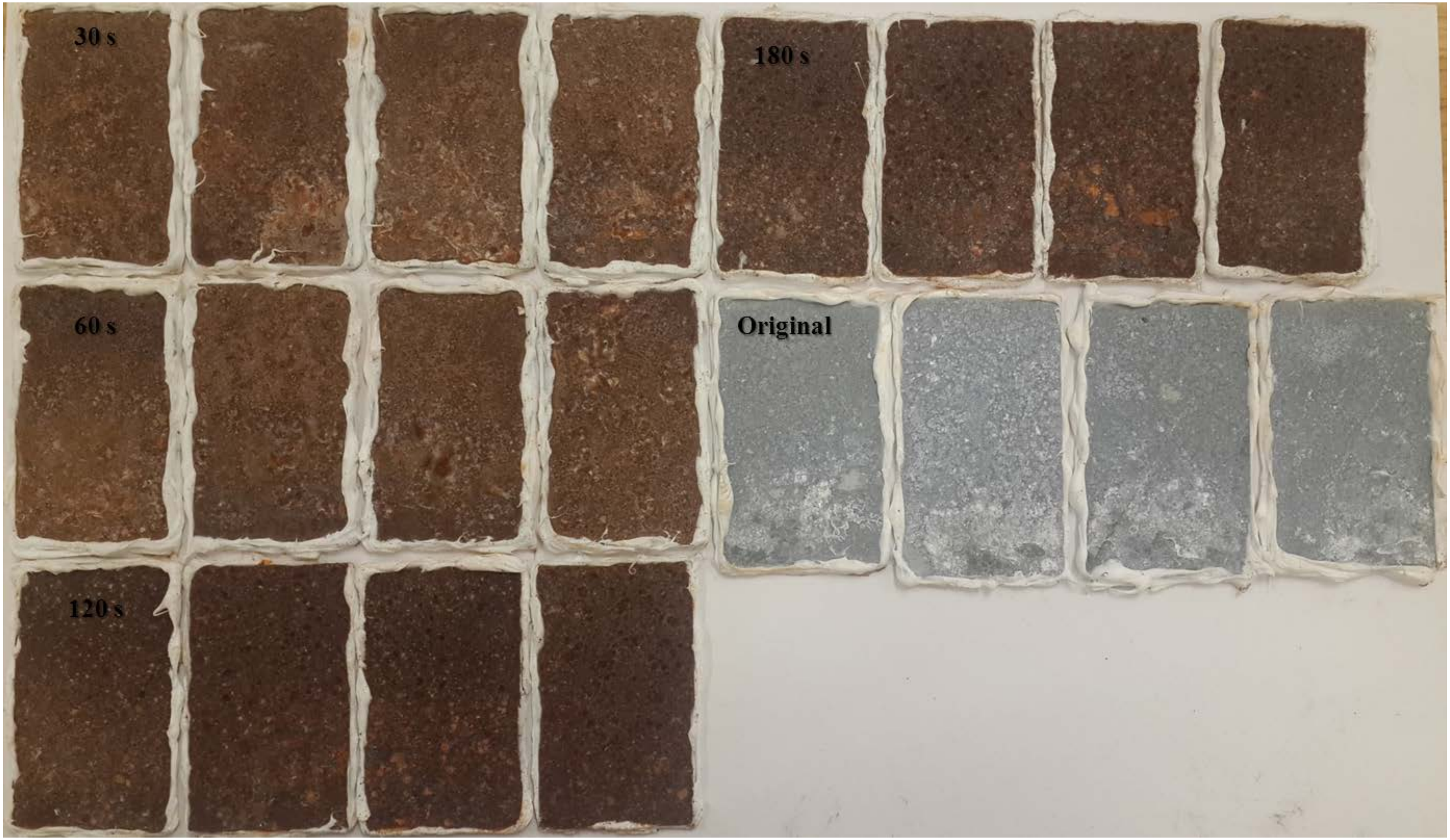
Coating Microstructure vs. Annealing Time – GI70

GI70 @ 900°C PAT – 6 week SAE J2334 Exposure



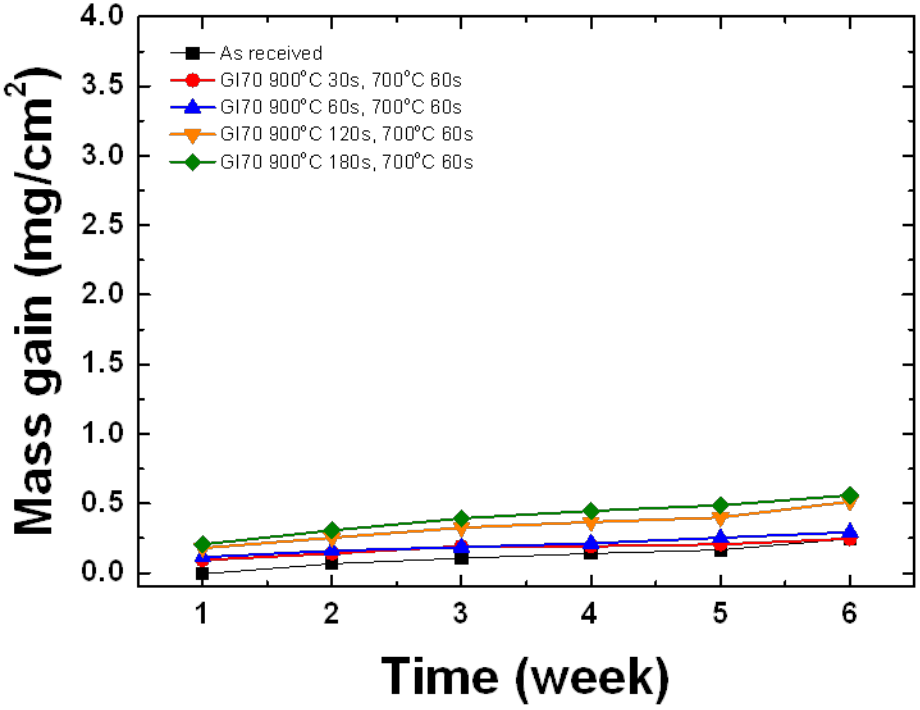
SAE J2334 Exposure Surfaces – GI70

GI70 @ 900°C PAT + 60s hold @ 700°C – 6 week SAE J2334 Exposure

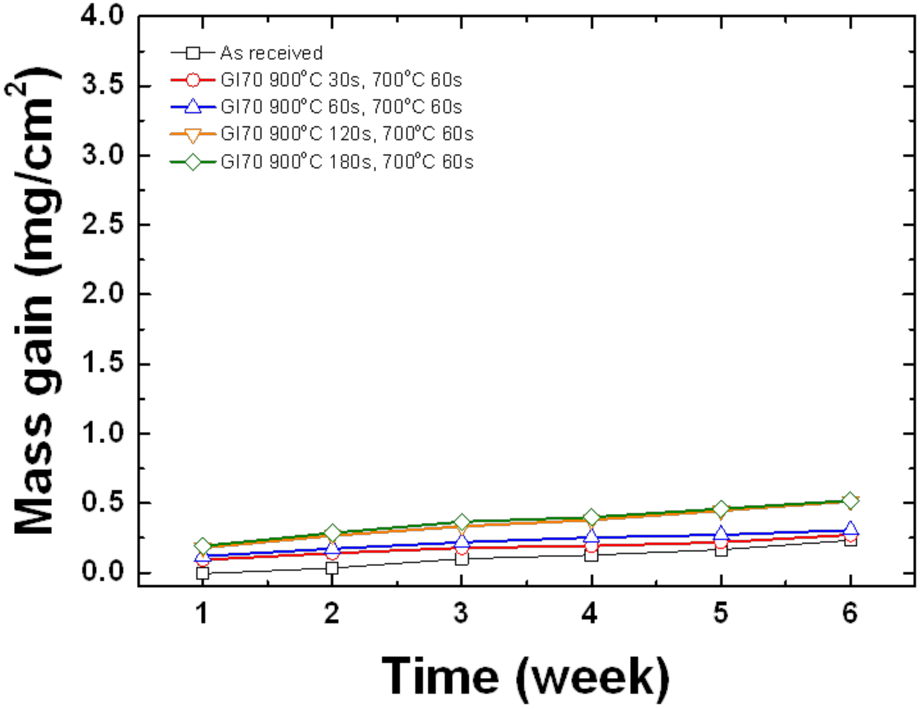


Weight Gain vs. Exposure Time – GI70 at 900ºC + 700ºC

GI70 Non-Scribed

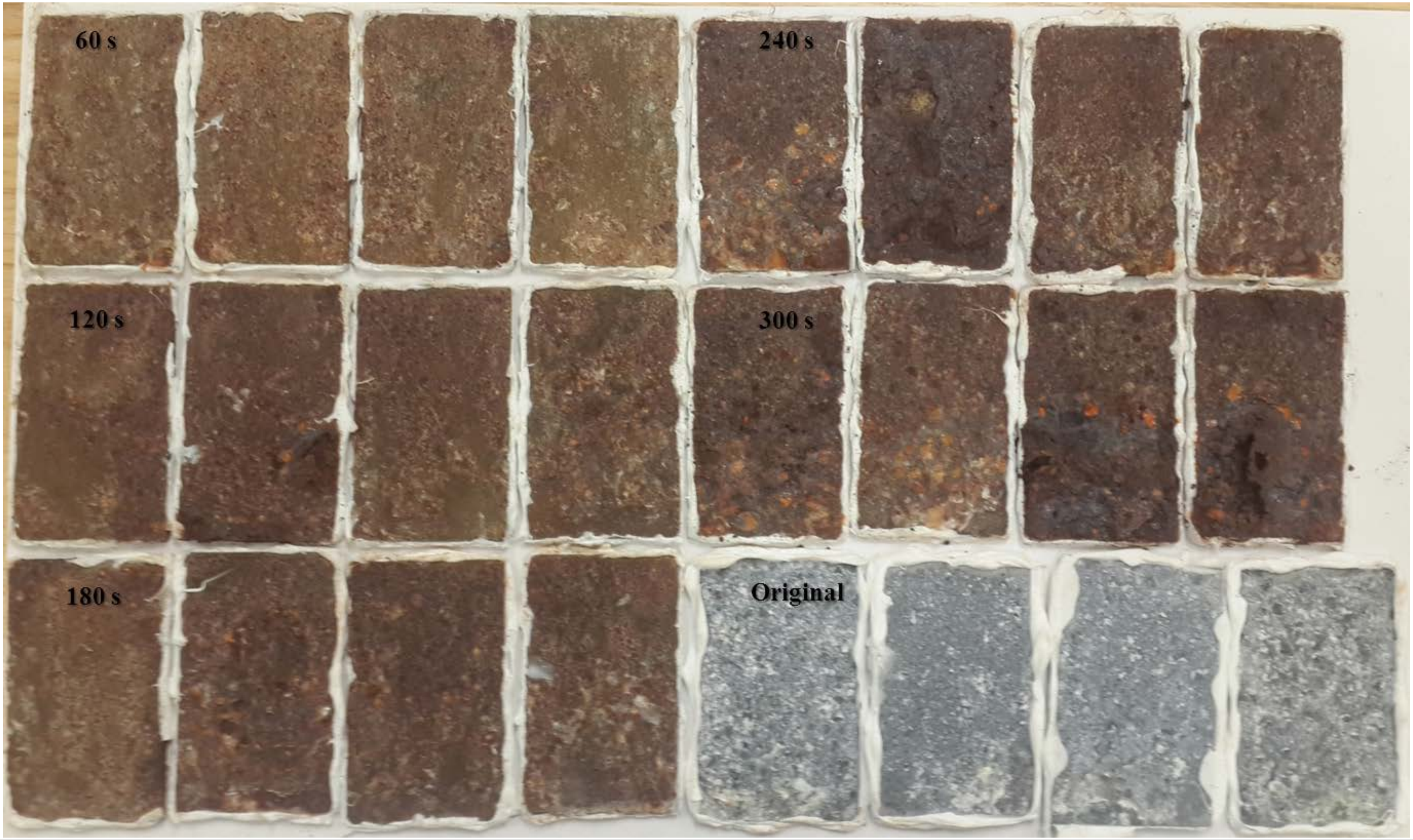


GI70 Scribed



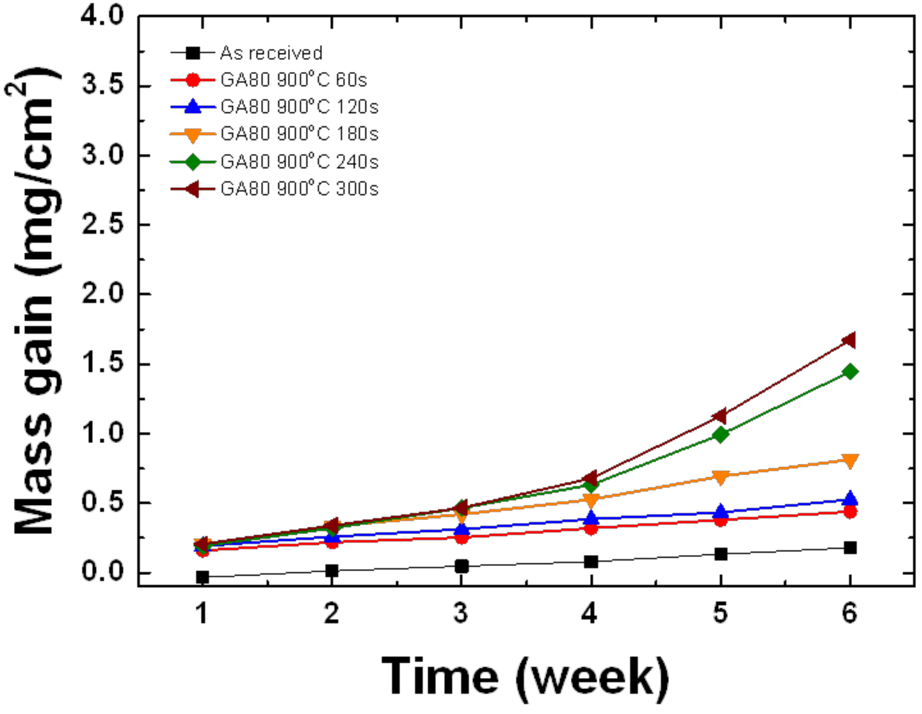
SAE J2334 Exposure Surfaces – GA80

GA80 @ 900^{o}C PAT – 6 week SAE J2334 Exposure

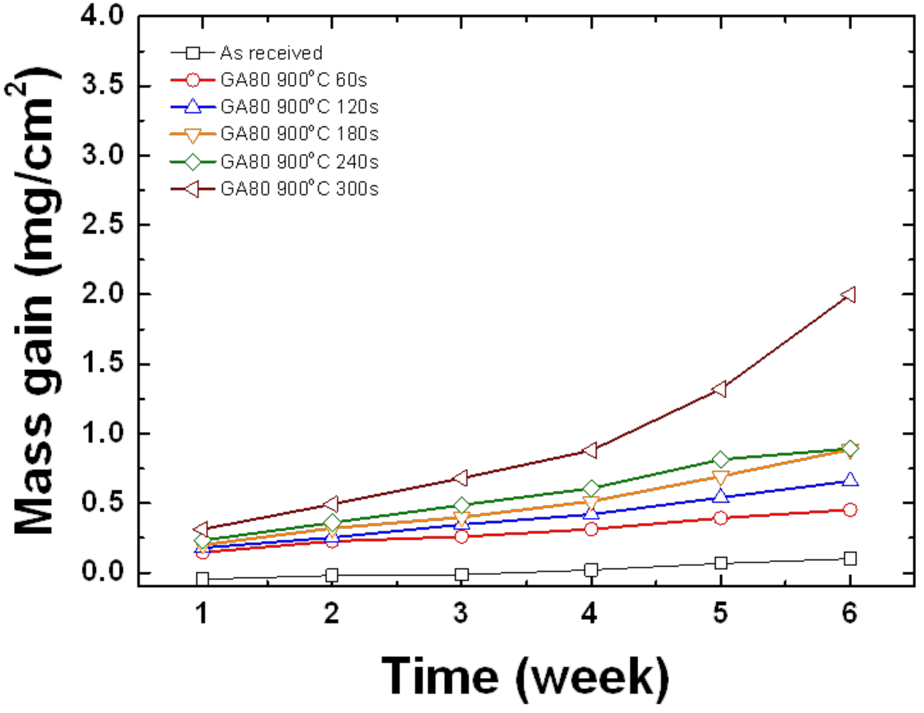


Weight gain vs. time – GA80 at 900ºC

GA80 Non-Scribed

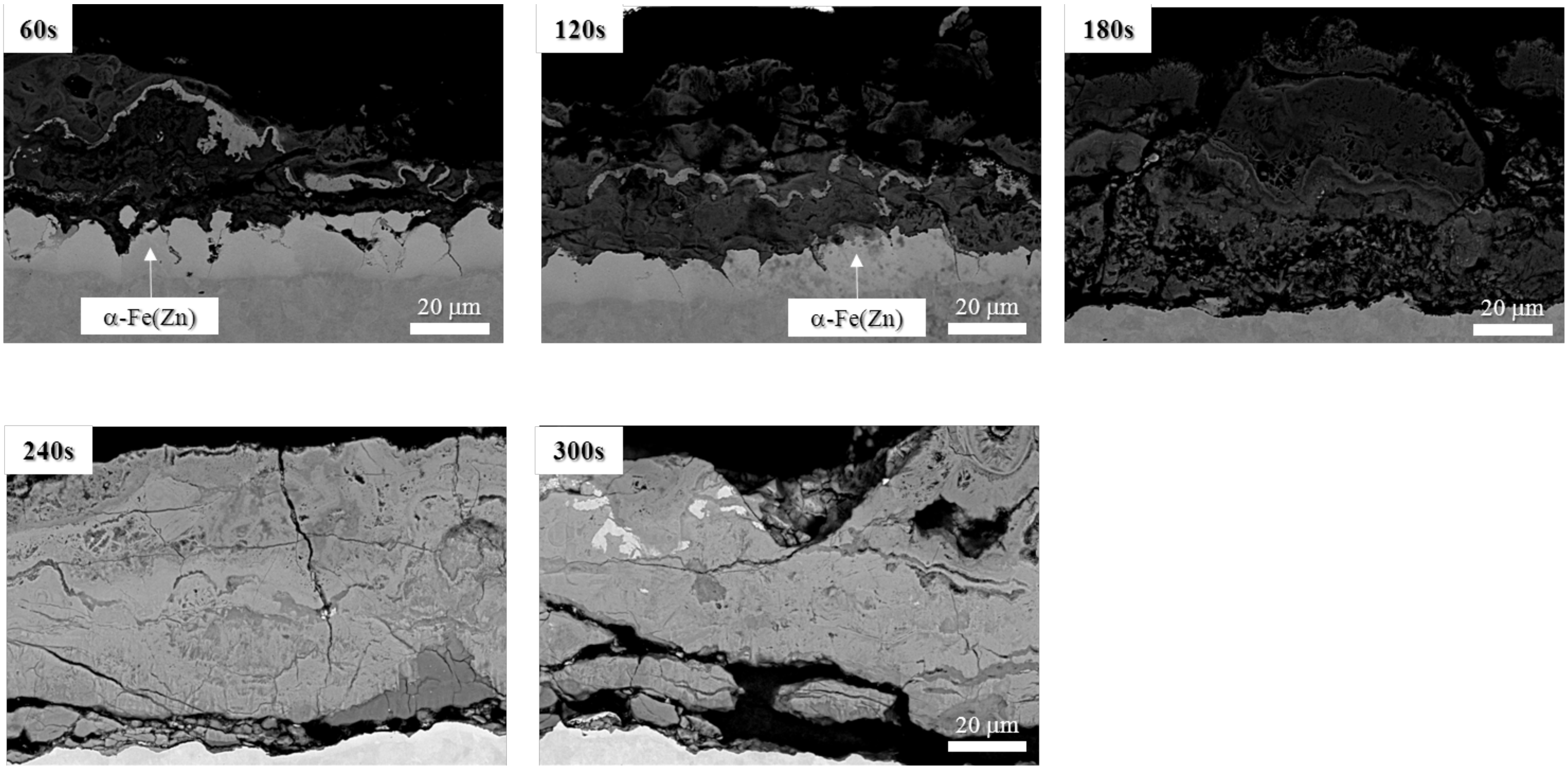


GA80 Scribed

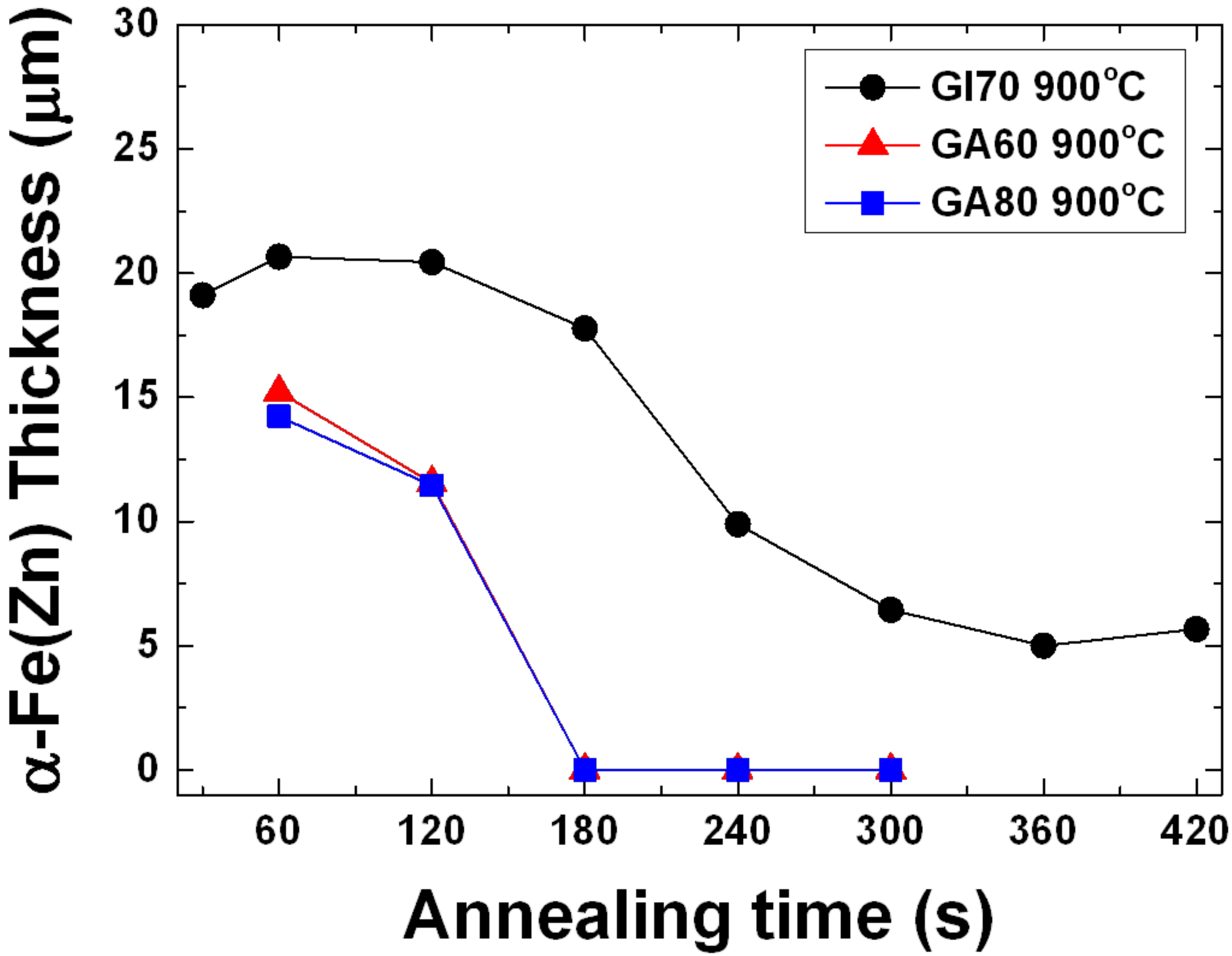


Coating Microstructure vs. time – GA80

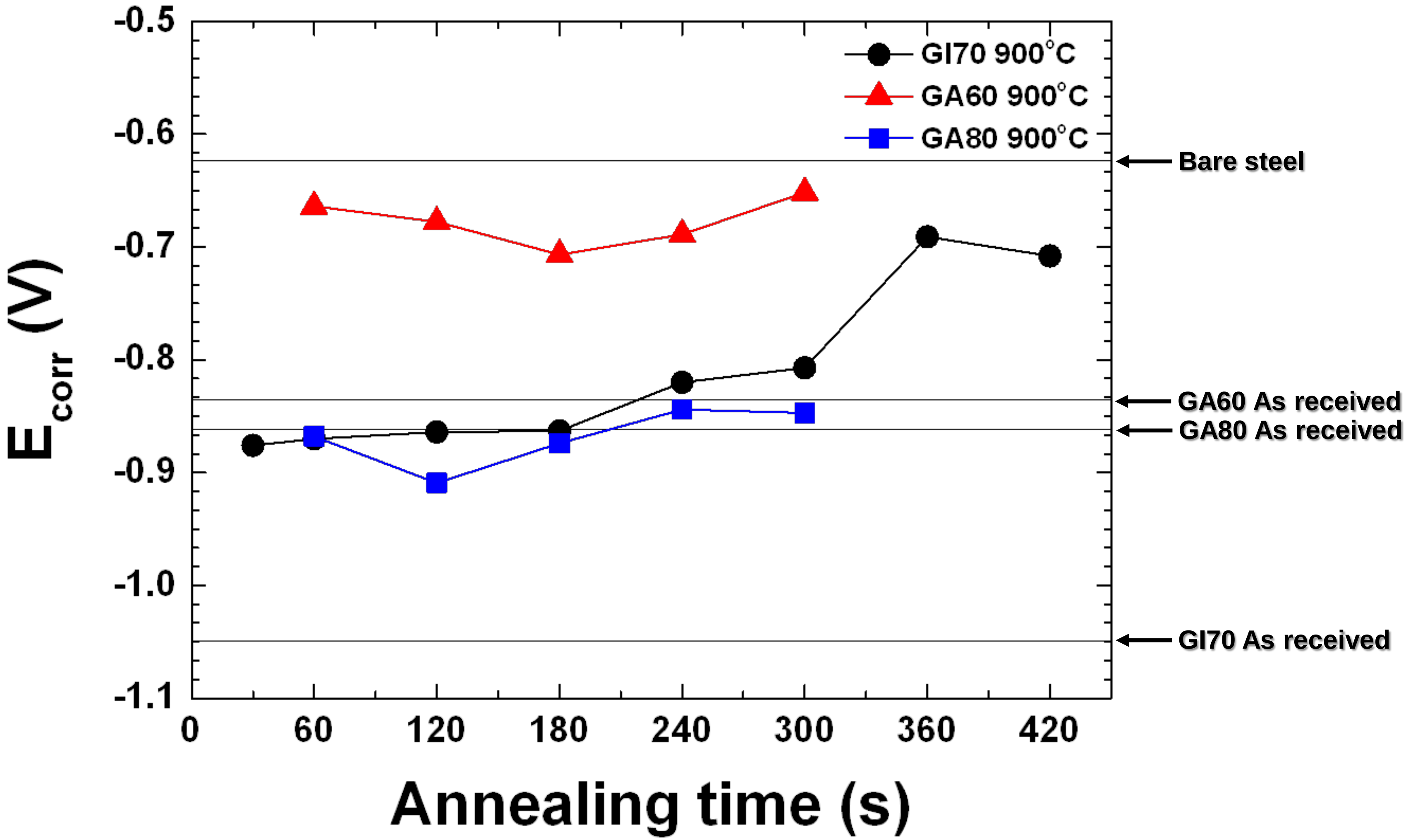
GA80 @ 900ºC PAT – 6 week SAE J2334 Exposure



Thickness of α-Fe(Zn) Layer After Exposure



E_{corr} vs. time



Task 3 – Summary

- **GI70 × 900°C coatings:**
  - **compared to the other coatings, the as-annealed GI70 showed good corrosion resistance**
  - **corrosion resistance deteriorated for annealing times of greater than 180s**
  - **potentiodynamic polarization tests showed that the as-annealed GI70 coatings should be cathodically protective with PHF steel.**
  - **E_{corr} increased with increasing annealing time and began to approach E_{corr} for the substrate**
  - **salt spray performance for annealing times of less than 180s was reasonable, problematic for greater than 180s**

Task 3 – Summary II

- **GA60 × 900°C coatings:**
  - **all GA60 coatings showed poor corrosion resistance.**
  - **potentiodynamic polarization test results showed that GA60 coatings were not likely cathodically protective for PHS steel.**
- **GA80 × 900°C coatings:**
  - **showed better corrosion resistance than GA60, but inferior to GI70**
  - **potentiodynamic polarization test results showed that the GA80 coating can be cathodically protective to PHS**
  - **the relatively thin αFe(Zn) layer vs. GI70 may contribute directly to the poorer corrosion performance**

Global Conclusions – Tasks 1 and 3

- **GI coatings are more effective for the production of cathodically protective αFe(Zn) layers than an equivalent GA coating**
  - **Zn source equivalency higher**
  - **proceed further using GI coating only?**
- **Coating weight has a strong influence on development of a cathodically protective αFe(Zn) layer – needs further definition**
- **Coating weight also has a strong effect on the amount of residual liquid in the coating for a given annealing time – needs further investigation**

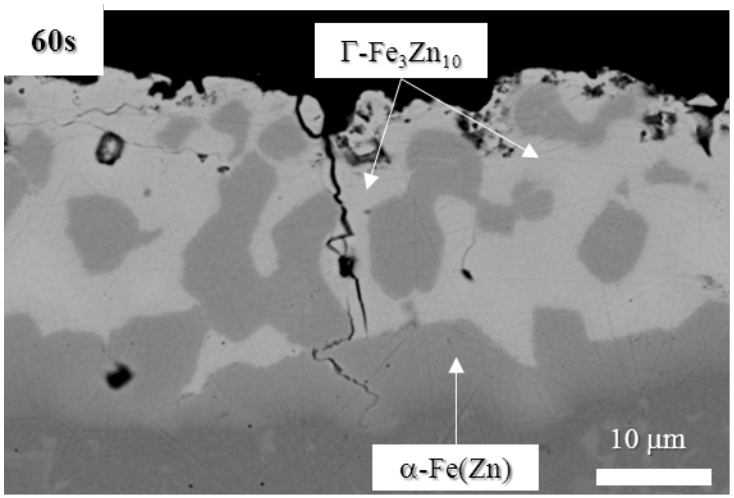
Future Work – Tasks 1 and 2

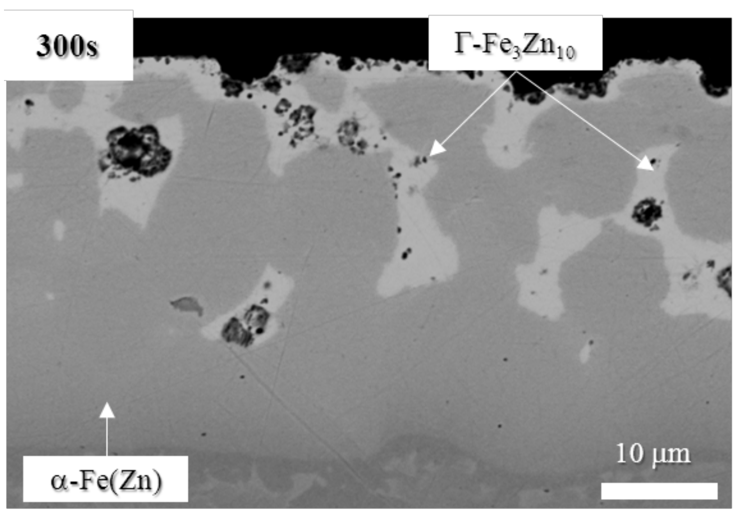
- **Task 1d – planar die forming trials to be started for all experimental materials**
  - **tensile properties – verify target properties are being met (UTS ≥ 1500MPa, %elongation ≥ 6%)**
  - **effect of αFe(Zn) layer and annealing time?**
- **Task 2 – will start following completion of planar die forming trials and preliminary corrosion tests.**

Appendices

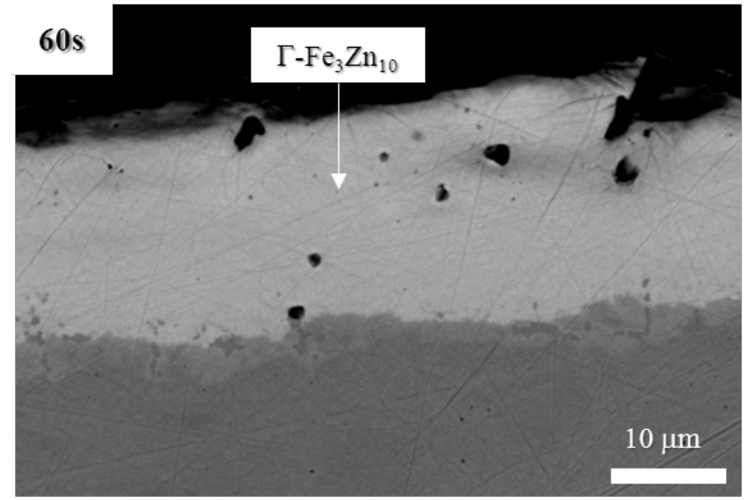
Coating Microstructure vs. time – GI120

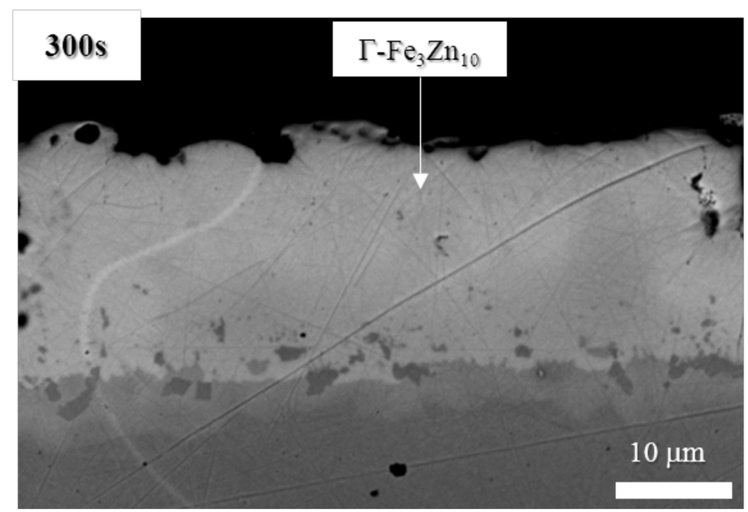
GI120 @ 900ºC PAT





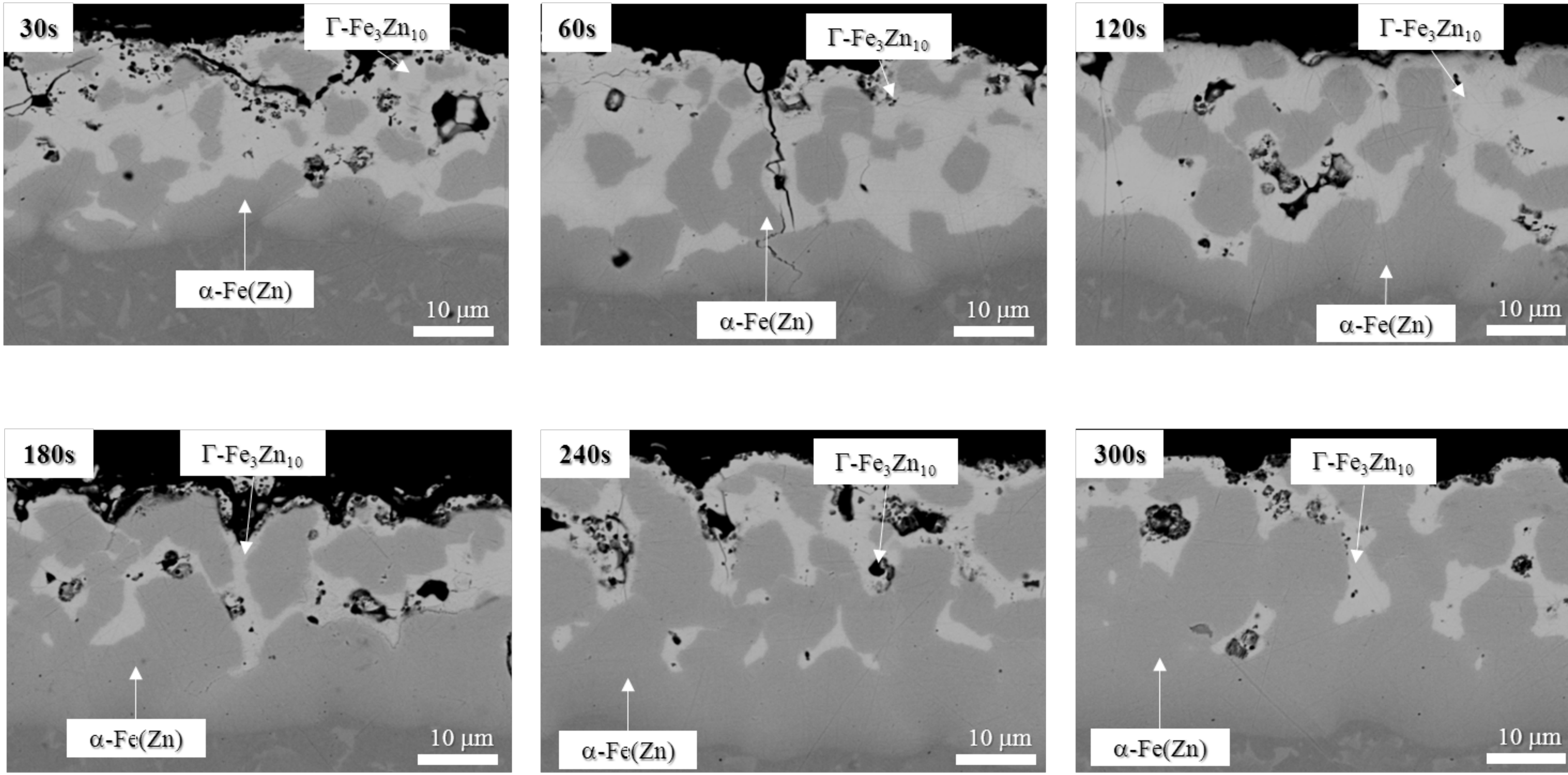
GI120 @ 700ºC PAT





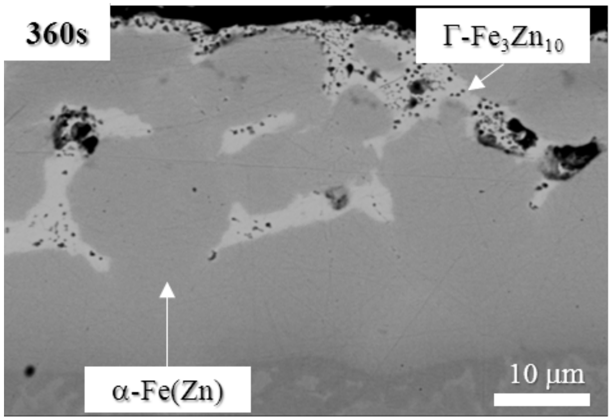
Microstructure vs. time – GI120 + 900ºC

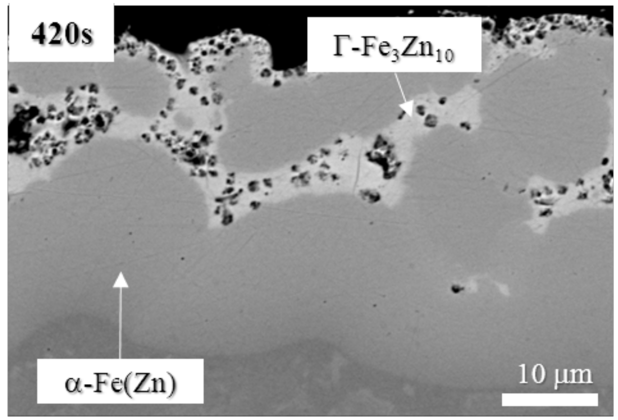
GI120 annealed @ 900ºC

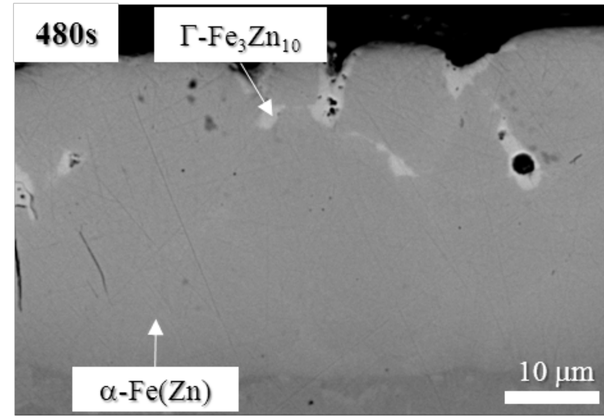


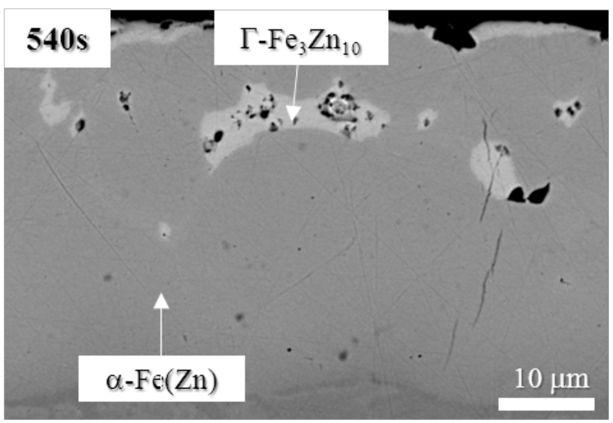
Microstructure vs. time – GI120 + 900ºC

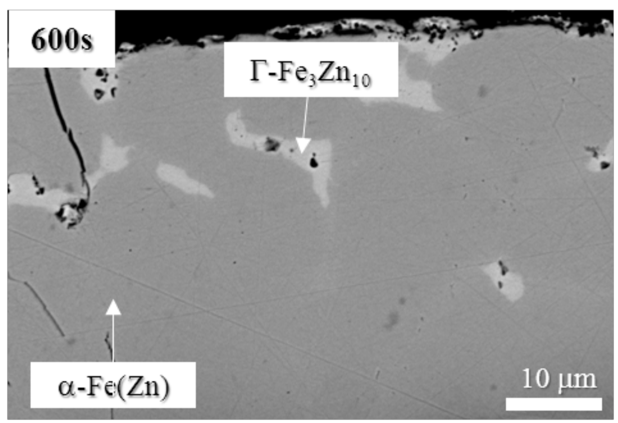
GI120 @ 900ºC PAT





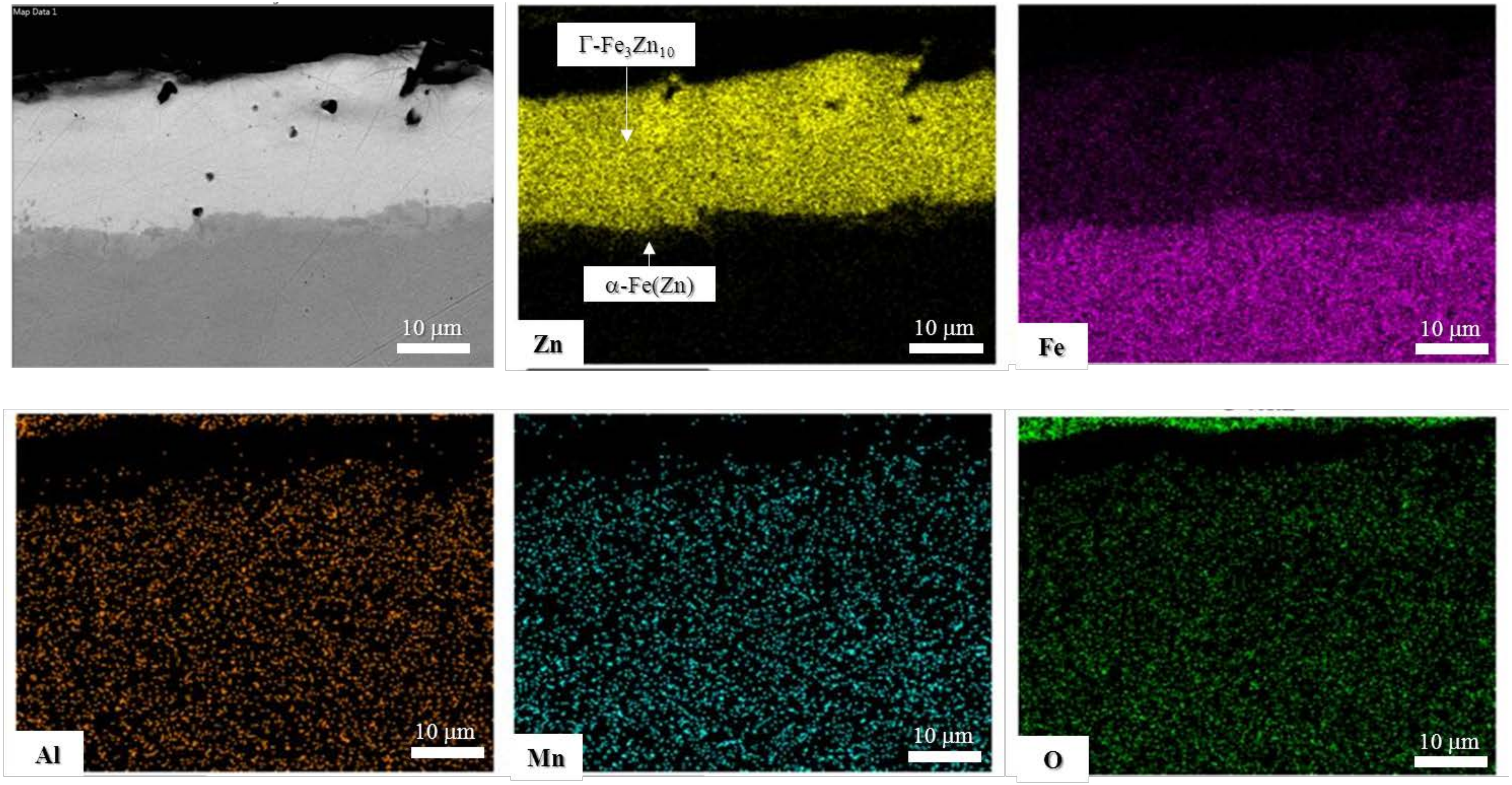






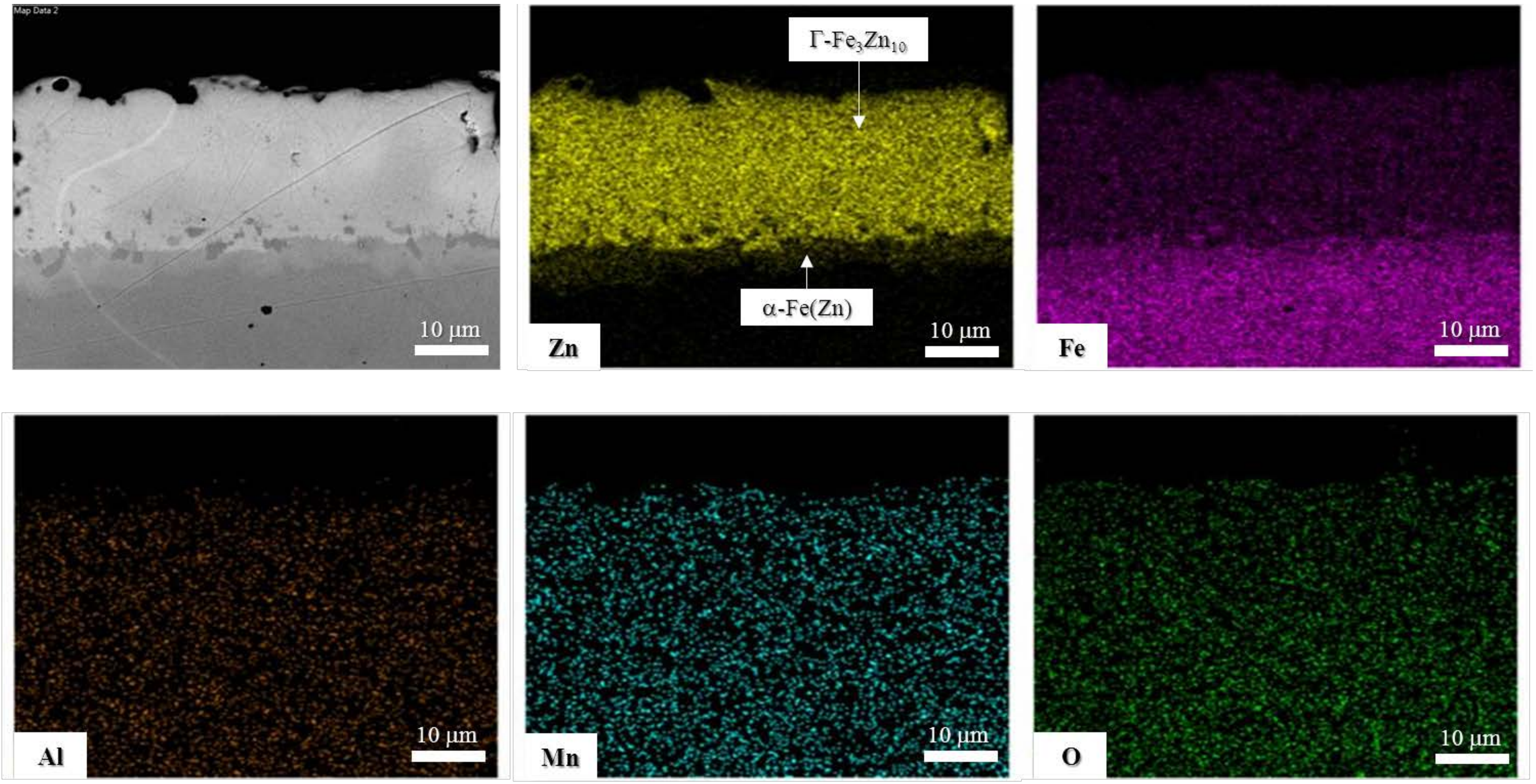
GI120 – 700ºC x 60s EDS maps

GI120 @ 700ºC PAT (60s)



GI120 – 700ºC x 300s EDS maps

GI120 @ 700ºC PAT (300s)



XRD Phase Analysis Summary – GI70

Quantitative XRD analysis

Phase ratio (%)	GI70																
	900^{o}C								900^{o}C and 700^{o}C						700^{o}C		
	30s	60s	120s	180s	240s	300s	360s	420s	30s	60s	120s	180s	240s	300s	60s	180s	300s
ZnO	1.2	1.9	1.8	2.2	3.7	2.9	7.8	6.7	1.3	1.6	2.5	3.8	3.0	3.3	0.9	1.0	1.4
Γ-Fe_3Zn_{10}	66.5	49.1	38.7	39.4	8.1	10.9	3.2	1.2	27.3	20.0	9.7	9.9	4.8	2.9	99.1	99.0	98.6
α-Fe(Zn)	32.3	49	59.5	58.4	88.2	86.2	89.0	92.1	71.4	78.4	87.8	86.3	92.2	93.8			
Phase	ZnO, α-Fe(Zn) Γ-Fe_3Zn_{10}								ZnO, α-Fe(Zn) Γ-Fe_3Zn_{10}						ZnO, Γ-Fe_3Zn_{10}		

XRD Phase Analysis Summary – GI120

Quantitative XRD analysis

Phase ratio (%)	GI120																
	900^{o}C								900^{o}C and 700^{o}C						700^{o}C		
	30s	60s	120s	180s	240s	300s	360s	420s	30s	60s	120s	180s	240s	300s	60s	180s	300s
ZnO	0.5	1.2	1.1	1.7	1.0	1.5	1.9	1.0	0.6	0.3	0.4	0.7	0.4	1.6	0.1	0.7	0.8
Γ-Fe_3Zn_{10}	74.6	72.6	68.7	58.5	50.3	49.1	41.5	54.1	67.5	60.1	59.2	36.4	43.8	38.0	99.9	99.3	99.2
α-Fe(Zn)	24.9	26.2	30.2	39.8	48.7	49.4	56.6	44.9	31.9	39.6	40.4	62.9	55.8	60.4			
Phase	ZnO, α-Fe(Zn) Γ-Fe_3Zn_{10}								ZnO, α-Fe(Zn) Γ-Fe_3Zn_{10}						ZnO, Γ-Fe_3Zn_{10}		

XRD Phase Analysis Summary – GA60 & GA80

Quantitative XRD analysis

Phase ratio (%)	GA60								GA80							
	900^{o}C					700^{o}C			900^{o}C					700^{o}C		
	60s	120s	180s	240s	300s	60s	180s	300s	60s	120s	180s	240s	300s	60s	180s	300s
ZnO	17.3	18.1	18.5	20.5	20.1	2.8	3.3	4.4	18.1	23.3	20.7	30.7	26.5	2.5	3.2	3.9
Γ-Fe_3Zn_{10}	5.7	3.4	2.9	0.9	1.9	97.2	96.7	95.6	50.8	38.1	47.0	35.8	1.7	97.5	96.8	96.1
α-Fe(Zn)	77.0	78.5	78.6	78.6	78.0				31.1	38.6	32.2	33.5	71.8			
Phase	ZnO, α-Fe(Zn) Γ-Fe_3Zn_{10}					ZnO, Γ-Fe_3Zn_{10}			ZnO, α-Fe(Zn) Γ-Fe_3Zn_{10}					ZnO, Γ-Fe_3Zn_{10}		

Corrosion test matrix

	GA60						GA80					
Annealing Temperature	**As received**	**900°C**					**As received**	**900°C**				
Annealing Time		**60s**	**120s**	**180s**	**240s**	**300s**		**60s**	**120s**	**180s**	**240s**	**300s**
Non-scribed Samples	2	2	2	2	2	2	2	2	2	2	2	2
Scribed Samples	2	2	2	2	2	2	2	2	2	2	2	2
Total Samples	4	4	4	4	4	4	4	4	4	4	4	4

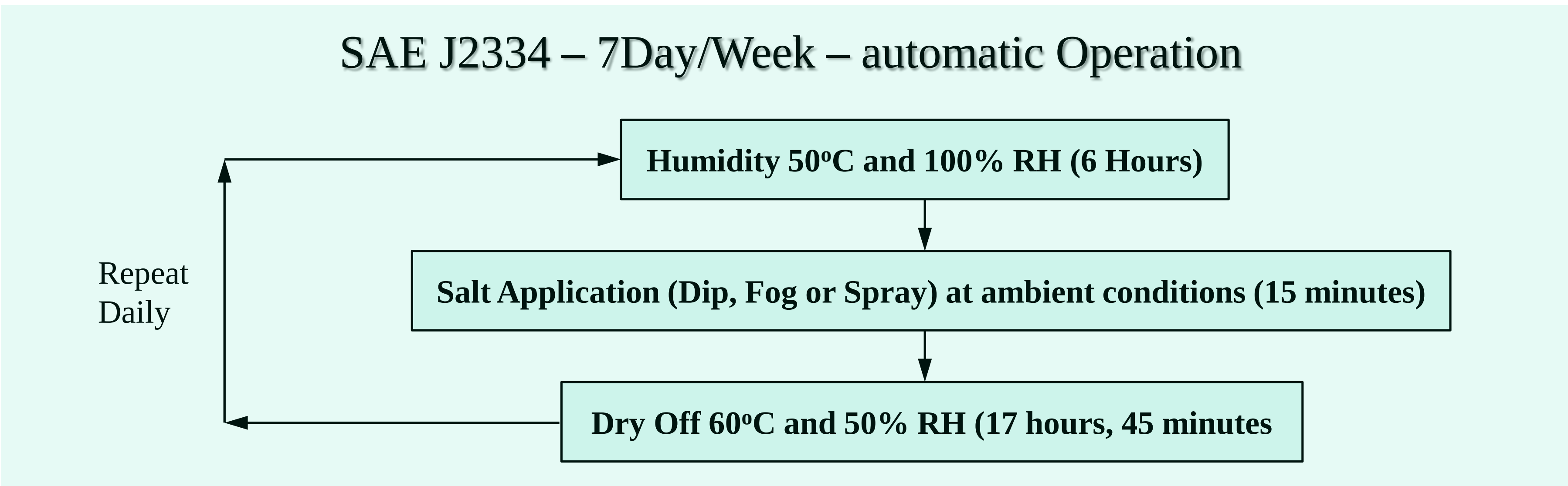
	GI70												
Annealing Temperature	**As received**	**900°C**								**900°C +700°C (60s)**			
Annealing Time		**30s**	**60s**	**120s**	**180s**	**240s**	**300s**	**360s**	**420s**	**30s**	**60s**	**120s**	**180s**
Non-scribed Samples	2	2	2	2	2	2	2	2	2	2	2	2	2
Scribed Samples	2	2	2	2	2	2	2	2	2	2	2	2	2
Total Samples	4	4	4	4	4	4	4	4	4	4	4	4	4

Corrosion test method - SAE J2334

The test will conduct according to SAE J2334 procedures. Key process parameters were:

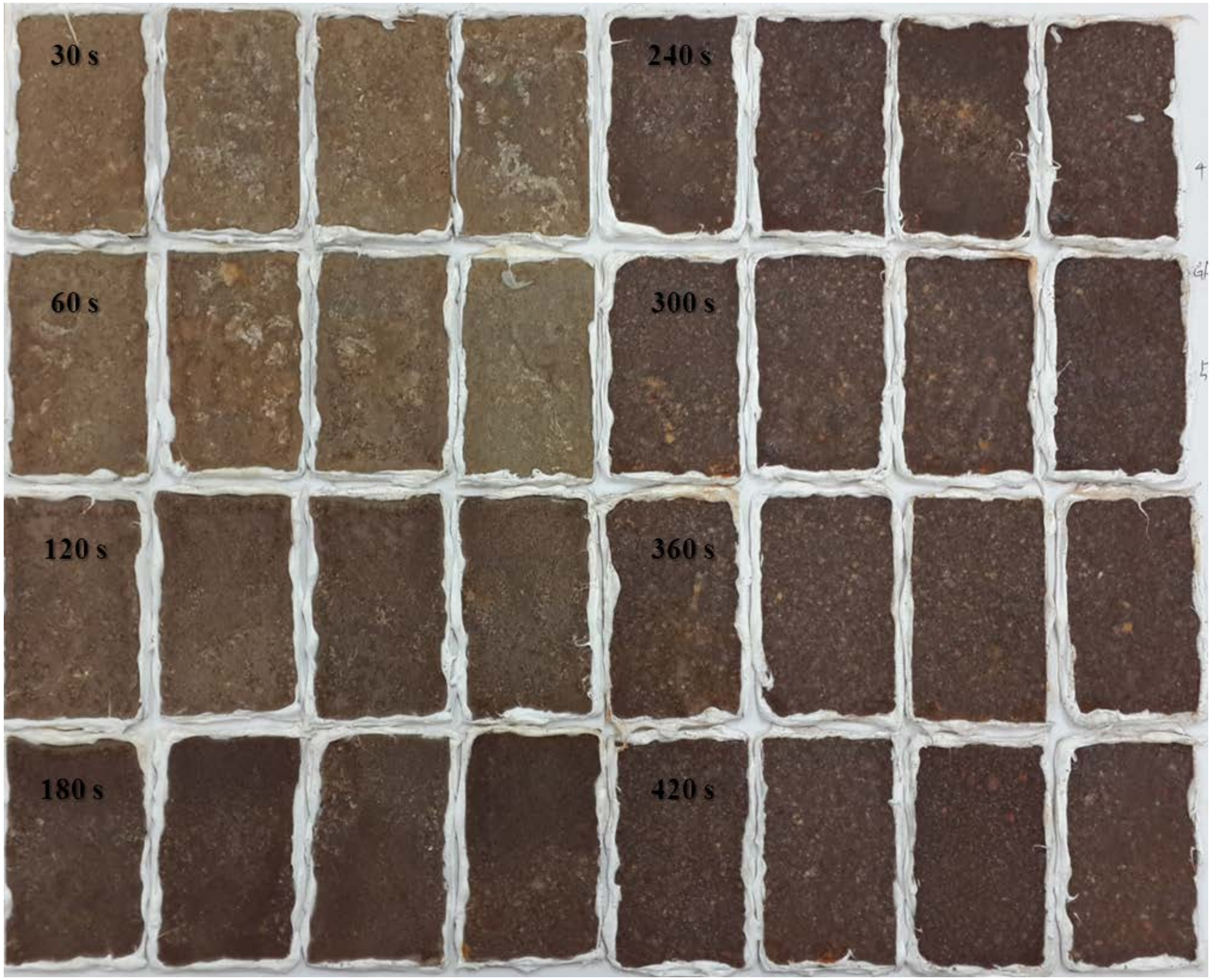
One 24 hour cycle in an enclosed chamber included:

- **6 hours exposure in 100% condensing humidity at 50^{o}C.**
- **15 minute exposure at 25^{o}C to a salt solution consisting of, 0.5% NaCl, 0.1% $CaCl_2$ and 0.075%$NaHCO_3$.**
- **17.75 hours exposure in a dry stage (60^{o}C, 50% relative humidity).**
- **Duplicate specimens were spaced from each other and inclined at 15^{o} from vertical**



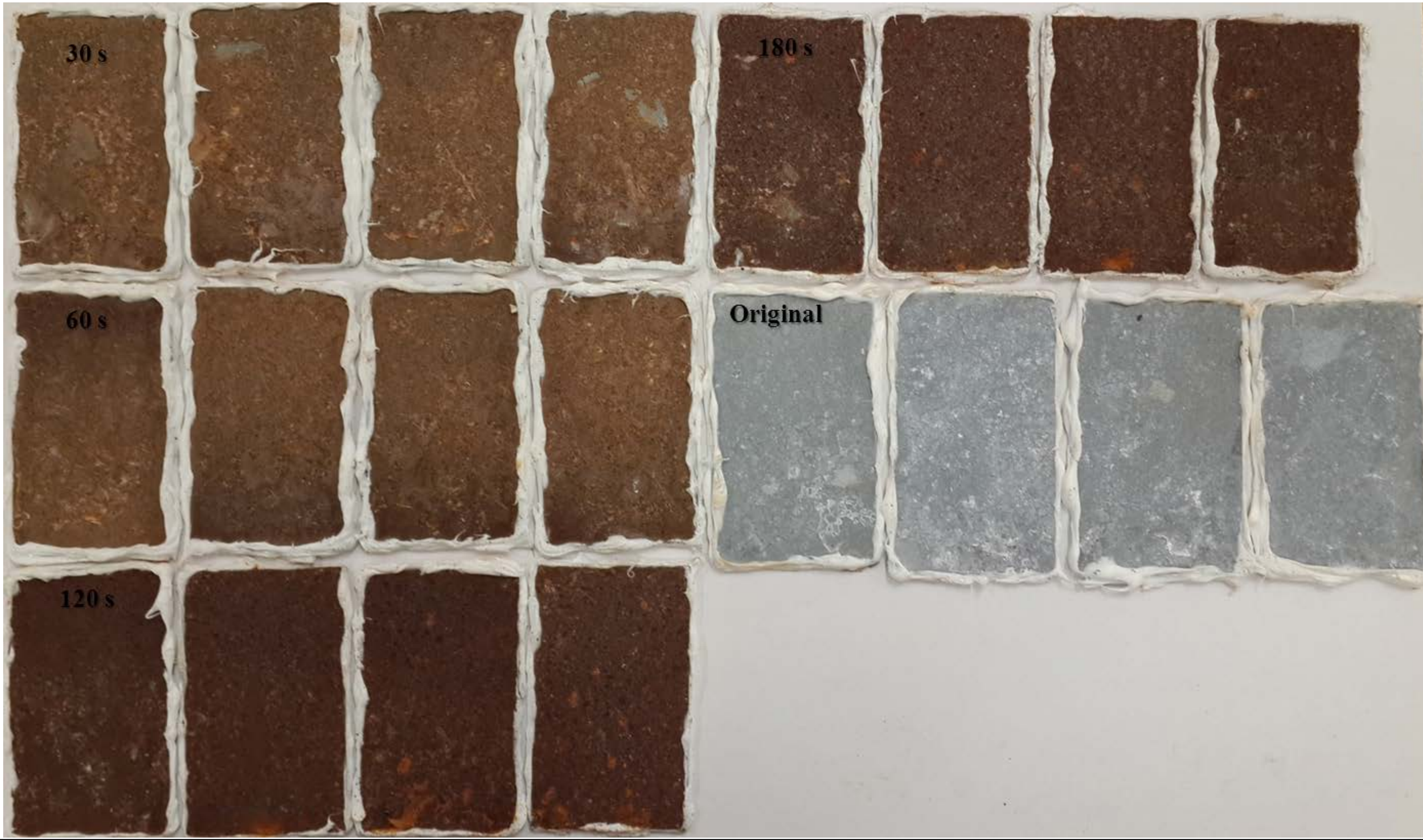
Sample Surfaces – GI70

GI70 @ 900^{o}C PAT – 3 week



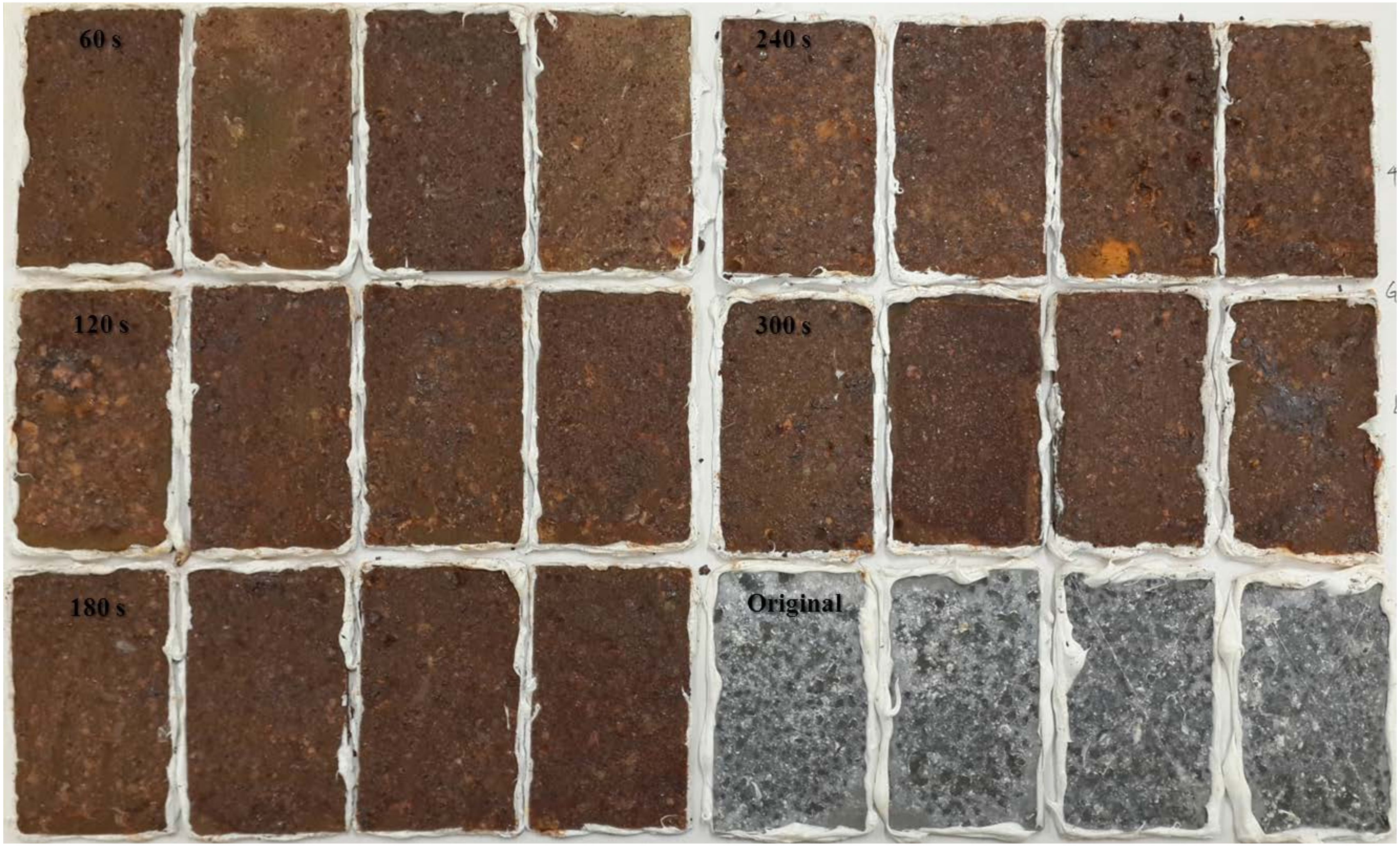
Sample Surfaces – GI70

GI70 @ 900ºC PAT + 60s hold @700ºC – 3 week



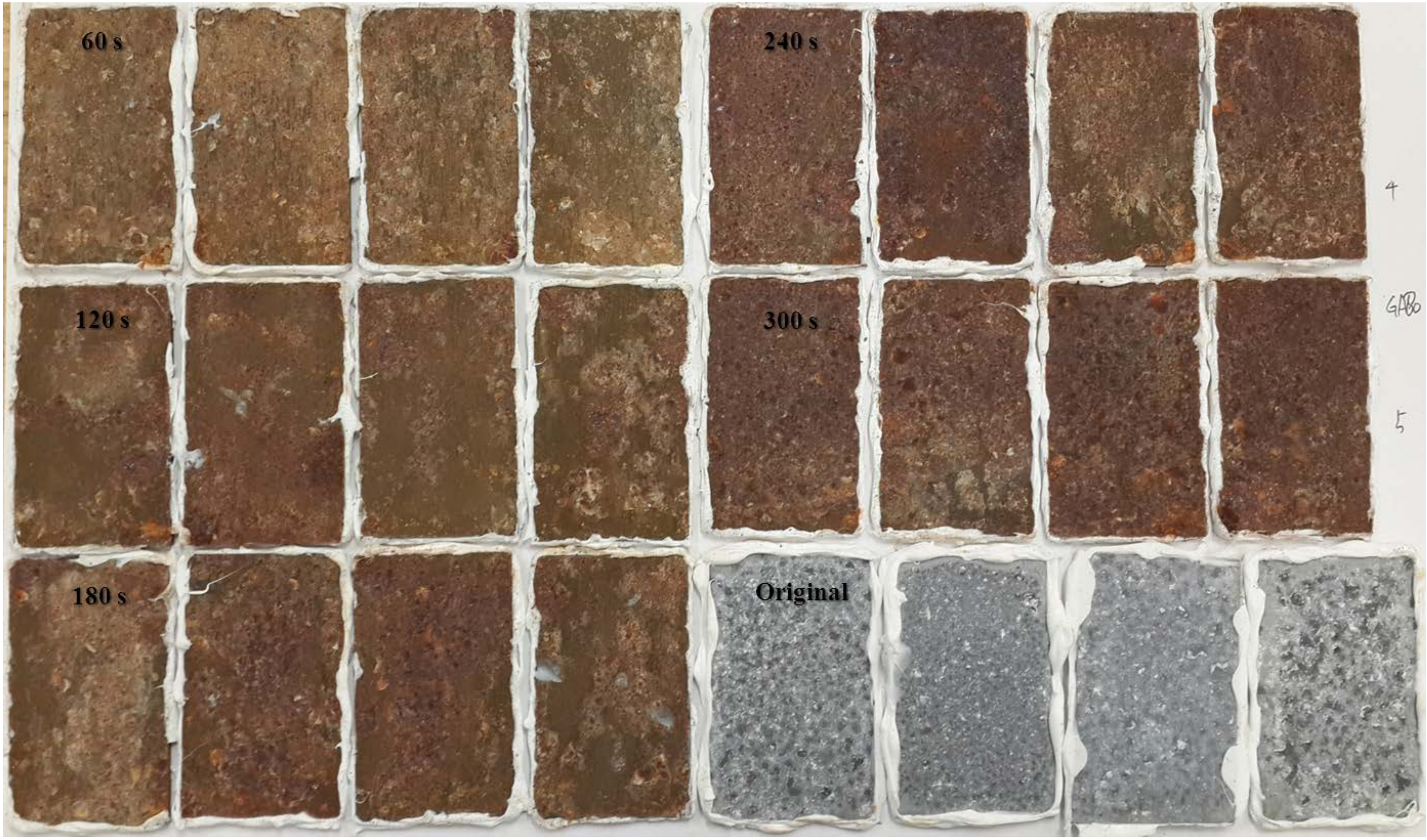
Sample Surfaces – GA60

GA60 annealed @ 900^{o}C – 3 week



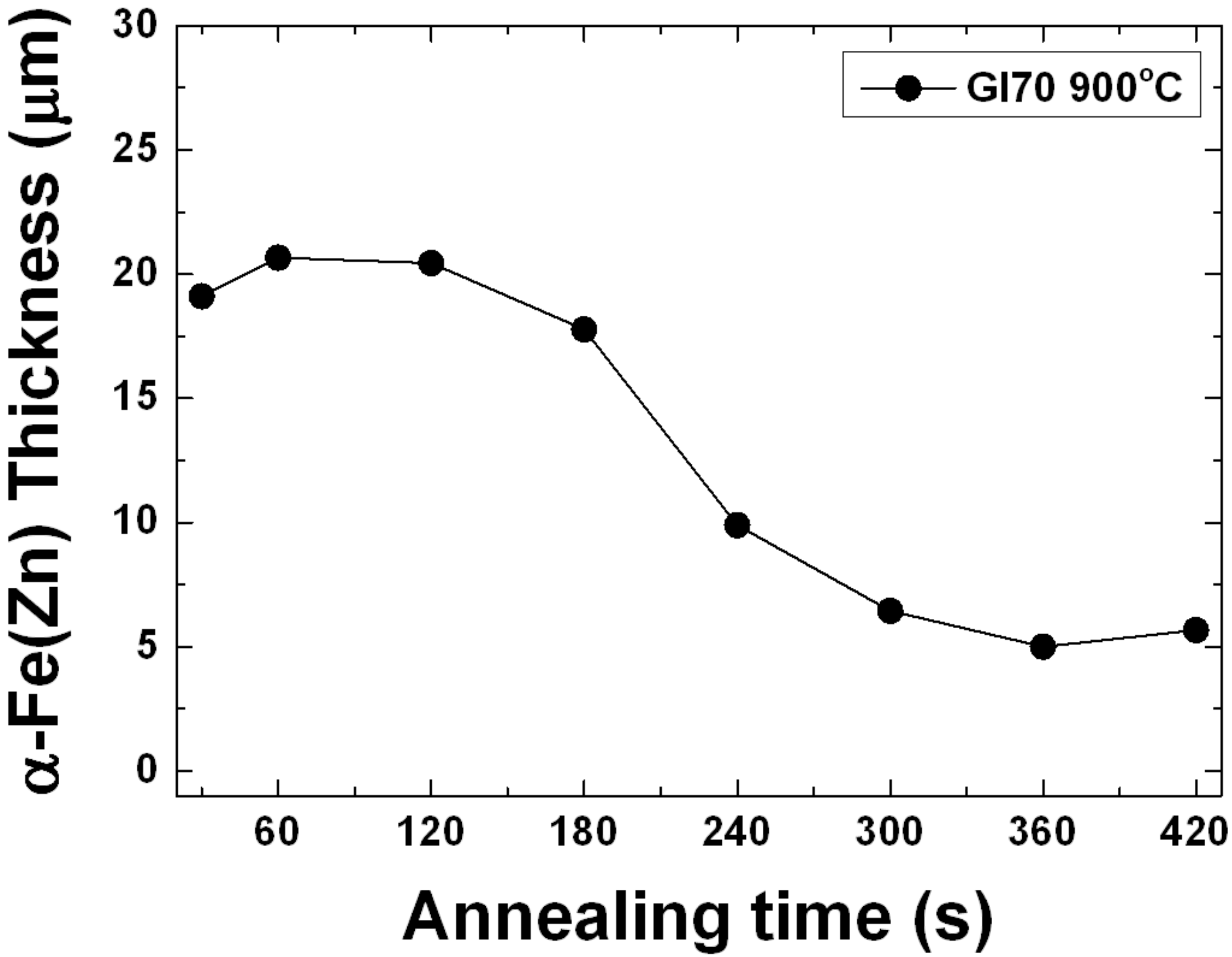
Sample Surfaces – GA80

GA80 @ 900°C PAT – 3 week



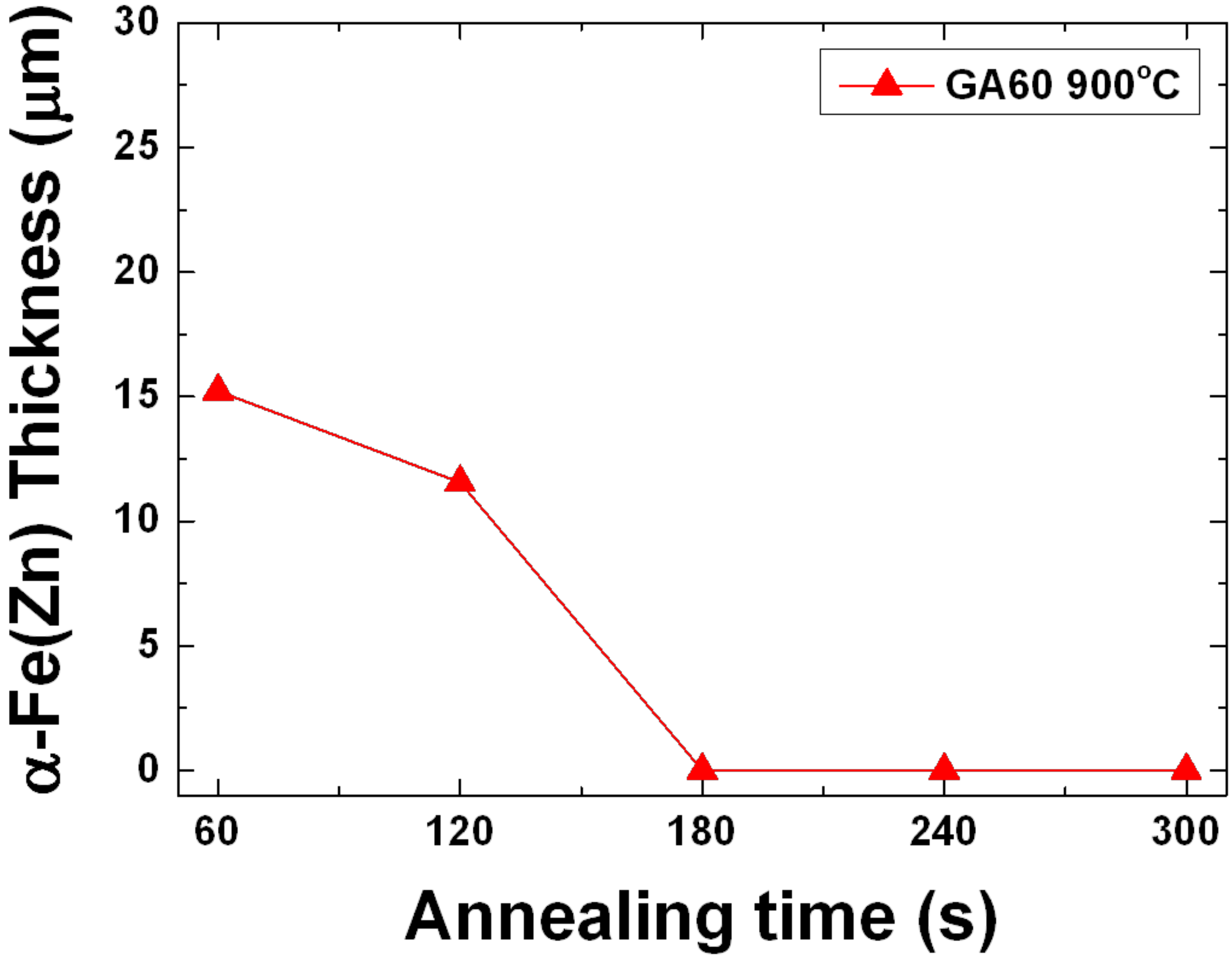
Thickness of α-Fe(Zn) Layer – GI70

GI70 @ 900^{o}C PAT



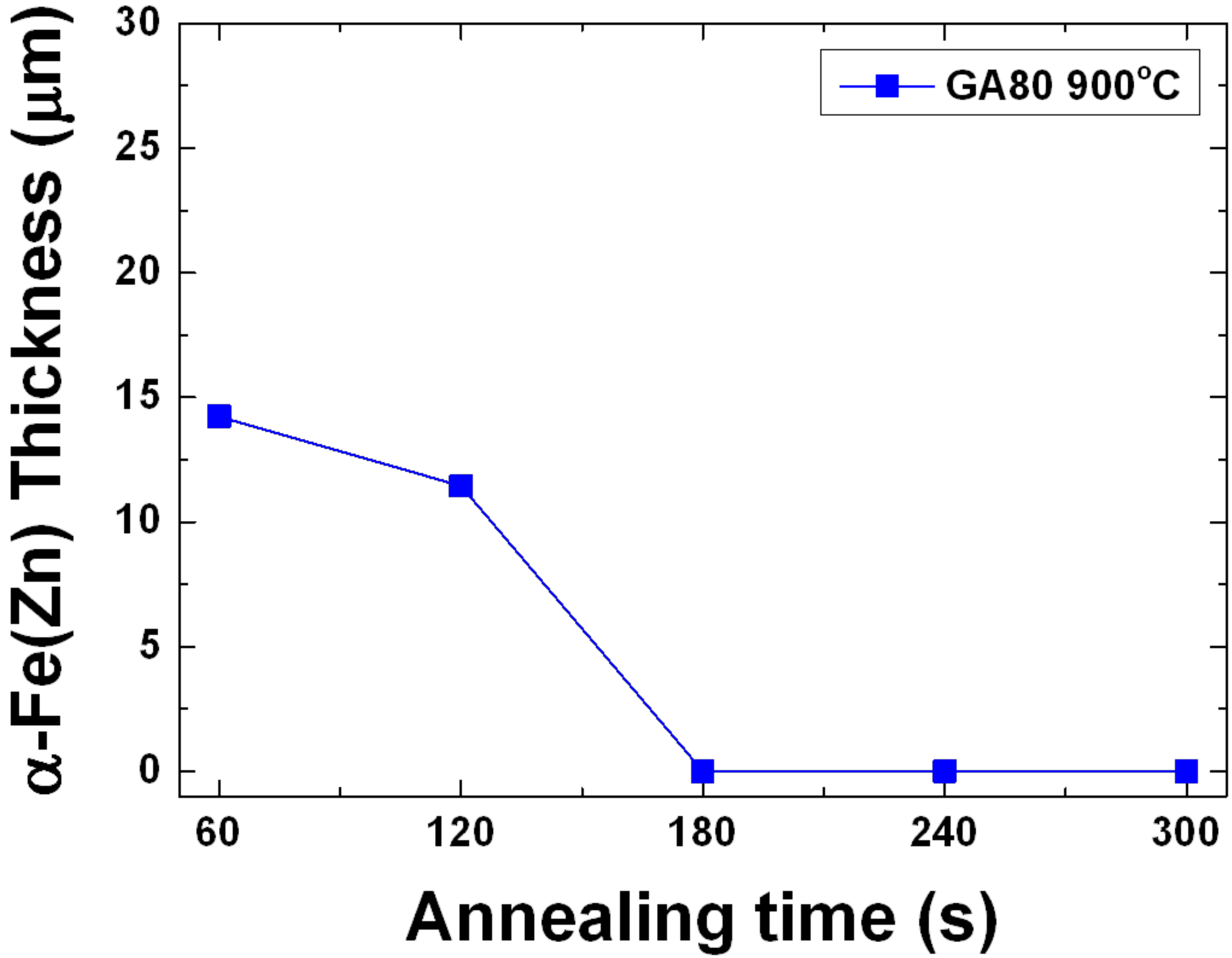
Thickness of α-Fe(Zn) Layer – GA60

GA60 @ 900°C PAT



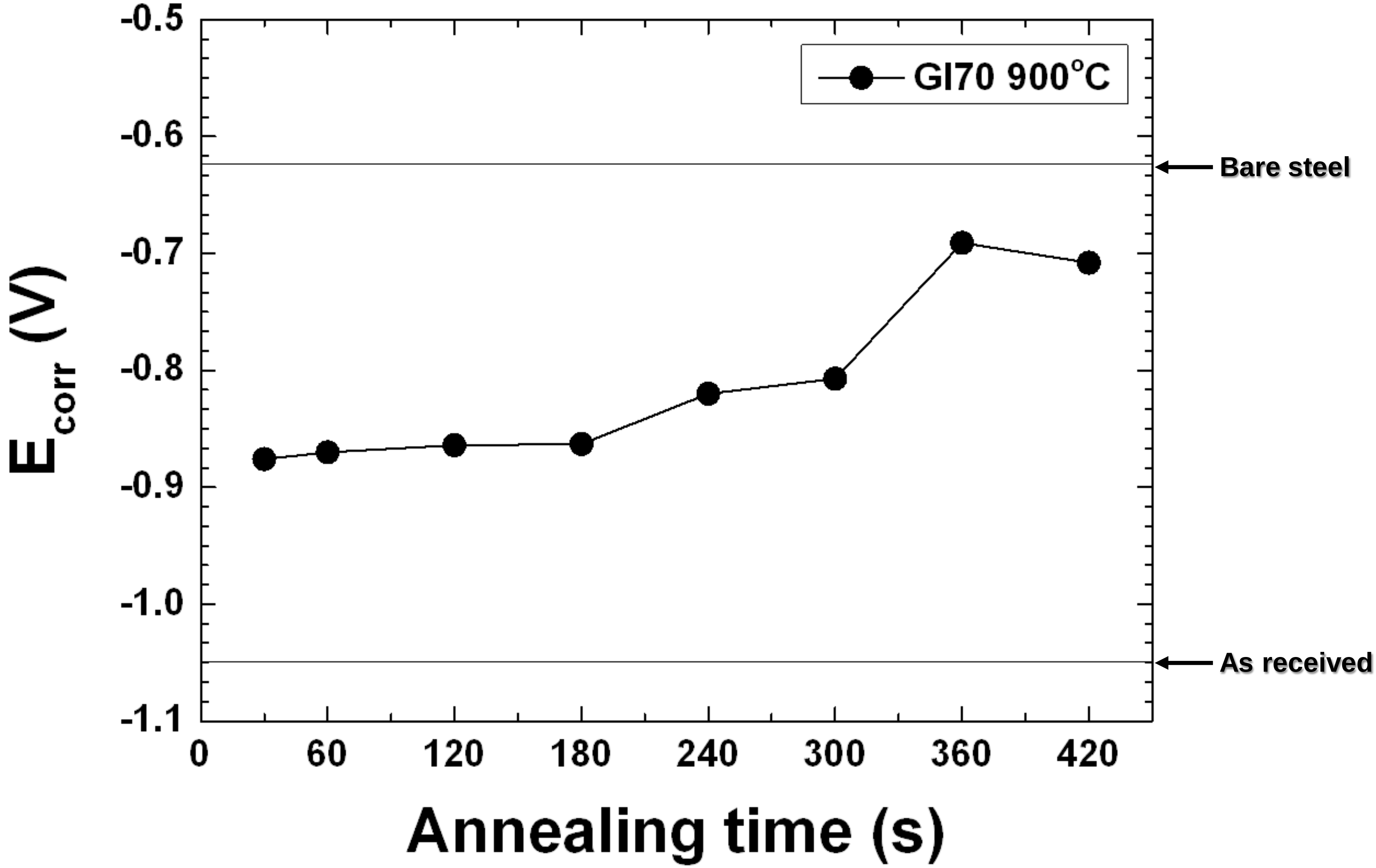
Thickness of α-Fe(Zn) Layer – GA80

GA80 @ 900°C PAT



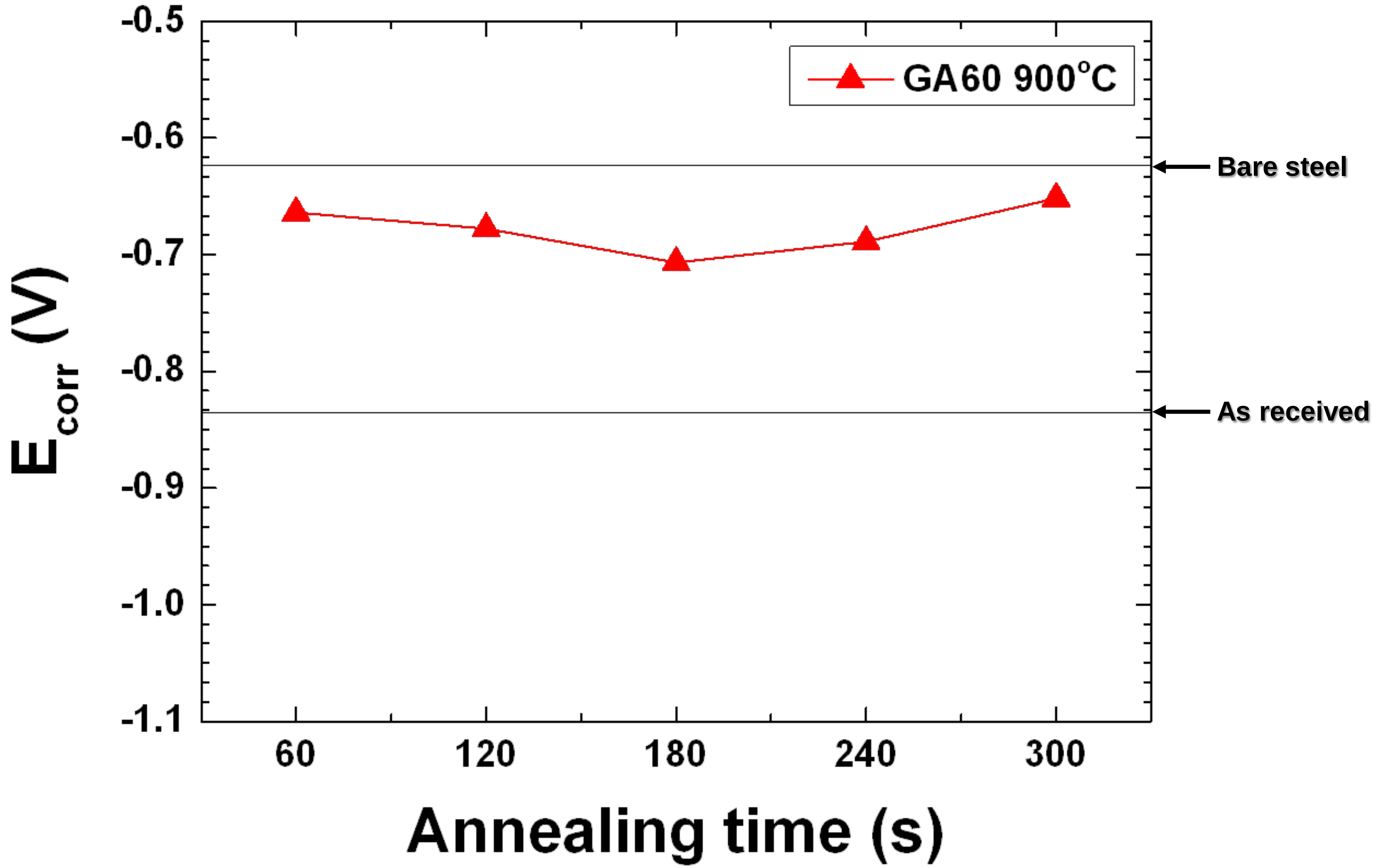
E_{corr} vs. Annealing Time – GI70

GI70 @ 900°C PAT



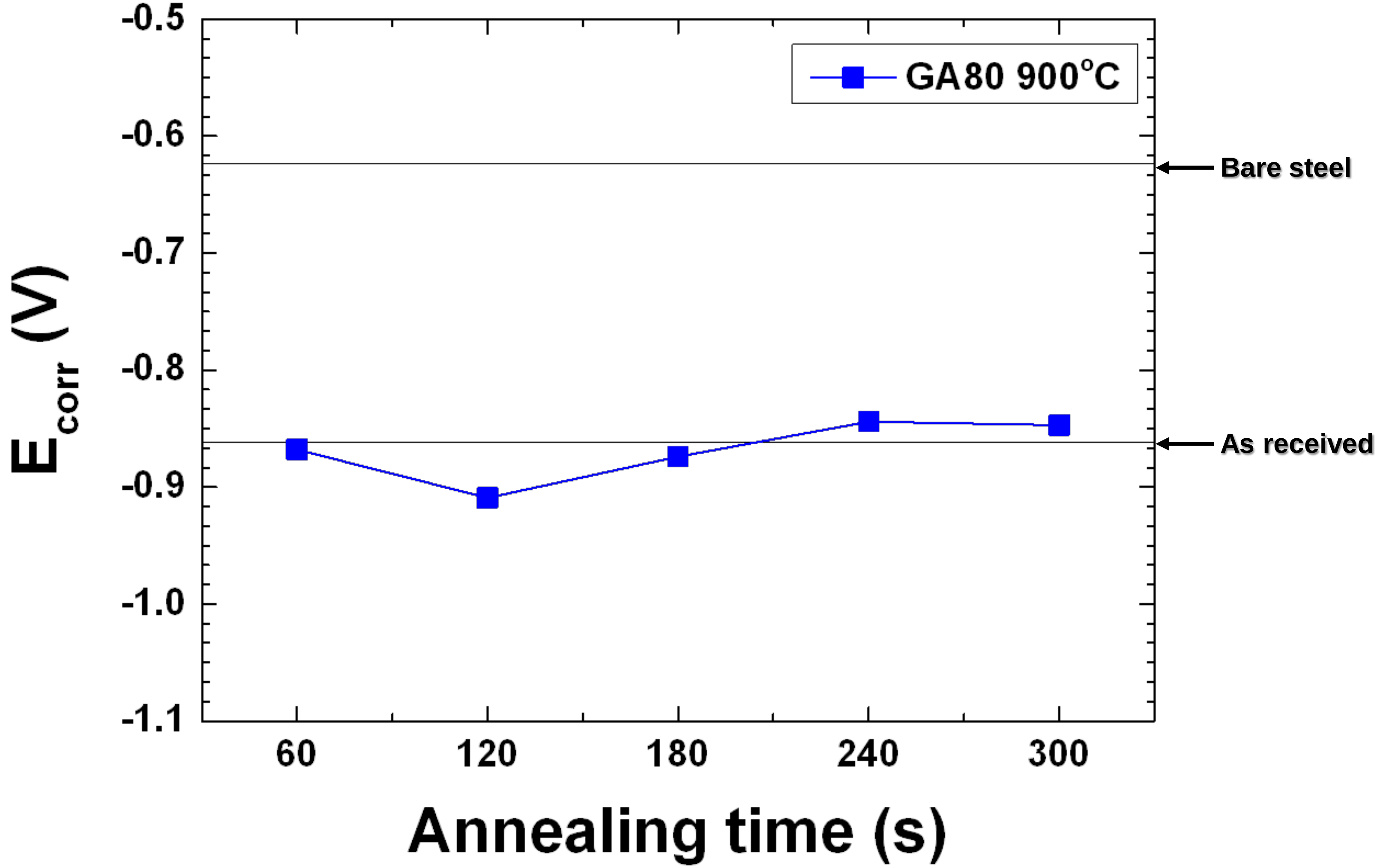
E_{corr} vs. time – GA60

GA60 @ 900^{o}C PAT



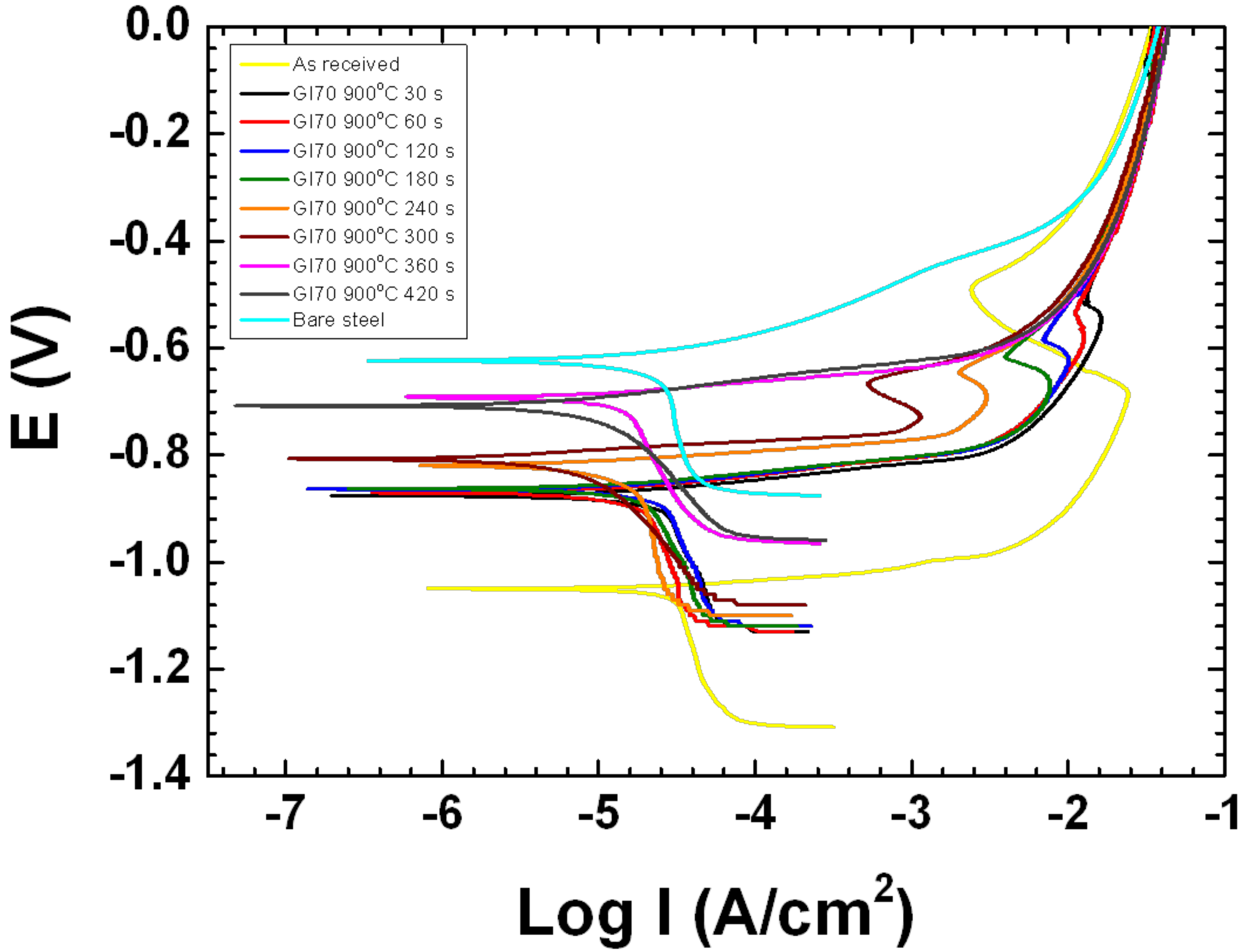
E_{corr} vs. time – GA80

GA80 @ 900°C PAT



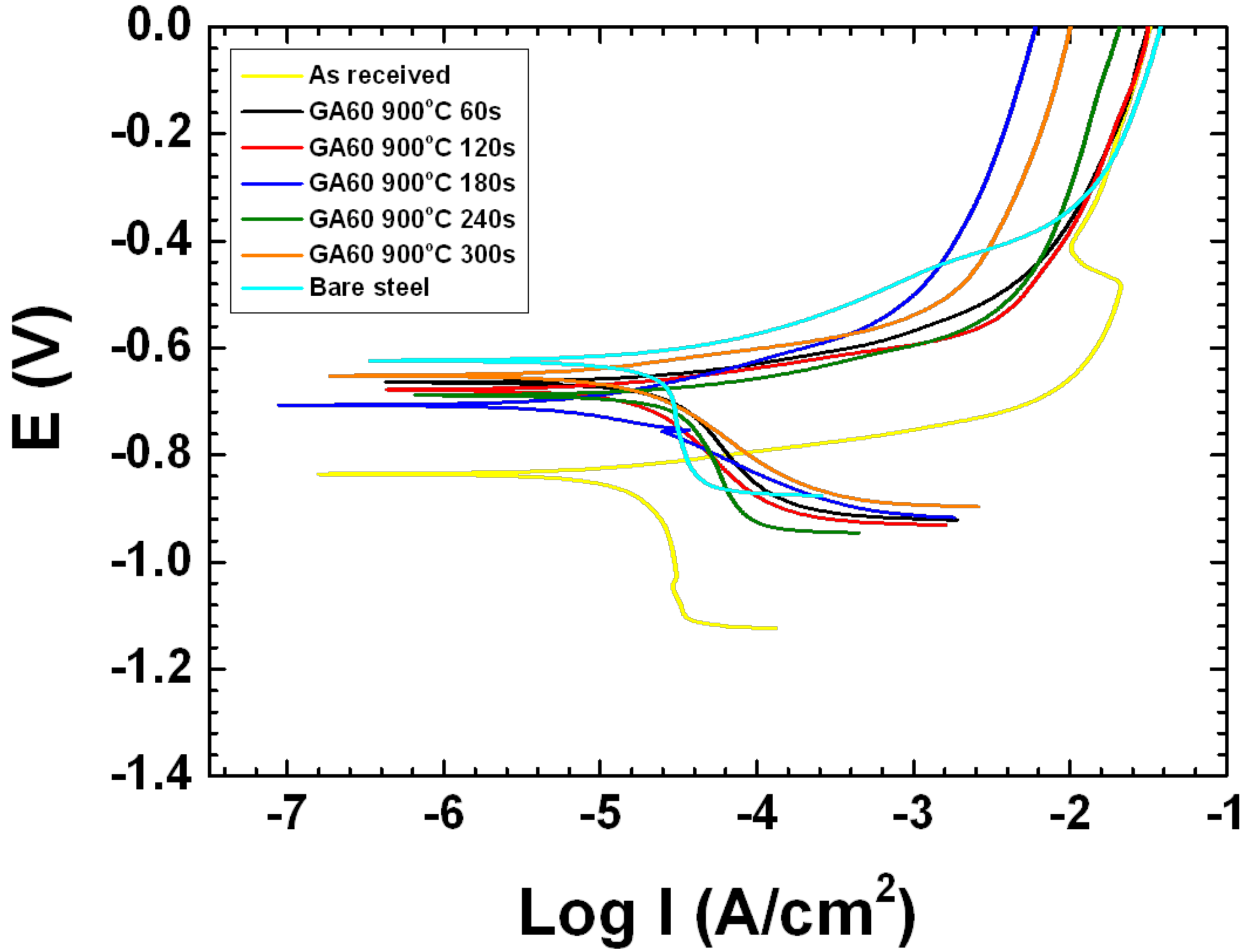
Polarization curve – GI70

GI70 @ 900^{o}C PAT



Polarization curve – GA60

GA60 @ 900^{o}C PAT



Polarization curve – GA80

GA80 @ 900ºC PAT