

Post-Annealing Adhesion Capability of the Chromium-Free Coating to Electrical Steels: Effects of Furnace Atmosphere and Substrate

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Effects of furnace atmosphere on the post-annealing adhesion capability of the chromium-free coating were investigated for electrical steels (ES) annealed in the "air-tight" furnace. It was revealed that both "oxygen-containing but absolutely dry" and "humidity-containing but absolutely oxygen-free" nitrogen atmospheres have no harm to the coating adhesion after annealing, which is opposed to the previous results from a study on the "non-hermetic" furnace. However, the coexistence of oxygen and humidity can trigger severe synergetic effects, alter the cross-sectional distribution of elements, and lead to coating adhesion failures. Hence, the furnace atmosphere of the annealing process should be carefully controlled. We also proposed a practical and efficient solution that can avoid the synergetic effects.

Keywords: Electrical Steel, Furnace, Atmosphere, Annealing, Coating, Adhesion

1. INTRODUCTION

Electrical steels (ES) are the Fe-Si alloys with special electromagnetic properties, constituting the core component of motors, generators, compressors, and transformers. Therefore, the performance of ES is critical to the energy conversion efficiency of these facilities.

For ES, the loss in the energy conversion process (generally referred to as "iron loss") is composed of "hysteresis loss" and "eddy current loss"⁽¹⁾. The alloy composition of ES mainly determines the former, while the latter is proportional to the square of the ES sheet thickness and inversely proportional to the resistivity of the ES sheet^(2,3).

Before being assembled as the core for the facilities mentioned above, ES must be cut into the designed shape by stamping. However, after this process, residual stress is left at the edges of the ES stampings and deteriorates the electromagnetic properties (e.g., iron loss increases). To remove the residual stress and restore the electromagnetic properties of ES stampings, an after-stamping heat treatment (usually at 700–850°C) is required. Such a heating process is called "stress-relieving annealing (SRA)"^(4,5).

Although annealing can restore or even improve the electromagnetic properties of ES stampings, it may also

damage the insulating coating on ES. Improper heat treatment usually causes coating adhesion failures and loss of interlayer resistance (electrical insulation between adjacent ES sheets), due to which the efficiency of the ES facilities is lowered and leads to abnormal temperature rises during operation.

Nevertheless, the heat-treating hardware and parameters (furnace type, furnace atmosphere, heating profile, positioning...etc.) are so diversified that the annealing results (adhesion and appearance of the coating) can be very different. Thus, among the working processes of ES, SRA is undoubtedly the most difficult to control. Variations or deviations in the above parameters usually result in poor annealing outcomes^(6,7). In previous studies on ES annealed in the "non-hermetic" furnace (with limited leakage of air)⁽⁸⁾, we have shown that the microstructure of the coating-substrate interface and internal oxidation of the ES substance (beneath the coating) are affected both by the furnace atmosphere and the substrate alloy composition.

To exclude the interference from ambient air, in this study an "air-tight" furnace was used. Therefore, the effects of the furnace atmosphere (oxygen (O₂), humidity (H₂O), and H₂) and substrate (alloy composition) on the post-annealing adhesion capability can be investigated qualitatively and quantitatively for the ES with chromium-free coating⁽⁹⁾.

2. EXPERIMENTAL METHOD

2.1 The Materials

Three kinds of ES sheets were used as the substrate for coating. As shown in Table 1, the main alloying elements Si and Al are ca 3.1~1.9% and ca 1.1~0.3%, respectively. The substrates were coated with a waterborne chromium-free (phosphate-based) paint and then baked by heating, after which the coating was cured. The thus coated ES samples are coded as S1, S2, and S3, respectively.

2.2 Thermal Treatment (Stress-Relieving Annealing)

An "air-tight" single-chamber furnace was used for thermal treatment. The ambient atmosphere can be completely expelled from the furnace by purging gas at a flow rate of 2 L/min. The furnace atmosphere was in-situ monitored and recorded by an on-line gas analyzer (Rapidox 7100).

The heating profile used for the thermal treatment on the samples is shown in Figure 1. The furnace was heated from room temperature to 750°C in 3 hours, kept at this temperature for 2 hours, and then cooled down naturally. The composition of the furnace atmosphere for heat treatments is listed in Table 2. Based on the initial dew point of the furnace atmosphere, experiments can be categorized into the D group with dry atmospheres (#D1, #D4, #D8, initial dew point <-30°C), and the H group with humid atmospheres (#H1 ~ #H9, initial dew point ~ 0°C).

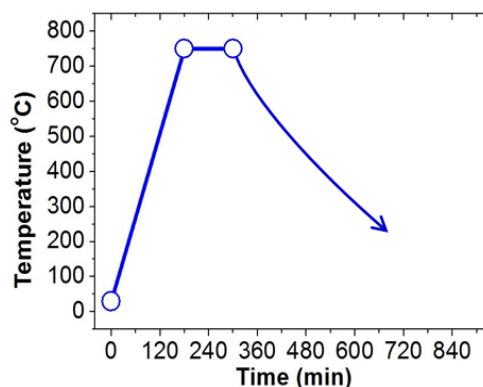


Fig.1. The heating profile for the investigated thermal treatments.

The purge gas for the furnace atmosphere was provided by a multi-channel humidifier that can precisely control the flow rate of component gases to generate the purge gas with the specified O₂ content and dew point. For example: the furnace atmosphere with 0.025 v/v% O₂ content and an initial dew point ~ 0°C was obtained by purging 0.01 L/min O₂/N₂ (5/95 v/v%, from the cylinder) and 1.99 L/min humidified (to dew point ~ 0°C) nitrogen (from the gas plant).

For each specified furnace atmosphere, all of the three samples were annealed in the same batch. The samples were positioned "individually and separately" in the furnace so that the coated surface of the samples could be exposed directly to the furnace atmosphere.

Table 1 The composition of the major alloying elements in the ES substrates of the investigated samples.

		The coated sample		
		S1	S2	S3
Alloy composition of the Substrate	Si	ca 3.1%	ca 3.0%	ca 1.9%
	Al	ca 1.1%	ca 0.6%	ca 0.3%

Table 2 The initial atmosphere composition for annealing experiments.

#	Initial composition (v/v%)		(D) Dry atmosphere initial dew point <-30°C	(H) Humid atmosphere initial dew point ~0°C
	[O ₂]	[H ₂]		
1	0	0	#D1	#H1
2	0.025	0	Not Tested	#H2
3	0.025	0.5	Not Tested	#H3
4	0.2	0	#D4	#H4
5	0.2	0.5	Not Tested	#H5
6	0.5	1	Not Tested	#H6
7	0.5	1.5	Not Tested	#H7
8	1.0	0	#D8	Not Tested
9	1.0	3.0	Not Tested	#H9

Therefore, the effects of the furnace atmosphere on the post-annealing adhesion capability of the coating can be clarified.

2.3 Adhesion Capability of Coating for Annealed Samples

After annealing, the coating adhesion capability to the substrate was evaluated with Scotch tape (type 600). Upon fast removal of the tape from the annealed sample, clean tape without stain and intact surface without substrate exposure stand for excellent adhesion. On the contrary, if coating adhesion is significantly damaged after annealing, bare substrate (peeling-off of the coating) and stains on the tape would show up. The post-annealing adhesion capability of the coating can thus be differentiated by the extent of substrate exposure and tape stains.

2.4 Cross-Sectional Analysis of the Coatings After Annealing

For the FIB / SEM / EDS analysis, specimens were first vapor deposited by a thin layer of platinum (Pt). Then the surface was milled by dual-beam focused gallium ion beams (DB-FIB) to cut out a rectangular hole, from which cross-sectional images can then be taken by scanning electron microscopy (SEM) at a magnification of 25,000X. The distribution of elements over cross sections can be revealed by mapping (energy dispersion spectroscopy, EDS): Fe map for the substrate, P map for the coating, and O map for evaluating the extent of oxidation. For the glow discharge spectroscopy (GDS) analysis, annealed samples were analyzed

directly without any pretreatment. However, vacuum suction locally on the surface (ca. 20 mm², by an O-ring) was required before the GDS analysis. The surface of sample S3 annealed in #H2 was very fragile and got partly peeled off before the analysis so GDS results were not available for this specimen.

3. RESULTS AND DISCUSSION

3.1 Effects of Furnace Atmosphere and Substrate on the Post-Annealing Adhesion Capability of the Coating

The composition of the investigated furnace atmospheres for the annealing of ES samples (S1, S2, S3) is listed in Table 2. The results of the tape test on annealed samples are summarized in Tables 3 ~ 7, from which the post-annealing adhesion capability of the coating can be differentiated between samples and furnace atmospheres.

3.1.1 The Individual Effects of "O₂" (#D1, #D4, #D8)

Practically, the leakage of air into the furnace usually interferes with the annealing process of ES stampings. The dependence of such effects on the substrate (alloy composition) had been revealed in our previous study on the non-hermetic furnace⁽⁸⁾. However, for such furnaces, the O₂ and humidity contents in the furnace atmosphere are simultaneously altered by the leakage of air. Therefore, strictly speaking, the individual effects of O₂ and humidity on the post-annealing adhesion capability of the coating cannot be differentiated and investigated separately by the non-hermetic furnace.

Table 3 Tape test results of the samples annealed in the dry atmospheres (initial dew point <-30 °C): the appearance of the annealed sample with tape torn off (scanned images).



















Initial dew point	#	Initial composition (v/v%)		Annealed sample after tape test		
		[O ₂]	[H ₂]	S1	S2	S3
<-30 °C	D1	0	0			
	D4	0.2	0			
	D8	1.0	0			

Table 4 Tape test results of the samples annealed in the dry atmospheres (initial dew point <math><-30^{\circ}\text{C}</math>): the appearance of the tape torn from the annealed sample (scanned images).

Initial dew point	#	Initial composition (v/v%)		Tape torn from the annealed sample		
		[O ₂]	[H ₂]	S1	S2	S3
<math><-30^{\circ}\text{C}</math>	D1	0	0			
	D4	0.2	0			
	D8	1.0	0			

In this study, to clarify the individual influences of "O₂" without the interference of humidity from the air, O₂/N₂ mixed gas (5/95 v/v%, from the cylinder) was used as the source of O₂ for the airtight furnace. For example, purging the O₂/N₂ mixed gas at a flow rate of 0.08 or 0.40 L/min with dry nitrogen (directly from the gas plant, dew point ca. -48 °C), and keeping the total flow rate at 2.00 L/min, dry furnace atmospheres (#D4, #D8) with 0.2 or 1.0 v/v% O₂ were obtained.

As shown in Tables 3 and 4, samples S1, S2, and S3 annealed in the pure nitrogen atmosphere (#D1) have excellent tape test results, so do the samples annealed in the dry atmosphere with 0.2 or 1.0 v/v% O₂ (#D4, #D8). Oxygen in #D4, and #D8 doesn't affect the post-annealing adhesion capability of the coating.

From Table 3, instead of showing the typical black/gray appearance characteristic for annealed stampings, samples S2 and S3 annealed in the oxygen-containing dry atmospheres (#D4, #D8) are however reddish brown (S1 is only slightly reddish). This means that the surface of these annealed samples has been oxidized after the annealing in the above atmospheres, and the organic components (i.e., contain the carbon element, the reason for the black/gray appearance after annealing) in the coating should have been mostly burned off. The coating material that remained on the surface of annealed samples under such oxygen-containing dry atmospheres (#D4, #D8) should be mainly inorganics.

Therefore, for samples annealed in an oxygen-containing dry atmosphere, the adhesion capability evaluated by the tape test is a combined result for "that of the residual inorganic components of the coating to the substrate" and "that of the oxidized substrate beneath the coating to the underlying un-oxidized substrate".

As a summary of Tables 3 and 4, the existence of O₂ itself doesn't affect the post-annealing adhesion capability of the coating for samples S1, S2, and S3 annealed in the oxygen-containing dry atmospheres (#D4, #D8). This is the apparent result of good adhesion between







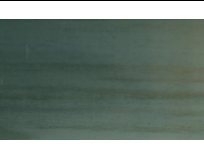
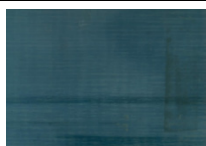

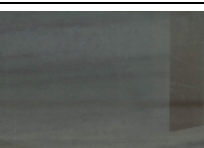
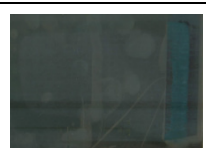
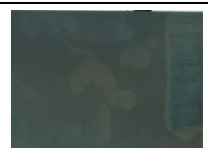

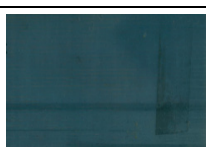
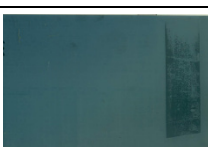
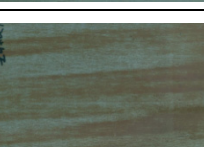
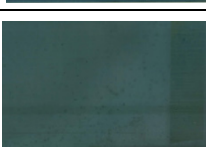
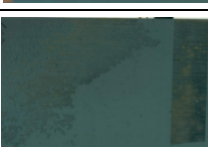
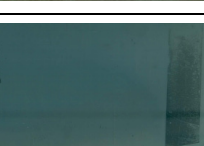
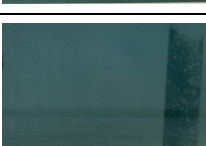
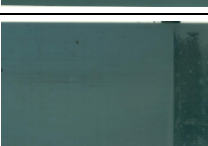
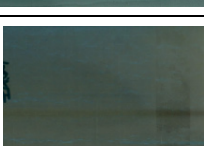
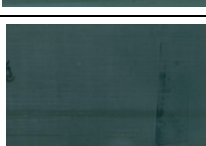
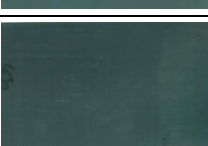
surface materials (the coating remained after annealing and the oxidized substrate beneath it) and the underlying matrix.

3.1.2 The Synergetic Effects of "O₂ + Humidity" (#H1, #H2, #H4)

In the previous section (#D1, #D4, #D8), we found out that small amounts (≤ 1.0 v/v%) of O₂ do not affect the post-annealing adhesion capability of the coating for samples annealed in the airtight furnace with dry atmosphere. However, such results oppose our previous study on the non-hermetic furnace: O₂ (introduced by "air leakage") damages the post-annealing adhesion capability of the coating and the extent of its influence is substrate (i.e., alloy composition) dependent⁽⁸⁾. Since air leakage would inevitably introduce humidity as well, the situation of the non-hermetic furnace is more complicated than expected.

To clarify the influences when O₂ and humidity coexist in the furnace atmosphere, experiments were also carried out for oxygen-containing but humid (initial dew point $\sim 0^{\circ}\text{C}$) atmospheres. The results (#H1, #H2, #H4) are summarized in Tables 5 and 6. For samples annealed in humid atmospheres that are oxygen-free (#H1), the post-annealing adhesion capability of the coating is all good. Obviously, in the absence of O₂, humidity in the furnace atmosphere (at levels like #H1) does no harm. However, if the humid furnace atmosphere is contaminated by O₂ (#H2, #H4), the post-annealing adhesion capability of the coating can be significantly damaged. That is, the "coexistence of O₂ and humidity" can trigger strong "negative synergetic" effects, just like what happened on samples S2 and S3 annealed in #H2 and #H4. It should be emphasized that at the dew point of $\sim 0^{\circ}\text{C}$, 0.025 v/v% O₂ (#H2, from the purge of 0.01 L/min O₂/N₂ (5/95 v/v%) mixed gas and 1.99 L/min humidified plant nitrogen) is enough to impose the synergetic effects. Such a low content of O₂ is far beyond the lower limit of detection for ordinary

Table 5 Tape test results of the samples annealed in the humid atmospheres: the appearance of the annealed sample with tape torn off (scanned image).

Initial dew point	#	Initial composition (v/v%)		Annealed sample after tape test		
		[O ₂]	[H ₂]	S1	S2	S3
0°C	H1	0	0			
	H2	0.025	0			
	H3	0.025	0.5			
	H4	0.2	0			
	H5	0.2	0.5			
	H6	0.5	1.0			
	H7	0.5	1.5			
	H9	1.0	3.0			

gas analyzers. Practically, the above findings can account for some cases where annealing went wrong with all the furnace parameters being kept “apparently normal”.

From the above results, neither “oxygen-containing but absolutely dry” nor “humid but absolutely oxygen-free” nitrogen atmospheres are damaging to the post-

annealing adhesion capability of the coating. However, as long as O₂ and humidity coexist in the furnace atmosphere (N₂-based), a trace amount of O₂ (0.025 v/v%) can fail the annealing! Besides, samples of substrates with lower Si and Al alloying contents (S2, S3) are more liable to be influenced by such synergetic effects.

Table 6 Tape test results of the samples annealed in the humid atmospheres: the appearance of the tape torn from the annealed sample (scanned images).

Initial dew point	#	Initial composition (v/v%)		Tape torn from the annealed sample		
		[O ₂]	[H ₂]	S1	S2	S3
0 °C	H1	0	0			
	H2	0.025	0			
	H3	0.025	0.5			
	H4	0.2	0			
	H5	0.2	0.5			
	H6	0.5	1.0			
	H7	0.5	1.5			
	H9	1.0	3.0			

Table 7 Summary of the tape test results for samples annealed in the humid atmospheres.

Initial dew point	#	Initial composition of the furnace atmosphere (v/v%)			Annealed sample after tape test*			Tape torn from the annealed sample**		
		[O ₂]	[H ₂]	[H ₂]/ [O ₂]	S1	S2	S3	S1	S2	S3
0 °C	H1	0	0	-	◎	◎	◎	◎	○	○
	H2	0.025	0	-	◎	XX	XX	◎	XX	XX
	H3	0.025	0.5	20	◎	◎	◎	◎	◎	◎
	H4	0.2	0	-	◎	X	X	◎	X	X
	H5	0.2	0.5	2.5	◎	◎	◎	◎	◎	◎
	H6	0.5	1.0	2	◎	XX	XX	◎	XX	XX
	H7	0.5	1.5	3	◎	◎	◎	◎	◎	◎
	H9	1.0	3.0	3	◎	◎	X	◎	X	XX

Sample : ◎ intact* ○ slightly exposed △ locally exposed X extendedly exposed XX completely exposed

Tape : ◎ no stain ○ slightly stained △ locally stained X extendedly stained XX completely stained

*Samples with no sign of coating peeling after the tape test were also regarded as intact even if the tape was stained.

3.1.3 Countermeasures to Suppress "The Synergetic Effects" of Humidity and Oxygen (#H3, #H5, #H6, #H7, #H9)

Practically, annealing is the most difficult to control among all the working processes of ES. And it is not easy to obtain a furnace atmosphere that is either "absolutely dry" or "absolutely oxygen-free" in mass-production factories (especially for the continuous lines). Therefore, the synergetic effects of "O₂ + humidity" introduced by

air leakage must be taken into consideration for the optimization of an annealing process.

Our previous study on the non-hermetic furnace⁽⁸⁾ had qualitatively revealed that the post-annealing adhesion capability of the coating on ES is correlated to the surface oxidation after annealing and hydrogen (H₂) can improve the annealing results. As it is hard to obtain ideal furnace atmospheres ("absolutely dry" or "absolutely oxygen-free"), as an alternative, H₂ can be

introduced into the furnace for better annealing results.

As shown in Table 2, the furnace atmospheres of experiments #H3, #H5, #H6, #H7, and #H9 contain "O₂ + humidity + H₂". From Tables 5 and 6, the introduction of hydrogen is indeed an effective method to improve the post-annealing adhesion capability of the coating for samples annealed in the furnace atmospheres that contain both humidity and O₂, as long as the H₂ content is "sufficient" (to consume the oxidizing component: O₂) to offset the negative synergetic effects of "O₂ + humidity". For example, even though hydrogen was introduced in experiments #H6 and #H9, the relative content ratio of [H₂] / [O₂] was however not high enough so the tape test on the annealed samples S2 and S3 still showed poor results.

For samples annealed in humid furnace atmospheres (#H1 ~ #H9), the tape test results are summarized in Table 7. As shown in the content ratio of [H₂] / [O₂], for furnace atmospheres with O₂ contents ≤ 0.5 v/v%, the H₂ content needs to be 3 times the O₂ content to completely suppress the negative synergetic effects of "O₂ + humidity". Moreover, the higher the O₂ content in the furnace atmosphere, the higher the [H₂] / [O₂] ratio is required.

3.2 Cross-Sectional Analysis of the Microstructure and Elemental Distribution of the Annealed ES Samples

The above results on samples S1, S2, and S3

annealed in the investigated furnace atmospheres show that both "humidity" and "O₂" are critical to the post-annealing adhesion capability of the coating. At the investigated content levels, neither "humidity" nor "O₂" can fail the adhesion "alone". However, the coating adhesion can be significantly damaged if humidity and O₂ coexist in the furnace (e.g., air leakage). And such synergetic effects can even occur at an extremely low level of O₂ (e.g., 0.025 v/v%) that is hard to be detected by ordinary gas analyzers.

To clarify how the furnace atmosphere affected the post-annealing adhesion capability, samples annealed in the humid atmosphere (initial dew point ~0°C): #H1 (humidity only), #H2 (humidity and trace O₂), #H3 (humidity, trace O₂, and H₂) were analyzed by FIB / SEM / EDS and GDS for the cross-sectional "microstructure" and "distribution of elements". The underlying reasons for good or poor post-annealing coating adhesion can thus be revealed, as described below.

3.2.1 "FIB / SEM / EDS" Cross-Sectional Analysis of the Annealed Samples

SEM images of the FIB cross sections are summarized in Table 8 for samples annealed in the humid (initial dew point ~0°C) furnace atmospheres: #H1 ~ #H3 (please note that a protecting platinum (Pt) layer was evaporated onto the surface of samples before FIB milling). The cross-sectional mapping of the elements O, Fe, and P are shown in Tables 9, 10, and 11, respectively.

Table 8 FIB / SEM cross-sectional images of the annealed samples from experiments #H1 ~ #H3 (initial dew point ~0°C)

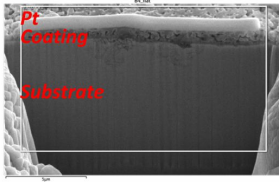
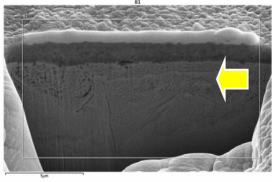
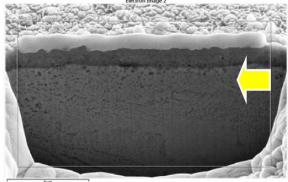
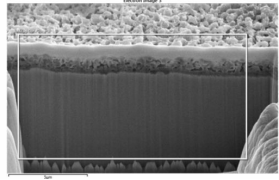
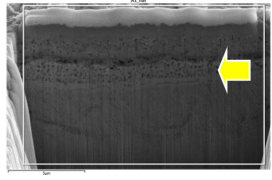
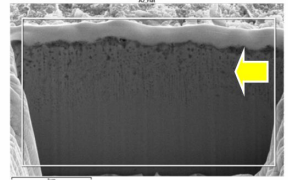
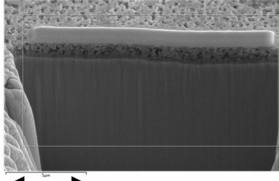
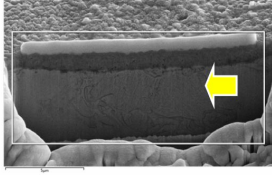
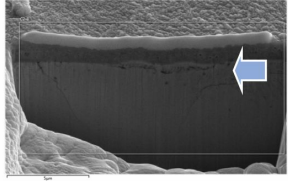
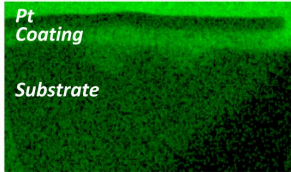
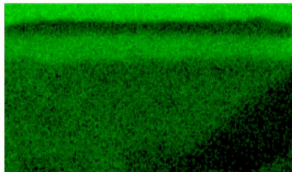
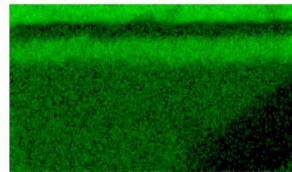
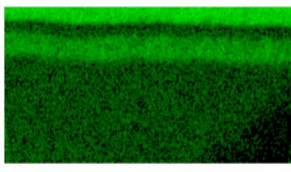
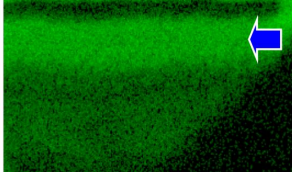
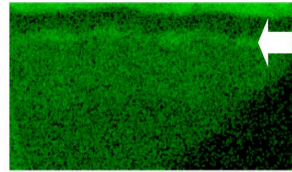
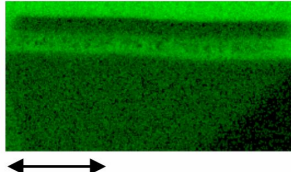
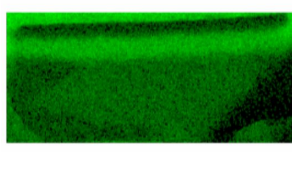
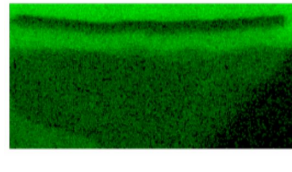
#	v/v%		S1	S2	S3
	O ₂	H ₂			
H1	0	0			
H2	0.025	0			
H3	0.025	0.5			

Table 9 The oxygen (O) mapping on FIB cross sections of the annealed samples from experiments #H1 ~ #H3 (initial dew point ~ 0°C)

#	v/v%		S1	S2	S3
	O ₂	H ₂			
H1	0	0			
H2	0.025	0			
H3	0.025	0.5			

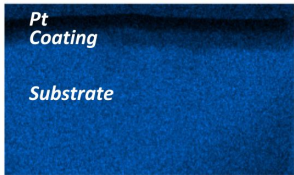
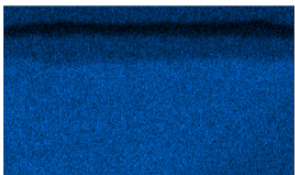
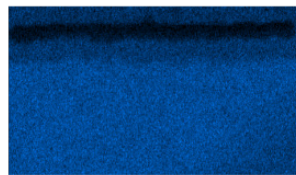
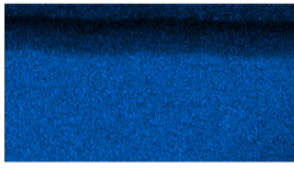
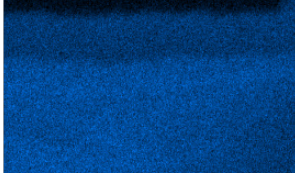
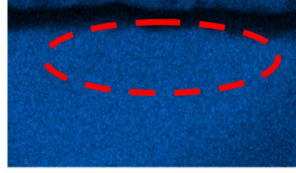
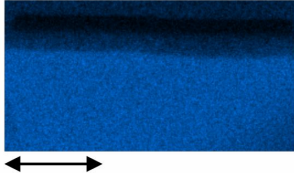


As shown in Table 8, after the annealing in #H1 (humidity only), #H2 (humidity and trace O₂), and #H3 (humidity, trace O₂, and H₂), the coating-substrate interface of sample S1 remains simple and clear. In contrast, for samples S2 and S3 annealed in the same conditions, the substrate has different morphologies in the surface region just beneath the coating (indicated by arrows) and in the underlying part. For thus annealed samples S2 and S3, the surface region of substrate just beneath the coating should have undergone some reactions by which a continuous phase (termed as “the inner reaction layer”) with different morphology and considerable thickness is formed. Nevertheless, for the sample S3 annealed in #H3 (humidity, trace O₂, and H₂), the inner reaction layer of the substrate (indicated by the blue arrow) is relatively thinner and the structure is less complicated.

Table 9 is the oxygen (O) mapping on FIB cross sections of samples annealed in #H1 (humidity only), #H2 (humidity and trace O₂), and #H3 (humidity, trace O₂, and H₂). Comparing Tables 8 and 9, the region that the O element spreads is mostly thicker than the coating itself (the coating also contains O). Obviously, after the annealing in #H1 ~ #H3, the surface region of the

substrate (just beneath the coating) has been oxidized and such a reaction is specifically called “internal oxidation”. Generally speaking, after the annealing in #H1 ~ #H3, the internal oxidation is much more obvious in samples S2 and S3 than in sample S1.

It is worth noting that the internal oxidation zone (IOZ) of S2 annealed in #H2 (humidity and trace O₂) is very thick (Table 9, the region indicated by the blue arrow). However, the IOZ of S3 annealed in the same batch is relatively thin and less concentrated (Table 9, the region indicated by the white arrow). Comparing the results of samples S2 and S3 annealed in #H2 in Tables 8 and 9, the thickness of the “internal reaction layer (Table 8)” and that of “IOZ (Table 9)” is not necessarily correlated. For example, a thick internal reaction layer was present in S3 annealed in #H2 (humidity and trace O₂), but O elements were however relatively concentrated just along the interface. Obviously, for samples annealed in #H2 (humidity and trace O₂), some kinds of reaction (e.g., “reduction”...) other than “oxidation” (formation of oxides, hydroxides, etc.) should also have occurred. Therefore, effects (i.e., the reactions initiated to the substrate) of humidity in the furnace atmosphere

Table 10 The iron (Fe) mapping on FIB cross sections of the annealed samples from experiments #H1 ~ #H3 (initial dew point ~0°C)

#	v/v%		S1	S2	S3
	O ₂	H ₂			
H1	0	0	<p>Fe Kα1</p> 	<p>Fe Kα1</p> 	<p>Fe Kα1</p> 
H2	0.025	0	<p>Fe Kα1</p> 	<p>Fe Kα1</p> 	<p>Fe Kα1</p> 
H3	0.025	0.5	<p>Fe Kα1</p>  <p>5μm</p>	<p>Fe Kα1</p> 	<p>Fe Kα1</p> 

are diversified and complicated, and how they affect can be significantly altered by the presence of trace O₂ (0.025 v/v% is sufficient).

Table 10 is the iron (Fe) mapping on FIB cross sections of samples annealed in #H1 (humidity only), #H2 (humidity and trace O₂), and #H3 (humidity, trace O₂, and H₂). Unexpectedly, the content of Fe in the surface (i.e., where the coating is) of annealed samples S2 and S3 is considerably high, while the surface Fe content in sample S1 annealed in the same conditions is significantly lower. Some Fe atoms have migrated upward from the substrate to the coating for samples S2 and S3 annealed in #H1 ~ #H3. For sample S3 annealed in #H2, the migration of Fe atoms is so significant that the coating-substrate interface has almost disappeared in the Fe map (indicated by the red dashed circle).

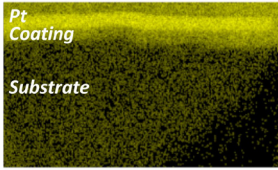
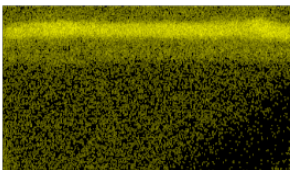
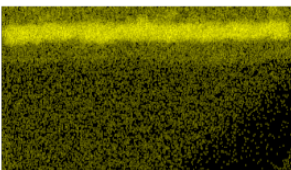
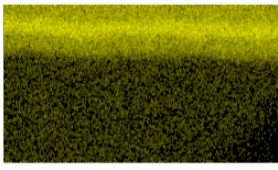
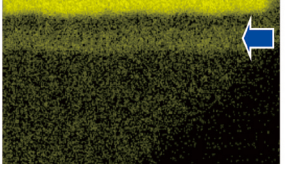
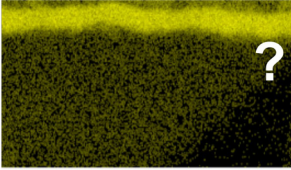
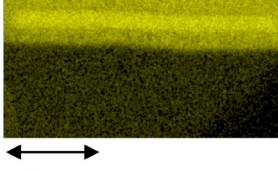
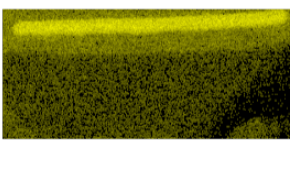
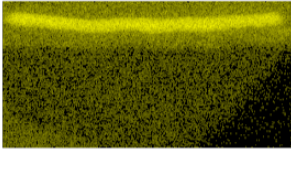
Table 11 is the phosphorus (P) mapping on FIB cross sections of samples annealed in #H1 (humidity only), #H2 (humidity and trace O₂), and #H3 (humidity, trace O₂, and H₂). Since the chromium-free coating is based on the phosphorus-containing material, the P map can indicate where the coating material is. As shown in

Table 11, most samples annealed in #H1 ~ #H3 have P atoms remaining in the original position (over the substrate), which means P atoms didn't migrate upon annealing.

However, for sample S2 annealed in #H2 (humidity and trace O₂), P atoms sunk into the substrate region beneath (indicated by the blue arrow), resulting in a continuous "phosphorus-deficient" band (the dark layer above the blue arrow) in the position where the coating was originally located. Moreover, for sample S3 annealed in the same condition, P atoms had even disappeared in the map (no sign of a P-rich zone, indicated by the white question mark) and the cross-section thus became entirely phosphorus-deficient.

According to the tape test results on samples annealed in #H1 ~ #H3 (Table 7), the samples with poor post-annealing adhesion (S2 and S3 annealed in #H2) are exactly those with "phosphorus deficiency" in the cross-section (Table 11). Therefore, the distribution of P atoms after annealing must be very critical to the post-annealing adhesion capability of the coating: an outmost P-rich band just on the surface of annealed ES (i.e., in

Table 11 The phosphorus (P) mapping on FIB cross sections of the annealed samples from experiments #H1 ~ #H3 (initial dew point $\sim 0^{\circ}\text{C}$)

#	v/v%		S1	S2	S3
	O ₂	H ₂			
H1	0	0	P K α 1 	P K α 1 	P K α 1 
			P K α 1 	P K α 1 	P K α 1 
			P K α 1 	P K α 1 	P K α 1 

5 μm

the original position where the coating should be) is required for good adhesion. If an extended phosphorus-deficient zone forms in the surface (i.e., where the coating originally is) upon annealing, it will eventually fail the coating adhesion.

From Tables 8 ~ 11, the reactions introduced by humidity and O₂ in the furnace atmosphere to the substrate are complicated and diversified. Trace O₂ with content as low as 0.025 v/v% in the furnace atmosphere can drastically change the interactions between humidity and substrate surface (beneath the coating), alter the coating-substrate interface, result in different morphologies/microstructures/distribution of elements, and ultimately destroy the post-annealing adhesion capability of the coating.

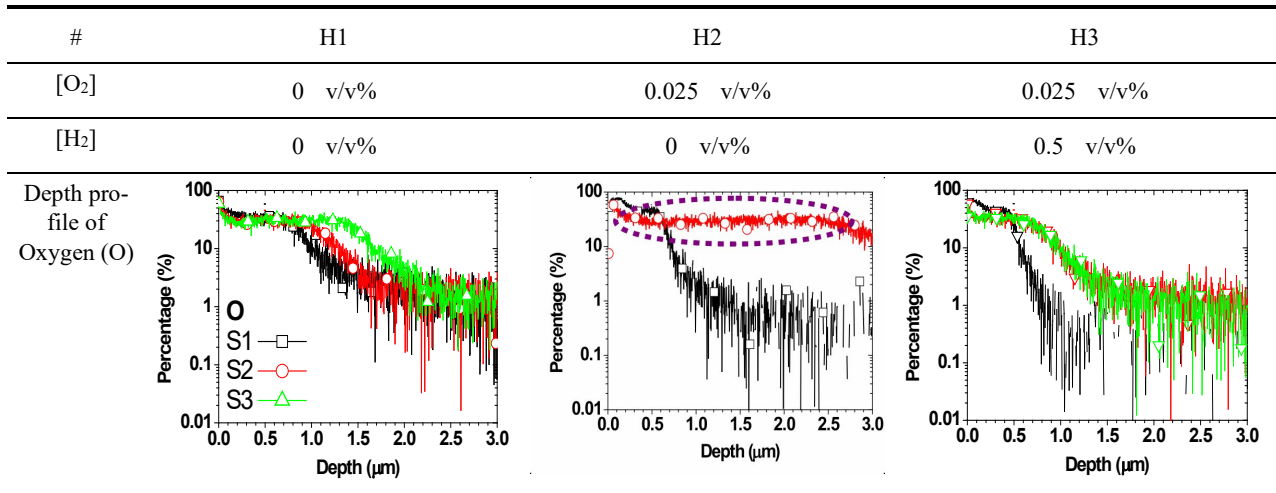
3.2.2 “GDS” Analysis: The Depth Profile of Elemental Distribution in the Annealed Samples

For samples annealed in humid atmospheres (initial dew point $\sim 0^{\circ}\text{C}$): #H1 (humidity only), #H2 (humidity and trace O₂), and #H3 (humidity, trace O₂, and H₂), the GDS depth profiles of elements "oxygen (O)", "iron (Fe)", and "phosphorus (P)" is shown in Tables 12, 13, and 14, respectively (please note the coating of S3 annealed in #H2 is too fragile, the surface had partly

peeled off before the GDS analysis and therefore results were not available for this specimen). To clarify the effects of the furnace atmosphere, samples annealed in #D1 (absolutely dry and oxygen-free) were also analyzed, the results are shown in Figures 2, 3, and 4.

Comparing Table 12 with Figure 2, the penetration depth of O atoms into the substrate is on average deeper for samples annealed in humid furnace atmospheres (#H1 ~ #H3) than those annealed in #D1 (absolutely dry and oxygen-free). That means "internal oxidation" did occur in the substrate surface (beneath the coating) for samples annealed in #H1 ~ #H3. The extent of internal oxidation differs between furnace atmospheres and substrates. The internal oxidation of annealed sample S1 was limited (#H1) or even almost absent (#H2, #H3). However, for sample S2 annealed in #H2, O atoms can penetrate the substrate as deep as ca. 2.6 μm (as indicated by the dotted circle in Table 12).

The depth profile of O atoms in sample S1 annealed in #H3 is very similar to that in this sample annealed in #D1 (absolutely dry and oxygen-free). This shows that the internal oxidation of sample S1 upon annealing can be prevented by the introduction of 0.5 v/v% hydrogen into the furnace atmosphere (to offset the negative synergetic effects of humidity and O₂). For samples S2

Table 12 The oxygen elemental GDS depth profile of the annealed samples from experiments #H1 ~ #H3 (initial dew point ~ 0°C) (Note: results were not available for sample S3 annealed in #H2 because of the poor coating adhesion.)**Fig.2.** The oxygen elemental GDS depth profile of the annealed samples from experiment #D1 (furnace atmosphere: dry pure nitrogen)

and S3 annealed in the same atmosphere #H3, the internal oxidation was however only mitigated (but not inhibited) in the presence of 0.5 v/v% hydrogen (from the comparison of results of #H3 and #D1 in Table 12 and Figure 2). The penetration depth of O atoms in samples S2 and S3 annealed in #H3 was both close to 1.0 μm , which had exceeded the thickness of the coating (Figure 2, since oxidation was absent in #D1 so the profile of O atoms is correlated to the coating with no doubt).

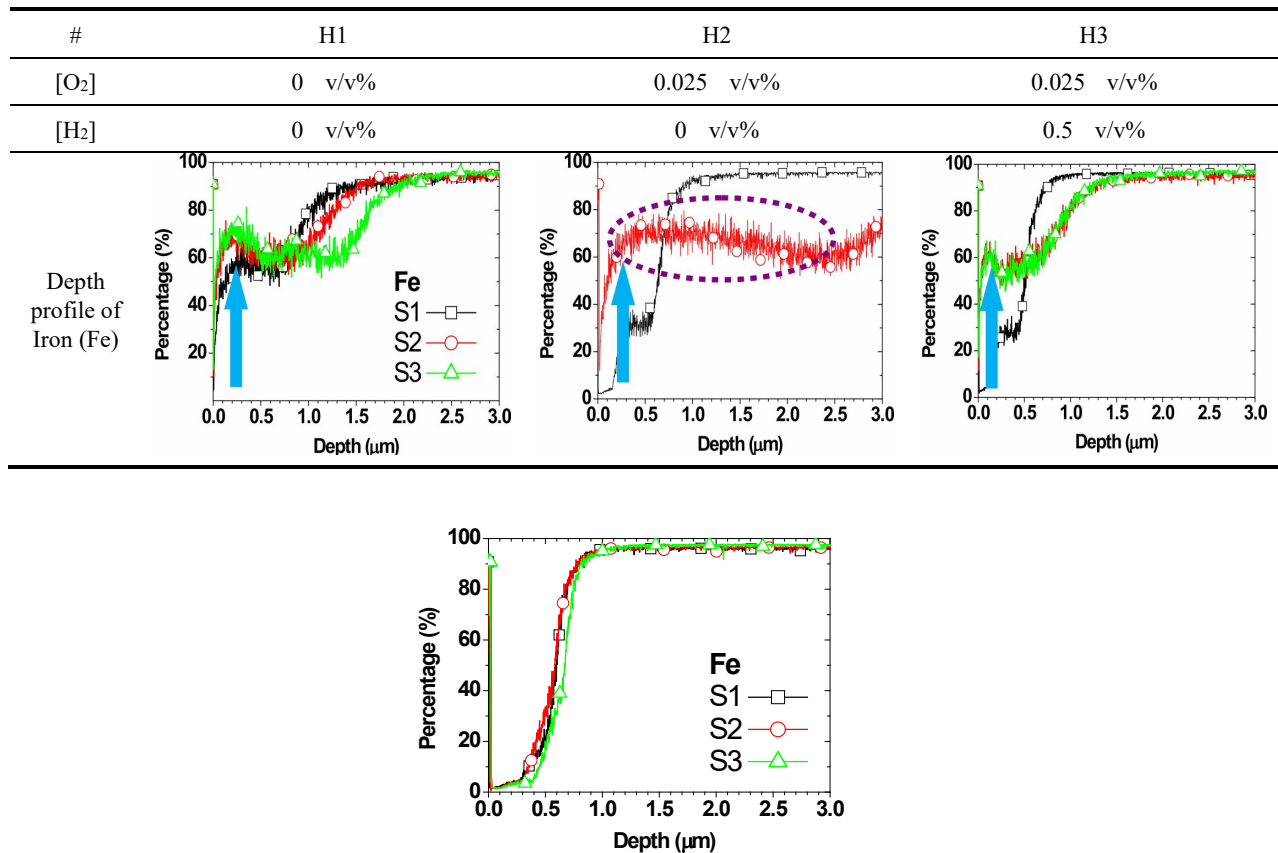
Comparing Table 13 with Figure 3, the surface Fe content is higher for samples annealed in humid furnace atmospheres (#H1 ~ #H3) than those annealed in #D1 (absolutely dry and oxygen-free) (indicated by the blue arrow), especially for samples S2 and S3 (the increased surface Fe content after annealing was less significant for S1, but still noticeable). Obviously, after the annealing in #H1 ~ #H3, some Fe atoms had migrated upward from the substrate to the coating position (depth \leq ca. 0.7 μm). As shown in Table 13, for samples S2 and S3 annealed in #H1 ~ #H3, the surface Fe content was as high as 40 ~ 70% and had become a main component of

the coating zone after the annealing. In contrast, Fe atoms stayed within the substrate for all the samples annealed in #D1.

In addition, for the sample S2 annealed in #H2 (humidity and trace O₂), the depth profile of Fe spanned from the very surface into the underlying part (by ca. 2.6 μm , as indicated by the dotted circle in Table 13). Such a result also implied that an extended internal oxidation of the substrate (beneath the coating) had occurred in this sample after the annealing (Tables 8 ~ 10 and Table 12).

Comparing Table 14 with Figure 4, an extended P profile from the coating to the substrate beneath is revealed in samples S2 and S3 annealed in #H1 (humidity only), #H2 (humidity and trace O₂), and #H3 (humidity, trace O₂, and H₂). Annealing in the above atmospheres triggered a downward migration of P atoms from the coating to the substrate. However, such migration was very limited in samples S1 annealed in #H2 and #H3 (S1 annealed in #H1 also showed such downward migration of P atoms).

It should be emphasized that: for the sample S2

Table 13 The iron elemental GDS depth profile of the annealed samples from experiments #H1 ~ #H3 (initial dew point ~0°C) (Note: results were not available for sample S3 annealed in #H2 because of the poor coating adhesion.)**Fig.3.** The iron elemental GDS depth profile of the annealed samples from experiment #D1 (furnace atmosphere: dry pure nitrogen)

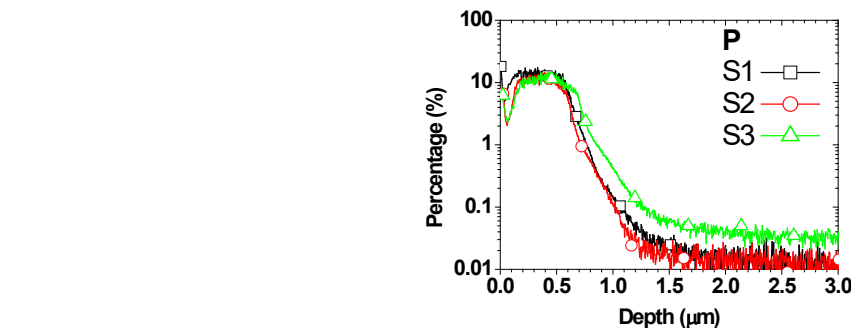
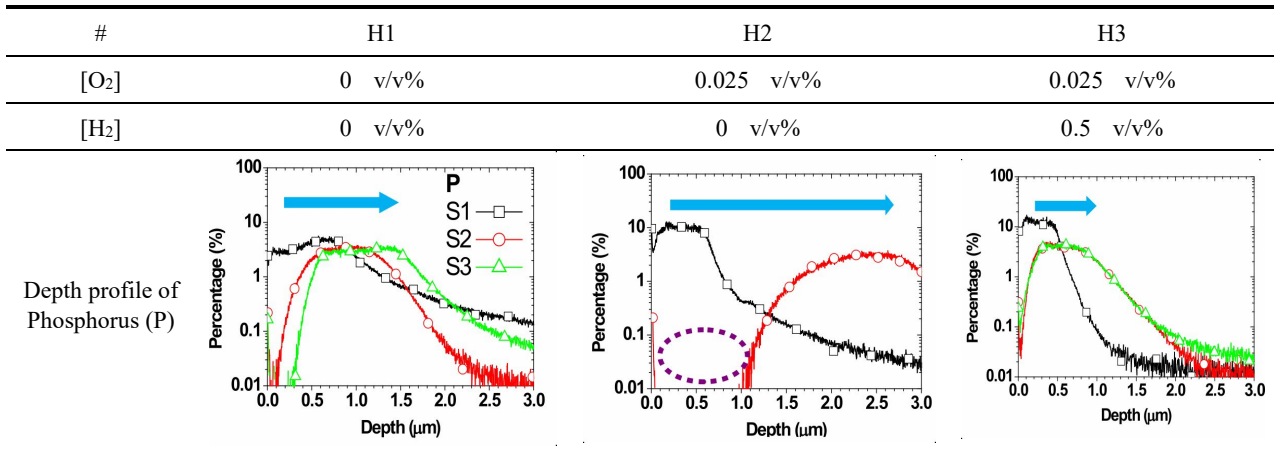
annealed in #H2, the P depth profile significantly sank into the substrate (shifted rightward in Table 14), and therefore a significant "phosphorus deficient" band was formed in the surface (as indicated by the dotted circle in Table 14). Such a result also proves the phosphorus mapping result of sample S2 annealed in #H2 (Table 11). Although the GDS analysis cannot be done for sample S3 annealed in #H2, in this case, a phosphorus-deficient zone that spreads much more deeply into the substrate is expected from the FIB/EDS results (Table 11).

From Table 7, the tape test results on samples annealed in humid atmospheres: #H1 (humidity only), #H2 (humidity and trace O₂), and #H3 (humidity, trace O₂, and H₂), the samples with poor post-annealing coating adhesion (e.g., S2 and S3 annealed in #H2) all have a phosphorous deficient zone in the surface (Tables 11 and 14). Therefore, the distribution of P atoms after annealing should be critical to the post-annealing adhesion capability of the coating. If an extended phosphorus-deficient zone forms in the surface (i.e., where the coating originally is) upon annealing, it will eventually fail the coating adhesion.

From the above FIB/SEM/EDS and GDS results, the negative synergetic effects of the coexistence of humidity and O₂ in the furnace atmosphere are the result of fatal changes in interfacial microstructure and elemental distribution of O, Fe, and P. In addition, we have also shown that introducing "sufficient" H₂ into the furnace atmosphere can protect the coating-substrate interface from being affected by humidity and O₂ (i.e., completely suppress the negative synergetic effects).

4. CONCLUSIONS

In this study, the post-annealing adhesion capability of the chromium-free coating was investigated for the coated electrical steels annealed in the "air-tight" furnace. It was shown that both "oxygen-containing but absolutely dry" and "humid but absolutely oxygen-free" furnace atmospheres (N₂-based) do not harm the post-annealing adhesion of the coating. However, this result conflicts with our previous study on the non-hermetic furnace: O₂ (from the leakage of air into the furnace) is damaging to the post-annealing adhesion of the coating. Such a contradiction is due to that air leakage introduced

Table 14 The phosphorus elemental GDS depth profile of the annealed samples from experiments #H1 ~ #H3 (initial dew point $\sim 0^\circ\text{C}$) (Note: results were not available for sample S3 annealed in #H2 because of the poor coating adhesion.)**Fig.4** The phosphorus elemental GDS depth profile of the annealed samples from experiment #D1 (furnace atmosphere: dry pure nitrogen)

not only O₂ but also humidity. More definitely, it was therefore the apparent results of “O₂ + humidity” but not the individual effects of O₂ alone that were investigated in the previous study on the non-hermetic furnace.

Unexpectedly, in this paper, results from the “air-tight” furnace revealed that the coexistence of humidity and O₂ in the furnace atmosphere can lead to strong negative synergetic effects, alter surface and interface reactions of the annealed samples, cause catastrophic changes in the morphology, microstructure, and elemental distribution around the coating-substrate interface, and ultimately result in failures of coating adhesion. It was also found that the influence of such synergetic effects is dependent on the alloy composition of the substrate.

According to the FIB / SEM / EDS and GDS analysis results on samples annealed in the furnace atmosphere with such negative synergetic effects (the coating adhesion of these samples was very poor), an extended “phosphorus (P) deficient” zone is present in the surface (i.e., where the coating should be). Therefore, the distribution of P atoms is very critical to the post-annealing adhesion capability of the coating: an

outmost P-rich zone just on the surface of annealed ES (i.e., in the original coating position) is required for good adhesion.

Practically, mass-production furnaces usually contain both humidity and O₂ (especially for continuous lines). To prevent the negative synergetic effects in such atmospheres, the introduction of “sufficient” H₂ into the furnace was proposed. We found out that, by this method, the coating-substrate interface in annealed samples can be well protected with little changes in morphology, microstructure, and elemental distribution. The H₂ content required to completely suppress the synergetic effects is ca. 3 times the O₂ content (for atmospheres with [O₂] ≤ 0.5 v/v%). However, a higher [H₂] / [O₂] ratio is needed for furnaces with higher O₂ content.

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