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Original Research Article

Examination of surface contamination and impurities in tinplate samples, both passivated and non-passivated

Amirhossein Meysami[1], Reza Amini Najafabadi[1,*], Ehsan Nemati Varnoosfaderani[2], Erfan Aghili[1], Aliasghar Foroughifar[3]

[1] *Materials Engineering Group, Golpayegan College of Engineering, Isfahan University of Technology, 87717-67498 Golpayegan, Iran*

[2] *Advanced Materials Research Center, Department of Materials Engineering, Najafabad Branch, Islamic Azad University, 85141-43131 Najafabad, Iran*

[3] *Department of Mechanical Engineering, Golpayegan College of Engineering, Isfahan University of Technology, 87717-67498 Golpayegan, Iran*

*** Corresponding author:** Reza Amini Najafabadi, r.amini@iut.ac.ir

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ABSTRACT: This study examined the surfaces of non-passivated and passivated tinplate samples, as well as the impurities present on them, using SEM, EDS, and GDOES. Additionally, solutions were analyzed using ICP in order to identify any correlations between the elements present in the solutions and on the strip surfaces. The results from GDOES indicated the presence of unwanted elements, such as Sn, S, Cr, N, P, Zn, Fe, Mn, C, and Si, on both the passivated and non-passivated sample surfaces. SEM analysis of the passivated sample revealed light and dark regions in parallel lines, which were observed ahead of the rolling direction. EDS analysis indicated that the light areas were rich in Sn while the dark areas were rich in Fe, and C was identified as an unwanted element in both areas. O and Cr were only found in the dark areas. EDS analysis of the impurities revealed Na, S, Cl, Ca, Mg, Si, N, and Al as unwanted elements. The results suggest that unwanted elements are transferred from the steel strip surface to different solutions in the tinplate line, causing pollution in various solutions.

KEYWORDS: tinplate surface; surface impurities; unwanted elements; passive

1. Introduction

Food contact surfaces play a critical role in ensuring food safety and quality[1–3]. As such, it is essential to identify and minimize potential sources of contamination, including the presence of unwanted elements on the surface of the tinplate. In identifying sources of pollution, several criteria are utilized, encompassing factors like chemical composition, environmental impact, and concentration levels[4,5]. Elements or compounds known for their harmful effects on the environment or human health are typically labeled as pollutants. However, the exclusion of substances such as viruses, bacteria, and certain compounds often stems from their biological nature or the focus on chemical pollutants. While these biological agents can cause contamination and health issues, they might not align with conventional pollutant definitions. In the context of addressing contamination on the surface of tinplate, the emphasis could be on chemical elements or compounds that adhere to the surface, potentially impacting its use or posing risks upon contact, thus prioritizing their identification and mitigation over biological contaminants. This focus allows for more effective control and management of contamination in industrial settings, aligning with the specific concerns related to surface pollutants in manufacturing or processing.

Previous studies have utilized various analytical techniques to investigate the surface layer of commercial tinplate[6–10]. For instance, in addition to the XPS method with argon ion sputtering used by Chen et al.[11], Sun et al.[12], and Azzerri et al.[13], other studies have employed techniques such as Raman spectroscopy[14], atomic force microscopy[15], and X-ray diffraction[16] to analyze the surface composition and structure of tinplate.

In this study, we employed SEM, GDOES, and EDS to investigate the presence of unwanted elements and components on both passivated and non-passivated samples of tinplate. These techniques allowed us to identify the different elements present on the surface and determine their distribution and concentration. We also utilized ICP to analyze the elements in the process solutions of the tinplate line, which helped us understand the sources of these unwanted elements and their correlation with the elements present on the polluted tinplate surface. The surface of tinplate is susceptible to contamination from a variety of sources. One major contributor is the use of raw materials that are not properly screened for impurities. Contaminants from the raw materials can find their way onto the surface of the tinplate during production, leading to an inferior product. Inadequate cleaning procedures can also be a source of unwanted elements on the surface of the tinplate. If the equipment used in the manufacturing process is not thoroughly cleaned between batches, residual contaminants can build up and transfer onto the surface of the tinplate. This can have a negative impact on the appearance and quality of the final product. Poor passivation techniques can also lead to the transfer of unwanted elements onto the surface of the tinplate. Passivation is a process used to create a protective layer on the surface of the tinplate, which helps prevent corrosion and other types of damage. If this process is not properly executed, contaminants can become trapped within the passivation layer and eventually make their way to the surface of the tinplate. To mitigate these issues, it is crucial to establish and maintain effective quality control measures throughout the production process. This includes rigorous screening of raw materials, implementing and enforcing thorough cleaning procedures, and ensuring proper execution of passivation techniques. By doing so, manufacturers can optimize their production process and deliver high-quality tinplate that is free from contamination. The novelty of this study lies in the comprehensive investigation of the presence of unwanted elements and components on both passivated and non-passivated tinplate samples using various analytical techniques such as SEM, GDOES, EDS, and ICP. While previous studies have used the XPS method with argon ion sputtering to analyze the surface layer of commercial tinplate, this study goes further by examining the potential correlation between unwanted elements in the solution used in the production and the elements present on the polluted tinplate surface. The findings of this study can contribute to the development of effective strategies to reduce the pollution of tinplate surfaces, improve production quality, and enhance customer satisfaction.

2. Experimental method

In this study, various methods were utilized to investigate the chemical composition and elements present on the surface of tinplate. Two types of samples were prepared, including non-passivated tinplate (free from any surface contamination) and passivated tinplate (with surface pollution), with dimensions of 50 mm × 50 mm × 0.25 mm and a coating mass of 2.8 g/m^2. Scanning electron microscopy (SEM) with the ZEISS EVO MA18 model from Germany was used to examine the samples using secondary electrons, electron back-scattered electrons, luminescence cathodes, and back-scattered separation detectors. For quantitative analysis, energy-dispersive X-ray spectroscopy (EDS) was utilized with the same device. To detect elements in solution samples, inductively coupled plasma spectrometry (ICP) with Integra XL construction company GBC Australia was employed. To investigate the chemical composition of the very thin layer on the surface of tinplate samples, glow discharge optical emission spectroscopy (GDOES) with the GDA 750 HR SPECTRUMA ANALYTIK GMBH company was used, which is capable of identifying up to 79 elements with a resolution of one nanometer in the analysis and can cover a depth of 200 microns. One of the novelties of this study is the utilization of GDOES to study the chemical composition of the very thin layer on the surface of tinplate samples. Moreover, the combination of SEM, EDS, ICP, and GDOES analysis provided a comprehensive understanding of the elements present on the surface of tinplate and their behavior in different solutions, which can be helpful in improving the quality and safety of food packaging materials.

3. Results and discussion

The surface morphology and microstructure of both passivated and non-passivated samples were examined using SEM and EDS analysis. The SEM and EDS results of the non-passivated sample are illustrated in **Figure 1** and **Figure 2**. The surface exhibits burrs, notches, and impurities. EDS analysis revealed the presence of O, Sn, and Fe, with Fe accounting for around 13 atomic%. As a result of the presence of impurities on the surface, further investigation was necessary. SEM analysis showed that impurities A and B were present on the surface of the non-passivated sample, as shown in **Figure 3** and **Figure 4**.

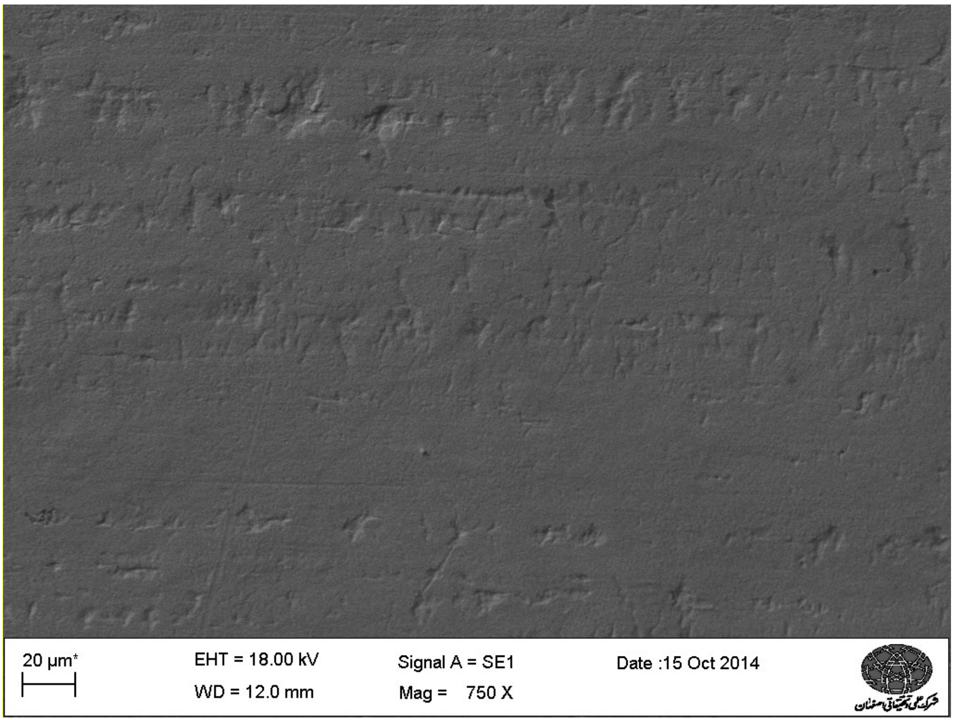
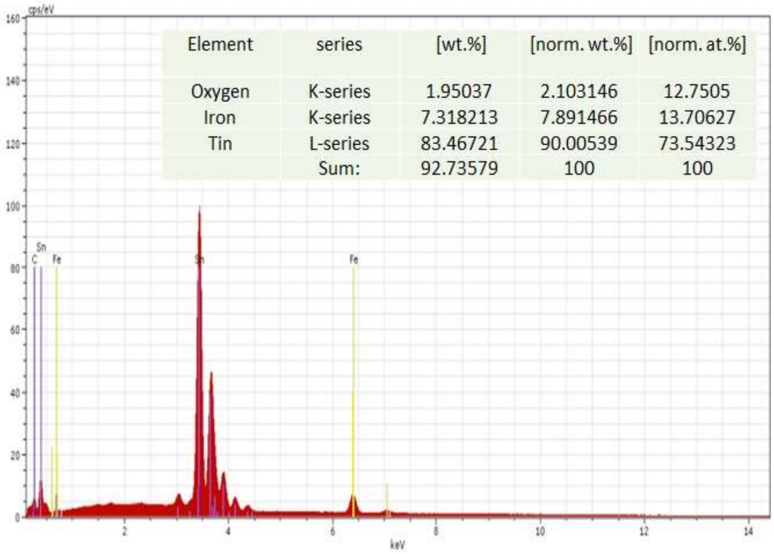


Figure 1. SEM of non-passivated sample.



Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]
Oxygen	K-series	1.95037	2.103146	12.7505
Iron	K-series	7.318213	7.891466	13.70627
Tin	L-series	83.46721	90.00539	73.54323
	Sum:	92.73579	100	100

Figure 2. EDS result of non-passivated sample.

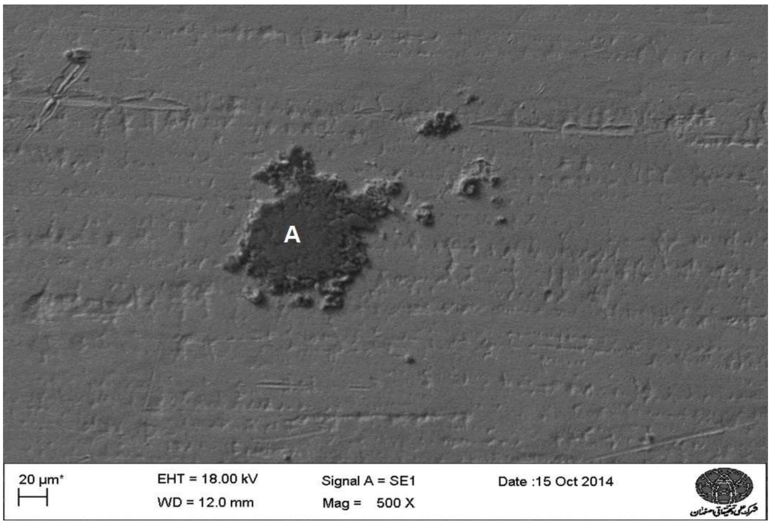


Figure 3. SEM of impurity (A) on the non-passivated sample.

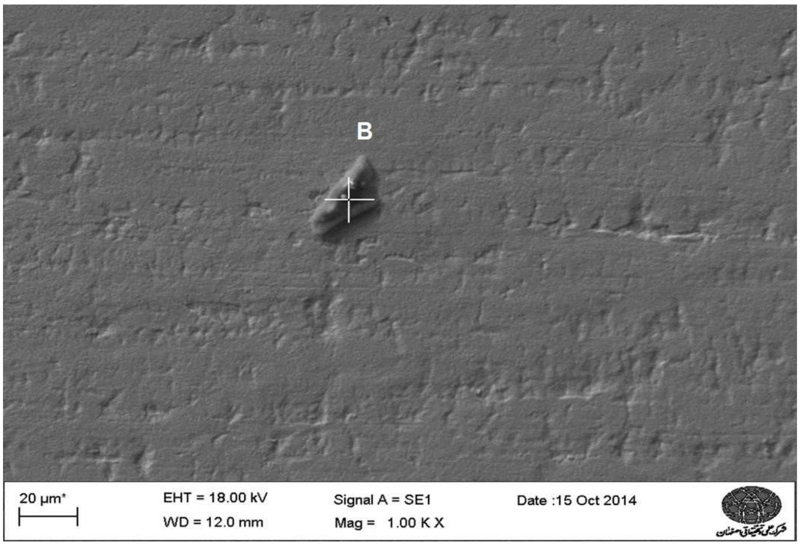
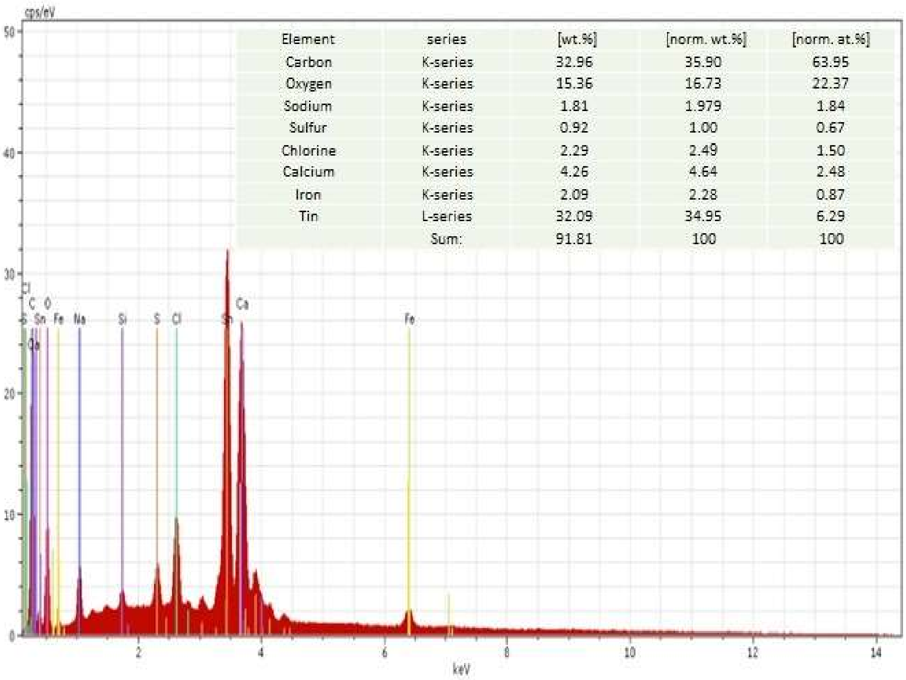


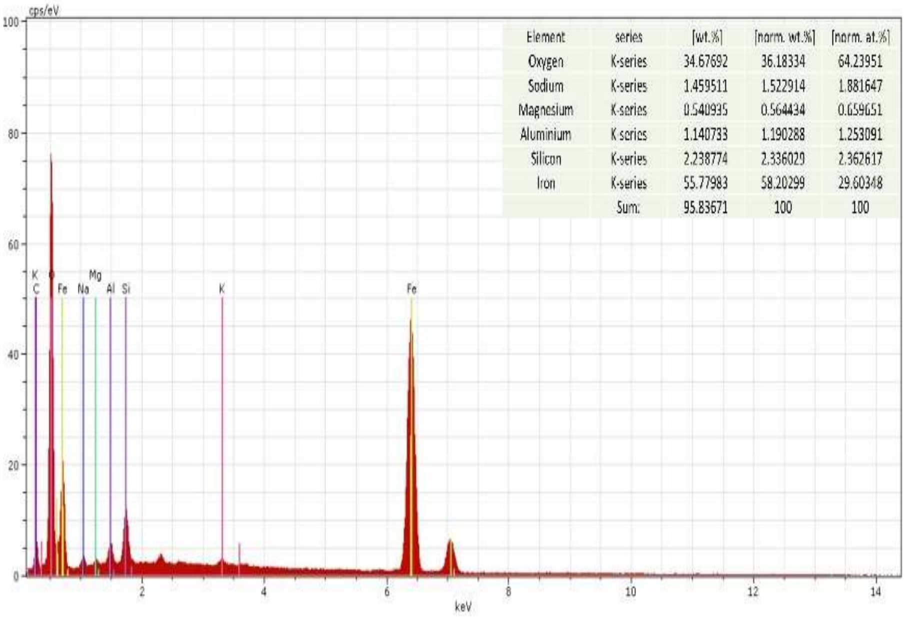
Figure 4. SEM of impurity (B) on the non-passivated sample.

The EDS analysis of these impurities (A and B) is presented in **Figure 5** and **Figure 6**. Unwanted elements, including Cl, O, Fe, S, C, Mg, Al, Si, Ca, and Na, were detected. The turbulence of the coating electrolyte may cause impurities to transfer to the strip surface. These impurities can then move to adjacent cells through the strip and contaminate their solutions as well.



Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]
Carbon	K-series	32.96	35.90	63.95
Oxygen	K-series	15.36	16.73	22.37
Sodium	K-series	1.81	1.979	1.84
Sulfur	K-series	0.92	1.00	0.67
Chlorine	K-series	2.29	2.49	1.50
Calcium	K-series	4.26	4.64	2.48
Iron	K-series	2.09	2.28	0.87
Tin	L-series	32.09	34.95	6.29
	Sum:	91.81	100	100

Figure 5. EDS result of impurity (A) on the non-passivated sample.



Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]
Oxygen	K-series	34.67692	36.18334	64.23951
Sodium	K-series	1.459511	1.522914	1.881647
Magnesium	K-series	0.540935	0.564434	0.659651
Aluminium	K-series	1.140733	1.190288	1.253091
Silicon	K-series	2.238774	2.336029	2.362617
Iron	K-series	55.77983	58.20299	29.60348
	Sum:	95.83671	100	100

Figure 6. EDS result of impurity (B) on the non-passivated sample.

The SEM result of the passivated sample is displayed in **Figure 7**. Dark and light parallel areas, indicating the rolling direction, were observed in **Figure 8**. The EDS analysis of the light and dark areas is presented in **Figure 9** and **Figure 10**, which confirmed that the dark areas were enriched in Fe with a high concentration of C as an unwanted element. Cr was also observed in the dark areas. The light areas were rich in Sn, with a high concentration of C as an unwanted element, similar to the dark areas.

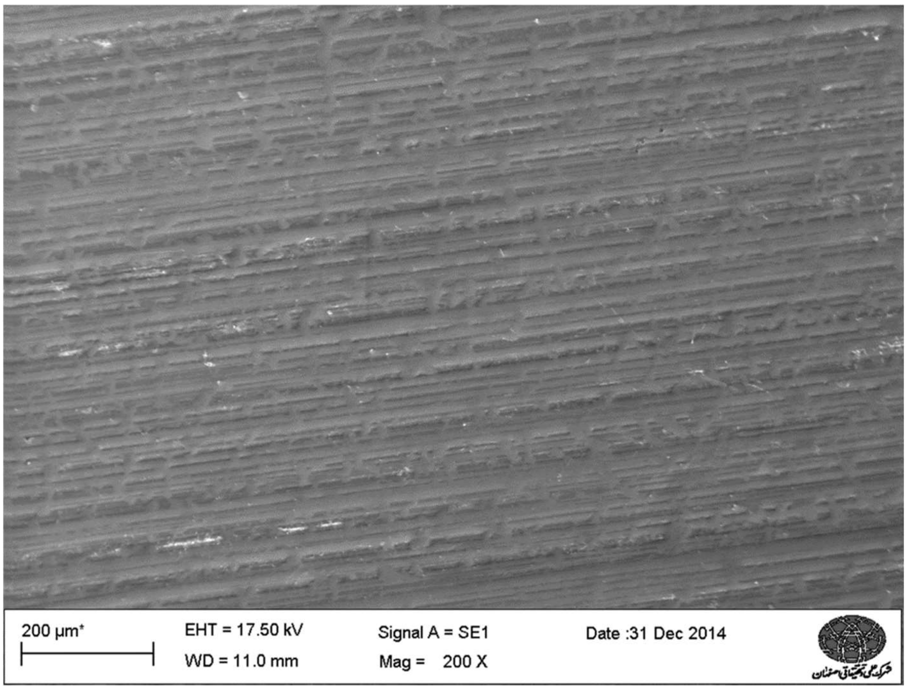


Figure 7. SEM of passivated sample.

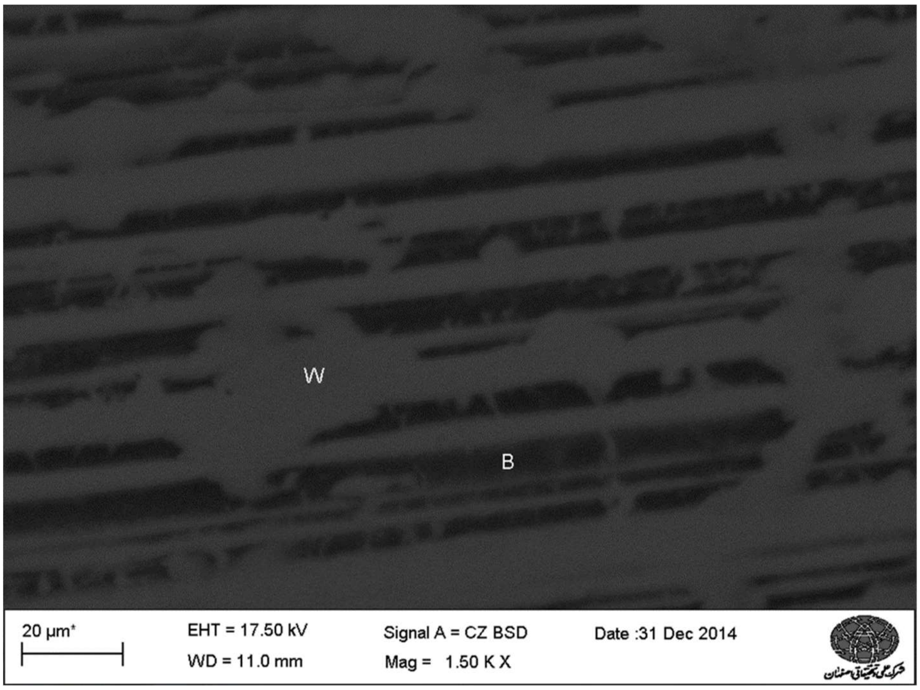
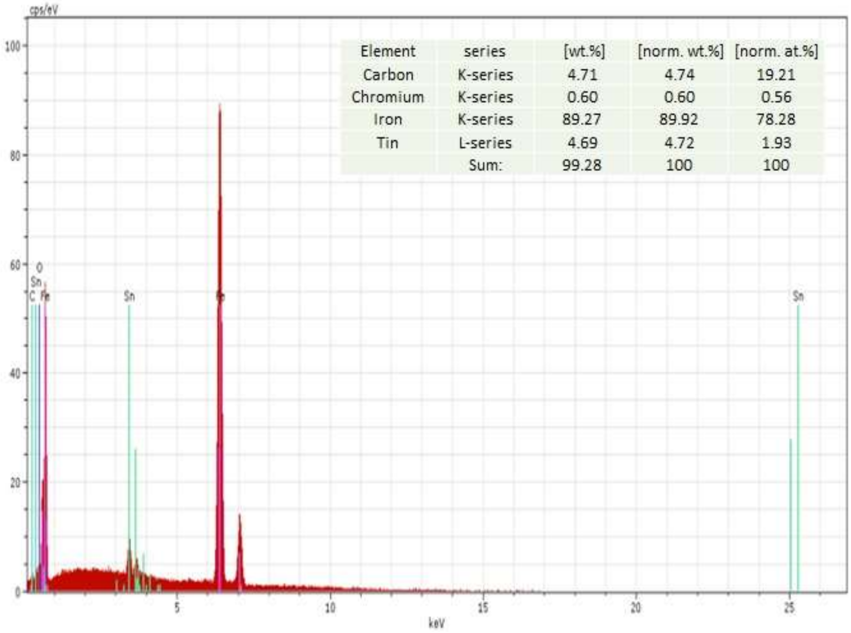
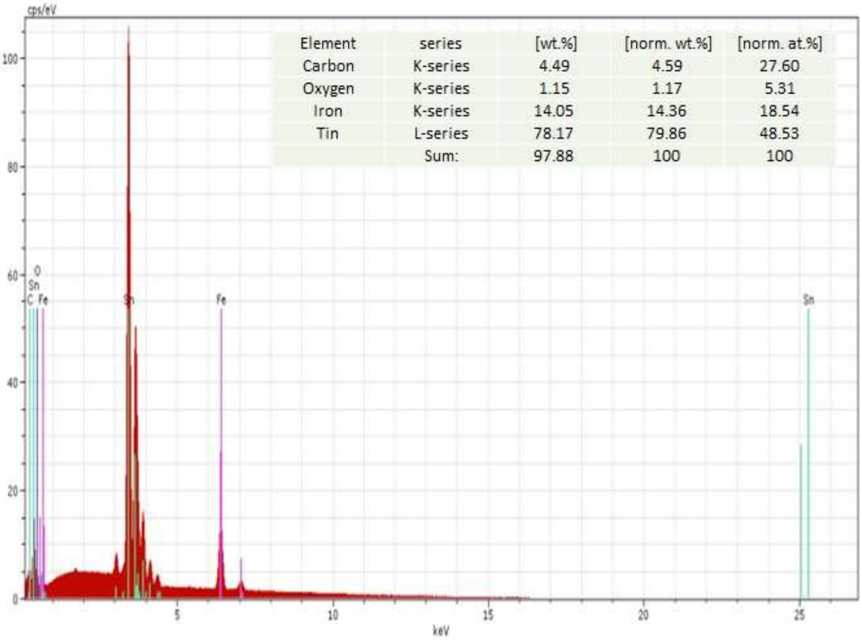


Figure 8. SEM of passivated sample on dark & light areas.



Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]
Carbon	K-series	4.71	4.74	19.21
Chromium	K-series	0.60	0.60	0.56
Iron	K-series	89.27	89.92	78.28
Tin	L-series	4.69	4.72	1.93
	Sum:	99.28	100	100

Figure 9. EDS of B point (dark area) on passivated sample.



Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]
Carbon	K-series	4.49	4.59	27.60
Oxygen	K-series	1.15	1.17	5.31
Iron	K-series	14.05	14.36	18.54
Tin	L-series	78.17	79.86	48.53
	Sum:	97.88	100	100

Figure 10. EDS of W point (light area) on passivated sample.

The oxygen content in the bright area depicted in **Figure 8** is relatively low. The relatively low oxygen content in the passive area of the tin plate can be attributed to the formation of a protective layer or film that impedes further oxidation. Tin plates often develop a passive layer. This layer acts as a barrier, reducing direct contact between the underlying metal and the surrounding environment. Consequently, the availability of oxygen for further oxidation reactions on the surface decreases, resulting in a relatively low oxygen content in the passive area of the tin plate. This protective layer helps maintain the metal's integrity while limiting the extent of oxygen interaction, thereby keeping the oxygen content comparatively low in the passive region.

There was no oxygen in the dark areas, but in the light areas, it was significantly present. Oxygen was observed due to the presence of the tin oxides SnO and SnO_2 on the surface. There was no Cr in the light areas. ICP has been used for investigating tinplate lines with different cell solutions and GDOES for the surfaces of passivated and non-passivated samples.

The chemical composition of the plating electrolyte is shown in **Table 1**. The elements Sn, S, C, and Fe in small amounts due to the dissolution of the steel strip are expected. This result is shown in the significant unwanted elements Fe, Pb, Mn, Cr, Si, and Ca. The source of the very high amount of Fe, Mn, and Si in the electrolyte is due to the frequent stoppages of steel strips in acidic plating electrolytes during the long age of this solution. At the time of the test, the solution to this study was about 12 years old.

Table 1. ICP result of plating electrolyte.

Element	Quantity (ppm)
Fe	3100
Pb	33.2
Zn	2.15
Mn	56.4
Cr	8.4
Sn	25,600
Si	10
Ni	4.6
Ca	8
S	260

The presence of Pb, Ca, and Cr is also caused by impurities in the raw materials PSA and ENSA, as well as tin anodes consumed during the life of the electrolyte. The chemical composition of the passivation solution is shown in **Table 2**. As expected, the main ingredient in the chemical composition of the solution is Cr. But the presence of Sn, Si, S, and Fe in concentrations is remarkable. According to the above results, the transmission of different elements from plating cells to the next cells by the strip surface is observable. Also, the high age of the plating electrolyte causes contamination of the solution due to the raw materials PSA, ENSA, and Sn anodes and strip stoppages.

Table 2. ICP result of passivation solution.

Element	Quantity (ppm)
Fe	3.90
Pb	0.30
Zn	0.10
Mn	0.75
Cr	1950
Sn	5.00
Si	4.00
Ni	0.50
Ca	0.50
S	5.00

The GDOES test was used for quantitative analysis of elements present on the surface layer of the sample. The results showed that for the non-passivated surface, S was detected in the first moment, and then Sn was exposed to large amounts as specified in **Figure 11**. N, P, Zn, C, and Fe were also present. In this experiment, Si and Mn were not observed. After the preliminary detection of C, it was reduced to zero by test time. In terms of priority element detection by the device, S, N, Sn, P, Zn, C, and Fe were detected on the surface in the first moments of the test. As mentioned above, a large amount of S, N, and Sn was available on the surface.

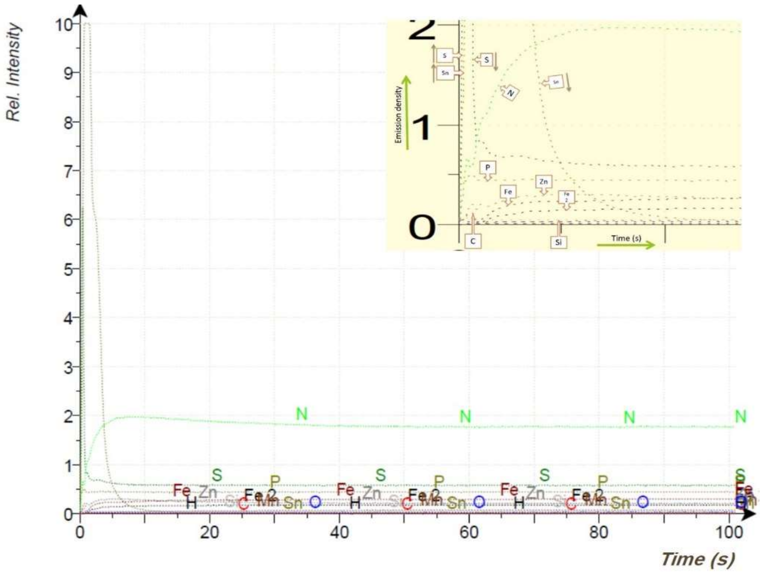


Figure 11. GDOES result of non-passivated sample.

The GDOES graph in **Figure 12** reveals the chemical composition of the pollution on the passivated surface. Upon closer inspection of the graph, high peak intensities of C, S, Zn, and Si were observed in the first moments along with abundant Sn, which declined over time. Cr also had a strong peak that completely dropped with time. Based on the peaks of N, P, Zn, Fe, and Si in the early moments, of the test, it can be concluded that in very thin profiles of the surface, Sn, S, Cr, N, P, Zn, Fe, Mn, C, and Si exist, representing the chemical composition of the pollution on the surface. In terms of priority element detection, Sn, S, N, P, Cr, Zn, Fe, Mn, and Si were the most apparent.

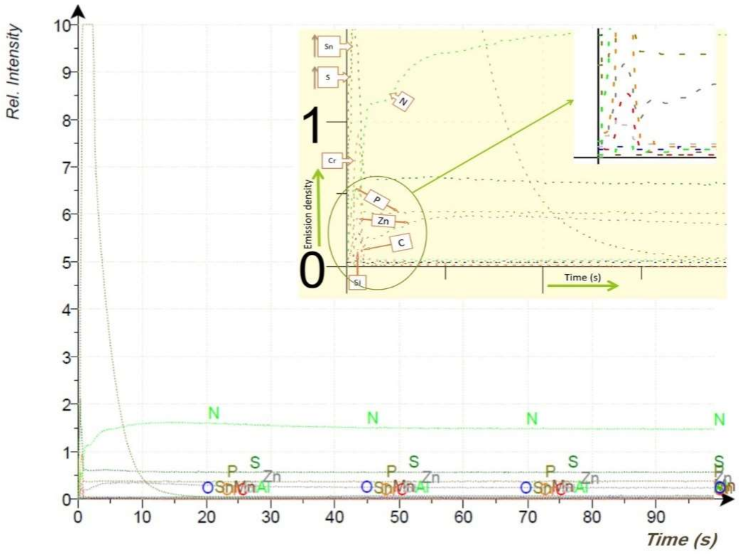


Figure 12. GDOES result of passivated sample.

Comparing the ICP results with the GDOES results shows remarkable similarities in the elements that represent the placement of unwanted elements on the Sn coating layer during electrolysis.

Applying a coefficient of 50 times on the display of S, P, and N, S and before Sn are revealed as the first element in the non-passivated sample in GDOES. This suggests that S exists on the surface of the entry strip to the passivation cell, which can prevent a correct cathodic dichromate passivation process and also dissolve in the passivating solution, infecting it as an unwanted element. S is also observable in the ICP results of the plating electrolyte as well as the passivation solution. According to GDOES analysis, nitrogen and phosphorus were found to be located beneath the strip surface, following the detection of sulfur and tin. The increase in nitrogen emissions and decrease in tin emissions suggest that the nitrogen source may be either the tin plating or surface melting sections. Phosphorus, on the other hand, is believed to have been transferred from the cleaning section to the plating section during strip processing. Si was observed in the passivation solution ICP results (**Table 2**) and contributed to an early peak in the GDOES results of the passivated sample (**Figure 12**). Cr, as well as Sn, S, N, and P, were detected in the passivated sample results. The presence of Sn in the GDOES results was attributed to its presence in the passivation solution rather than the coating process. The sequence of element detection in the passivated sample revealed the interference of C and Zn in the passivation process, with C and Zn being detected after Cr. The significant presence of C in both the EDS and GDOES results of the passivated sample indicates that the strip carries a certain amount of plating electrolyte as it passes through the cells in the line.

The experimental findings necessitate several key recommendations to enhance food packaging material quality and safety. These include the implementation of stringent monitoring protocols throughout the manufacturing process, focusing on critical stages like passivation, and refining processes to minimize the transfer of unwanted elements between different manufacturing cells. Thorough evaluation of raw materials before their use, alongside establishing stringent quality assurance measures and investing in ongoing research to explore alternative surface treatment methods, are also crucial. By adopting these measures, the study aims to reduce the presence of contaminants on tin plate surfaces, ultimately ensuring safer food contact and compliance with stringent regulatory standards. This proactive approach not only mitigates risks associated with potential contamination but also fosters long-term consumer confidence in the safety and quality of packaged food products.

4. Conclusion

The outcomes from the previous chapter's discussions are as follows:

The SEM analysis of passivated samples uncovered rolling grooves on the surface, displaying alternating dark and light areas. The tall areas in the dark regions contained elevated levels of Fe and unwanted C, while both dark and light areas revealed the presence of Cr. The light regions, rich in Sn and significant amounts of unwanted C but lacking O, indicated the presence of Sn oxide in these areas. The melting process on the surface resulted in differential Sn thickness between dip and tall regions due to the liquid Sn filling the lower areas. For non-passivated samples, impurities adhered solely to the Sn layer, indicating transfer from plating cells. EDS analysis of these impurities showcased unwanted elements in sequence—O, Fe, Cl, S, C, Mg, Al, Si, Ca, and Na. The ICP analysis of plating electrolyte coating uncovered significant unwanted elements caused by the steel strip stoppage during its 14 years of use, alongside impurities in raw materials (PSA, ENSA, Sn anode). GDOES highlighted the detection sequence—S, N, Sn, P, Zn, C, and Fe—on non-passivated samples, indicating their transfer between cells. Passivation solution ICP results emphasized Cr as the major element, with notable amounts of Sn, Si, S, and Fe. S, N, and P were detected beneath the surface layer in both passivated and non-passivated samples, while GDOES of passivated samples indicated initial high-intensity peaks of various elements, diminishing over time due to surface pollution's chemical composition. These findings suggest the transfer of unwanted elements from previous process cells during passivation electrolysis, adsorbing on the surface due to polarization and compounding surface elements at the passivation cell entrance.

Author contributions

Conceptualization, AM and RAN; methodology, ENV; software, AM; validation, RAN, AF and EA; formal analysis, AM; investigation, ENV; resources, AM; data curation, ENV; writing—original draft preparation, ENV; writing—review and editing, AM; visualization, RAN; supervision, RAN; project administration, RAN; funding acquisition, RAN. All authors have read and agreed to the published version of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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