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Effect of Lithium Ratio on Adherence Performance of Vitreous Enamel Coatings

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Abstract

Vitreous enamels which exhibit superior engineering properties such as high temperature resistance, thermal stability, high hardness, abrasion resistance and chemical inertness are frequently preferred types of coatings for improving the surface properties of metallic materials and increasing their corrosion resistance. The raw materials used in production and the oxides formed in the structure play a decisive role in the end product properties of the coating. Lithium is an essential element in vitreous enamel production that increases wetting ability without decreasing chemical resistance. It is also used as flux, nucleating agent and viscosity reducer. Lithium-containing vitreous enamels are often used for coating metals in different usage areas, for instance kitchen utensils, ovens, water heaters, thank to their low melting point and high adherence performance. Due to high cost, production and supply restrictions, lithium is being used to reduce the use of glass-ceramic structures. In this study, the effect of lithium ratio on adherence performance of vitreous enamel coatings was investigated. Vitreous enamel frit containing lithium in different proportions was prepared and applied on metallic surfaces. Chemical characterization analysis of the prepared frit were performed. The effect of lithium ratio on microstructure, acid and temperature resistance, refractoriness, surface properties and coating adherence performance of coatings were investigated.

Lityum Oranının Emaye Kaplamaların Yapışma Performansına Etkisi

Anahtar kelimeler
Emaye; Frit; Lityum; Yapışma Performansı

Öz

Yüksek sıcaklık dayanımı, ısıl kararlılık, yüksek sertlik, aşınma direnci ve kimyasal inertlik gibi üstün mühendislik özellikleri gösteren emayeler, metalik malzemelerin yüzey özelliklerinin iyileştirilmesi ve korozyona karşı direncinin arttırılması amacıyla sıklıkla tercih edilen kaplama çeşididir. Üretimde kullanılan hammaddeler ve yapıda oluşan oksitler, kaplamanın son ürün özellikleri üzerinde belirleyici rol oynamaktadır. Lityum, emaye üretiminde kimyasal dayanıklılığı azaltmadan ıslatma kabiliyetini artıran önemli bir elementtir. Ayrıca ergitici, çekirdeklenme elemanı ve viskozite azaltıcı olarak kullanılmaktadır. Lityum içeren emayeler düşük ergime noktası ve yüksek yapışma performansları sayesinde mutfak gereçleri, fırınlar, su ısıtıcıları gibi farklı kullanım alanlarındaki metallerin kaplanmasında sıklıkla kullanılmaktadır. Yüksek maliyeti, üretim ve tedariğinde kısıtlamalar olması nedeniyle lityumun cam-seramik yapılarda kullanımının azaltılması üzerine çalışmalar yapılmaktadır. Bu çalışmada lityum oranının emaye kaplamaların yapışma/tutunma performansına etkisi araştırılmıştır. Farklı oranlarda lityum içeren emaye fritleri hazırlanmıştır, metalik yüzeyler üzerine uygulanmıştır.

Hazırlanan fritlerin kimyasal karakterizasyon analizleri gerçekleştirilmiştir. Kaplamalarda lityum oranının, mikroyapı, asit ve sıcaklık dayanımı, refrakterlik, yüzey özellikleri ve kaplama yapışma performansına etkisi incelenmiştir.

1. Introduction

Vitreous enamels, also known as porcelain enamels, are glassy structure coating materials obtained by applying one or more layers on metallic surfaces (Andrews *et al.* 2011). In addition to increasing corrosion and acid resistance, high temperature resistance of enameled surfaces, enamel coatings are often preferred to achieve various aesthetic surface properties such as desired color, brightness, opacity (Andrews *et al.* 2011, Rossi *et al.* 2015, Scrinzi and Rossi 2010). They have a wide range of use in the industry, for example kitchenware, water heaters, heat exchangers, silos. (Andrews *et al.* 2011, Rossi *et al.* 2019).

Vitreous enamels consist of two main products as frit and mill additives (Andrews *et al.* 2011, Rossi *et al.* 2014). Frits are glassy structures obtained by dissolving different oxides such as sodium oxide (Na_2O), boron oxide (B_2O_3), alumina (Al_2O_3), nickel oxide (NiO), cobalt oxide (CoO), lithium oxide (Li_2O) in Silicon Oxide (SiO_2) (Andrews *et al.* 2011, Dietzel 1981). Mill additives are those such as pigments, clays, quartz, which can preferably be added according to the desired end product properties and application method of the enamel coating. Enamel coatings are generally produced by two basic methods: wet and electrostatic applications. In wet application, the frit and mill additives are made into aqueous solution and applied to the metal surface by dipping or spraying. In electrostatic application, it is ensured that the frit and mill additives, if any, are ground to the appropriate grain size to adhere to the metal surface by electrostatic theory. In both methods firing is made at 750-870 °C after application (Conde and Damborenea, 2016).

The adherence performance of enamel coatings depends on the enamel-metal interface relationship (Andrews *et al.* 2011). Increased bonding at the interface positively affects adherence performance. There are four basic theories on adherence mechanism (Eppler and Eppler, 2000):

I. Mechanical Theory

Mechanical theory is the approach in which the adherence mechanism is related to the surface area. It is based on the approach that as the surface area increases, the enamel will interact with the metal surface more and the metal surface will oxidize at the firing temperature to diffuse into the softened enamel and form dendrites. (Eppler and Eppler 2000, Greenhut and Haber 2000).

II. Chemical Theory

Chemical theory is an approach based on thermodynamic behavior of materials. During firing, the enamel melts and dissolves the oxidized iron layer on the surface. FeO enamel from metal surface reduces CoO and NiO to metallic forms (Isiksacan *et al*. 2015, Eitel 1976)

III. Electrolytical Theory

When enamel melts between iron and cobalt, a galvanic formation occurs. In this case, the iron becomes negative and the cobalt becomes the positive pole. By melting, a current from iron to cobalt occurs. It is composed of angled cavities with galvanic current. Enamel is filled and mechanically adherence (Dietzel 1981, *King et al. 1959)*

IV. Diffusion Theory

At high temperatures, where the metal ions in the glass and the atoms in the metal are relatively mobile, there is a constant change in the glass-metal interface. Metal ions from glass spread to metal, gain electrons and become metal atoms.

Metal atoms are dispersed on the glass and ionized. Thus, a dynamic equilibrium is formed at the glass-metal interface with the appropriate oxide of the glass base metal. This balance contributes to adherence performance (King *et al. 1959)*.

Lithium is not used as direct adhesion promoter such as nickel and cobalt in enamel (Andrwes *et al.* 2011, Shieu *et al.* 1999). Lithium is used in vitreous enamel production to increase wetting ability without reducing chemical resistance and also used as flux, nucleating agent and viscosity reducer (Andrews *et al.* 2011). Increasing importance of energy storage with advancing technology has increased lithium prices. In addition, there are restrictions on the supply of lithium by government regulations. Therefore, studies are being carried out to reduce the lithium content in glass-ceramic structures without loss of mechanical and chemical properties.

In this study, frit obtained by using lithium carbonate which is used as raw material in different ratios were applied to metal surfaces by electrostatic method without mill additive and effect of lithium ratio on enamel coating adhesion performance was investigated.

2. Materials and Methods

2.1 Frit Preparation

In this study, T16 frit, which is the commercial product of Gizemfrit, was used. The lithium carbonate ratio in the frit was assumed to be 100%, and mixtures containing 75% 50% and 25% lithium carbonate, the remaining amounts of other raw materials, were prepared and named as L100, L75 and L50 and L25 according to the lithium carbonate ratios. The mixtures were melted in a crucible at 1200-1400 °C for 45 minutes and cooled by pouring into water. The obtained frit was milled in 300 g batches with a total weight of 750 g alumina balls with a diameter of 1-1.5 cm and 1 ml silicone oil in a 300 RPM mill for 15 minutes. The milled frit was passed through a 80 mesh (197 micron) sieve. Atomic absorption spectrometry (PG Instrument PG-990 AAS) analysis were performed for the determination of lithium content and XRF (Bruker AXS S8 Tiger) analysis were performed for the determination of oxide composition of prepared frits.

2.2 Metal Coating

Prepared milled frits, 10x10cm and 0.5mm thickness DC01EK (EN10027–1) norms of the plate, electrostatic method with the front surface of 6 g of the back surface of 4 grams of one layer was applied. Surface preparation processes for example primer frit, acid washing and nickel flashing were not performed. Frit-coated plates were fired in a laboratory type furnace (Protherm - PLF110) at 820°C for 4 minutes. The fired plates were cooled at room temperature.

2.3 Color Measurement and Citric Acid Testing

SCE color measurement (Konica Minolta - Spectrophotometer CM-700d) of enamel coated plates was performed. Then citric acid test was performed in accordance with EN ISO 28706-1 standard. The solution was prepared by adding 10 g of citric acid in 100 ml of bidistilled water. 4 ml of the prepared mixture was applied to each sample and closed by cap to avoid evaporation for 15 minutes. The surface was washed with water and dried at room temperature.

2.4 Coating Thickness and Adhesion Test

The thickness of the enamel coatings was measured and the locations of similar thicknesses were marked for adhesion testing. Adhesion test was carried out in accordance with BS EN 10209 standard. A hemispherical punch with a diameter of 1.5 kg and a diameter of 22 mm was placed on the sample surface at a height of 300 mm.

2.5 Optical Microscopy and Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy Analysis (EDS)

Areas subjected to adhesion testing were imaged with optical microscope (Olympus LC30 - SZ61TR). Samples were then taken from the untested areas of the plate and SEM (JEOL JSM-6060) - EDS (IXRF-EDS-2004) analysis were performed. The acceleration voltage is 15 kv and the working distance is 14 mm. BSE images were taken from the sample surfaces at x100, x250, x500 and x750 magnifications. In addition, EDS analysis were taken from various points of sample surfaces at x750 magnification. Section images were taken as SE at x500, x750 and x1000 magnifications.

3. Results and Discussion

AAS and XRF analyzes were performed to determine the oxide composition and lithium content of the frit after melting. In the analysis, it was measured that the lithium oxide content in the frit composition decreased with the decrease of lithium carbonate ratio without altering other raw material amounts and melting-cooling parameters (Table 1). With the decrease of lithium ratio, the ratios of R_2O, RO and RO_2 groups increase.

As the lithium content decreases in frit composition, discoloration and hardening are expected to decrease. By keeping the firing parameters constant, the energy required to melt the lithium which has become residual has caused the enamel surface to burn and darken. SCE color measurements with the spectrophotometer shown in Table 2 confirm this approach.

The acid resistance of enamel coatings varies according to the acid type. Silica ratio is the most important parameter determining the acid resistance of the enamel. The effect of lithium ratio on the acid resistance of enamels is negligible. As shown in Figure 1, the citric acid resistance of the enamel containing different amounts of lithium is similar.

Table 1. XRF and AAS Results of Prepared Frit

		L100	**L75**	**L50**	**L25**
R_2O	**Na_2O, K_2O**	12,65	12,93	12,95	13,24
RO	**BaO, MnO, CoO, CuO, CaO**	6,85	7,18	7,16	7,07
R_2O_3	**B_2O_3, Fe_2O_3, Al_2O3, Sb2O3**	18,54	18,22	17,60	17,92
RO_2	**SiO_2, TiO_2**	58,26	58,40	59,68	59,78
RO_3	**MoO_3**	0,30	0,31	0,30	0,32
R	**F**	0,50	0,76	0,73	0,76
	Li_2O	2,90	2,20	1,58	0,91
	Total	100,0	100,0	100,0	100,0

Table 2. SCE Colour Measurement Result

	L100	**L75**	**L50**	**L25**
L	10,120	10,190	8,63	7,390
a	-0,950	-0,920	-1,43	-1,270
b	-8,130	-7,200	-6,26	-5,470

The adhesion test of enamels is carried out according to the standard classification specified in BS EN 10209 (Figure 2). L100 and L75 samples showed good adhesion. However, as lithium content decreased, adhesion performance decreased (Figure 3). The reason for the decrease is that with the decrease of lithium, the glass-ceramic structure does not show the desired properties as in the standard sample. Lithium is used as a melter in enamel structures. The lithium depletion hardens the glass-ceramic structure. In addition, expansion coefficient and wetting ability are reduced. The hard glass-ceramic structure cannot be homogeneously distributed to the metal surface during cooling after firing and cannot form any bonding mechanism with the surface. SEM images from cross-sectional surfaces support this approach.

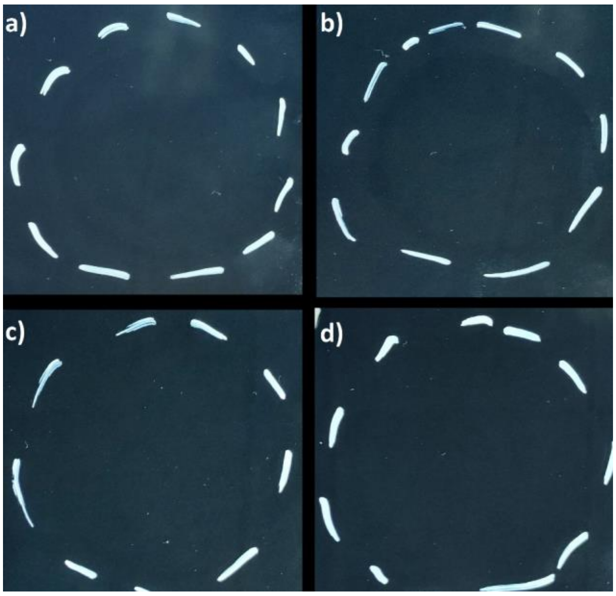


Figure 1. Enamel Citric Acid Test Images
a)L100 b)L75 c)L50 d)L25

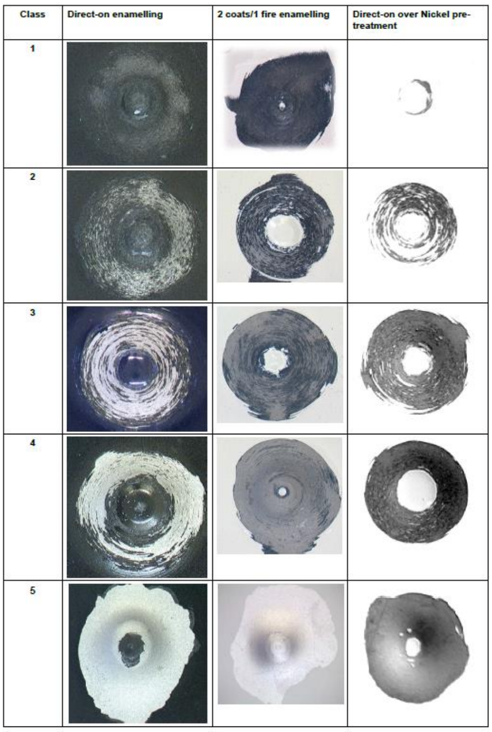
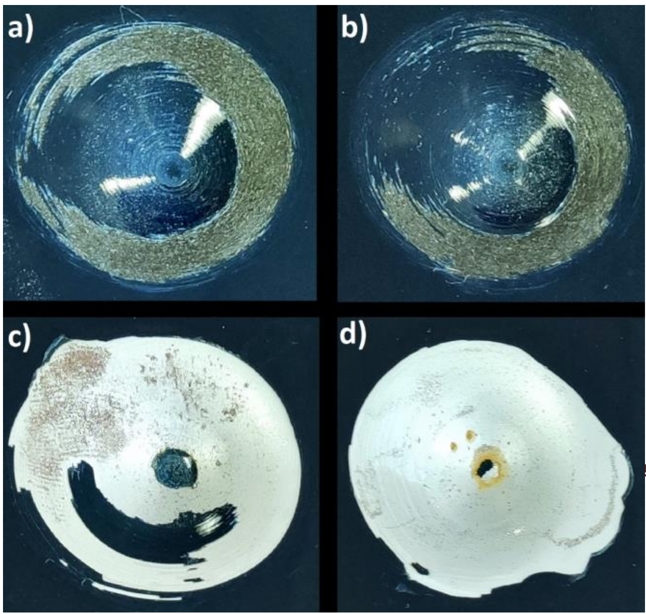


Figure 2. Adhesion Performance Classification Examples



according to BS EN 10209

Figure 3. Adhesion Test Image of Samples
a)L100 b)L75 c)L50 d)L25

Figure 4 shows the optical microscope images of the samples after the adhesion test. As the lithium rate decreased, adhesion decreased, while the rate fell below 50%, adhesion was not observed. In the L50 and L25 samples, after the test, the enamel coating was completely removed to reveal the base metal. In addition, with the reduction of the lithium content, the impact areas of the enamel coating began to detach larger parts of the edges during the test.

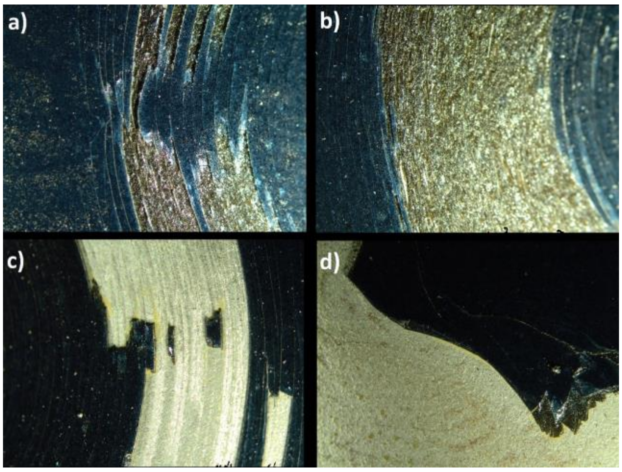


Figure 4. Optical Microscopy Images after Adhesion Testing of Samples a) L100 b) L75 c) L50 d) L25

Although the lithium content decreased, the thermal behavior of the glass-ceramic structure has lost homogeneity with the given energy remaining constant. Therefore, residual stresses and microfractures have formed in the enamel structure. During the adhesion test, the resulting defects affected enamel coating breakages and separation from the metal surface, and no homogeneous image could be obtained as seen in the L50 sample.

When the SEM images of the L100 coded standard sample were examined, no residues or defects were observed except for pit defects due to firing (Figure 5). As shown in Figure 6 and Table 3, field EDS results are consistent with the frit composition.

Elt.	Line	Intensity	Error	Conc	Units
		(c/s)	2-sig		
O	Ka	134.96	7.346	43.091	wt.%
Na	Ka	44.13	4.201	6.935	wt.%
Al	Ka	24.63	3.138	2.879	wt.%
Si	Ka	307.30	11.084	34.690	wt.%
K	Ka	16.29	2.552	2.544	wt.%
Ti	Ka	17.88	2.674	3.882	wt.%
Mn	Ka	5.38	1.467	1.849	wt.%
Fe	Ka	5.62	1.499	2.288	wt.%
Zn	Ka	1.29	0.717	1.533	wt.%
Zr	La	0.93	0.610	0.310	wt.%
			Total:	100.000	wt.%

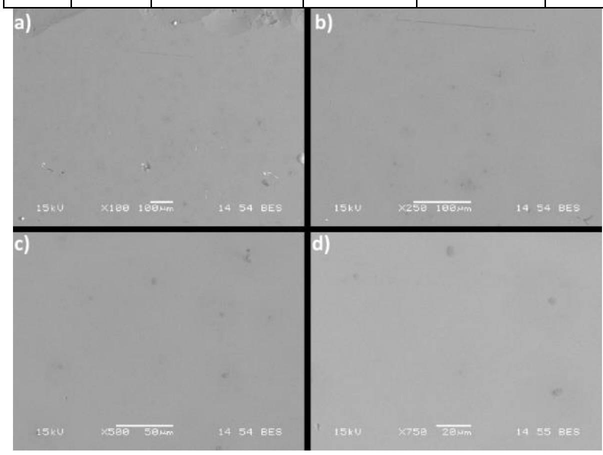


Figure 5. SEM images of the L100 sample at different magnifications a) x100 b) x250 c) x500 d) x750

Table 3. EDS Analysis of L100 at x750 magnification

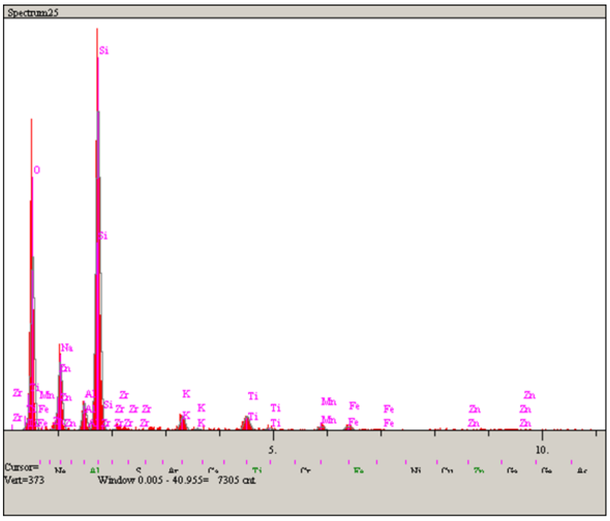


Figure 6. EDS analysis graph of L100 sample at x750 magnification

With the reduction of lithium, the hardness of the enamel coating was increased, thus reducing the surface wetting ability. As seen in Figure 7, surface defects began to become clearer as lithium content decreased.

Another factor affecting the coating performance of enamel coatings is the surface properties of the base metal. Residues of organic compounds and corrosion on the base metal affect the adhesion performance of the enamel. Reduction of the lithium content reduces the diffusion of the enamel to the surface and increases the ability to cover defects from the base metal.

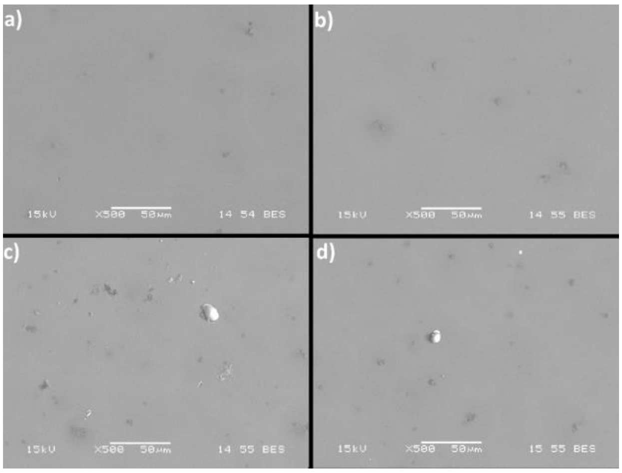


Figure 7. SEM images of the samples at X500 magnification

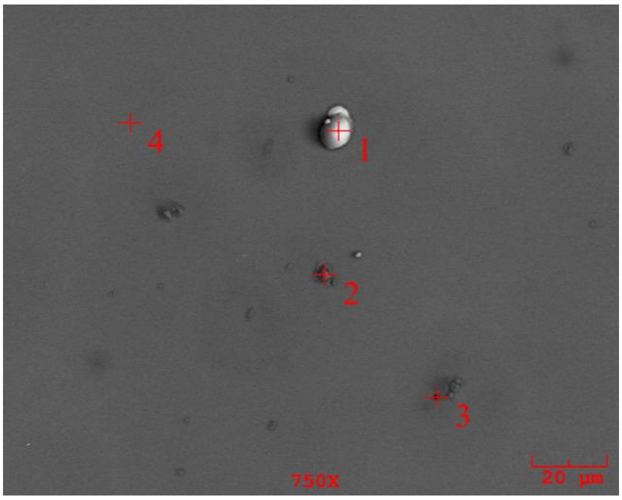


Figure 8. EDS Analysis Points of L25 sample at x750 magnification

Some differences are observed as a result of EDS analysis from different regions of L25 sample

(Figure 8). In SEM images, elements with a high atomic number give a brighter image. When the EDS analysis of point 1 (Table 4-a) is considered, it is understood that the element which gives a bright image is iron. This region, which is greater than the amount of iron oxide in the enamel composition, is understood to be due to the degradation of the coating performance of the enamel and the failure of the base metal to cover surface defects.

In Figure 8, the results of EDS analysis points 2 and 3 show similarity and high amounts of aluminum are observed (Table 4-b, Table 4-c). Although there is no change in the amount of alumina entering the frit structure compared to the standard sample, there are two possibilities for the presence of high amounts of aluminum on the sample surface. The first option is the inclusion of alumina as an inclusion from the furnace refractories to the frit structure during melting due to unchanged melting parameters. The second option is the alumina contamination between the frit and the homogeneous distribution of alumina inclusions in the powder during grinding due to the fact that the grinding parameters do not change and the frit hardness due to lithium reduction increases.

As shown in Table 4-d, EDS analysis on the normal surface of the enamel is similar to the oxide composition.

Table 4. EDS analysis of L25 Sample at x750 magnification
a) 1.point b) 2.point c) 3.point d) 4.point

a)

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
O	Ka	192.94	8.782	33.301	wt.%
Na	Ka	0.00	0.000	0.000	wt.%
Al	Ka	2.41	0.983	0.325	wt.%
Si	Ka	8.96	1.892	1.044	wt.%
K	Ka	1.83	0.856	0.224	wt.%
Ti	Ka	4.12	1.283	0.614	wt.%
Mn	Ka	0.95	0.617	0.248	wt.%
Fe	Ka	189.81	8.711	63.054	wt.%
Zn	Ka	0.60	0.491	0.598	wt.%
Zr	La	2.44	0.987	0.592	wt.%
			Total	100.000	wt.%

b)

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
O	Ka	155.76	7.892	35.527	wt.%
Na	Ka	24.18	3.110	2.523	wt.%
Al	Ka	576.63	15.185	47.225	wt.%
Si	Ka	79.51	5.638	9.464	wt.%
K	Ka	14.50	2.408	1.778	wt.%
Ti	Ka	4.32	1.315	0.732	wt.%
Mn	Ka	1.38	0.742	0.366	wt.%
Fe	Ka	1.86	0.862	0.583	wt.%
Zn	Ka	1.70	0.826	1.570	wt.%
Zr	La	0.86	0.588	0.232	wt.%
				100.000	wt.%

b)

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
O	Ka	149.31	7.728	47.659	wt.%
Na	Ka	21.96	2.964	3.411	wt.%
Al	Ka	14.08	2.373	1.558	wt.%
Si	Ka	338.90	11.642	36.118	wt.%
K	Ka	17.22	2.624	2.634	wt.%
Ti	Ka	21.26	2.916	4.539	wt.%
Mn	Ka	4.24	1.302	1.433	wt.%
Fe	Ka	3.29	1.147	1.317	wt.%
Zn	Ka	0.38	0.389	0.443	wt.%
Zr	La	2.76	1.051	0.889	wt.%
			Total	100.000	wt.%

d)

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
O	Ka	134.21	7.326	36.281	wt.%
Na	Ka	35.26	3.755	4.388	wt.%
Al	Ka	352.80	11.879	34.552	wt.%
Si	Ka	144.59	7.605	18.396	wt.%
K	Ka	11.30	2.126	1.613	wt.%
Ti	Ka	4.86	1.395	0.957	wt.%
Mn	Ka	1.12	0.668	0.344	wt.%
Fe	Ka	1.73	0.832	0.630	wt.%
Zn	Ka	2.04	0.904	2.184	wt.%
Zr	La	2.11	0.918	0.657	wt.%
			Total	100.000	wt.%

As shown in Figure 9, a strong intermetallic bond was formed at the enamel - metal interface in the standard sample. In Figure 10, the bond at the interface was preserved despite the decrease in the lithium content. As Figures 11 and 12 show, although the proportion of nickel and cobalt-containing oxides increases as the lithium content decreases, the probability of bond formation at the interface is get weakened and the bonded areas remain less than the non-bonded areas. Figure 12 also shows surface defects in the enamel coating. The hardening of the frit with the reduction of lithium, micro-fracture during cooling can not provide stability.

Adhesion test results confirm cross-sectional SEM images. The adhesion tests of the L100 and L75 samples with storng enamel-metal bonds at the interface scored high and the adhesion tests of L50 and L25 samples scored the lowest according to the standard.

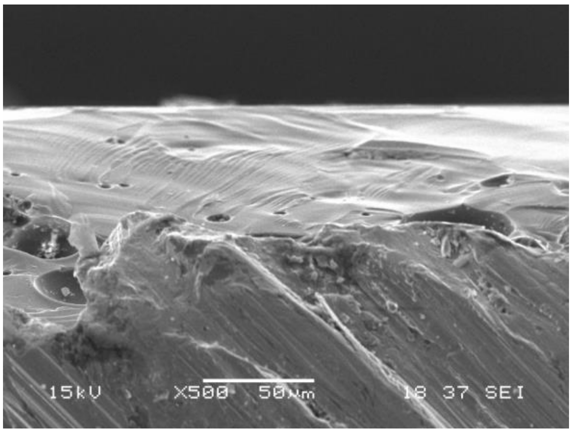


Figure 9. L100 Cross section SEM Image

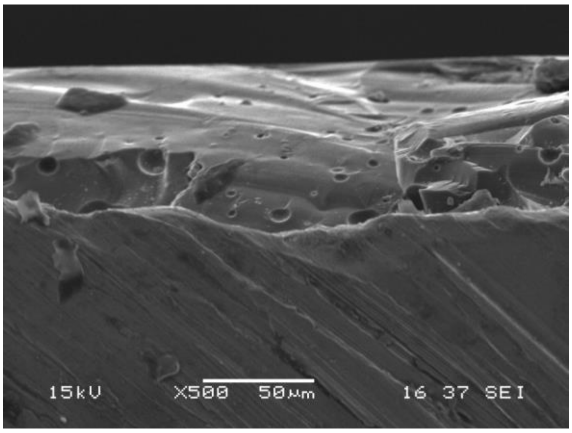


Figure 10. L75 Cross section SEM Image

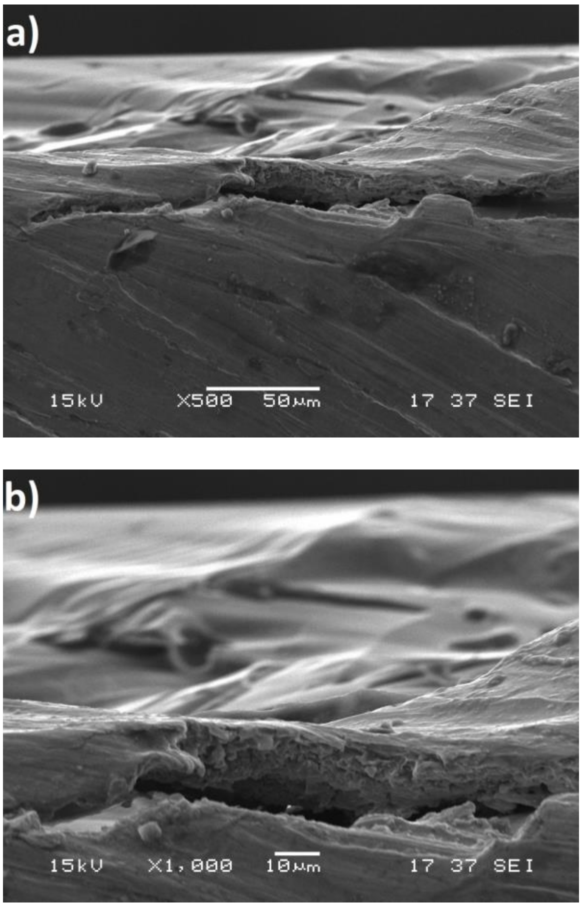
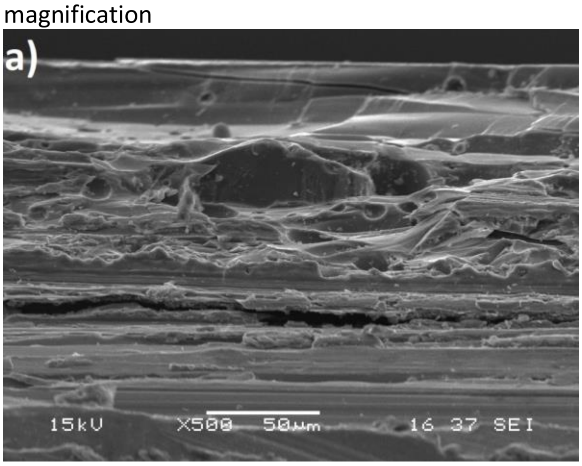


Figure 12. L50 Cross Section Image a) x500 b) x1000 magnification



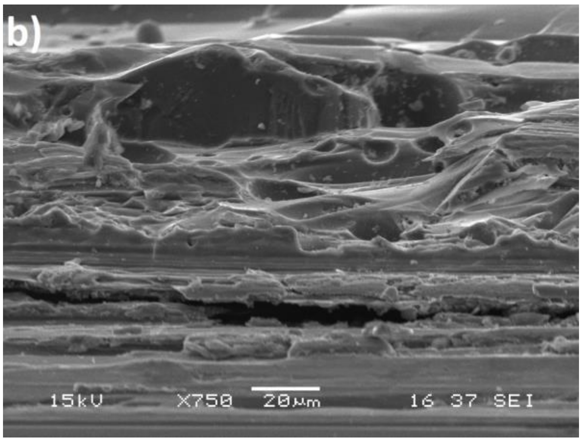


Figure 13. L25 Section SEM Image a) x500 b) x750 magnification

4. Conclusions

In this study, frit containing different ratios of lithium carbonate was prepared and applied on metal surfaces by electrostatic method. Adhesion, color and citric acid tests were performed on enamel coated plates. The samples were imaged by optical microscope and microstructure examination was performed by SEM-EDS analysis. As a result of the tests and analyses, it was observed that the lithium ratio decreased and intermetallic bond formation decreased at the enamel-metal interface. The adhesion test performance of the samples with low intermetallic bonds was found to be low. Furthermore, with the reduction of the lithium content, the sealing performance of the surface defects of the base metal of the enamel decreased. Due to the increase in hardness, the frit became brittle, the surface wetting ability decreased and the micro-fractures in the enamel, except for the decrease in bonding to the metal surface.

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