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Investigation of Nickel Effects on Matt Cast Iron Enamel

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Abstract:

Cast iron is the generic name for iron-carbon alloys containing more than 2% carbon content. It can melt at low temperatures compared to steel and has low cost. The surfaces of cast irons, which can be used in many areas from construction to kitchen equipment, are coated with enamel to prevent corrosion, increase wear resistance and easy to clean. Enamels are glassy coating materials obtained by adding various oxides such as Al_2O_3, B_2O_3, ZrO_2, NiO, CoO into SiO_2. The raw materials used and the oxides formed during production have a direct effect on the end product properties of the enamel. NiO and CoO are the most essential oxides affecting the bonding performance of the enamel to the metallic surface. Although NiO has little effect on glassy structures, it improves the adherence performance. It is also effective on the aesthetic appearance of the enamel. It gives a dark color to the enamel and prevents fish scale defects, with the latest regulations, the use of nickel in enamels has been restricted for health and environmental safety reasons. For this reason, studies have started to develop a new generation of nickel-free enamels suitable for regulations. In this study, the development of enamel that can be applied to cast iron surfaces having a matt appearance that does not contain nickel and the effect of nickel on enamel properties were investigated. In the existing frit compositions, new frit recipes were prepared, which did not contain nickel and were applied to cast iron surfaces by wet application method. Heating microscopy analysis of prepared frit was performed. Microstructure, chemical abrasion resistance, color properties, surface properties, coating adherence performance, and the effect of nickel on these properties were investigated

.**Keywords:** Enamel; Cast Iron; Nickel Free Enamel; Metal Coatings.

DOI:

1. INTRODUCTION

Cast iron is an iron-carbon alloy containing more than 2% carbon. Low melting temperature, high castability, low production cost, high viscosity and easy formability are advantages of cast iron [1,2]. However, low wear resistance and corrosion resistance, low chemical resistance and toxicity are the disadvantages of cast iron. Due to its high heat capacity, cast iron has recently become popular in kitchen equipment. The non-stick and cleanability of cast iron kitchen equipment is low, it also has low corrosion and acid resistance. Therefore, it causes toxicity and metal migration.

Enamel coatings are used to improve the surface properties of cast iron kitchen equipment. Enamel coatings are glassy coating materials that can be applied to metal surfaces in one or more coats [3]. Enamels have a glassy main phase, called frit, obtained by dissolving different

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Acta Materialia Turcica

Volume 4, June 2020, Pages 10-17

oxides in silicon oxide. The metal oxides dissolved in the main phase has different functions. For example, the lithium oxide has a flux and a thermal stability regulator. While cobalt oxide is an adherence enhancing agent, boron oxide acts as a refractory [3].

Nickel oxide is a type of oxide which directly affects the end product properties of enamel coatings. It darkens the color of the coating, accelerates the passage of hydrogen through the litter metal, and prevents fish scale defect [4]. Besides being a hard metal oxide, it reduces the viscosity by increasing the iron oxide content in the enamel and prevents easy softening of the enamel. However, recent regulations restrict the use of nickel oxide in food contact products [5]. Briefly, it causes the accumulation of nickel in the body by causing migration, which means metal ion transfer to the body [6]. In addition to causing cancer, it causes allergic reactions on the skin. In this study, the effect of nickel on enamel coating was investigated by removing nickel oxide from the frit of matt cast iron enamel used in food contact products. Standard enamel and nickel-free enamel are applied to the gray cast iron by wet spray application. The color, gloss values of the prepared samples were measured and the effect of citric acid and impact test on the coating performance was examined. For microstructure analysis, SEM-EDS analysis was performed. In addition, XRF, AAS and Heating microscope analyzes were performed to investigate the effect of nickel on frits.

2. EXPERIMENTAL PROCEDURE

The study is carried out in Gizem Frit R&D Center (Hendek/Sakarya). The general flow chart of the study is shown in Figure 1.

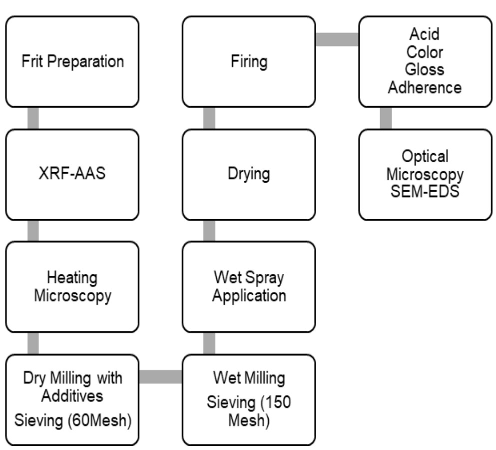

Figure 1. Production and Study Process Flow Chart.

2.1. Frit Preparation and Analysis

The frit code ZB3008 used in Gizemfrit's commercial, matt enamel was accepted as the standard sample. The mixture obtained by removing nickel oxide from the raw materials forming the standard frit was melted at 1400°C for 40 minutes, and ZB3008-Nifree frit was obtained by cold cooling method. XRF (PG Instrument PG-990 AAS) and AAS (Bruker AXS S8 Tiger) analyses were performed to determine the oxide compositions of the standard and nickel free frit. The behavior of the frit was examined under heating microscope (Misura® 3 HSM/ HSML).

2.2. Enamel Preparation and Milling

The prepared frit was ground in a ball mill made of alumina-zircon balls with a total weight of 800 grams for 10-12 minutes and sieved through 80 mesh sieves until the grain size suitable for pistol application was reached with the additives specified in Table 1. Milled raw materials were formed with 30% solution by adding tap water and hydrated in a ball mill consisting of alumina-zircon balls having a total weight of 320 grams for 1 minute and sieved through a 150 mesh sieve.

Table 1. Intended Use and Additive Ratios of Mill Additives.

Mill Additives	Intended Use	Additive Ratios*
Quartz	Refractory	10-15%
Molybdenum Trioxide	Adherence Agent	0,001-0,005%
Black Pigment	Colors	0,01-0,10%
Red Pigment	Colors	0,001-0,005%
Clay MT510	Refractory	0,01-0,10%
Sodium Nitride	Electrolytic	0,001-0,005%
Boraks	Flux	0,001-0,005%
Bentonite	Floating Agent	0,001-0,005%

*Additive ratios are used in different ratios to reach the suitable viscosity for with wet spray application.

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2.3. Wet Spray Application and Firing Parameters

The blend, which was made suitable for wet spray application, was applied on sandblasted 10x10cm gray cast iron plate. It is allowed to dry at 320°C for 5 minutes to form the biscuit. The dried enamel plate was fired at 750°C for 11 minutes.

2.4. Tests and Analyses

The color properties and brightness values of the fired samples were measured with spectrophotometer (Konica Minolta - Spectrophotometer CM-700d). Citric acid resistance test according to the EN ISO 28706-1 standard, adherence test according to the BS EN 10209 standard were performed, and optical microscope images of the spot where the adherence test was applied were taken. Surface and cross-sectional SEM-EDS (Phenom Pro X) analyses of the samples were also performed.

3. RESULTS and DISCUSSION

3.1. Oxide Composition and Heating Microscopy

XRF and AAS results of prepared frits are shown in Table 2. With the removal of nickel from standard frit, the proportions of other oxides increased in similar ratios.

When the heating microscope results of the frit were examined, it was seen that the softening point of nickel-free frit was higher than the standard. The increase of refractories such as silicon oxide and boron oxide improved the thermal resistance of the frit and increased the amount of energy required between the sintering and softening points. After passing the softening point, the frit has become spherical at lower temperatures by removing a hard metal oxide such as nickel oxide from the structure. Consequently, there has been a decrease in the hemispherical and melting points.

3.2. Aesthetic Properties and Surface

In industrial enamel production, it is desirable to have maximum silicon oxide amount in the frit due to its low cost and improved acid resistance. The ideal ratio of silicon oxide is determined by Seger formula. In enamels containing silicon oxide below the ideal ratio, there are problems such as burning due to overfiring and decrease in acid resistance. In the enamel containing silicon oxide, which is above the ideal ratio, there are defects such as unfiring, surface defects, deterioration in color and gloss.

In the nickel-free frit, the brightness value decreased due to the increase of the silicon oxide amount above the ideal ratio and the glassization of the enamel could not be completed. In addition, nickel oxide is used in the enamels as darkening agent. With the removal of nickel, the L value of the coating decreased and the color darkens (Table 3). Changes in the oxide compositions can cause surface defects such as pinhole or pits. There were no faults on the surface by removing nickel from the enamel composition (Figure 3).

Table 2. Oxide Compositions of Standard and Ni-Free Frits.

		Standard Frit	**Ni-Free Frit**
R_2O	Na_2O, K_2O, Li2O	13,40	13,52
RO	CaO, MgO, CoO	12,09	12,23
R_2O_3	B_2O_3, Fe_2O_3, Al_2O_3	16,23	16,39
RO_2	SiO_2, TiO_2, ZrO_2	55,81	56,38
RO_3	MoO_3	0,27	0,27
R	F	1,19	1,21
	NiO	1,01	0,00
	Total	100,0	100,0
	NO_2	0,96	0,97

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Acta Materialia Turcica

Volume 4, June 2020, Pages 10-17

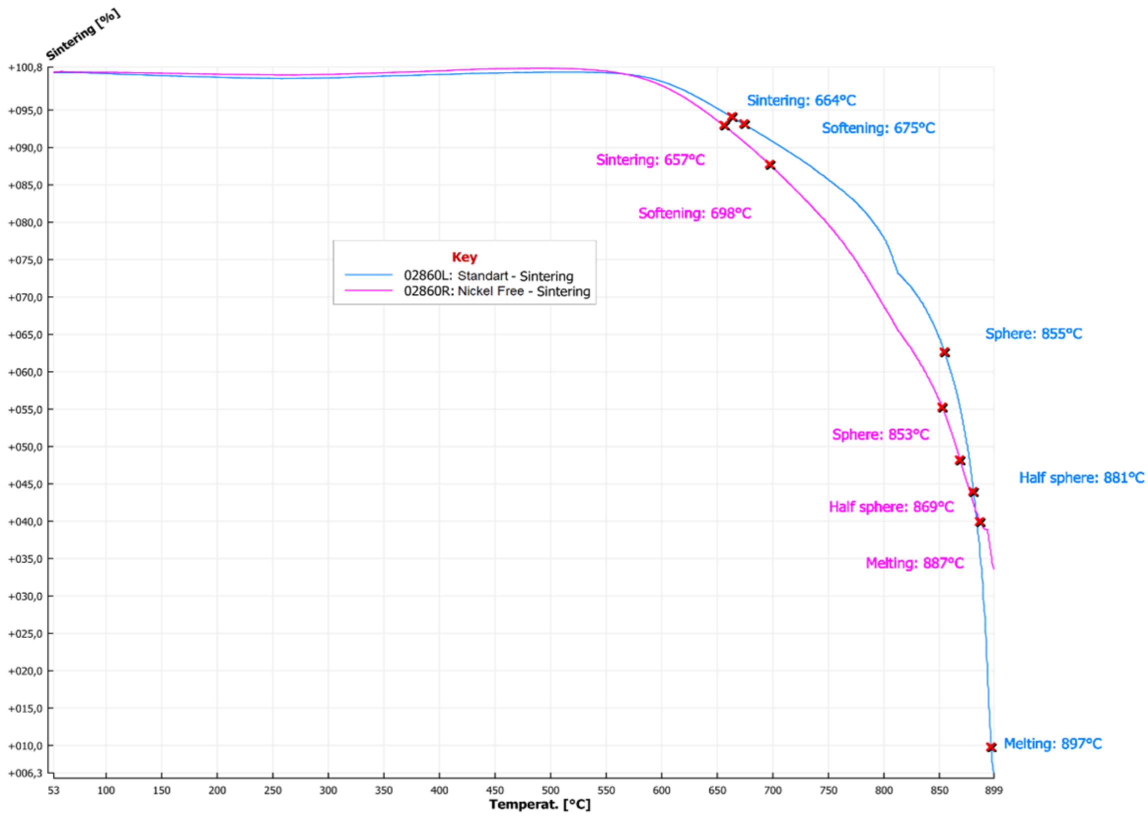

Figure 2. Heating Microscope Time-Sintering Graph.

Table 3. SCE D65, SCI D65 Color and Gloss Measurement Results.

	SCE D65			**SCI D65**			
	L	a	b	L	a	b	Gloss (°60)
Standard	29,24	0,48	-0,34	30,67	0,42	-0,35	5,2
Nickel Free	30,25	0,44	-0,53	31,54	0,38	-0,53	4,3

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Volume 4, June 2020, Pages 10-17

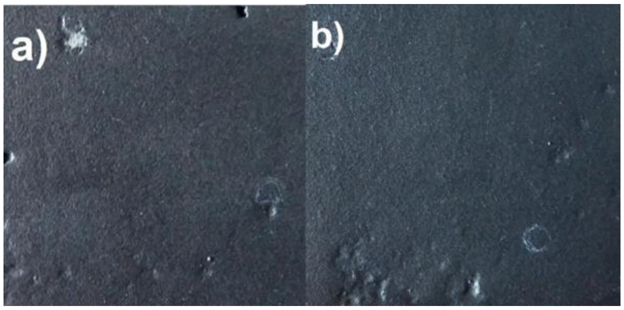

Figure 3. Surface Image **a)**Standard Sample **b)**Nickel-free Sample.

3.3. Acid Resistance

Glassy structures have higher acid resistance than the rest of the materials (except HF). Therefore acid resistance of enamel coatings depends on the amount of silicon oxide. With increasing SiO_2 ratio in enamel compositions, the amount of glassy phase increases. Therefore the acid resistance of the enamel coating has improved with the increase of SiO_2. However, increasing the ratio of alkaline earth metal oxides which react easily with acids such as CaO, MgO in structure decreases acid resistance. The test of 10% citric acid solution did not show a change in acid resistance by removing nickel (Figure 4). The reason for this is that while the ratio of silicon increases, the proportions of earth alkali metal oxide increase by the same amount.

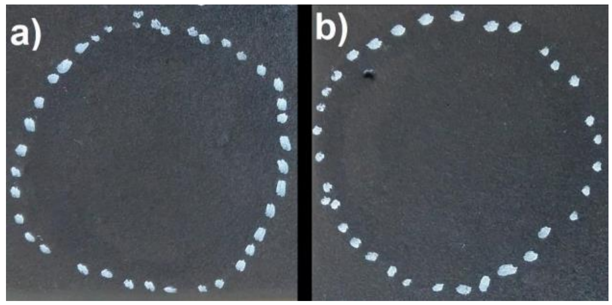

Figure 4. Surface Image after Citric Acid Test **a)**Standard Sample **b)**Nickel-free Sample.

3.4.Adherence Test

Adhering mechanisms and adherence performance at the enamel coatings and metal interface depend on the proportions of nickel and cobalt oxides. Cobalt oxide is a stronger adherence agent than nickel oxide.
By removing nickel from the frit, the cobalt oxide became more dominant in the structure and increased its adherence performance (Figure 5 and 8).

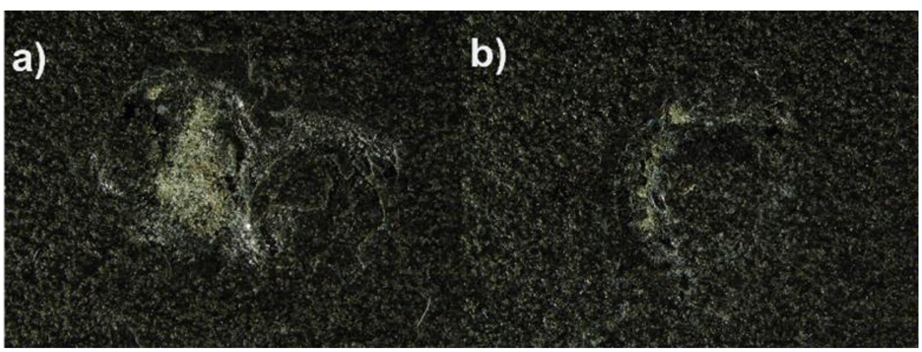

Figure 5. Surface Optical Microscopy Image after Adherence Test **a)** Standard Sample **b)** Nickel-free Sample.

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3.5. SEM-EDS Analysis

After the tests and analyzes, SEM analysis was performed on the coating surface and enamel-metal section interface. The EDS analysis results of the standard sample are similar to the analyzed oxides composition (Figure 6). By removing nickel from the frit composition, more micro-defects are seen on the surface of the nickel-free sample since the thermal stability of the structure is impaired (Figure 7). However, the resulting micro-defects did not cause visible results on the surface (Figure 3). If the oxides in the enamel are not dispersed homogeneously, the defect of accumulation of metal oxides appears. Metal oxide accumulation due to this defect was observed in the standard sample. (Figure 6-d). In addition, Nb, which is an impurity in frit raw rutile titanium material, caused deposits on the surface with iron with the removal of nickel (Figure 7-c).

At the cross-sectional views, both of the coatings pro vided complete adherence with the metal (Figure 8). The enamel-metal interface of the nickel-free sample is rougher. The galvanic interaction of the cobalt to the base metal, dominated by the removal of nickel from the structure, increased the amount of electrolytic adherence resulting in roughening.

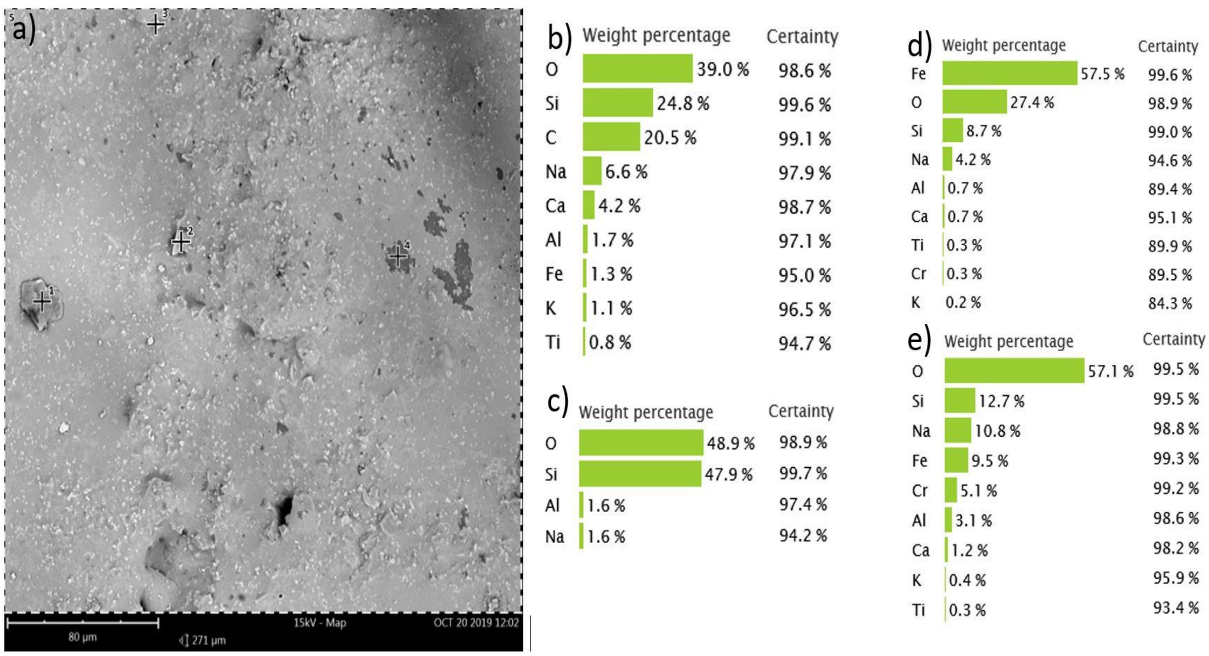

Figure 6. Surface SEM Image of Standard Sample and EDS Results **a)** BSD Image **b)** Spot1 EDS Result **c)** Spot2 EDS Result **d)** Spot3 EDS Result **e)** Spot4 EDS Result.

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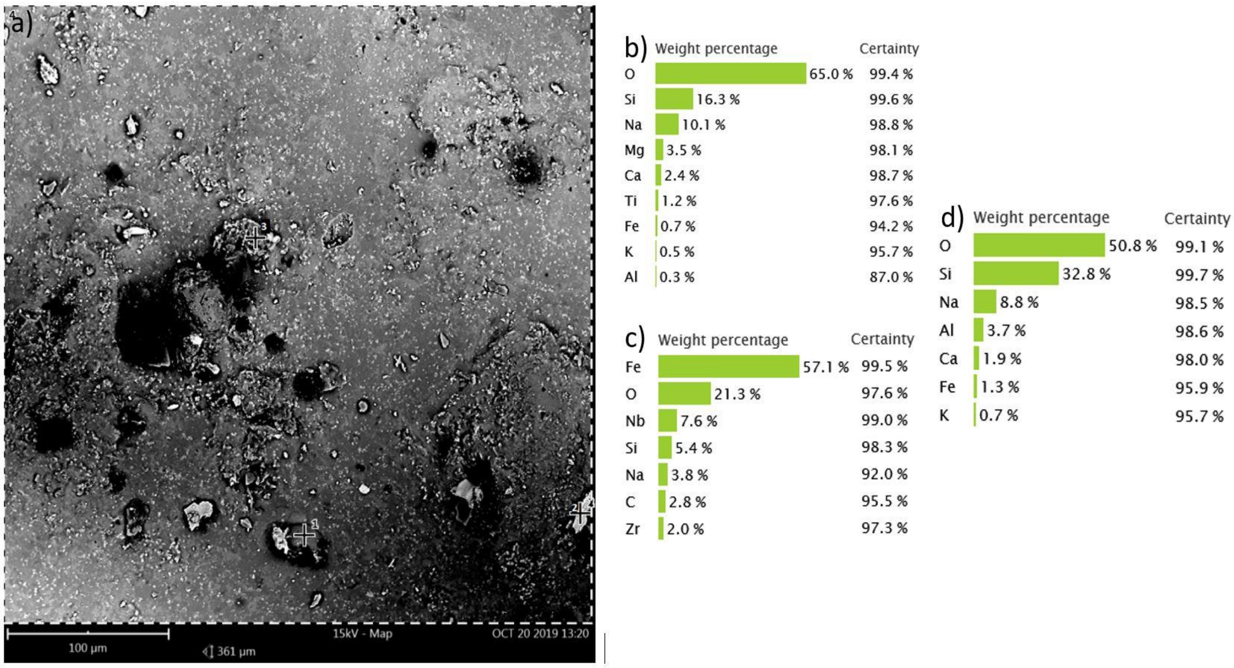

Figure 7. Surface SEM Image of Nickel Free Sample and EDS Results **a)** BSD Image **b)** Spot1 EDS Result **c)** Spot2 EDS Result **d)** Spot3 EDS Result

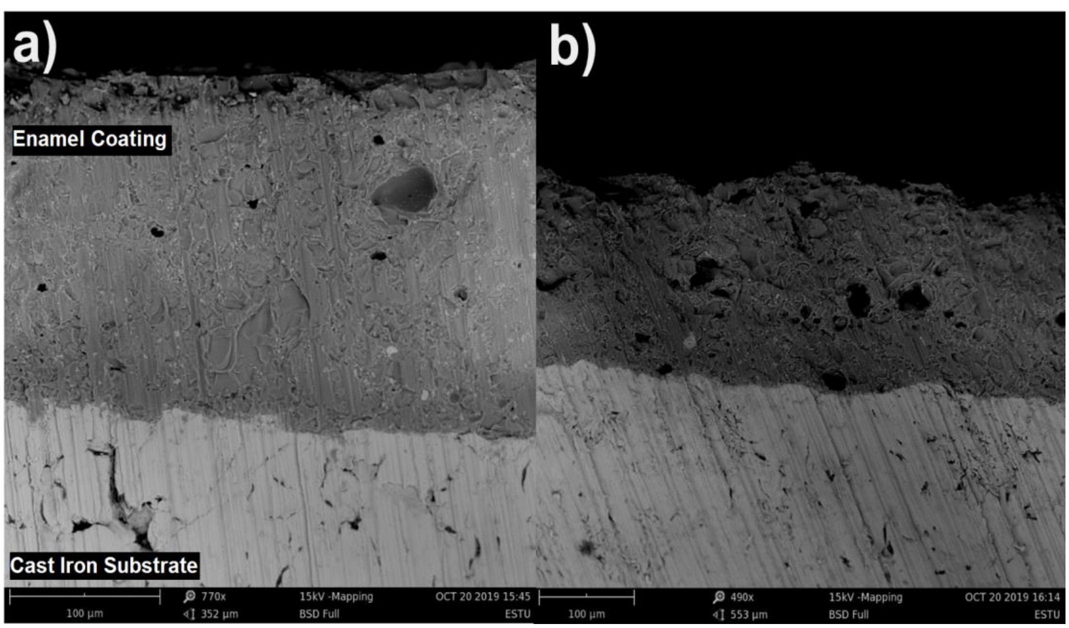

Figure 8. Surface SEM-Back Scatter Electron Image **a)** Standard Sample **b)** Nickel-free Sample.

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Acta Materialia Turcica

Volume 4, June 2020, Pages 10-17

4. CONCLUSIONS

In this study, the effect of nickel on matt enamel applied on cast surfaces with wet application was investigated. Heating microscopy was applied to enamel frit. Adherence, color and citric acid tests were performed on enamel coated plates. The samples were imaged by optical microscope and surface examination was performed by SEM-EDS analysis.

As a result of the tests and analyzes,

- Sintering, sphere, half sphere and melting point was decreased by removed nickel from frit but softening point is increased.
- It was found that did not negative affect the adherence performance of nickel cast iron enamels.
- It did not affect acid resistance.
- The color of the coating was whitened by the removal of nickel.
- When the microstructure was examined, micro-defect were seen by removing nickel but these micro-defects did not cause visible defect on the surface.

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