

REPUBLIC OF TURKEY
YILDIZ TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF SCIENCE AND ENGINEERING

EFFECT OF ZrO_2 AND ZrB_2
ON THE EROSION / CORROSION BEHAVIOR
OF GLASS-CERAMIC COATINGS

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MASTER OF SCIENCE THESIS
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Aykut AK



Dedicated to my family

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LIST OF SYMBOLS

$\text{\AA}$	Ångström
A	Area exposed to attack
K	Cavitation number
$^{\circ}\text{C}$	Celcius Degree
c	Constant related to the curvature of the dynamic meniscus
q	Cooling rate of the glass
w	Corrosion rate in millimeter per year
v	Corrosion rate per unit area
q_c	Critical cooling rate
ρ	Density of solution
Q	Dissolution rate
A_{80}	Elongation
M_f	Final mass
GPa	Gigapascal
T_g	Glass transition temperature
g	Gravity constant
h	Hours
J	Joule
K	Kelvin
kN	Kilonewton
X_{Lv}	Liquid vapor volume
T_L	Liquidus temperature

MPa	Megapascal
μm	Micrometer, unit
mm	Millimeter
r	Normal anisotropy coefficient
T_N	Nose coordinates of temperature
δt	Nose coordinates of time
$\text{Pa}\cdot\text{s}$	Pascal Second, unit of viscosity
P	Poises
S	Rate of shear
F	Shearing stress
m^2	Square meters
M_s	Starting mass
T	Temperature
R_m	Tensile Strength
ν	The flow velocity through the restriction
V	The maximum acceptable velocity in erosion mechanism
$P_{\min}$	The minimum pressure occurring in the vicinity of the restriction
u	The rate at which the substrate withdraws from the solution
$n_{20/D}$	The refractive index of water at 20°C for the D line
P_{vap}	The vapour pressure of the liquid
h	Thickness of film
t	Time
$\emptyset$	Time for corrosion calculation
ΔW_A	Total loss in mass per unit area

η	Viscosity of solution
W	Watts
R_e	Yield strength



LIST OF ABBREVIATIONS

BOF	Basic Oxygen Furnaces
BT	Bessemer – Thomas
CAD	Computer-aided design
CAM	Computer-aided manufacturing
DSC	Differential Scanning Calorimetry
EAF	Electric Arc Furnaces
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier transform infrared
GCC	Glass-Ceramic Coatings
GCs	Glass-Ceramics
GPS	Global Positioning System
HCl	Hydrochloric acid
ICP	Inductively Coupled Plasma
NACE	National Association of Corrosion Engineers
NaOH	Sodium Hydroxide
SEM	Scanning Electron Microscope
SM	Siemens – Martin
TGA	Thermogravimetric Analysis
UV	Ultraviolet
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
1C/1F	One coat one fire

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Effect of ZrO_2 and ZrB_2 on the Erosion / Corrosion Behavior of Glass-Ceramic Coatings

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Department of Metallurgical and Materials Engineering

Master of Science Thesis

Supervisor: Assoc. Prof. Buğra ÇİÇEK

Glass-ceramic materials are an important part of our daily life, from the most critical parts of space shuttles to cookwares in our kitchen. Enamel coatings, which cover the largest area among glass-ceramic coatings, are preferred because of their aesthetic and anticorrosive properties. Although these coatings are resistant to corrosion due to their ceramic nature, they have a certain lifespan like any other material in corrosive environments such as hot water, alkali, acid. In order to increase this resistance, erosion and corrosion mechanisms should be well understood. It is known that the corrosion resistance of glass-ceramic enamel coatings can be increased by ceramic doping. However, it has critical importance which material and how much will be used in doping. ZrB_2 and ZrO_2 ceramic additives are advanced ceramics that are subject to corrosion research due to their anticorrosive behavior in high-temperature applications. These additives were added into the glass-ceramic enamel coating by 2wt.%, 6wt.%, and 10wt.% during milling to the vitrified compositions before controlled crystallization. The positive

and negative effects of these additives on enamel corrosion were investigated in 5% by mass of hot NaOH and 10% by volume of cold HCl. During the analyses, thermal and crystallographic examinations, microstructural examinations and the amount of elements released to the corrosive solution were investigated. As a result, both ceramic additives improved the basic corrosion resistance of the enamel structure at different levels, while weakening the acid resistance. Although ZrB_2 crystals decompose at around 660°C and released gas, its decomposition in the enamel structure was limited and preserved its crystal form in the structure. The basic mechanisms that ensure the adherence of enamel containing Nickel and Cobalt to the steel surface have also been determined by microstructural studies and mechanical examinations.

Keywords: Glass-ceramics, erosion, corrosion, zirconium diboride, zirconium dioxide

ZrO₂ ve ZrB₂'nin Cam-Seramik Kaplamalar Üzerinde Erozyon / Korozyon Davranışlarına Etkisi

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Cam-seramik malzemeler uzay mekiklerin en kritik parçalarından, mutfağımızdaki pişirme gereçlerine kadar günlük yaşantımızın önemli bir parçasıdır. Cam-seramik kaplamalar içerisinde en geniş alanı kapsaya emaye kaplamalar gerek estetik gerekse antikorozyon özelliklerinden dolayı tercih edilirler. Bu kaplamalar seramik doğasından ötürü her ne kadar korozyona karşı dirençli olsalarda sıcak su, baz, asit gibi korozyon ortamlarında her malzeme gibi belirli bir kullanım ömürleri vardır. Bu direncin artırılması için erozyon ve korozyon mekanizmalarının iyi anlaşılması gerekmektedir. Cam-seramik emaye kaplamaların korozyon dayanımının seramik katkılandırma ile artırılabilirdiği bilinmektedir. Ancak katkılandırmada hangi malzemenin ne kadar kullanılacağı kritik öneme sahiptir. ZrB₂ ve ZrO₂ seramik katkıları, yüksek sıcaklık

uygulamalarında sergiledikleri antikorozyon davranışları sebebiyle korozyon araştırmalarına konu olan ileri seramiklerdir. Bu katkılar cam-seramik emaye kaplama içerisine kontrollü kristalizasyon öncesi camlaştırılmış kompozisyonlara kütlece %2, %6 ve %10 olarak öğütme esnasında eklenmiştir. Kütlece 5%'lik sıcak NaOH ve hacimce %10'luk soğuk HCl ortamlarda bu katkıların emaye korozyonuna olan pozitif ve negatif etkileri incelenmiştir. Analizler sırasında termal ve kristalografik incelemeler, mikroyapı incelemeleri ve aşındırıcı solüsyona geçen elementlerin miktarı incelemeleri yapılmıştır. Sonuç olarak, her iki seramik katkı da emaye yapısının bazik korozyon direncini farklı seviyelerde geliştirirken asit dayanımını zayıflatıcı etki göstermiştir. ZrB_2 kristalleri 660°C civarında bozunma reaksiyonu vererek gaz çıkışı yapmasına rağmen emaye yapısı içerisindeki bozunması sınırlı kalmış, yapı içerisinde kristal formunu korumuştur. Nikel ve Kobalt içeren emayenin çelik yüzeye yapışmasını sağlayan temel mekanizmalar da mikroyapı incelemeleri ve mekanik incelemeler ile saptanmıştır.

Anahtar Kelimeler: Cam-seramikler, erozyon, korozyon, zirkonyum diborür, zirkonyum dioksit

Corrosion is the one of the most important issue in the world. Every year, there is loss of life and property due to corrosion, and for a sustainable world, the materials must be recycled without corrosion. Ceramics, metals, polymers and composites, which are the four common types of solid form materials in our world, can all corrode in one way or another. As a result of this corrosion, the materials either become unusable or their performance decreases. The corrosion rate of each material varies depending on the usage area and environmental factors. For example, glass, which is known as one of the most inert material, corrodes and dissolves in a few hours when contact with Hydrogen Fluoride (HF), while this acid can be stored in polyethylene bottle for years. Similarly, glass can withstand temperatures up to 600-700°C, while polypropylene loses its durability after 130°Cs and becomes vulnerable. In other words, we can say that the corrosion resistance of materials is a relative concept depending on the environment and usage conditions. Nature is one of the most aggressive corrosive environments in the long run. Factors such as water, wind and sun can give great shapings to nature through erosions / corrosions. Non-oxide metals such as steel, in particular, begin to return to its stable oxidic structures when it encounter water-heat. This situation can damage their mechanical strength and visual structure, which is their intended use. In order to prevent this damage, the steels are covered with various materials. Glass-ceramic coatings can withstand erosion under heat, water and mechanical abrasion for a long time against other coating types. While the glass-ceramic coating protects the steel, the steel continues to maintain its mechanical strength, thus achieving the longest durability against the corrosive environment. The subject of glass ceramics will be examined in detail in the following sections, and enamel coatings are the most common type of glass-ceramic coating and probably exist in our homes. These glass-ceramic enamel coatings are obtained by mixing and melting oxides such as SiO_2 , Na_2O , CaO , Li_2O , B_2O_3 etc. or their minerals in certain compositions. According to these compositions, the

erosion/corrosion resistance of the coating can be adjusted. Erosion/corrosion resistance of glass-ceramic coating reaches maximum levels with production methods and recipe compositions. In fact, due to cost and international regulations, composition and production methods have been squeezed into an even narrower area, and new ways have been sought to increase strength. The method of doping with advanced ceramics has emerged as a popular method in increasing mechanical and chemical resistance in recent years. Especially a few advanced ceramic particles show great promise in this field. Efficiency of ZrO_2 and ZrB_2 ceramic particles as both healthy and erosion/corrosion resistant has been proven by international academic studies. However, detailed studies on the corrosion resistance performance of these particles in glass-ceramic coatings are scarce.

Another important feature of the enamel coating, which protects the surface of the steel against corrosion, is the bonding with steel. If glass-ceramic coating cannot maintain its physical presence on the metal or it burst out at the slightest impact, there will be no point in increasing the corrosion resistance of the coating. For this reason, the adherence of glass-ceramic coatings to steel will also be examined in this study. Adherence is very important in terms of both performance and cost and the cost part will be better understood when it comes to the multilayer color applications.

1.1 Literature Review

There are many studies on the corrosion and adherence of glass-ceramics. Although some of these are made on different application areas such as ceramic glazes, the fundamental mechanisms are the same and they are helpful for understanding the corrosion of steel enamel.

Chena et al. [1] worked on corrosion of $\text{SiO}_2\text{--B}_2\text{O}_3\text{--Al}_2\text{O}_3\text{--CaF}_2\text{--R}_2\text{O}$ ($\text{R}=\text{Na}$ and K) enamel with addition of 0, 2.5, 5 wt. % of ZrO_2 substituting for SiO_2 . This advanced ceramic additive is known as an inert and corrosion resistant material. Two kinds of corrosive solutions were chosen; 30% (vol.) H_2SO_4 and 3 wt.% NaOH solutions. Solutions were heated up to 80°C . For the analysis, they used Scanning-Electron

Microscope (SEM) - energy dispersive X-ray spectroscopy (EDS) to surface inspection. Electron probe microanalysis technique was used to inspect the gel layer, laser scanning confocal microscopy was used to inspect the corroded surface morphologies. After 14 days corrosion, leached gel surface was inspected. Si and S were quite higher than the content of Na, Al, K, Ca, Co, Zr. Additionally, Na and K were completely leached out. Replacing SiO_2 with ZrO_2 greatly improved alkaline resistance of enamel more than by two times. It is not only changed the alkaline resistance amount but also changed the mechanism of corrosion. Nevertheless, ZrO_2 made worse the enamel surface against to acidic environment in 30 vol% sulfuric acid.

Li et al. [2] prepared a paper about corrosion studying method of enamel coating. TiO_2 - ZrO_2 consisting of enamel compositions sintered at different temperatures as 780-810-850-900-1000°Cs onto the SAPH440 high strength steel. They used 3.5 wt.% NaCl solution as a corrosive environment. Also, Nickel Oxide (NiO) and Cobalt Oxide (CoO) were added into the composition to boost adherence with steel and to make it more aesthetic. In order to evaluate the corrosion, X-Ray Diffraction (XRD), SEM, Scanning Electrochemical Microscopy, and Electrochemical Measurement Methods (Potentiodynamic polarization, Mott-Schottky curves) were used. As a result of this study, corrosion resistance and mechanical properties of enamel coating deeply connected to the porosity of surface and this porosity is decreased with time and temperature. But too much temperature over the 900°C make the enamel boils and causes too many holes and cracks in the surface so corrosion resistance decreases. *Li et al.* [3] studied very similar work before. This time they worked on effect of powder particle size of enamel slurry on mild steel at one temperature as 780°C against to 5 wt.% NaCl solution. Particle sizes were arranged by different milling time 350 μm , 149 μm , 74 μm , 44 μm , 37 μm and 33 μm . Evaluation methods were as same as before. In the conclusion of their work, enamel coating with 44 μm particle size demonstrated the best corrosion resistance. Thick particles couldn't be packed densely so couldn't fill the voids enough.

Yu *et al.* [4] studied corrosion of enamel with the presence of 2.5 wt.% CaF_2 . In this work, molten aluminium at 750°C was chosen as a very harsh corrosive environment. Frits are obtained and milled to under $10\mu\text{m}$ then coated onto 304 stainless steel and fired at 1000°C for 2 min. Also, bulk enamel is produced without any coating procedure. XRD, Differential Scanning Calorimeter (DSC), SEM/EDS, and Thermodynamic Equilibrium methods were used to evaluate the results. In conclusion, crystallization of enamel is affected by presence of CaF_2 . Cristobalite is the only detectable phase in the presence of CaF_2 while α -quartz and cristobalite were obtained during the absence of CaF_2 . This fluoride breaks down the bridging oxygen and by this way lower the melting temperature of enamel. During the corrosion α -quartz transform to β -quartz and this transformation leading to porosity and cracks in the coating surface. Corrosion is accelerated by these defects. CaF_2 also reduces wettability. Corrosion resistance of enamel surface was increased by addition of 2.5 wt.% CaF_2 .

Samiee *et al.* [5] describe the effect of bubble structure on enamel coating adherence and chemical durability. They worked on two basic formulations containing cobalt (CCE) and cobalt-free (CFE). The enamel coating is made of SiO_2 , B_2O_3 , Na_2O , K_2O , Li_2O , CaO , TiO_2 , CuO , MnO_2 , NiO , CoO , F_2 , and Fe_2O_3 . Chemical compositions are also shared in the work and two enamel have different compositions. According to the paper, there is a direct proportion between bubble concentration and spatial connectivity. Interconnected bubbles help gases out and bonding strength. Steels with 0.021% C content were chosen for work and cleaned chemically then enamel slurry was applied to the surface by wet spraying method with $350\mu\text{m}$ fired thickness. The specimens were fired at 870°C for 5 min (CCE) or at 890°C for 2 min (CFE). For adherence evaluation, an impact test was used according to EN 10209. For chemical durability evaluation, boiler corrosion cells were used according to ISO 2743 standard with 20 vol.% HCl solution. Fourier transform infrared (FTIR), SEM-EDS, and Optical Microscope equipments helped to understand the corrosion mechanism. In a conclusion, cobalt improved adherence, but cobalt-free enamel has better resistance to chemical corrosion thanks to higher connectivity of the network, not-connected bubbles, and fewer

non-bridging oxygens. The CCE glass network has a dissolution mechanism while the CFE has an ion-exchange mechanism. During the corrosion, bubble structure, dimensions, connectivity, and concentration are important parameters for durability.

Salman et al. [6] worked on the chemical durability and crystallization process of glass-ceramics. Li_2O (33%mol) - B_2O_3 (17%mol) - SiO_2 (50%mol) glass-ceramic system was used with partial replacements of GeO_2 instead of SiO_2 , F_2O_3 instead of B_2O_3 . This GC system is hard to control due to the volatility of B_2O_3 and Li_2O . Differential Thermal Analysis (DTA) and XRD were used to evaluate crystalline structures. Samples were exposed to hot 0.1N HCl solution at 95°C for 3h. Higher Fe_2O_3 content increases the dissolution because it makes non-bridging oxygens. In conclusion, Transition (T_g) and softening (T_s) temperatures of the main formulation were fallen by GeO_2 and Fe_2O_3 . Crystallization of glass at different heat treatments with different additions could provide fine-grained microstructure and this increases the chemical durability of lithium borosilicate glass-ceramic.

Wang et al. [7] studied the corrosion behavior of Zirconium Diboride (ZrB_2) coating. 201 Stainless steel was chosen as substrate and galvanostatic depositions in $\text{NaCl-KCl-K}_2\text{ZrF}_6\text{-KBF}_4$ molten salts was chosen as a coating method. The corrosion behavior of coating was investigated in 6061 molten aluminum at 800°C for up to 120 hours. The thickness of ZrB_2 coating was set as $25\mu\text{m}$. ZrB_2 coating remain uncorroded after 72h contact while the uncoated steel was corroded after 2h. At the end of the 96h and 120h, only local defects like pitting corrosion were observed at the steel surface, the rest of the coating was still resisting connectedly.

Yadav et al. [8] prepared a ZrB_2 coating by solid-state borothermal reduction route synthesis and applied it onto 304 stainless steel by doctor blade technique. The wet coating, having 150nm average particle size, was cured at 150°C for 6 h. Corrosion studies were evaluated using the linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) measurements. Corrosive solutions with 1, 7, and 13 pH were prepared by using Na_2SO_4 , H_2SO_4 , and NaOH . According to the results, ZrB_2 films exhibited good anti-corrosive performance according to the uncoated steel in strong acid, strong alkaline, and neutral media.

Korneev et al. [9] characterized the ZrB_2 and Zr- B-N coatings with their corrosion resistance. ZrB_2 was applied on VK6M (WC–6%Co), nickel alloy by Magnetron sputtering in Ar and Ar–15% N_2 atmospheres method. Corrosion potential and corrosion current density measurements in H_2SO_4 and NaCl solutions demonstrate corrosion performance of the coating. Also, oxidation strength was inspected at 600-800°C. According to the results, Zirconia-based coating decreases the oxygen diffusion to the substrate. Zr content in the coating structure boosts the corrosion resistance while the boron and Nitrogen content having the opposite effect because of the rapid formation and volatilization of BOx and NOx .

Cha et al. [10] investigated adherence performance and bubble structure of Nano-Nickel Oxide (NiO) added enamel coating. After obtaining the CoO/NiO-containing frit composition, Nano NiO was mixed into the enamel slurry with 0-0.5-1.0 wt. % ratios. Enamel slurries were applied onto 0.08% C sheet steel then fired at 870°C for 5 min. To inspect adherence strength, ball-drop test in accordance with the ASTM B916-01 and SEM-EDS analyses were applied. As a result, Nano NiO addition increased the amount and volume of dendrite arms at the interface. It also assists Fe-ions to move from steel to coating side. With the increasing amount of NiO, the sizes of bubbles also increased. In addition, Fish-Scale tendency was decreased by the addition of Nano NiO.

1.2 Objective of the Thesis

The thesis primarily aims to increase the erosion/corrosion strength of a specific enamel surface after understanding this mechanism of glass-ceramic coating containing NiO/CoO. To increase this resistance, Zr (O, B) $_2$ advanced ceramic additives, which have proven themselves with studies in the field of corrosion resistance, is used. As a criterion, the boiler basic solution and acidic solution at room temperature are used to simulate the erosion/corrosion resistance in the most realistic way. In addition to the standard enamel composition, it is tried to obtain a more durable structure than the reference sample in terms of boiling solution resistance in each trial. Another aim of the thesis is to understand the intermetallic bonding mechanism that provides adherence between steel and

glass-ceramic coating. For this purpose, adherence tests and examinations will be carried out simultaneously with the erosion/corrosion studies.

1.3 Hypothesis

Although there are studies on the resistance of ZrB_2 ceramic to corrosive environments as coating or bulk, such an application or research has not been encountered in the enamel coating works. In addition to ZrB_2 , it is known that ZrO_2 increases the corrosion resistance of the glass structure in the enamel structure. However, understanding how the increase in the percentage of zircon in resistance to alkali corrosion causes a change in the enamel structure will increase our awareness of corrosion resistance in this type of coating. In addition, with this study, the sintering behavior of ZrB_2 in the glass-ceramic structure and subsequently its behavior against alkali and acidic attack will be compared with ZrO_2 , which is a close relative of this material and has proven itself in this field. Thus, the reasons for the improvement or deterioration in corrosion resistance can be analyzed relatively. In addition to all these, since Zr, B, and O elements are already present in the chosen frit composition, so, it is expected that these materials will have better compatibility with the structure than other materials.

2.1 Glass-Ceramics (GCs)

The discovery and definition of glass-ceramics is made by famous glass chemist Dr. S.D. Stookey in the 1950s. Dr. Stookey defined glass-ceramics as "Glass-Ceramics are made by first melting and forming special glasses containing nucleating agents and then causing controlled crystallization of the glass." [11]. However, the fact is, this definition was made on this date doesn't mean that such materials didn't exist in the previous years. It is known that in the 1700s and even earlier, scientists obtained dense ceramic materials by crystallizing glass. This material was noticed and studied in detail and commercialized by Dr. Stookey as a new type of material. He had been doing a silver precipitation experiment using lithium silicate glass for permanent photographic image work in that laboratory. The reason for using lithium silicate is that lithium glasses are more chemically stable. Stookey keeps the glasses at around 450°C for precipitation work, one night the furnace temperature rises to 850°C. Stookey, who thought that the glass was melted and the furnace was ruined, saw that the sample remained unmelted and as it had left. While removing the glass from the furnace, accidentally dropped to the ground and the glass doesn't break, on the contrary, it sounds like metal. After this abnormal event, Stookey examines the glass. Knowing the importance of crystals with low expansion coefficient over the studies on the near-zero thermal expansion of β -spodumene in previous years[12]. Stookey continues his studies on this subject and works with crystals such as titania, zinc sulfide, etc. In his works with Titania, he sees the strength of Titania-doped aluminosilicate glass-ceramics and commercializes it through Corning Ware®, a product used even in rocket nose cones is launched.

These glass-ceramics have been developed over the years and their usage areas have increased. With the developments in other ceramic, glass, metal, and nano

material fields, all fields have been intertwined and glass-ceramic materials have become mixed with glass-crystal composites. A current definition of glass-ceramics is made by Deubener et al.: *“Glass-ceramics are inorganic, non-metallic materials prepared by controlled crystallization of glasses via different processing methods. They contain at least one type of functional crystalline phase and a residual glass. The volume fraction crystallized may vary from ppm to almost 100%”*.

According to the current definition of glass-ceramics, the first step is to melt and shape the glass structure. This stage is not achieved only by melting the glass. With methods such as Sol-gel and vapor deposition, which have become widespread in today's technology, these first two stages can be reached even before reaching the melting point, even below the glass transition temperatures. The glassy transformation can be determined from the peaks in the DTA/DSC curves. Endothermic orientations in the curves indicate glassy transition and exothermic orientations indicate crystallization. With XRD, the glass structure can be directly confirmed by the absence of crystalline peaks. However, XRD's percentage of crystal detection is not sensitive enough to go down to ppm levels, so this method is discussed according to the new definition. Time-Temperature-transformation graphs are very helpful in understanding the transformation of glass-ceramics. According to Figure 2.1, if glass is desired to be obtained in the melt-quenching method, the cooling rates should be larger than the critical ones ($q \geq q_c$). According to Uhlmann's classical theorem, there is a correlation between the onset of crystallization and the ratio of the crystal fraction of one part per million ($X = 10^{-6}$). The basic transformations in the graph in Figure 2.1 are also based on these ratios.

In the graphic;

q : indicates the cooling rate of the glass,

q_c : gives the critical cooling rate, $q_c: (T_L - T_N) / \delta t$

T_g : Glass transition temperature,

T_L : Liquidus temperature,

T_N and δt : The nose coordinates that can change according to nucleation mechanism.

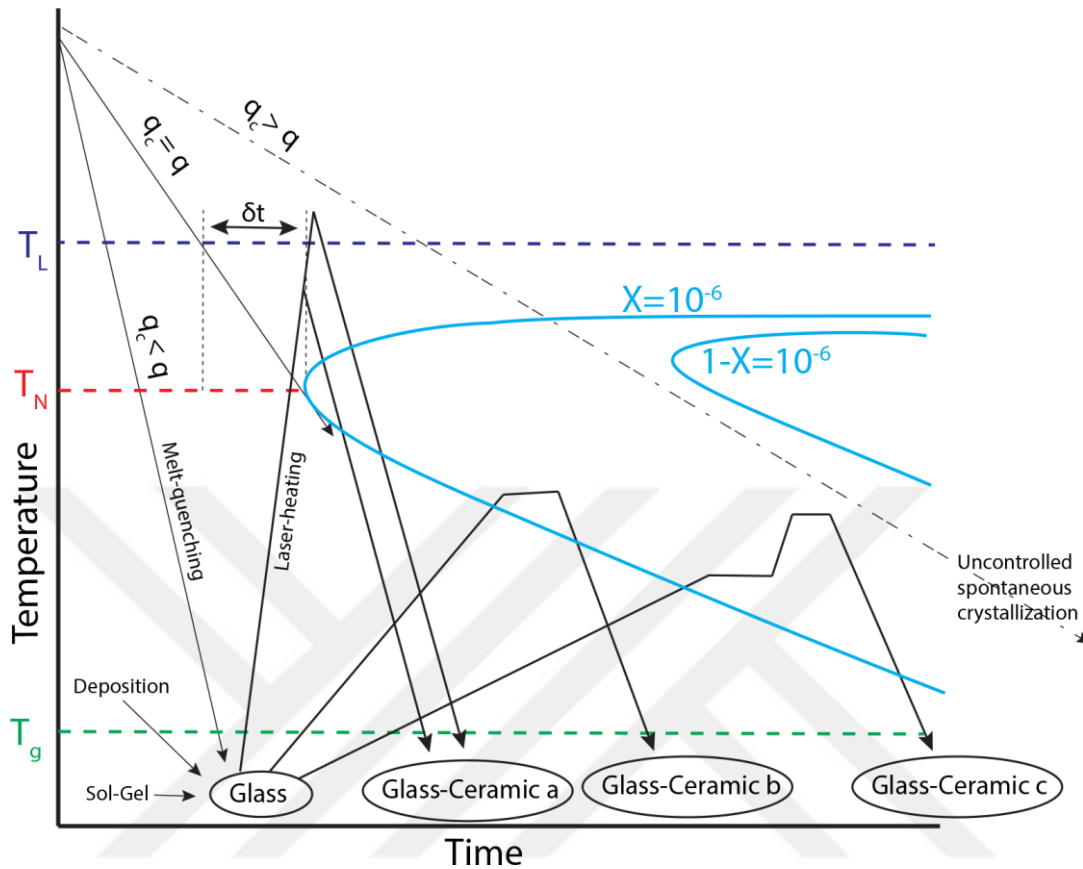


Figure 2.1 Time-temperature-transformation diagram for glass-ceramic formation

2.2 Formation of GCs

- **Pressing**

In this technique, pressure between a mold and a plunger is used to shape the glassware. Pressing equipment can vary such as air vacuum, metal presses, etc.

- **Casting**

To use this ancient method, the glass viscosity must be low and the temperature must be above the glass transition temperature. This method is used in dental applications.

- **Spinning (Centrifugal Casting)**

The difference between this method from the standard casting method is the need for a conical mold that can rotate. The viscosity must be between 30 and 100 Pa s. in this process[13]. Television bulbs of the old cathode ray tube technique were produced in this way.

- **Rolling**

In the rolling method, molten glass is poured and rolled on a water-cooled press table. Ideal viscosity should be set at 700–1000 Pa s. Flat glasses can be produced in this way[13].

- **Float Process**

The float or Pilkington process, which is currently most commonly used in flat glass production, is the basic forming in a molten tin bath. While the molten glass comes out of the furnace belly, it is flattened and strengthened in the tin bath at relatively low temperatures. The flat glass continues on the same conveyor line, enters the annealing lehr line, reduces its tension, and continues.

- **Direct Forming or Reforming of Glass-Ceramics**

In some cases, glass-ceramics can be obtained from the ceramic phases. The residual glass phases soften, allowing shaping.

2.2.1 Applications

- **Technical Applications**

Radomes are the first commercially available glass-ceramics. It is a structural, weatherproof enclosure that protects the radar antenna. Radom glass-ceramic attenuates to a minimum the electromagnetic signal transmitted or received by the antenna, it is sensitive to radio waves. low dielectric loss, low dielectric constant, low coefficient of thermal expansion, high strength, and high abrasion resistance must be required for this type of usage [14].

Photosensitive and etched patterned materials are produced for use in electronics, chemistry, acoustics, optics, mechanics, and biology in extremely

sensitive miniature sizes. These kinds of glass-ceramics are generally derived from the $\text{SiO}_2\text{--Li}_2\text{O}$ system. The parent glass contains Ce^{3+} and Ag^+ ions. The compositions exposure to UV, so photoelectrons cause the oxidation of Ce^{3+} to Ce^{4+} , Ag^+ to Ag^0 . During the heat treatment at 600°C (Beall 1993), crystal phases become precipitated by controlled crystallization[15]. The final product is obtained by etching lithium metasilicate crystals with dilute hydrofluoric acid. These refined glassy bodies were commercialized by Corning Glass under the Fotoform® trademark. The non-etched structure was commercialized under the name Fotoceram® with a few changes.

Machinable GCs are glass-ceramics based on fluoromica. The most known machinable commercial glass-ceramic is MACOR® which is containing fluorophlogopite phase ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$). Boundary retainers on the spaceships, electrical insulators, suction feedthroughs, microwave-type component screens, field-ion microscope parts, seismograph coils, gamma-ray lens frames are known examples that Macor is used in[16].

Magnetic memory disk substances are also made of GCs. Canasite, lithium disilicate, spinel–enstatite, and spinel are the most known GC used for this purpose. Nano-structured fracture toughness and young modules are important parameters for this kind of material. For example, Gahnite type, ZnAl_2O_4 , or spinel, MgAl_2O_4 , or the solid solution of both types of crystals must be smaller than $0.1\mu\text{m}$, fracture toughness of enstatite is above $1\text{MPa}\cdot\text{m}^{0.5}$, spinel–enstatite material, which is the best-known option for magnetic memories, has Young's modulus of 100–165 GPa that is actually high according to the other GC materials[13].

$\text{SiO}_2\text{--Al}_2\text{O}_3\text{--Li}_2\text{O}$ system are used to produce substrates for **Liquid Crystal Displays** used in personal laptop computers. If the wavelength of the visible light is bigger than crystallite size, the GCs become transparent, and crystals demonstrate almost the same refractive index as the parent glass.

- **Consumer Applications**

β -Spodumene Solid-Solution GCs used for kitchen applications and cooking dishes that could withstand high-temperature fluctuations because of the thermal

shock-resistance nature comes from low thermal expansion coefficient property. These products were developed and commercialized with the addition of TiO_2 and ZrO_2 by different companies[17].

β -Quartz Solid-Solution GCs are based on the **β -Spodumene Solid-Solution** GCs. The household market demanded more aesthetic products than **β -Spodumene**. So **β -Quartz Solid-Solution** GCs were white, translucent, and even highly transparent. It is used to produce bowls, teapots, glasses, cups, etc under name of borosilicate glass called Pyrex®[17].

• **Optical Applications**

Telescope Mirror Materials required near-zero coefficient of thermal expansion because of temperature fluctuation. **β -Quartz Solid-Solution** GCs meet this requirement.

Lithium metasilicate/lithium disilicate glass-ceramics with approx. 20 μm thickness was used to produce Integrated Lens Array[17].

Luminescent Glass-Ceramics **are becoming very popular because of their energy efficiency and** less loss of data. Cr-Doped Mullite for Solar Concentrators, Cr-Doped Gahnite Spinel for Tunable Lasers and Optical Memory Media, Rare-Earth (such as Ytterbium, Erbium, Praseodim, etc) Doped Oxyfluorides for Amplification, Up conversion, and Quantum Cutting, Chromium (Cr^{4+})-Doped Forsterite, **β -Willemite**, and Other Orthosilicates for Broad Wavelength Amplification, Ni^{2+} -Doped Gallate Spinel for Amplification and Broadband Infrared Sources, Yttrium-(gadolinium)-aluminate garnet glass-ceramic Phosphor for White LED were good examples for luminescent GCs[13].

Optical Components such as Fiber Bragg Grating Athermalization, Laser-Induced Crystallization for Optical Gratings and Waveguides, Ferrule for Optical Connectors, Transparent ZnO Glass-Ceramics with Controlled Infrared Absorbance and Microwave Susceptibility were also made of different crystal-based GCs[18].

- **Medical and Dental Glass-Ceramics**

Two different applications are made under this title: implantology (medical prostheses) and materials used in restorative dentistry (dental prostheses)[19]. Implantology is used to fabricate medical prostheses for orthopedics, head and neck surgery, dental implants, and root fillers. A common feature of all those is inserted into the human body. The materials used in restorative dentistry are not implanted in the body. Instead, they are used to restore natural teeth. Dental inlays, crowns, bridges, and veneers are good examples of this category. Although these two categories seem similar, the materials are completely different from each other. Implantological materials must be biocompatible and bioactive. The biologically active hydroxycarbonate apatite layer found in bioactive materials allows bonding with bones and even soft organs. Implant materials can be exposed to mechanical forces, so strengths such as compression, tensile, shear, toughness, Young's modulus may be needed. Visual features are often overlooked. Unlike implant materials, restorative dental application materials must be aesthetic and should look like natural teeth, have high abrasion and corrosion resistance, and should not react with any kind of chemicals that can be found in foods and beverages. The production of both types of materials also requires a lot of attention. Dimensional precision should be at the micrometer level and the surface properties after production should be completely smooth or rough at the desired level. Different production methods can be used for these materials like sintering, molding, or machining using computer-aided design (CAD)/computer-aided manufacturing (CAM) techniques.

- **Electrical and Electronic Applications**

Mica-type GCs are used for Insulator materials. These materials exhibit high dielectric constants. $\text{SiO}_2\text{--TiO}_2\text{--Nd}_2\text{O}_5$ and $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--PbO}$ GC systems are used with sintered ceramics to have composite material that exhibits a high dielectric constant. These inorganics are mixed with binder resin (butylmethacrylate), a solvent (toluene), and a plasticizer (dibutylphthalate) and applied onto a smooth flat surface by Doctor Blade Technique with thickness from

0.1 to 0.3 mm then heated at 400°C to burn out the organics and sintered at 900°C to obtain mechanically strong dense material. Circuit patterns are siren printed on the surface after mixing the organics[20].

Electronic Packaging also uses GC systems. $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$ and $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--ZnO}$ systems are used for this purpose together with advanced ceramics such as ZrO_2 to obtain composite materials. This packaging system has been used for multilayer chip carriers in the special computers of IBM.

Special GCs are developed for Dielectric Glass-Ceramics for GHz Electronics. In the microwave wireless communication business, dielectric oxide ceramics have proven a game-changer. They make resonator and antenna components for a variety of applications, including mobile phones and GPS systems. However, these ceramics have some drawbacks that are unrelated to their electrical properties, most notably porosity, which causes metallization issues, and inhomogeneity, which causes performance degradation. For these reasons, glass-ceramics in the $\text{SiO}_2\text{--B}_2\text{O}_3\text{--TiO}_2\text{--ZrO}_2\text{--La}_2\text{O}_3\text{--RE}_2\text{O}_3$ system have been designed that match the requirements of existing ceramics while also being exceedingly homogeneous and free of porosity. Glass compositions are typically tailored to precipitate either $\text{La}_2\text{Ti}_2\text{SiO}_9$ or $\text{La}_4\text{Ti}_9\text{O}_{24}$, or both.

- **Architectural Applications**

Nippon Electric Glass develops the most important glass-ceramic for building applications under the Neopariés™ trademark[21]. The following is how the glass-ceramic is made: Granular glass particles are used to create a foundation glass. The granular glass is shaped into flat or curved panels in a tunnel furnace at temperatures of up to 1100°C in a completely automated process. Sintering of the granular glass takes place at 850°C during the heat treatment. Wollastonite crystallizes at temperatures above 950°C. These kinds of materials have to have some essential properties such as weathering resistance, zero water absorption, lighter in weight than natural stone building materials, harder than natural stone, etc. This category also comprises fire-resistant windows.

- **Glass-Ceramics for Energy Applications**

Glass-ceramics are a key component of several programs aimed at improving the efficiency with which energy is produced and managed. Glass-ceramics are used for energy generation in at least three areas: (i) solar energy efficiency, (ii) battery components, and (iii) solid oxide fuel cells[22]. Cathode, anode, and electrolyte are the components of batteries and GCs can substitute for three of them efficiently. For Example, the parent glass from which this phase is formed has a batch composition of $\text{Li}_2\text{O}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5-\text{Nb}_2\text{O}_5$. The glass was melted in a reducing environment, and then heat treatment was used to start the crystallization process. LiFePO_4 precipitated in a continuous phase as a result of this technique. This crystal is chemically resistant to charge-discharge intercalation cycles and has a greater thermal conductivity in the glass-ceramic state than when formed via solid-state reaction. As a result, the glass-ceramic battery has lower internal resistance and greater high-rate discharge performance than a LiFePO_4 ceramic battery.

- **Coatings and Solders**

The importance of thin and thick films is growing in today's technologies. A wide variety of glass-ceramic coatings are made so that special substrates can maintain their performance or improve surface properties. These coatings can be made by traditional methods such as powder coating sintering, as well as by effective and economical methods such as sol-gel coating. Especially with the sol-gel method, coatings can be applied effectively to shaped surfaces of different materials such as aluminum, glass, wood, polymer in the desired thickness. Also, non-coating materials such as bulk glasses, ceramics, aerogels, fibers, nanopowders can be produced with this technique. Sol-gel processing can create fluorhectorite, $\text{LiMg}_2\text{LiSi}_4\text{O}_{10}\text{F}_2$, which can be used to make mica glass-ceramic films. In addition, when the fluorhectorite glass-ceramic was exposed to water, it spontaneously gelatinized, generating a fine sol-gel dispersion. This could be dried to a film, but water could easily dissolve the film and recreate the gel. Donald (2007) reviews glass-ceramic-to-metal seals for energy and biological applications and explains

the underlying concepts necessary for glass-to-metal seal viability. Seals for the microelectronics sector were produced using the P_2O_5 - Na_2O - BaO system and the SiO_2 - Li_2O system, respectively. Glass-ceramics with a phosphate base is preferred for hermetic seal applications when combined with aluminum or copper. Lithium disilicate glass-ceramics have been created as high-strength seals.

Most of the commercial glass-ceramic coatings comprise ceramic glaze and enamel coatings. Both glass-ceramic types are obtained by pulverizing glassy parts called Frit, applying them on a ceramic or metal substrate, and sintering them. Since the expansion coefficients and surface properties of ceramics and metals are different from each other, the oxides used as raw materials in glaze and enamel also differ. Therefore, the melting and sintering temperatures of these two glassy structures also differ from each other. Ceramic glaze frits are vitrified at $1500^\circ C$ and sintered at $1200^\circ C$. Enamel frits are vitrified at $1300^\circ C$ and sintered at $800^\circ C$.

Enamel coatings are obtained by bonding the glass powder to the metallic substrate (Sheet steel or cast iron) by sintering/crystallization at 780 - $880^\circ C$. Enamel frit is obtained by melting the oxides such as SiO_2 - B_2O_3 - Li_2O - K_2O - CaO - NiO - CoO etc or their minerals at $1300^\circ C$ s and quenching it. Every oxide in that composition serves a special purpose. In this part, a question may arise as to whether all these oxides can be mixed and applied to the metal surface without melting, and glass ceramics can be obtained. At this point, it is necessary to return to the definition of glass-ceramics. To obtain this type of glass-ceramic, you must first obtain a homogeneous glass structure. In frit production, cheaper minerals are generally preferred instead of oxides. Oxides, which may contain carbonate, sulfate, and crystalline water, are reduced during glass production and move away from the structure, leaving a homogeneous relaxed structure with low gas content. This provides a frit structure with better surface properties for the coating, low porosity, and a short firing time at low temperatures. The most important feature of the composition to be selected is the coefficient of thermal expansion. If the thermal expansion coefficient of the glass-ceramic coating is not compatible with the metallic substrate, a continuous glass-ceramic coating cannot be obtained. In addition, adhesion agents such as NiO , CoO can be included in the frit composition

to ensure or strengthen the bonding between metal and glass-ceramic coating. Enamel coatings have a very wide of application areas. properties of enamel coatings listed in figure 2.2

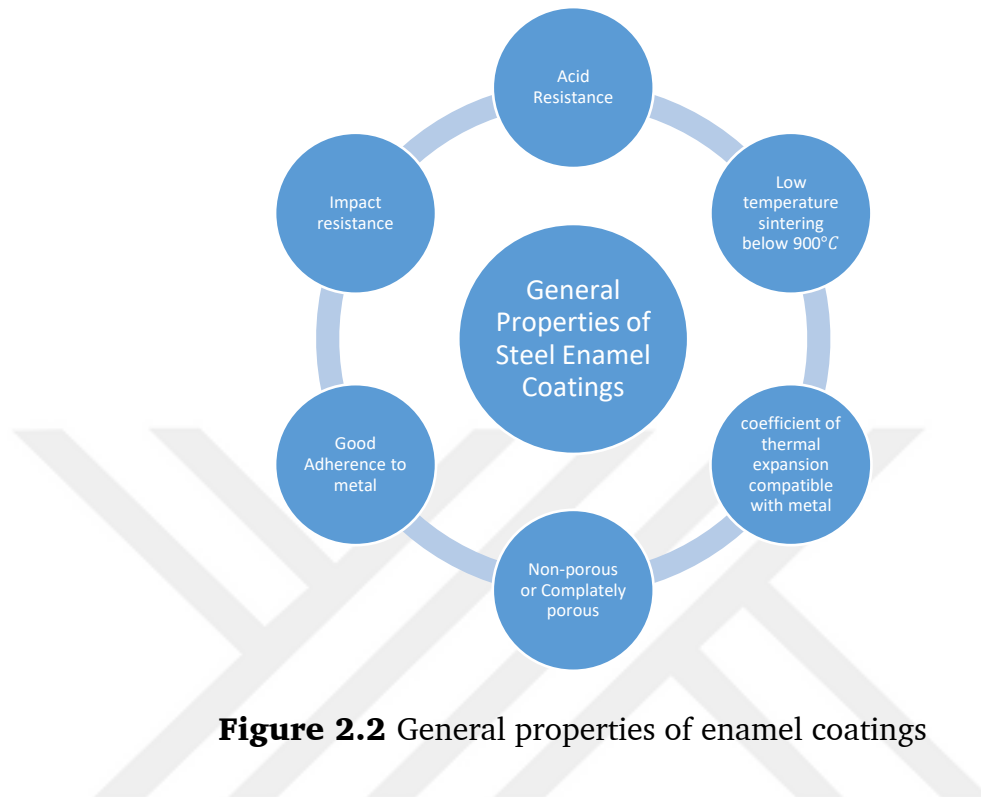


Figure 2.2 General properties of enamel coatings

The properties of enamels differ according to their application areas. While features such as aesthetic expectation, acid resistance, low porosity come to the fore in cookware, features such as greater porosity and good sintering come to the fore in catalytic coatings. So, frit structures used vary according to different applications areas.

2.3 Enamel Frits

Frit is a kind of granulated or broken glass containing nucleating agents, which is rapidly cooled by water or water-cooled cylinders. To understand the concept of frit, we must first understand the concept of glass.

According to Hasanuzzaman et al. [23], “a glass is a non-crystalline solid exhibiting the phenomenon of glass transition.” When a material lacks long-range regularity or uniformity in the arrangement of its molecular elements on a scale

bigger than a few times the size of these groups, it is said to as amorphous. In vitreous silica, for example, the average spacing between silicon atoms is roughly $3.6\text{\AA}$, and there is no order between these atoms at distances greater than about $10\text{\AA}$. When exposed to moderate stresses, a solid is a stiff substance that does not flow. A solid is defined as a substance having a viscosity greater than or equal to around 10^{15}P (Poises) [24]. To better understand, glass is often generated during the solidification step of the melting process. Crystallization does not have time to occur due to quick cooling. As the temperature drops further, the viscosity of the liquid increases, resulting in progressive freezing and solidification of the liquid. Specific volume as a function of temperature may be used to explain the connection between crystal, liquid, and glass.

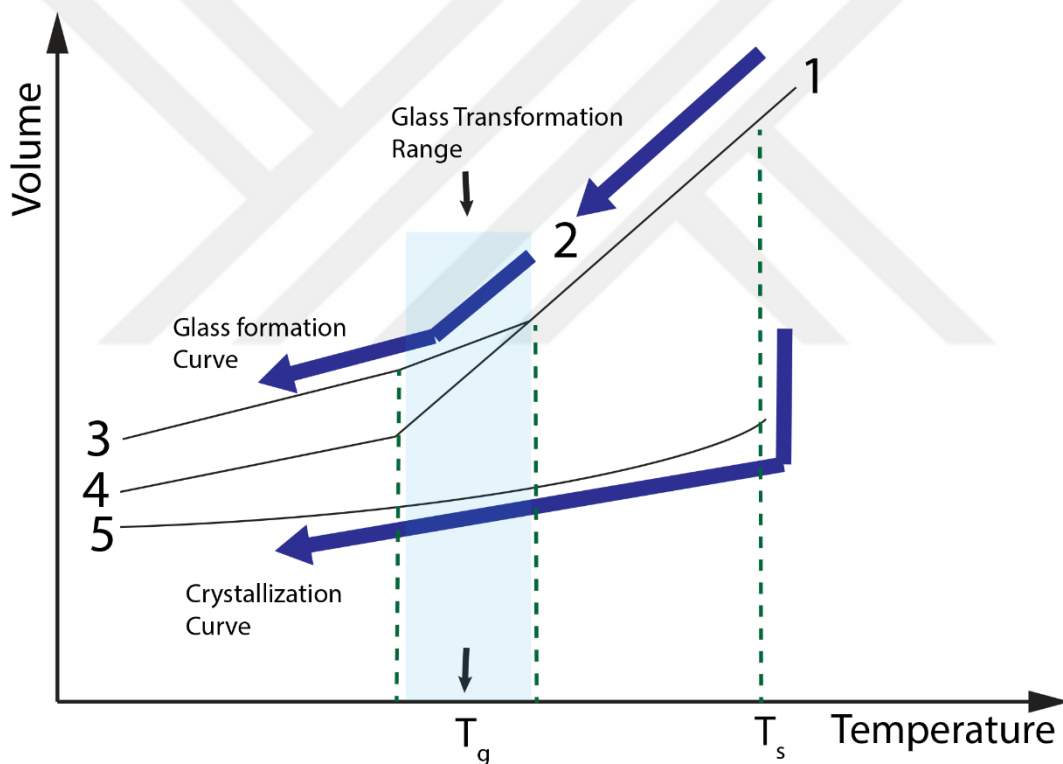


Figure 2.3 Glass transition range [23]

Two facts might occur while cooling from a high temperature (T_s) at the point of solidification. If the liquid crystallizes, there is a discontinuous change in volume at the melting point, or if crystallization is avoided, the liquid passes to a

supercooled state (between T_s and T_g) (Figure 2.3) and the volume of the liquid decreases steadily until the expansion coefficient decreases at a temperature range known as the glass transformation range. The glass structure does not relax below this temperature range, and the expansion coefficient is generally the same as that of the crystalline solid. The glass transition temperature, T_g , is the point where the curves for the glassy state and the supercooled liquid connect.

The first step for glass production is to determine the appropriate chemical composition. Glass contains 5 types of ingredients while creating these compositions: **Network formers, flux, property agent, colorant, and fining agent**. Of course, if we wanted to obtain glass-ceramic, nucleating agents are also necessary and can be put in the property modifier group. The one oxide used in these groups can serve more than one purpose. For example, although alumina is used as a glassmaker, it also supports the structure as a property agent and even affects the color properties.

Today, the most widely used **network maker** commercially is known as silica. In these commercial glasses, B_2O_3 and P_2O_5 are also used as glass formers along with silica. Along with these, GeO_2 , Bi_2O_3 , As_2O_3 , Sb_2O_3 , TeO_2 , Al_2O_3 , Ga_2O_3 , and V_2O_5 oxides are also all used as glass formers. However, for some special oxides such as GeO_2 , it may be necessary to decrease the cooling time to obtain glass. S, Se, and Te act as glassformers in chalcogenide glasses[24]. BeF and ZrF are also included in the class of halide glassmakers. 1700°C and above temperatures may be required to melt glass network makers. **Fluxes** are used both to save energy and to reduce the viscosity of the glass. The most known is Na_2O and PbO , but PbO has been restricted due to its harmful effects on the environment and health. The use of flux reduces the cost, but too much use reduces the chemical stability of the glass structure. So, this lowers the corrosion resistance. At this point, **property agents** are added to the structure to improve the chemical and other properties of the glass. Alkaline earth and transition metal oxides can be used for this purpose. **Colorants** consisting of 3d transition metals or the 4f rare earth metals can be used to control the color of the glass. To facilitate the elimination of bubbles from the melt, **fining agents** are mixed into the structure. As_2O_3 and

Sb_2O_3 , K and Na Nitrates, NaCl, fluorides including CaF, NaF, and Na_3AlF_6 , and a variety of sulfates are all used as fining agents[24]. These materials are frequently present less than 1 wt% and are handled as if they had a very negligible impact on the final glasses' characteristics.

Mole calculations are made by determining the ratios of all these raw materials according to the multiple glass phases desired to be obtained. Masses are created over these calculations. These materials, which are mixed homogeneously after the weighing, are melted in a smelter. Since the raw material, calculations, melting, and cooling conditions for each glass structure change, the next sections will proceed through enamel glasses, in other words, frits.

2.3.1 Enamel Frit Types

Enamels differ from each other according to the purpose of use. These differences may occur according to corrosion resistance, aesthetic properties, porosity, ease of cleaning, kind of substrate, and even the type of application. The change of these properties is achieved by changing the frit structure of the enamel. To start from the fundamental, the structure of the frits should first be chosen according to the substrate on which enamel will be applied. The most common and commercial of these substrates are flat glass frits, container glass frits, aluminum frits, cast iron frits, and steel sheet frits. Properties of these frits are exhibited in Table 2.1.

Table 2.1 Properties, compositions and usage areas of different kind of enamel frits

	Flat Glass Frits	Container Glass Frits	Aluminum Frits	Cast Iron Frits	Sheet Steel Frits
Main Market	Household ovens, control panels, refrigerators, spandrel panels, shower screens, advertising, internal glass doors, and partition tabletops, kitchen cabinets, wall cupboard doors, display cabinets, etc.	Glass beverage containers, beer bottles, etc.	Aluminum cast and sheet applications such as decorating the interior and exterior of buildings	Pots, pans, bathtubs, grills, stoves	Water heaters, silos, tanks, architectural panels, stoves, writing boards, household ovens, oven trays, built-in sets, barbecues, pots, cups, bathtubs, Sanitary ware, chemical reactors, luvos, self-cleaning ovens, plows, street signs, oil refinery pipes,
Ingredient	ZnO, Bi ₂ O ₃ , SiO ₂ , ZrO ₂ , TiO ₂ , Na ₂ O, B ₂ O ₃ , Li ₂ O, K ₂ O, CaO, Al ₂ O ₃ , SnO ₂ , MgO etc. [25].	WO ₃ , P ₂ O ₅ , Bi ₂ O ₃ , Sb ₂ O ₃ , MoO ₃ , SiO ₂ , B ₂ O ₃ , Al ₂ O ₃ , Na ₂ O, ZnO, ZrO ₂ , TiO ₂ , BaO, SrO, La ₂ O ₃ , CeO ₂ , Y ₂ O ₃ etc [26].	SiO ₂ , B ₂ O ₃ , P ₂ O ₅ , Na ₂ O, K ₂ O, Li ₂ O, V ₂ O ₅ , NiO, Sb ₂ O ₃ , MnO ₂ , etc. [27].	SiO ₂ , Fe ₂ O ₃ , Al ₂ O ₃ , B ₂ O ₃ , CaO, MgO, ZnO, NiO, CoO, Na ₂ O, K ₂ O, Li ₂ O etc. [28].	SiO ₂ , Al ₂ O ₃ , B ₂ O ₃ , CaO, MgO, ZrO ₂ , TiO ₂ , NiO, CoO, Na ₂ O, K ₂ O, Li ₂ O, P ₂ O ₅ , CuO, MnO, F etc.

Table 2.2 Properties, compositions and usage areas of different kind of enamel frits (continued)

Average Expansion Coefficient (C.O.E.)	$<60 \times 10^{-7} \text{ K}^{-1}$	$70-90 \times 10^{-7} \text{ K}^{-1}$	$160 - 185 \times 10^{-7} \text{ K}^{-1}$	$105-115 \times 10^{-7} \text{ K}^{-1}$	$80-120 \times 10^{-7} \text{ K}^{-1}$
Firing Temp	670-710°C, 35-40 second/mm of thickness, fast heating and fast cooling	560-640°C, 90 min firing cycle	520-560°C, 5-10 min	750-850°C, 10-15 min	820-880°C, 4-15 min

Steel enamels are also diversified according to their purpose of usage. Enamels can be applied in different coat and firing cycles, such as single coat, double coat, and triple coat. In multi-layer applications, the ground coat is usually applied first, as the cover coat doesn't adhere to the metal.

The main purpose of the use of **ground coat enamels** is to provide a strong adherence with the metal. Generally, there is no aesthetic expectation from these black and dark-colored enamels. When used, they eliminate the surface defects caused by the steel sheet and provide a clean and optimum surface for the cover coats to be applied later. It can be prepared as a single frit or multi frit. If a single frit is prepared, the frit formulation remains within a limited range to adjust hardness and fusion. Quartz, feldspar, and borax, which are the three fundamental components in the structure, should remain within a certain mole range as in figure 2.4 according to the triple-phase diagram[29]. The percentage of the sum of this triple-phase should be between 92 – 75% wt. of the overall mass[30]. Frits with a high proportion of feldspar become hard and viscous. Such structures can create an orange peel appearance on the surface. It increases the mechanical and chemical resistance of the structure. Also, adding too much quartz to the structure

increases the hardness a lot. The bubbles in the frit take longer to dissolve. If it is not melted in enough time, it makes a fish scale defect on the enamel surface. It is necessary to fire such structures at high temperatures for a long time. Apart from these phases, raw materials such as cobalt oxide, nickel oxide, cryolite, copper oxide, and soda are also entered. We will examine the oxides given by these minerals and their uses in the following sections. In enamel compositions prepared with two or more frits, at least one of the frits used must be a hard frit and at least one of them should be a soft frit. Other frits will be selected according to the purpose of use and will add function to the structure. For these other frits to fuse without separating among themselves, they must contain relatively high levels of fluorine and barium.

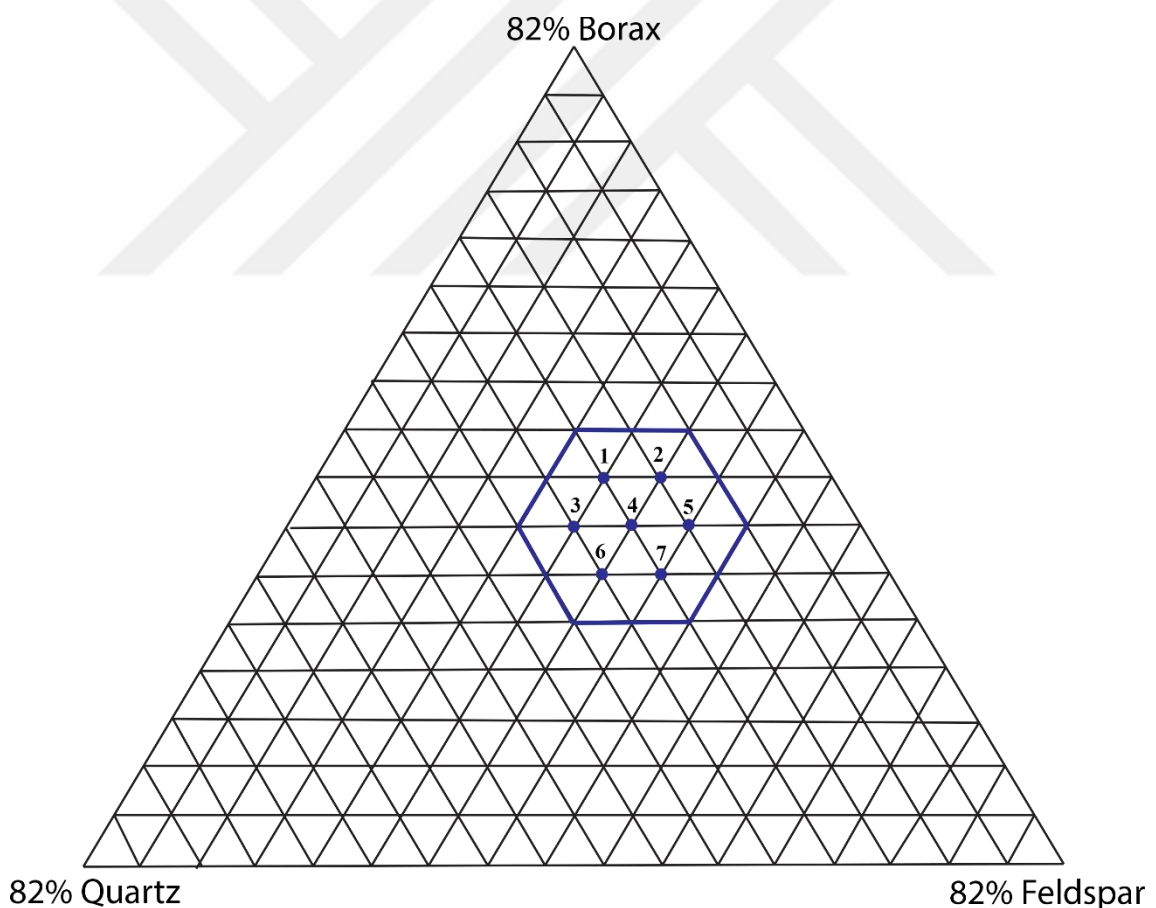


Figure 2.4 Limitations in composition

Clean-only ground coats, also known as Liberty Ground Coats, are intended to replace the acid pickling system applied to the steel before coating. Acid etching and Ni deposition methods have adverse effects on the environment and human health, consume clean tap water, and take time to apply. With the clean-only method, the frit composition containing high Ni and Co provides very good adherence to the metal without the need for this pickling and Ni deposition process.

By changing the chemical composition of the frits in these single or multiple frit compositions or by adding different chemical compounds, enamels with different properties such as **citric acid-resisting enamel surfaces, easy-to-clean enamel, pyrolytic enamel, grill enamel** can be obtained[31].

Unlike other enamel surfaces, **Catalytic Enamel surfaces** have high porosity and a non-glassy surface. The purpose of the use of these enamels is to oxidize the residual oils remaining in the household oven at low temperature, thus allowing the surface to be partially self-cleaned with heat at approx. 250°C. It contains a high amount of heavy metals such as Fe, Al, Cr, Mn, Cu. The melting temperature of these frits is around 1450°C and is higher than other frits[32]. Their hardness is high. They are applied onto a hard character ground coat.

Colored or colorable cover coat enamels with a low porosity vitreous surface occupy a large part of the current enamel market. In this class, we can put self-colored frits, transparent frits, semi-transparent frits, and majolica frits. **Self-colored frits** are used in areas such as ovens, pots, bathtubs, and writing boards. Clear, bright, fluorescent-looking blue, green, cream, etc. colors as well as reflective effective surfaces are obtained. By using **transparent or semi-transparent frits** together with oxidic pigments, dark, vivid, and pastel colors are obtained. Especially with semi-transparent frits, pastel tones can be captured more easily. **Majolica frits** are also self-colored, but since the opacity level is low, the frit color becomes evident as the coating thickness increases[33]. It exhibits gradient color transitions with a shadow effect on embossed surfaces.

Enamel reactors are usually employed in the chemistry, petroleum, insecticide, drug, dyes and pigments, and nutrition sectors, among other things. These frits exhibit piezoelectric resistance, alkaline resistance, acid resistance, and impact resistance. In the gas preheaters, also known as **Luvo**, enamel frits are used to decrease hot air corrosion.

Perhaps the most corrosive substance we encounter in daily life without realizing it is hot water. The water heaters, used to heat tap water, are a highly corrosive environment as they contact to hot water containing corrosive ions such as Na, Ca, K, P, Cl for years. The type of steel that will maintain this environment will corrode in a short time and become unusable. **Alkaline resistant frits** have been developed for this purpose. Structures containing relatively high amounts of SiO_2 , Na_2O , ZrO_2 , TiO_2 have high hardness[34].

2.3.2 Frit Formulation

The behavior of materials in nature with each other under normal conditions changes when conditions change. Depending on factors such as temperature, pressure, vibration, materials can react chemically with each other, dissolve or decompose in each other. All of these dissolutions and reactions take place in certain phases and rates. Since it is very difficult to determine the phases and ratios of all interactions in nature, phase diagrams have been created to show the combinations of materials that we use most and that are useful to us[35].

Frit making is basically based on the same foundation as glass making, as mentioned before. The starting point of this basis is the phase diagrams of the glass. Appropriate raw materials should be entered in the right proportions for the crystals that are aimed to be formed in the glass. Frit formulations are also explained in Enamel Frit Types section (See section 2.3.1)

2.3.3 Frit Raw Materials

Frit raw materials are divided into four main groups: bases, acids, amphoters and others.

2.3.3.1 Bases

Used as a flux, they contain the chemical formula R_2O and RO .

- **Lithium Oxide (Li_2O)**

It is one of the oxides that increase the expansion the most. It reduces the melting temperature and viscosity. Since the cost is high, the amount of usage is tried to be reduced. Lithium Carbonate (Li_2CO_3), Spodumene ($LiAlSi_3O_8$) and Lithium cobalt oxide ($LiCoO_2$) are the main raw material sources[36][37].

- **Calcium Oxide (CaO)**

CaO , which has a very high melting temperature alone, turns into an active flux when soda and potash are added, improving oxidation and reduction. It causes a matte effect when entered too much. It improves the acid and abrasion resistance of the surface. Calcite ($CaCO_3$) and Calcium Fluoride (CaF_2) are the main raw material sources[38].

- **Sodium Oxide, Soda (Na_2O)**

It decreases the melting temperature by increasing the coefficient of expansion. It exhibits very good fusing behavior, especially with boron. When used excessively, it reduces the chemical resistance of the structure. Sodium Carbonate (Na_2CO_3), Sodium Nitrate ($NaNO_3$), Borax ($Na_2B_4O_7 \cdot 5H_2O$), Albite ($NaAlSi_3O_8$) in products containing Aluminum and Silicon, Sodium silica fluoride (Na_2SiF_6) in fluorinated products are used as mineral sources[36].

- **Magnesium Oxide, Magnesite (MgO)**

It is one of the oxides with the highest melting point ($2800^\circ C$). It lowers the melting temperature together with other oxides. It increases the viscosity of the molten glass and the brittleness of the final surface. It is often preferred to obtain a matte surface. Magnesium Carbonate ($MgCO_3$) and Magnesium Oxide (MgO) are the main raw material sources[39].

- **Potassium Oxide (K_2O)**

Its contribution to thermal expansion is high, though not more than Na_2O , and it increases viscosity more than Na_2O . In high-temperature applications, it exhibits a bright and lively surface if it is cooked well enough. Potassium Carbonate (K_2CO_3), Potassium Nitrate (KNO_3), Potassium Feldspar (KAlSi_3O_8), Potassium Silica Fluoride (K_2SiF_6) are the main mineral sources[36].

- **Barium Oxide, Baria (BaO)**

Even at low rates, it develops gloss, elasticity, mechanical strength, and corrosion resistance. Provides vibrant colors with pigments. It is used to give a matte effect. Too much use reduces corrosion resistance. Barium Carbonate (BaCO_3) and Barium Nitrate ($\text{Ba}(\text{NO}_3)_2$) are commercial mineral sources[40].

- **Strontium Oxide, Strontia (SrO)**

When it is replaced with some CaO , it increases the surface gloss due to its high refractive index. Since its expansion coefficient is lower than other fluxes, it reduces structural tension and reduces cracking. accelerates the removal of bubbles in the melt. SrCO_3 is a common commercial mineral[41].

- **Zinc Oxide (ZnO)**

It gives glossy and brilliant surfaces as lead does. It has a high refractive index and slightly increases corrosion resistance. ZnO is available for commercial sale[42].

2.3.3.2 Acids

They are glass network makers. They contain the chemical formula RO_2 .

- **Silicon Dioxide, Silica (SiO_2)**

It is the fundamental glassmaker in frit composition. More than 30wt.% is used in most of the frit. Its ratio to other elements in the structure determines the mechanical, thermal, and chemical properties of the frit structure. Quartz and silica sand are commercial minerals, but also partially found in other minerals such as feldspar[43].

- **Titanium Dioxide, Titania (TiO_2)**

It has low solubility in the silica glass matrix and is a nucleating agent. increases the opacity and refractory properties of the structure. It is used in the production of white top floor frits. It increases the acid resistance of the structure. It is commercially available in rutile and anatase forms[44].

- **Zirconium Dioxide (ZrO_2)**

It is one of the most refractory oxides known, reduces thermal expansion, increases opacity. Increases chemical resistance. Zircon silicate (ZrSiO_4) and Zircon dioxide (ZrO_2) are available commercial minerals[2].

- **Cerium Oxide (CeO_2)**

They are used with SiO_2 to lighten the color of direct enamel surfaces. It is used in self-colored gray enamel frits. CeO_2 mineral is commercially available[45].

2.3.3.3 Amphoteres

Oxides exhibit both acidic and basic properties. They can be used for different purposes.

- **Aluminum Oxide, Alumina (Al_2O_3)**

Increases the chemical durability of the glass structure. It is highly refractory and increases the viscosity of the glass, in this way the flow rate of the molten glass can be controlled. It dissolves well in the glass structure of SiO_2 , reduces the phase separation, and does not affect the transparency[46]. Pure Alumina is not a good source of Al_2O_3 . Instead, commercially available Albite ($\text{NaAlSi}_3\text{O}_8$), Potassium Feldspar (KAlSi_3O_8), and Spodumene ($\text{LiAlSi}_3\text{O}_8$) are used.

- **Boric Oxide (B_2O_3)**

Boric Oxide is another kind of flux material with low thermal expansion and surface tension. It is very efficient in adjusting the melting temperature of frit structures. It gives vivid colors on the surface and reduces cracking. Although Na_2O is a better melter, its use is restricted because of its high expansion coefficient. Boric oxide also improves the thermal shock resistance. B_2O_3 may

create a powerful eutectic with Barium Oxide, allowing for the creation of shiny, flowing enamels that solidify at temperatures under 500°C[43].

2.3.3.4 Others

- **Fluorine (F)**

It is a kind of flux, although it improves the acid resistance up to certain ratios in the recipe, it worsens it after that ratio. It increases the vitality of the surface and gives a shiny surface. It is volatile, so the time factor is important in frit melting. Potassium Silica fluoride (K_2SiF_6), Sodium Silica fluoride (Na_2SiF_6), Calcium Fluoride (CaF_2) are commercially available minerals[47].

- **Nickel Oxide (NiO)**

It improves the adherence of the enamel frit to the steel. It is a strong colorant for frit and gives a dark- navy blue color. Because of the hazardous effect on health and environment, usage of this heavy metal is restricted in Europe and some other areas. NiO and Ni_2O_3 are commercially available oxides[10].

- **Cobalt Oxide (CoO)**

It develops adherence just like NiO. It gives dark-blue color to frit. Little amount of it is used in white enamel. Lithium cobalt oxide ($LiCoO_2$), cobalt oxide (CoO), and Cobalt Carbonate ($CoCO_3$) are commercially available[5].

- **Iron Oxide, Ferric Oxide (Fe_2O_3)**

By acting like alumina in the frit structure, it hardens the structure and increases the viscosity. Enamel tends to be yellow-brown. It increases the fluidity at high temperatures and gives a clean appearance to the frit. It causes unwanted contamination on light-colored and transparent frits. It is available as commercial Ferric Oxide[48].

- **Cupric Oxide (CuO)**

Gives the frit a green color. Improves the adherence of enamel to steel. It reduces thermal expansion, viscosity, and melting point. CuO is commercially available[49].

- **Phosphorus Pentoxide (P_2O_5)**

Provides color stabilization on frits containing titanium. It has a tendency to crystallize, increases opacity, improves hydrophobic properties by increasing surface roughness. Mono-Ammonium phosphate ($NH_4H_2PO_4$) and Sodium tripolyphosphate ($Na_5O_{10}P_3$) are available as commercial minerals[50].

- **Antimony Oxide (Sb_2O_3)**

Antimony oxide is used as an opacifier in porcelain enamel compositions. It is very easy to reduce it in the composition. The glass industry uses this oxide as a decolorizing and fining agent to clarify glasses and as a stabilizing agent in the production of emerald green glass. Antimony has a low thermal expansion[51].

- **Chromium Oxide (Cr_2O_3)**

It is used to give a green color to frits. Decreases adherence level with metal. The dissolution in the glass network is not good, it can decompose from the structure. Chrome Oxide is commercially available[52].

2.3.4 Frit Melting & Cooling Down

After the frit, raw materials and their weights are determined, automatic or manual weighing is made. Mixing homogeneously just before entering the furnace is one of the most important parts of frit production. All minerals should be mixed homogeneously without grinding. During this mixing process, the humidity in the mixer or the air should be at room conditions or less, and no solid, liquid, or gaseous pollution should be transmitted from the outside. The mixture is taken to the feeding silo to enter the furnace and is fed into the furnace at a certain speed, with the help of an adjustable helix. The parameters in the furnace are as follows; Furnace type, feeding speed, furnace temperature, firing time, inner pressure, furnace internal inclination, heat source, air source (O_2 , air, or mixture) used. It must have sufficient firing time for the minerals entering the furnace to form a glass network homogeneously and to oxidize. This situation can also be called infusion or maturation. During the melting, the batch structure becomes more fluid by rupturing or distorting the fairly normal SiO_4 lattice. To lower the

softening point, B_2O_3 is added, which causes part of the Si–O bonds to break and an irregular network to develop[53]. Alkali and alkaline earth metals are introduced into the lattice to further disrupt the network. More bonds are broken when fluorine is added to the frit; an oxygen atom (–O–) that links two Si or B atoms is replaced with a fluorine atom which, since it is monovalent, cannot unite two Si or B atoms and so causes bond rupture. To formulate low-firing enamels, knowledge of pertinent phase diagrams and eutectics is beneficial.

Along with carbonates, sulfates, crystals, and physically bound water, some F and B also try to move away from the structure by passing into the vapor phase during the melting process. To facilitate this degassing process, the refining agents mentioned in the previous sections in glass can be used. Although the gas is removed from the structure during the melting of the glass, small bubbles are present in the frit even at the end of cooling. Rapid cooling is essential for the vitrification of frits. In frit production, this cooling is generally done in two ways; quenching the melt in the water or passing it between water-cooled cylinders and obtaining it as sheets. In the second method, the sheets are crushed into small pieces with the help of a crusher.

2.4 Substrates Selection & Pretreatments

Substrate selection is an area that needs to be as meticulous as glass-ceramic coating production to obtain a good enamel surface and good adherence. No matter how high performance the coating is, if it cannot adapt to the substrate, errors such as cracking, fish scale, chip-off, blistering, etc will occur. Glass-ceramics can be coated on almost most of the materials (see Section 2.1.2 for areas of use). There are low-carbon steel sheet types specially produced for steel sheet enameling. When determining the type of steel, the intended use of enamel should be considered. Acid resistance, corrosion resistance, mechanical strength, thermal shock, hot-cold resistance, color-exterior appearance, hygiene, and easy-to-cleaning, etc.

2.4.1 Steel Production, Properties & Qualities for Enamelling

2.4.1.1 General Properties of Steels

Iron is divided into two groups in terms of its common usage area. Cast iron and steel. Cast iron is a material with a carbon content of over 2.1% and most of this carbon is composed of graphite. The high carbon content in cast iron makes it nearly impossible to shape this material by another method. The mold filling properties of cast iron are good because of its good fluidity. Compared to steel, it conducts very well, has a high heat capacity, is quite brittle, and has vibration-damping properties. Steel is a material with a carbon content of less than 2.1% and this carbon in chemical bond with Fe is named Cementite. These two basic iron materials can be divided into hundreds or even thousands of different branches[54].

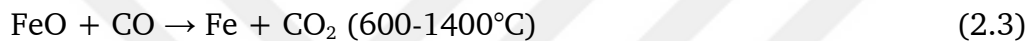
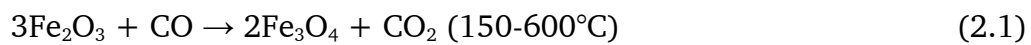
Phase diagrams are the starting point of metal production in crystalline metals as well as in glass and ceramics. Pure iron is in the α -iron or ferrite phase at room temperature. As the amount of carbon increases, the formation of cementite (Fe_3C) crystals increases, and the microstructure of the steel changes[55]. The steel microstructure can also be adjusted with alloying elements and through heat treatments. The microstructure of the steel affects many properties from the hardness of the steel to its ductility, mechanical properties, corrosion behavior, welding ability, etc[54].

Since steels are mostly used for mechanical strength, they are exposed to all kinds of forces. Various test methods have been developed to measure their mechanical resistance against these forces. Tensile and compressive strengths, shear strength, buckling, fatigue, creep, toughness, hardness, and ductility are the most important mechanical properties and all these properties are interdependent. Alloying elements, production method, heat treatments also directly affect these properties [54].

2.4.1.2 Steel Production

Steel production is made from two types of raw material sources, primary and secondary. The primary raw materials are minerals. Minerals such as hematite,

magnetite, limonite are used to produce pig iron. The secondary raw material source is steel scraps. Steel production can be made by using these two raw materials separately or together. Pig iron production is obtained by melting coke, ore, and limestone together in blast furnaces at temperatures up to 2000°C. The ore is obtained employing pelleting, sintering, or briquetting of minerals with or without additives[56]. Limestone facilitates the oxidation of the gangue inside and separates it from the metal. Coke is both a heat source and a good reducing agent. Coke performs its main reducing role simply according to the following reactions[57];



The reduced molten steel is drawn from the lowest belly of the blast furnace. Slag floating on the metal is discharged separately.

There are four methods used to produce steel from the pig iron obtained in this way; Bessemer – Thomas (BT), Siemens – Martin (SM), Basic Oxygen Furnaces (BOF), and Steelmaking in Electric Arc Furnaces (EAF). BT and SM methods have been replaced by BOFs and EAFs due to their slow production speed and/or low efficiency[58]. The working principle of EAF is melting by passing an electric arc through the scrap metal with the help of graphite electrodes. Most of the time, pig iron is put into the crucible along with the scrap to maintain the chemical balance. Carbon reduces Fe-oxide to metallic Fe according to the above reactions. In basic oxygen furnaces, pure oxygen is blown into the molten pig iron coming from the blast furnace, and all impurities such as carbon, in particular, Si, P, S in the structure are oxidized at approximately 1700°C and joining to the slag[57].

2.4.1.3 Steel Shaping & Design for Enamelling

The shaping of metals is traditionally done by 5 methods; plastic forming, powder metallurgy, welding, machining, and casting. These methods can be used singly or in combination. Plastic forming can be done above or below the crystallization

temperature of the steel, taking advantage of the ductility of low carbon steels. The plastic forming method is divided into types such as forging, rolling, extrusion, drawing, bending, cutting, deep drawing. By using these methods, steel producers can introduce products in the form of Round bar, Hexagonal bar, Plate, Sheet, and Profile[59]. While these 5 shapes are not restrictive, they are the most traded shapes on the market.

Steel sheets are obtained by rolling Steel slabs, blooms, or billets. If the production is made by the continuous casting method, the molten metal is cooled to a certain degree and fed to the rolling mills. Hot rolling is the heating of the steel to 50-100°C above the recrystallization temperature (400-700°C) and thinning by progressing between the rolling mills. During hot rolling, the crystals are rearranged during the process due to temperature[60]. The final surface quality is not good compared to cold rolled. Metal buildings, railroad hopper cars, and railcar components, water heaters, tubes, pipes, agricultural equipment, etc. are made by this method. In the cold rolling process, steel is passed between the rollers after being coated with a lubricant, usually at room temperature. For this reason, the surface quality is very high. Since there is no heating process, work hardening occurs in the structure during the rolling process. Cold rolling is a more expensive process than hot rolling. Exhaust pipes, computer shells, household electronic furnitures, shelving, tubing, thin blades, steel drums, lawnmowers, pans, pots, etc. are made by this method.

Steel Enamel manufacturers usually take their steel as sheet metal roll and give the final shape themselves. Some companies get the metal in a shaped form and only coat with enamel. Firms that make the final forming of steel sheets generally use two methods; die-stamping and welding.

2.4.1.4 Common Steel Qualities for Enamelling

Steel standards for enameling are referenced to **EN 10025** or **EN 10111** for hot rolled steel, and **EN 10209** for cold-rolled steel sheets. The general properties of the most commonly selected steels according to these standards are shown in Table 2.2[61][62].

Table 2.2 Properties of enamel quality steels

Cold Rolled Steels						
Quality	Max C %	Max Ti	R_e Max (MPa)	R_m (MPa)	A₈₀ % (Min)	r avg. (Min)
DC 01 EK	0.08	-	270	270-390	30	-
DC 04EK	0.08	-	220	270-350	36	-
DC05EK	0.08	-	220	270-350	36	1.5
DC06EK	0.02	0.3	190	270-350	38	1.6
DC07EK	0.02	0.2	253	270-472	42	-
DC03ED	0.004	-	240	270-370	34	-
DC04ED	0.004	-	210	270-350	38	-
DC06ED	0.02	0.3	190	270-350	38	1.6
Hot Rolled Steels						
Quality	Max C	Max Mn	R_e (MPa)	R_m (MPa)	A₈₀ % (Min)	
DD11	0.1	0.6	170-340	<440	24	
S240EK	0.1	0.6	>240	360-430	27	
S300EK	0.1	0.6	280-420	360-500	25	

DC01EK, DC04EK, DC06EK and DC07EK are generally perfectly compatible with 1coat/1fire and 2coat/2fire. DC04EK, DC06EK, DC07EK, DC03ED, DC04ED are more suitable for 2coat/1fire system. DC05EK is produced especially for bathtub manufacturing. DC07EK is very good at deep drawing applications. DC04EK is generally preferred for domestic appliances (cooking, laundry, stoves, etc.), architectural panels (interior and exterior). DC03ED and DC04ED are suitable for

direct white coating applications after pickling and Ni deposition on the metallic surface. DC04ED is also usually preferred in the production of self-cleaning pyrolytic household ovens[63].

Hot-rolled steels are used for water heaters, tubes, and pipes. However, they tend to make fish scale defects so to prevent this, they are coated only one side with alkaline resistant enamel. Thus, during the enamel firing, the gases in the steel can easily come out from the other uncoated side. On the other hand, in this type of steel, there may be a decrease in yield strength after enamel firing. S240EK and S300EK steels are specially produced to maintain this strength. S240EK is preferred in water-heater bottoms due to its good drawing properties. S300EK is mostly used in water-heater bodies. This kind of steel needs sandblasting procedure before the coating[64].

2.4.2 Sheet Steel Pretreatments

Sheet steel pretreatments can be made for different purposes. These purposes can be surface cleaning, etching, pickling, increasing the surface area, and changing the surface chemistry (Ni deposition). In the pre-treatments carried out just before the enamel coating of the steel, several of these can be used consecutively, or it may be sufficient to use only one of them. Different cleaning processes could be applied as stated in figure 2.5.

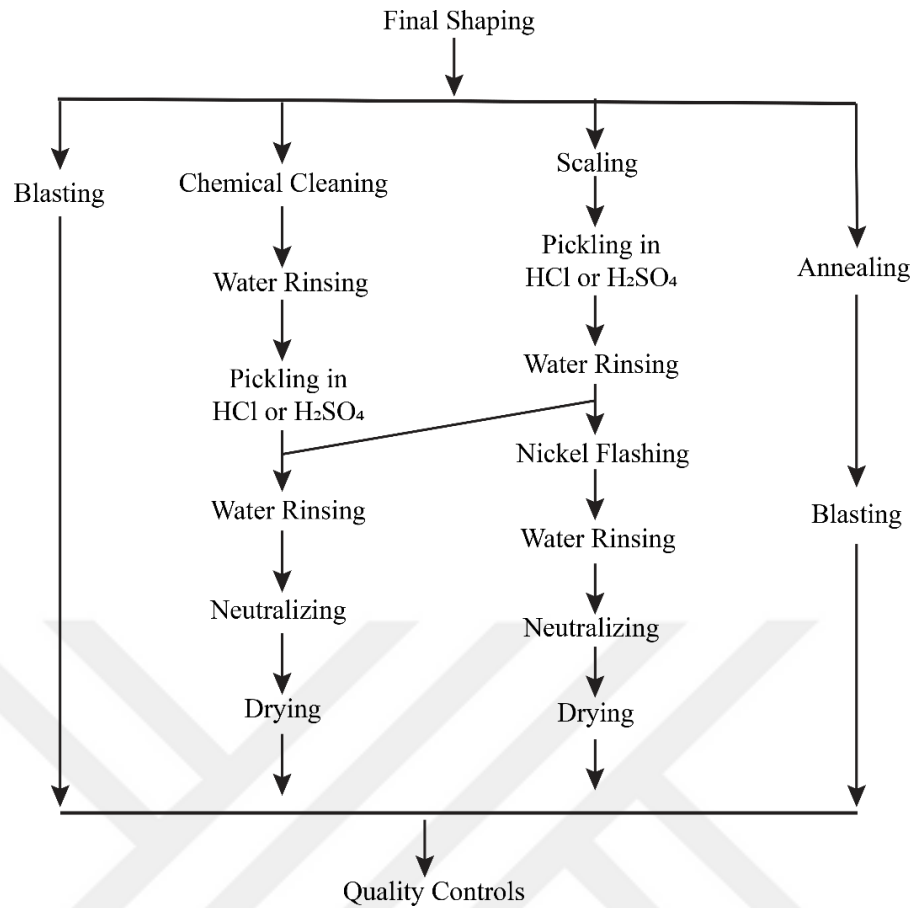


Figure 2.5 Preparation flow sheet for the metal for enamelling[29].

2.4.2.1 Surface Cleaning

Sheet steel comes from the manufacturer as oil-coated to prevent rust. This oil is deposited on the metal about 0,2-0,4 g/m². Also, there could be mineral oil on the surface that comes from the metal shaping section[65]. Cleaning of the surface of sheet steel from this oil and dirt comprises two main phenomena; saponification and emulsification. Saponification is basically transformation of oil to soap and glycerine together with a cleaner solution. Emulsification makes the oil droplets and takes them in the cleaner solution. These two phenomena work together during the cleaning process. Inorganic compounds such as Sodium Hydroxide (NaOH), Sodium metasilicate (Na₂O.SiO₂.5H₂O), Trisodium Phosphate (Na₃PO₄.12H₂O), Sodium Carbonate (Na₂CO₃), and ammonia (NH₄OH) are used in alkaline cleaning baths. In addition, compounds such as Sodium oleate, resin

soaps, Potassium linoleate are also used as colloidal materials in cleaning solutions. Keeping the cleaning solution at a temperature between 40-90°C will accelerate the degreasing reaction[65].

Electrolytic cleaning is also accelerating the degreasing. The metal piece is made the cathode and the metal tank becomes the anode. In this case, bath chemistry must be arranged to provide efficient current and cleaning.

After the cleaning alkaline bath, a hot water bath at 60-70°C should be applied to remove saponified oils. Otherwise, this residue could make a defect on the enamel surface.

If the metal surface is too oily, it is recommended to use Trichloroethylene (TCE) and Perchloroethylene (PCE) before the alkaline bath. However, it is not a common procedure[29].

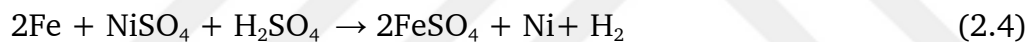
2.4.2.2 Pickling

In the Pickling process, an acid solution is used to remove rust and scale from the steel piece. The process also makes etching so increases the surface area which develops bonding between enamel and steel. Sulfuric acid (H_2SO_4) and Hydrochloric acid (HCl) acid are the two most commonly used acids in this process. Sulfuric acid works faster than other acids and is cheaper. Generally, 6-9% vol. of the solution is used around 67°C. If acid is necessary for 1C/1F applications, H_2SO_4 should be used, and approx. 50-55 gr/m² material should be removed from the metallic surface. However, it is inconvenient to use hot acid steam due to the damage it causes to human health and equipment[29]. Since HCl works at room temperature, it is preferred when a cold application is desired. Phosphoric acid is not preferred because of its high cost, but its importance is increasing in the application of single-coat white enamel. When phosphoric acid is used before the nickel deposition process, it increases the surface quality, the damage to the equipment is lower than other acids, and the amount of Fe removed from the part is less. In addition to these, adding some iron pyrites or sodium thiosulfate, or sodium sulfide into the pickling solution accelerates the pickling process[66].

After the acid pickling bath, if there will not be Ni deposition, Water Rinsing and Neutralizing are essential before drying. Neutralizing is done for three purposes: Neutralization of the acid residues left on the surface after the acid bath, precipitation of the Fe salts formed on the sheet surface after the acid bath, and separation as $\text{Fe}(\text{OH})_3$, preventing the oxidation of the steel surface, which becomes activated and unprotected after the acid bath, by covering it with a protective soda-borax film. Soda-Borax solution is the most common neutralizer solution. The bath is used hot at about 70°C .

2.4.2.3 Nickel Deposition

Ni deposition or Ni-Dip is used to improve adherence in single coat enamel applications. Fishscale and copper head problems are also eliminated with the process. The part is immersed in a $70\text{-}90^\circ\text{C}$ bath containing $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ salt is electrolytically coated with Ni. The stoichiometric reaction is done according to the equation below. Before this process, pickling, and after the Ni-Dip, rinsing-neutralization should be done[67].



2.4.2.4 Sandblasting

The blasting process is applied for increasing the surface area and cleaning the surface. The hard particle is blown to the metallic surface by pressurized air and gives damage to the surface. Alumina, silica sand, and steel grit are generally used as hard particles for this purpose. The sheet steel must be hard and thick enough to resist hard particle shots. Sandblasting also called shot blasting or blasting, is essential for cast iron enameling. It decreases the blistering defect, increases the enamel surface quality and adherence between cast iron and enamel[68].

2.5 Enamel Coating Methods for Steel

Enamel coating methods are traditionally divided into two: wet coating methods and dry coating methods. Among the wet coating methods, wet spraying, dip coating, and flow coating are the most used methods in the industry. In addition to these, although not used much, there are electrostatic wet spray, plastering,

and electrophoretic methods. As a dry coating method, the electrostatic powder coating method dominates the market and its use is increasing. Apart from traditional methods, there are also expensive but proven studies such as thermal coating [69]. In all coating methods, the glassy frits must be ground and fine to apply the coating. After the coating process, if the coating is made with the wet method, it is ensured that the enamel takes its final appearance by drying and then firing in the air at a gradually increasing temperature. The fact that heating and cooling curves of the enamel firing furnace must be smooth, homogeneous, sufficient, and evenly distributed to obtain the best performance and surface quality for GC enamel.

2.5.1 Preparation

The preparation comprises the preparation of the mixture according to the coating method. It consists of four steps, determining additives, weighing, milling, and checking. Additives are chosen according to the coating method so they will be explained in every coating method separately. After choosing the application method and weighing the additives, all materials in the batch are milled together to obtain powder or slurry (or Enamel suspension or wet enamel).

The basis of milling is based on crushing. In crystalline and amorphous solids, fractures first develop in stress zones. Stress zones can be at the macro level such as cracks, crevices, bubbles, or in microzones such as dislocations and grain boundaries[70]. According to Hook's law, Atoms give back the energy they received when the bonds are subjected to such little tension that they don't break. When rupture occurs, the stored energy transforms into free surface energy, or in other words, the potential energy of newly formed surfaces of atoms. During milling, 4 fundamental forces are applied to the solid particle: compression stress, shear stress, impact stress, and collision stress. Ball milling is generally used efficiently in the enamel industry. It is the name given to the mills whose grinding media contains metal or ceramic balls. The working principle is, the fed material moves together with the balls, and the balls grind the ore by free falling. By this method minerals or frits with 3-10mm particle size, can be milled down to 5-20 μ m

range. However, particle sizes are not homogeneous, instead, distribution in different sizes with different ratios[70]. One of the most important factors in ball mills is the ball material. The factors that should be considered when choosing ball material are stated in figure 2.6.

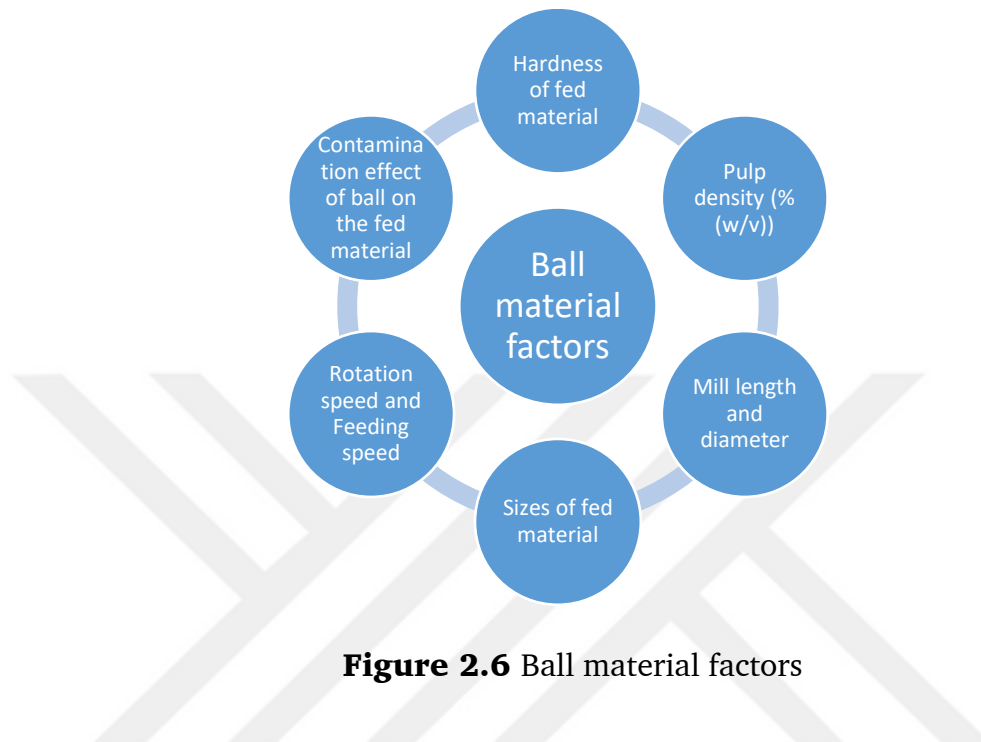


Figure 2.6 Ball material factors

Alumina, agate, glass, and Yttria stabilized Zircon materials are widely used as ball material in the ceramic and glass industry. Another important factor in the selection of ball material is below 0.1%wt of iron percentage, otherwise, it may damage most of the properties of the milled product, especially the color.

In general, the ball charge rate in wet and dry grinding is 40% of the internal volume of the mill. However, the ball charge rate can be slightly increased in dry grinding. Neikov provides useful more information about milling[70].

After milling, it is checked whether the powder obtained has the desired particle fineness. Here, it is practical to calculate the percentage remaining on the sieve. The ratio of the product remaining on the sieve after sieving from a certain amount of ground product taken on the sieve to the product placed first is considered as the over sieve ratio or the Bayer of the product. In wet applications, it is done according to Bayer Scale using the 150 mesh or 325 mesh sieves. The electrostatic

powder is applied according to the amount of grams remaining on the 45µm sieve. However, particle size distribution measurement can also be performed, which gives a more precise result. In addition to the particle size, tests such as contamination control and chemical composition tests are also done at this stage.

During the batch preparation, mill additive selection and rate of them is one of the most important section for properties of enamel coating.

In wet applications, five kinds of mill additives are used for different purposes listed in table 2.3.

Table 2.3 Wet enamel mill additives

Type	Additive Example	Function
Suspending Agents	Clay	It ensures that the ground frit grains can be suspended without bottoming out. It is a suspension builder
	Bentone, Bentonite	Bentonite is artificial, bentone is natural. Their suspending ability is higher than clays, but their cost is also higher.
	Silica Fume	It gets different names under different brands. Since they are very thin and light, they increase the consistency by swelling. They are added as clay aid.

Table 2.3 Wet enamel mill additives (continued)

Suspending Agents	Carboxymethyl cellulose	It is added to help clay in slurry. It swells in water and increases the mud consistency too much.
Electrolytes	Sodium Nitrite Potassium Nitrite	It dissociates into ions in water and increases the wet pick-up value (explained in the next section) of the enamel mud.
	Borax	Sets the flow rate and time of the enamel mud. Boric acid reduces aging relatively.
	Potassium Carbonate	Decreases enamel slip flowing time
	Sodium Aluminate	It ensures the homogeneous distribution of frit particles.
	Magnesium Sulphate	Increases the wet pick-up value
Refractory Materials[71]	Quartz Potassium Feldspar Zircon Silicate	They provide mechanical strength by increasing the firing temperature.

Table 2.4 Wet enamel mill additives (continued)

Pigments[65]		They are used to give color to the enamel coating. They are inorganic metal oxides and insoluble in water.
Other Agents	Zinc Sulfide, Copper Oxide, Nickel Oxide, Aluminum Hydroxide, Cerium Oxide, etc.	They are used to give special properties to enamel surfaces and structures.

2.5.2 Coating Methods

Coating methods could be wet, dry, or with different methods depending on the developing technology. In the enamel industry, coating methods in wet applications are generally chosen as wet spraying, dip coating/flow coating, electrostatic wet spraying, electrophoretic coating, and plastering methods. Dip/flow coating and spraying are the most commonly used in wet applications.

In dry methods, the most common method is the electrostatic powder coating method and its use is getting more common. In this method, the frit and additives are milled with a polymeric resin. Then, the particles, which are charged with negative charge with electrostatic guns, are sent to the grounded steel part with the help of pressurized air. Charged particles hold homogeneously the flat enamel surfaces. In this method, there is a restriction for some parts because of the Faraday Cage problem.

Dip Coating

Dip coating is a simple traditional method of applying a homogeneous thin film of liquid or liquid-like slurry onto a substrate, notably tiny slabs, cylinders, or other shapes where the perfectly uniform film thickness is not required for solidification

into a coating. The fundamental flow is constant, and the film thickness is determined by the struggle between viscous, capillary (surface tension), and gravity forces. The flow characteristics in the liquid bath and evaporation can affect thickness and homogeneity. The thicker the layer is deposited when the faster the substrate is extracted[72]. Using volatile solutes and combining quick enough drying with the basic liquid flow helps mitigate this. The physics becomes more sophisticated, theoretical process performance prediction becomes more difficult, and process control becomes more demanding. The film (coating) may or may not solidify during the dip-coating process[73]. When the substrate is a long, flexible sheet or filament, the process can also be done in a continuous line. There are five stages in the dip-coating process as also seen in figure 2.6[72]:

- Dipping,
- Start-up,
- Deposition,
- Drainage,
- Evaporation.

The film thickness in dip coating method is calculated by equation below[74];

$$h = c \frac{\eta u^{\frac{2}{3}}}{x_{Lv}^{\frac{1}{6}} (\rho g)^{\frac{1}{2}}} \quad (2.5)$$

Where:

c : a constant related to the curvature of the dynamic meniscus (0.944 for Newtonian liquids)

h : Thickness of film

x_{Lv} : Liquid vapor volume

ρ : Density of solution

g : Gravity constant

u : The rate at which the substrate withdraws from the solution.

η : Viscosity of solution

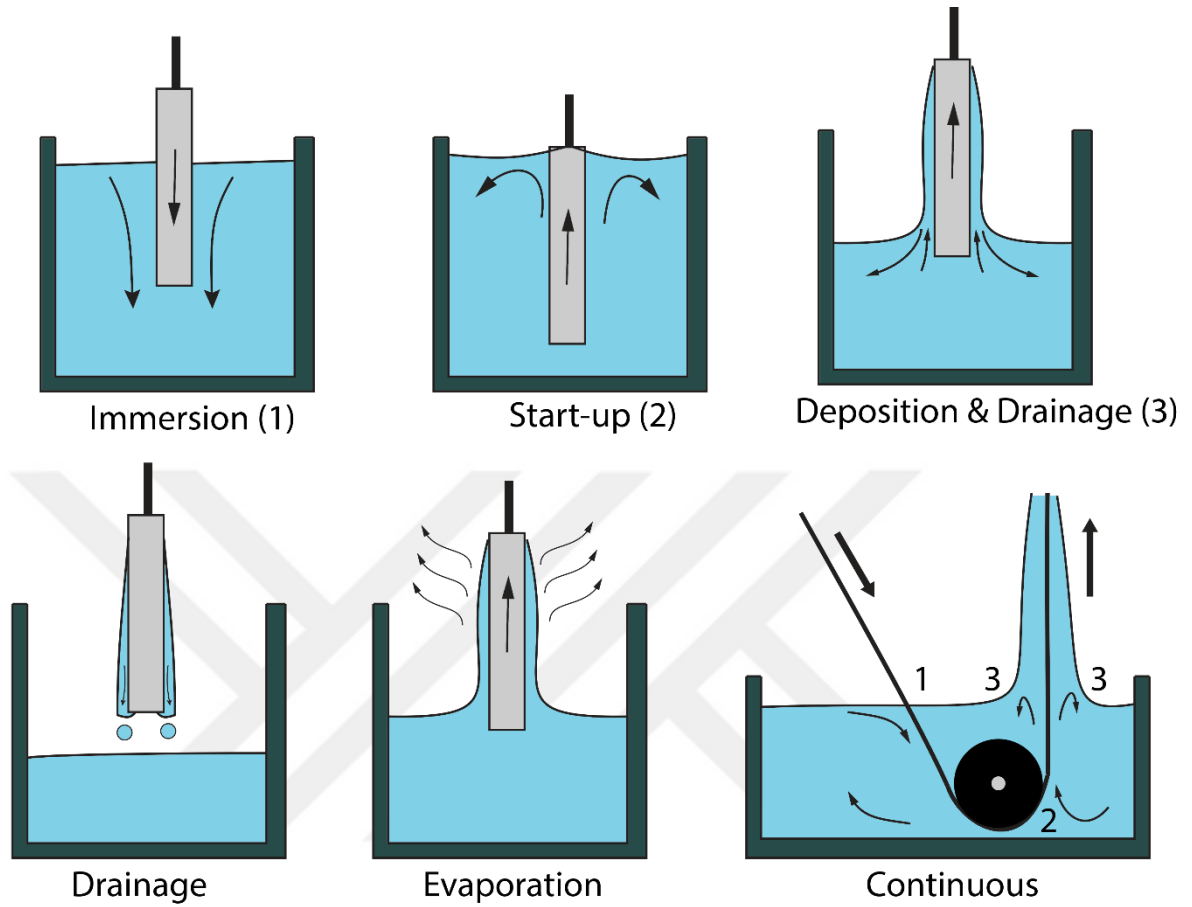


Figure 2.7 Dipping procedure

2.5.3 Rheological Properties of Enamel Slips

Fluids are generally divided into two: Newtonian and Non-Newtonian. To show the difference clearly, it is necessary to examine the viscosity behavior of that liquid. Viscosity is its resistance to mobility and is mathematically represented as:

$$\frac{1}{\text{Viscosity}} = \text{Mobility}$$

Also, viscosity can be determined by the Rotational Viscometers and calculated by the equation below:

$$F = \eta \cdot S \quad (2.6)$$

Where:

F: shearing stress

S: rate of shear.

Enamel slips are Non-Newtonian liquids. In addition, it may exhibit some of all of the plastic, pseudo-plastic, and dilatant liquid properties. These three liquid types are the classes of the consistencies of liquids[29].

The thick frit grains that make up the enamel don't have the ability to suspend or dissolve in water on their own. For this reason, it is essential to use suspending agents as a mill additive in all kinds of wet applications. Clay is generally used as a suspending agent for enamel slips. Electrolytes such as Borax, Sodium nitrite, are used to assist to arrange the rheological behaviors of slips. The types, amounts, and particle size distribution of these additives determine the rheological characteristics of the enamel slips.

Since the suspending stability of enamel coatings is low, there are some things to be considered in the preparation of the enamel suspension before proceeding to the coating process. Before moving on to these parameters, it is necessary to mention a few concepts that should be known in the dipping process of wet enamel. These are wet pick-up, rate of set (flow time), and density. These three parameters must be strictly controlled for a homogeneous and defect-free enamel coating at the desired thickness.

Wet pick-up is the weight (gram) of the wet enamel slip remaining on the square meters metal surface after the dipping and draining process. Sheet metal is dipped into an enamel slip and let it drain. After the draining, the weight of the wet slip is weighed in (metal must be tared beforehand). The rate of the set is flow time. Generally increasing draining time decreases the wet pick-up. Decreasing density increases the draining time and decreases the wet pick-up. Particle size distribution is also changing all these parameters.

In order to efficiently use soluble materials such as electrolytes, or salts, as mill additives, it is necessary to ensure the dissolution of these electrolytes. The most

common method of accelerating solubility is prolonged mixing. Mixing an electrolyte-containing enamel slip for a certain period before using it in the dipping process allows the salts to fulfill their duties and to reach the desired rheological values. However, too much mixing or keeping a prepared enamel slip without being used for a long time also causes problems such as aging, agglomeration, and separation in the enamel, which may affect the application and the surface quality of the enamel. In addition to these, water is the basic material for making wet enamel is also important. The conductivity values, pH, and the ions contained in the water also affect the wet pick-up values of the enamel.



EROSION / CORROSION OF GLASS-CERAMICS

3.1 Introduction to Erosion / Corrosion

Almost all metallic, ceramic, polymeric, and composite materials in nature are prone to corrosion in some way. In some cases, this takes minutes, while others take centuries. The concept of corrosion is completely relative and is used for situations where dissolution and decomposition have negative and undesirable meanings. While oxidation of metals is an undesirable situation when the mechanical properties of metallic materials are used and considered as corrosion, in some metals such as aluminum, oxidation of the surface is seen as a critical factor for protection from corrosion development. In other words, with a good understanding of the corrosion mechanism and a good preparation of material engineering designs, the rate of corrosion can be slowed down and even benefit from corrosion. During the production of glass-ceramic coating materials, which are the basis of this thesis, the liquid phase sintering, crystal growth, and the dissolution of the raw materials in each other are all based on corrosion. In addition, the etching process during metallographic sample preparation, the separation of sodium and boron-rich phases by selective leaching to produce silica glasses (commercially Vycor™), and the bonding of biomaterials with the bone are based on corrosion. In addition to these, understanding the mechanism of vitrification and corrosion mechanism is critical for nuclear waste, which is one of the biggest threats to the environment, to be neutralized and remain uncorroded in nature for thousands of years. International institutions such as the National Association of Corrosion Engineers (NACE International) raise awareness about the corrosion in the world and provide engineering training on corrosion.

Although there are no clear lines separating corrosion mechanisms in glasses, ceramics, and glass-ceramics, there are some differences. When we get down to

the basics, dissolution corrosion, which is one of the most frequently used terms in the corrosion of inorganic materials, can include galvanic cell corrosion, grain boundary corrosion, diffusion, and stress corrosion, which we know from metals.

Although erosion is generally perceived as corrosion, its mechanism of the process is fundamentally different. While corrosion develops mostly through chemical effects and reactions, erosion develops mostly through physical effects. The word erosion comes from the French word "érosion" and its meaning is wear. Erosion, which is generally considered a geological process, is used to describe the wear and transportation of rocks in nature by wind and water fluids. During the transport of water and air fluids from one place to another, friction and impact forces are applied to the material that resists the movement. The solid particles in these fluids increase the effect of these forces and erode particles from the surface of the resisting material. For erosion to occur, a moving fluid must be present in an environment. The combined processes of erosion and corrosion are called "**tribocorrosion**" by the metallurgists.

3.2 Ceramic Corrosion

Ceramic corrosion proceeds through dissolution mechanisms. According to Surendranathan, there are 5 types of dissolution mechanisms in ceramic materials [75];

3.2.1 Congruent dissolution by simple dissociation.

If the ceramic material dissolves in this way, the ratio of ions contained in the dissolved chemical is equal. The decomposition of NaCl as Na^+ and Cl^- is a good example of this situation. In this way, the thinning of the material will be the same at every point and the concentration profile on the surface of the material will always remain the same. This dissolution type is independent of pH and does not form a protective layer on the material surface. The concentration profile on the surface is shown in Figure 3.1.

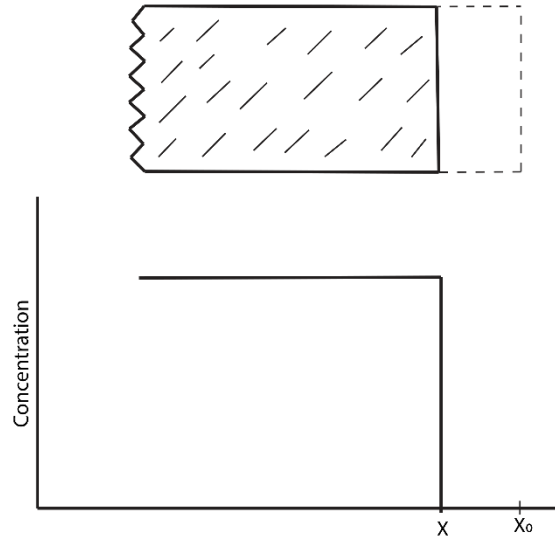


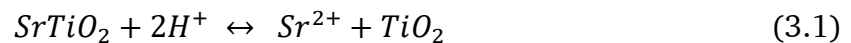
Figure 3.1 Representation of congruent dissolution by simple dissociation

3.2.2 Congruent dissolution by chemical reaction with the solvent

This type of dissolution occurs by acid-base reactions or hydrolysis reactions as a result of a solvent attack on the surface. Hydrogen ions attack the crystal immediately at low pH levels, whereas hydrolysis takes over at neutral pH levels. No protective solid reaction products are occurred on the surface [76].

3.2.3 Incongruent dissolution with the formation of crystalline reaction products

In this type of dissolution, the solvent and the ceramic surface react to form a new crystalline product on the surface. The dissolution of strontium titanate with acid is a good example of this phenomenon.



Dissolved Sr^{2+} ions are transferred into the solution and move away from the surface, leaving TiO_2 crystals behind. Since TiO_2 is insoluble in acid, it continues to exist on the surface. In this way, the surface chemistry and physical structure of the material will be different from the main ceramic. The concentration profile is shown schematically in Figure 3.2

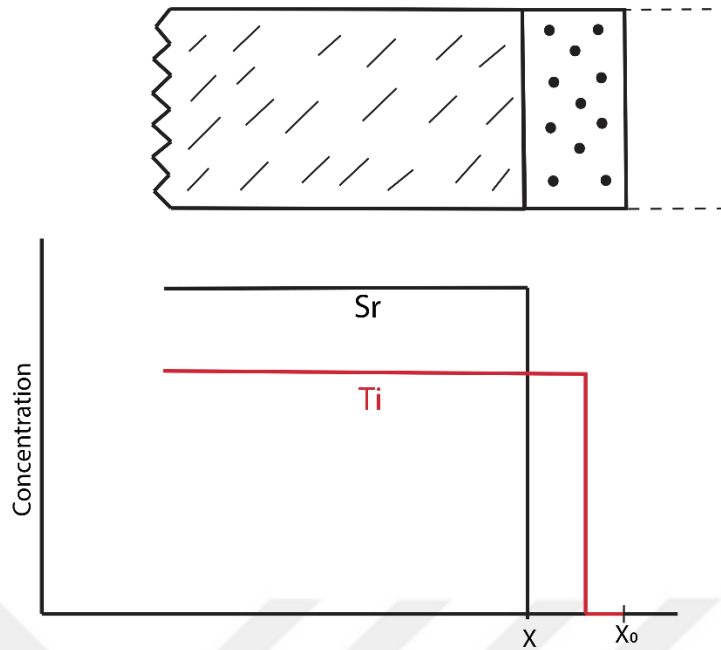
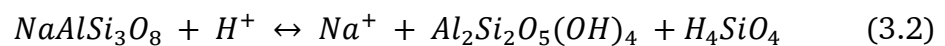


Figure 3.2 The concentration profile incongruent dissolution with the formation of crystalline reaction products

3.2.4 Incongruent dissolution with the formation of noncrystalline layer

In this type of dissolution, gel formation is observed on the crystal surface as a result of the contact of the crystal with the solvent. The reaction of Sodium aluminosilicate with acid is a well-known example.



As a result of the reaction, the silicon tetrahedral compound with Na^+ ions is separated from the structure and mixed into the solution. The remaining gel layer reduces the reaction/corrosion rate on the surface. In the final surface chemistry, while Al and Si elements decrease, the percentage of Al element increases. The concentration profile is shown schematically in Figure 3.3.

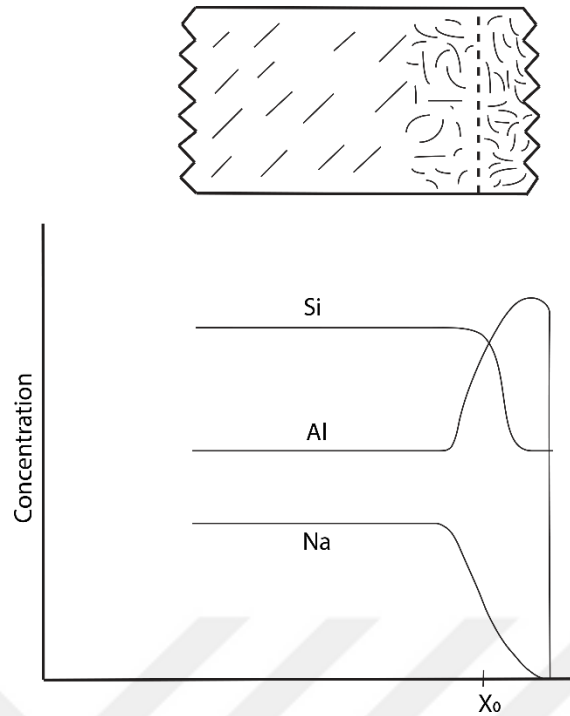
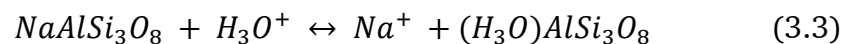


Figure 3.3 Concentration profile incongruent dissolution with the formation of the noncrystalline layer

3.2.5 Ion Exchange (Selective Dissolution)

It is based on the principle that an ion in the main crystal passes into the solution, while an ion from the solution participates in the crystal structure. A different dissolution mechanism of the Sodium Aluminosilicate mineral can also be an example of this type.



In the final surface chemistry, the Al/Si ratio retains its initial ratio. The concentration profile is shown schematically in Figure 3.4.

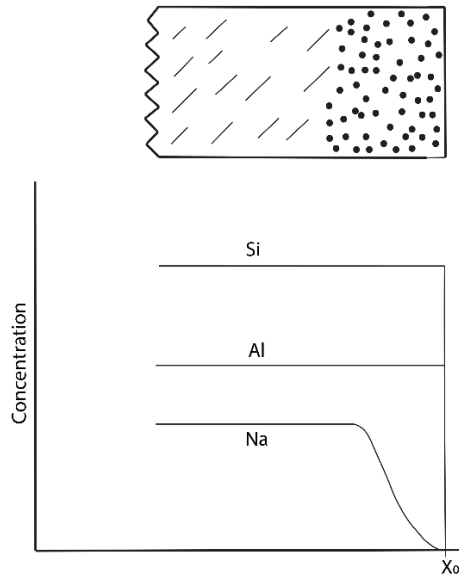


Figure 3.4 concentration profile of selective dissolution

3.3 Glass Corrosion

The interaction of alkali silicate glasses with water solution is commonly thought to be the consequence of two separate processes: initial diffusion-controlled extraction of alkali ions from the glass network (Ion exchange), and degradation of the glass matrix itself [77][75][78]. The first reaction is defined as an ion exchange (interdiffusion $\text{Na}^+ / \text{H}^3\text{O}^+$ or Na^+ / H^+) mechanism or due to water diffusion into the glass network, and the alkali release is square root time-dependent. Alkali diffusion continues to take place over time, raising the depth of depletion. The rate of alkali release to the medium reduces as the depth of alkali depletion increases. When this occurs, matrix dissolution takes over as the primary response.

During the corrosion of silicate glasses in the water environment, various layers are formed at the glass-water interface. Dealkalization of this interface facilitates the dealkalization and thus the dissolution of the matrix glass. The dealkalization of the interface depends on the following parameters [79];

- Diffusion rate of alkalis in this layer
- Layer Porosity

- Layer thickness
- pH of the solution.

Silica can be leached from a glass as a consequence of ion exchange with protons from the solution, or when hydroxyl ions from the solution attack the matrix's siloxane bonds. At low pH, the former process dominates, whereas at high pH, the latter. There are five distinct categories of leached glass surfaces [80]. Table 3.1 shows these classifications. When metal hydrates or hydrated silicates are present in Types I, II, and III, the reaction layer that develops have poor solubility. These layers are frequently protective, preventing further corrosion.

Table 3.1 Classification of glass corrosion [80].

Leached Surface Models for Glasses		
Type 1	Thin hydrated layer; $< 5 \text{ \AA}$	Best durability
Type 2	Alkali-depleted surface layer	Good durability
Type 3	Cation-rich layer next to solution and silica-rich layer adjacent to bulk	Good durability
Type 4	Non-protective layer with high silica content	Bad durability
Type 5	No layer formation	Worst durability

Researches state that the pH of the liquid is the most critical factor affecting glass durability. Ion exchange is the major process at pH 5, whereas matrix dissolution is the dominating mechanism at pH > 9 [81]. Corrosion is minimal between pH 5 and 9. Figure 3.5 shows a schematic representation of this. When the metal-oxygen bond is widely correlated to H^+ or OH^- ions, dissolution is quick, and it is minimal in neutral circumstances.

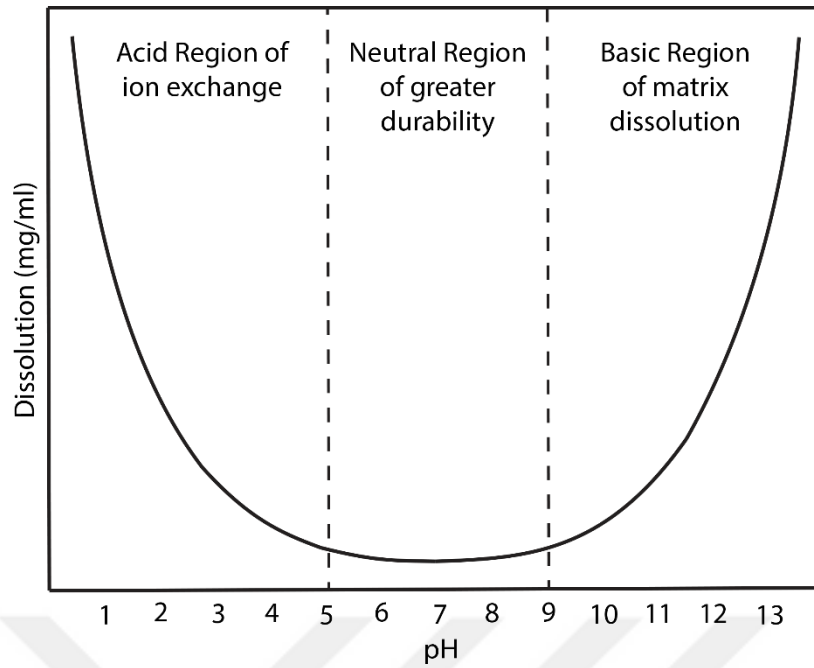


Figure 3.5 Schematic representation of glass corrosion according to pH

As the number of dissolved alkali ions in the solvent medium (water) increases, the relative amount and activity of H^+ ions decrease. This situation, which increases pH, accelerates the dissolution rate of the silica network. The pH of the solution should be kept constant to calculate the exact dissolution coefficients of the glass structure during the experiments. This is possible with buffer solutions or automated titration systems.

Hoganson and Heally (1962) described a mathematical model for corrosion rate of silicate glass in HCl (%10 vol.) which corrosion rates depend on time and temperature as below[82]:

$$W = a\theta^{b_2} \exp(-b_1/T) \quad (3.4)$$

Where,

W = weight loss,

a = experimentally determined coefficient,

b_1 = experimentally determined coefficient,

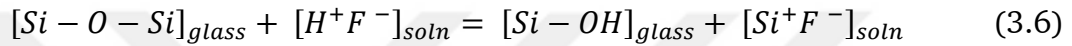
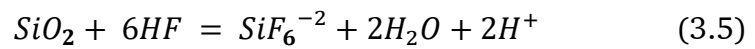
b_2 = experimentally determined coefficient,

θ = time, and

T = temperature

This equation, which includes temperature and time in the calculations, assumes uniform surface corrosion and does not include mechanisms. Corrosion, which is acceptable in practical applications, may be insufficient in dissolutions involving different mechanisms.

HF is a strong acid that can completely dissolve the glass structure within hours. The dissolution reactions for silicates and the glass surface are as follows:



3.4 Glass-Ceramics Corrosion

Since glass-ceramics are multiphase materials, more than one dissolution mechanism takes place simultaneously. While the glass phase is considered a homogeneous system, the ceramic phases may be more than one. When examining the corrosion behavior of glass-ceramics, besides the dissolution mechanisms of glass and ceramics, two more important factors come into play: grains and grain boundaries. Since grain boundaries are more active than grains, they form a kind of galvanic cell model in which grain boundaries serve as anode and grains as cathodes [75].

Since glass-ceramics can consist of a wide variety of crystal and glass structures, it is not possible to describe dissolution by several mechanisms. Knowing the phases of each glass-ceramic structure and making the examinations accordingly will give the most accurate result. However, several mechanisms can be mentioned for the erosion and corrosion of the glass matrix. During dissolution, alkali ions in the glass structure are replaced by H^+ and H_3O^+ in the solvent. During this dissolution, the silicate structure is broken and the silica begins to dissolve. When the solvent is saturated with the dissolved ions, the ions begin to precipitate into

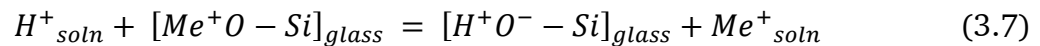
grain boundaries, pores, and high-energy areas on the glass surface. The solvent medium that attacks the pores formed on the precipitate surface causes pits on the glass surface. Erosion is the result of intermittent exposure of the glass surface to liquid-vapor and flow.

3.5 Enamel Coating Corrosion

Enamel coatings have glass, ceramic, and grain boundary phases after firing. In enamel, outside the grain boundary, the corrosion resistance of the amorphous structure is considered better than the crystalline structure[75]. When these coatings come into contact with any solution, the alkalis in the structure pass into the solution. For this reason, the thickness of the alkaline-poor layer (gel or solid) formed on the surface varies depending on the composition of the enamel, the contact time with the solution, the temperature of the environment, and the pH of the solution.

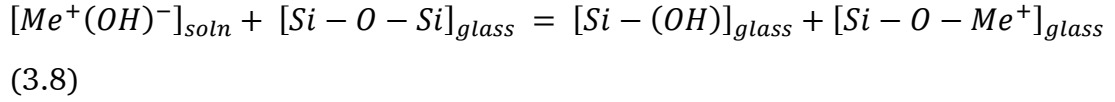
3.5.1 Ion Exchange (Neutral or Acidic media)

In scenarios where the enamel surface comes into contact with neutral or acidic solutions, alkalis in the enamel structure are transferred into the solution and equal amounts of H^+ ions are added to the structure, depending on the congruent dissolution rule, and the ion exchange mechanism mentioned before takes place.



3.5.2 Hydroxyl Attack (Basic media)

The situation is different in basic solutions. OH^- ions, which dominate the ion balance in the solution, attack the silica-rich layer. The reaction takes place according to the formula below.



As can be understood from the formula, Oxygen, which has a strong double bond structure with silicon, has a single bond structure as a result of the reaction. Water molecules reacting with this open oxygen form the Si(OH) structure. OH ions reproduced as a result of the reactions, continue the reactions, making the process autocatalytic.

3.5.3 Kinetics & Computational Corrosion

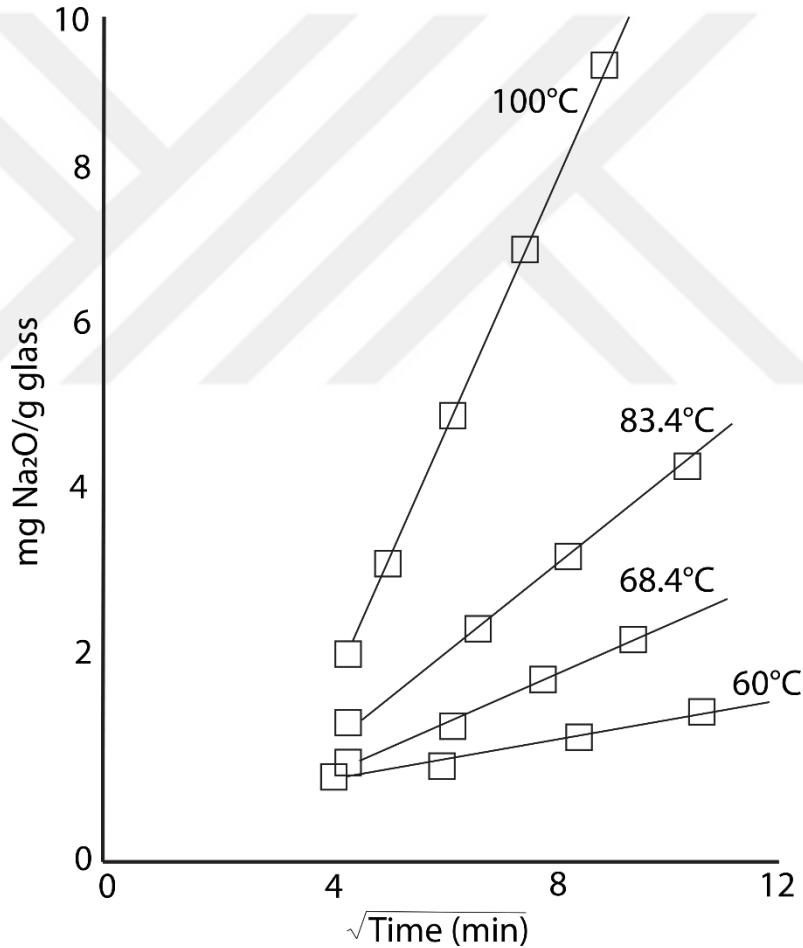


Figure 3.6 Dissolution profile according to the time and temperature of solution

At short periods and low temperatures, the rate of alkali extraction in the ion exchange process varies linearly with the square root of time[83][84]. The

concept of time and temperature directly affects the amount of dissolution of alkalis. As can be seen in Figure 3.6, the dissolution profile becomes steeper in trials with increasing temperature, that is, the time-dependent increase rate of Na_2O dissolution increases.

Mathematical modeling of these dissolution patterns can be represented by rate equation as below:

$$Q = a\sqrt{t} + bt \quad (3.10)$$

where t is the time and, a and b are constants. As t approaches 0, the limiting slope is 0.5, and as t approaches infinity, the limiting slope is 1. Over a short period of time, generally linear plots of $\log Q$ vs. $\log t$ would be anticipated, with slopes ranging from 0.5 to 1.

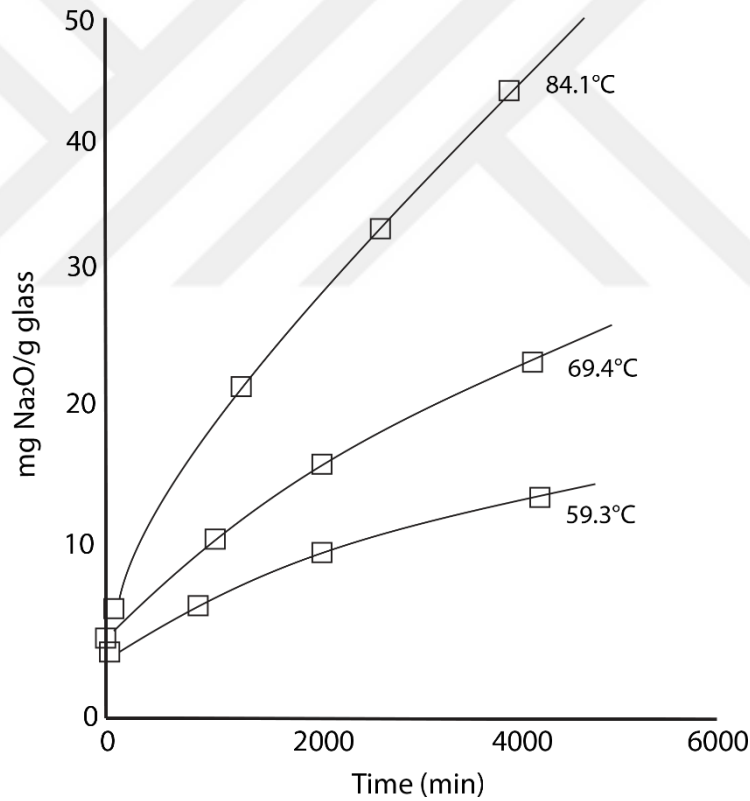


Figure 3.7 Long-time water leaching of $15\text{Na}_2\text{O} \cdot 85\text{SiO}_2$ glass[85].

The linear increase in long-term exposures (Figure 3.7) manifests itself after a certain period of time. Temperature affects the rate of dissolution as it directly influences the reaction kinetics under all conditions[75].

We have already mentioned the effect of pH on dissolution. When the hot citric acid test was performed on the enamel of the boiler tank, the slope was around 0.5 as seen in figure 3.8. In the figure, we see the dissolution rates of the enamel composition of different solutions at different pHs.

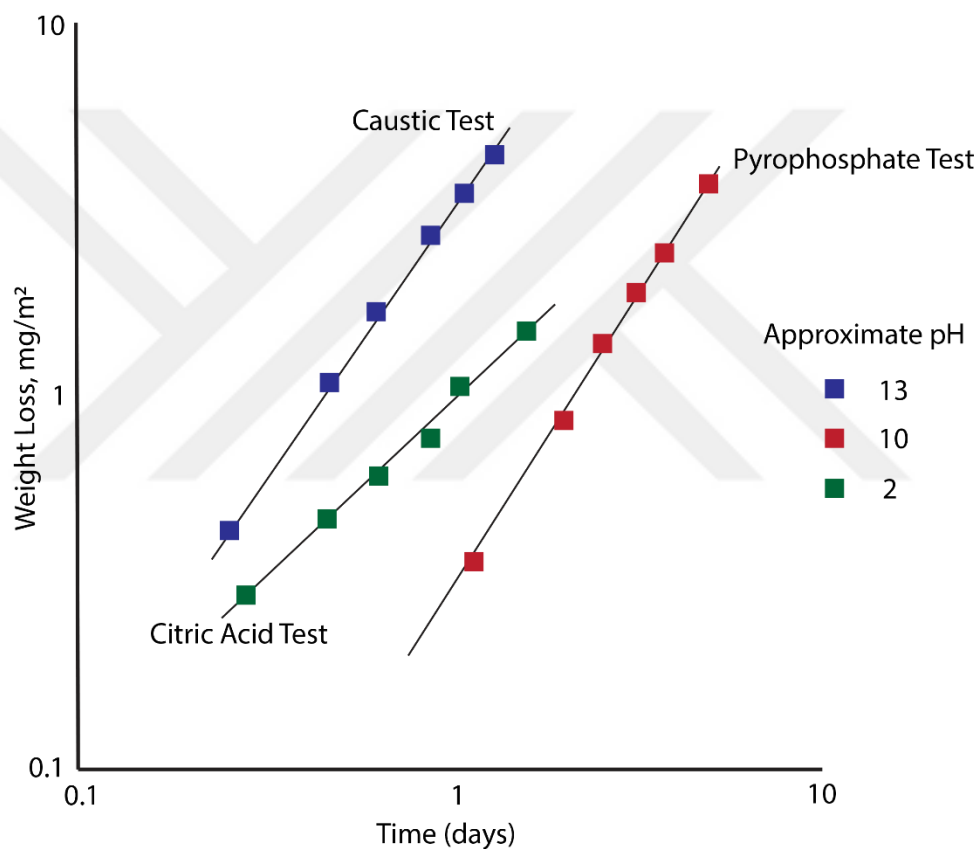


Figure 3.8 Weight loss data at 65°C–66°C for enamel. (From T. M. El-Shamy, Ph.D. Thesis, University of Sheffield, 1966.)

Thus, temperature, time, and pH are responsible for 90% of the corrosion on the enamel surface. The pH of the water that is standing still in the pores on the water surface or on the total surface will increase over time(Figure 3.8). Since the pH of the moving water can remain more stable, stagnant water causes more

corrosion[53]. However, the erosion effect caused by moving water should not be overlooked.

Besides pH, time and temperature, there are also secondary factors for corrosion rates[86]. The ions in the solution also directly affect the corrosion rate. Complexions such as citrate and acetate act as buffers by adjusting the pH balance, activity and reducing the corrosion rate (Figure 3.9). Some other ions can interact with the Si-(OH) formed on the enamel surface and increase the corrosion rate.

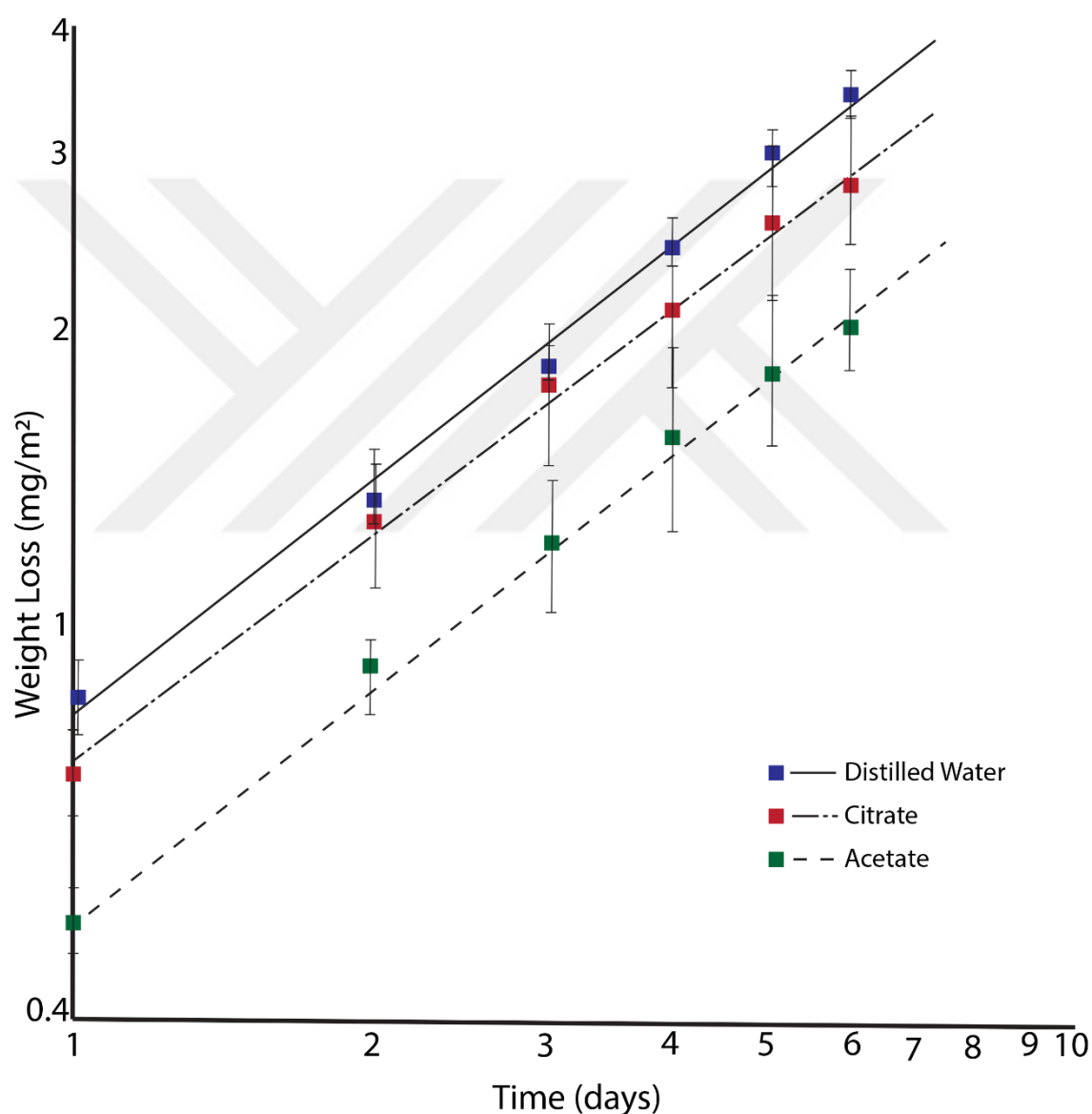


Figure 3.9 Weight loss in water and in two buffered solution

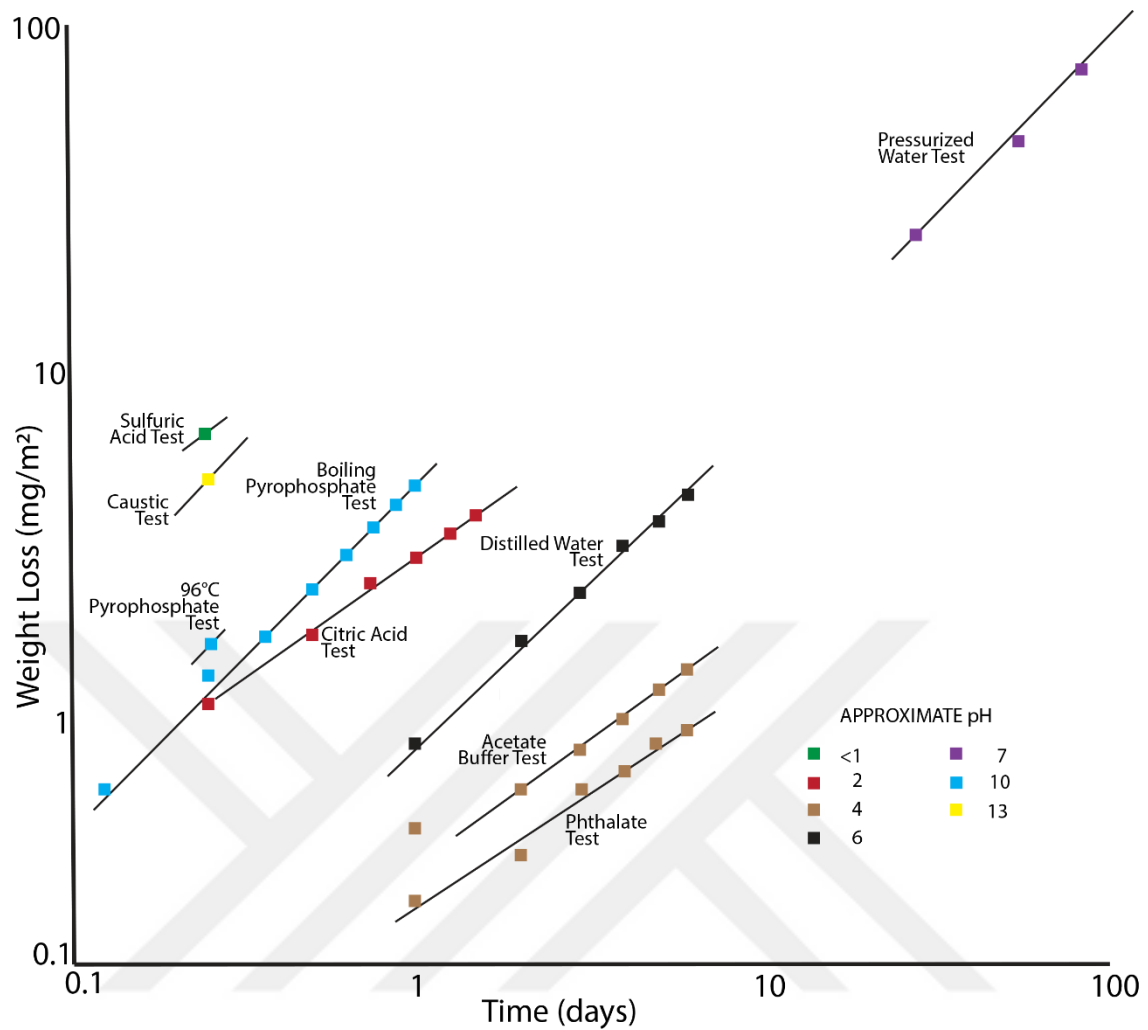


Figure 3.10 Weight loss data from 93 to 104 °C

The findings in Figure 3.10, which depicts the corrosion due to leaching of a boiler tank enamel at 93-100° C, illustrate these impacts (David E. Clark). As the pH is raised from less than 1 for the 5 percent sulfuric acid test to 2 for the 50 percent citric acid test to 4 for the phthalate test, a consistent drop in corrosion rate is seen. These curves have slopes of around 0.6, which is typical of ion exchange-dominated corrosion.

3.5.4 Compositional & Mill Additive Effect

Since ion exchange is directly related to the compounds in the structure, a figure of merit (FM) calculation is made to measure the durability of the enamel structure. Accordingly, if the ones with a high general resistance to corrosion are evaluated as "good" and those with low resistance as "bad", the calculation is made over molar concentrations as follows [85][75]:

$$Good = 2(Al_2O_3) + (SiO_2) + (TiO_2) + (ZrO_2) + (SnO_2)$$

$$Bad = 2[(Li_2O) + (Na_2O) + (K_2O) + (B_2O_3) + (P_2O_5)] + (MgO) + (CaO) + (SrO) + (BaO) + (F) + (ZnO) + (PbO) \quad (3.11)$$

$$FM = Good/(Bad)^{1/2} \quad (3.12)$$

The alkalis in the enamel structure are the first elements to dissolve in water according to the ion exchange process, and the solubility of each alkaline oxide is different from the other.

The presence of alkaline earth ions reduces the durability of the coating, but not as much as alkalis. Sodium oxide and boric acid both leach with an acid attack. The Na_2O/B_2O_3 ratio varies according to the enamel type and is usually constant[87][88]. Replacing alkali with alkaline earth on a mole-for-mole system tends to increase durability. The role of ZnO on acid resistance is a bit hazy[89][90]. It has a lower solubility than alkalis or alkaline earths, but a higher solubility than SiO_2 or related oxides[90]. Elements such as barium, calcium, zinc, lead strengthen the structure of the silica network and reduce the solubility of the structure in an alkaline environment[88]. CdO reduces acid durability[91].

Besides the addition of SiO_2 , TiO_2 , and ZrO_2 , Al_2O_3 additions are very useful for enhancing acid resistance. The only time alumina isn't advantageous is when the percentage becomes very high, causing certain Al^{+3} to shift from 4 to 6 coordination[92][93][94][95].

Alkali silicate glasses can be made more durable by adding up to 12% B_2O_3 [94]. However, in general, adding B_2O_3 into the coating composition significantly reduces acid resistance[96][95]. Only alkalis have worse durability than B_2O_3 [97].

Acid durability is also significantly reduced by additions of P_2O_5 and F, which disrupt the coating's silicate network[98][99]. As mentioned in the previous sections, homogeneity is one of the most important factors in glass-ceramic coatings, especially in enamel coatings. Glass-ceramic structures are prone to phase separation due to the complex compounds they contain. Compositions containing B_2O_3 and oxides of alkaline earth metals exhibit phase separation either at micro or macro scale[100][97]. While the amount of SiO_2 is high in one of these dissociated phases, the amount of alkali and alkaline earth borate is high in the other. The coating durability will be determined whether the borate phase is interconnected[101].

Acid resistance is affected by mill addition, firing routes, and the furnace atmosphere. This resistance is harmed by an increase in clay and alkaline electrolyte, and it is further harmed by firing. From this perspective, organic suspending agents are superior to clays, although other criteria must also be considered. Similarly, replacing 1% milling clay with 0.25 percent more colloidal bentonite is advantageous. Also, quartz addition into the mill improves heat resistance, and acid resistance is improved if the firing temperature is raised enough to dissolve this silica in the glass efficiently[88]. Quartz, clay, and opacifiers added as mill additives increase water resistance when the enamel is sufficiently sintered.

Condeand and Damborenea state that, in frits, divalent calcium and barium oxides are generally preferred over monovalent sodium and potassium, in terms of increasing water resistance[88]. In addition, oxides of pentavalent and tetravalent metals also have a positive effect on the water resistance. Although the effect of B_2O_3 and fluorine is aimed at reducing the stability of the structure, this may vary depending on the frit composition.

Bottles can be chilled in a dilute SO_2/SO_3 environment to boost chemical resistance in the glass bottle business[102]. Vitreous enamel has been seen to have a similar effect. A thin coating of $-OH$ groups or $-OH-H_2O$ (hydronium) ions are thought to be adsorbed on the surface of burned enamel. In the presence of sulfur

oxides, these ions are converted into $-\text{OSO}_2$ or $-\text{OSO}_3$, which are more resistant to acid attack. It's well known that the acid resistance of initially fired enamel increases with age, owing to the enamel's contact with SO_2/SO_3 in the environment.

The Cathodic Protection method is also used to increase corrosion protection in enamel-coated water heater systems. An electrochemically active noble metal type anode installed in the hot water tank and supplied by a chosen amount of current going from the anode via the water to the tank protects the tank from the corrosive effects of water[103].

3.6 Erosion Effect

Erosion is a complicated process influenced by a variety of factors, and even little changes in operational circumstances can have a substantial impact on the damage it produces. This might result in a situation where substantial erosion rates occur in one production system but little erosion happens in other systems that appear to be quite comparable. This complicates erosion control, especially for individuals who are unfamiliar with how erosion happens. Erosion also heavily depends on the design of parts [104]. Erosion is commonly seen in ship propellers, hydraulic systems, pumps, valves, pipes, flotation cells, hydro cyclones, and water heaters systems, and if the mechanism is not understood it makes the parts unserviceable. The liner materials in coal liquefaction facilities and industrial boilers where coal is conveyed directly as a fuel in water or oil are prone to severe erosion. Particles traveling at high speeds in corrosive gases at temperatures as high as 1000°C cause erosion in coal gasification and catalytic cracking systems.

According to Barton, 4 main phenomenas cause erosion: Particulate erosion, Liquid Droplet Erosion, Cavitation Erosion, and Erosion-Corrosion[104][105]. While these are adjusting the erosion rate, some may be more effective, while others may be less effective, depending on the conditions.

3.6.1 Sand and Particulate Erosion

The following are important factors that influence the rate of particle erosion:

- **Hard particle emergence and flowrate of particle**

The solid particles formed in the container, pipe, or parts trigger more particles to break off from the surface, increasing the total number of particles in the part. The sand transport mechanism is a critical component of erosion control in production systems. Gas systems are more prone to erosion than liquid systems because they run at high speeds (>10 m/s) [104]. Sand particles, on the other hand, can be captured and transported in the liquid phase in wet gas systems. Slugging, in particular, can produce high velocities regularly, potentially speeding up erosion. Sand may collect during periods of low flow if the flow is unstable or operating circumstances change, only to be flushed from the system when high flows occur. This and other flow mechanisms may concentrate sand, resulting in higher erosion rates in certain portions of the production system pipework.

- **Velocity, Viscosity, and Density of the Fluid**

The rate of particle erosion is strongly influenced by the particle impact velocity. The erosion rate is commonly assumed to be proportional to the particle impact velocity raised to a power, n . (typically n ranges between 2 and 3 for steels). When erosion is a problem, the particle impact velocity will be near to the fluid carrying the particle's velocity. As a result, erosion is most likely to occur where the fluid flow velocity is greatest. When these circumstances exist, even small increases in fluid velocity can result in significant increases in erosion rate.

Particles in thick viscous fluids are more likely to be transported around barriers by the flow than to collide with them. In low viscosity, low-density fluids, on the other hand, particles prefer to move in straight lines, colliding with the walls when the flow direction changes. Particulate erosion is thus more common in gas flows, partially due to the low viscosity and density of the gas, and partly due to the greater velocities of gas systems.

- **The particle's size, shape, and hardness**

The size of the particles has the largest impact on erosion since it determines how many particles hit a surface. The fluid carries very minute particles

(approx. 10 μ m) that seldom touch the walls. Larger particles have a tendency to move in straight lines and reflect off surfaces. Large particles (>1mm) travel slowly or settle out of the carrying fluid, therefore they are unlikely to cause significant harm.

It is a known fact that hard particles will cause more erosion. Sharp particles do greater damage than rounder ones, according to research.

3.6.2 Liquid Droplet Erosion

Droplet erosion is clearly limited to moist gas and multiphase flows that may produce droplets. Droplet size, impact velocity, impact frequency, and liquid and gas density and viscosity are all elements that influence erosion rate. It's difficult to forecast the rate of droplet erosion since many of these quantities are unknown in real-world settings. It's also worth noting that many of these variables are difficult to control in laboratory studies. As a result, when extending lab test results to field circumstances, extreme caution is essential[106].

The most practical approach is to identify whether droplet erosion could be in progress and then act to alleviate the problem. Salama & Venkatesh state that solids-free erosion only occurs at very high velocities[107]. High velocities cause unacceptably high-pressure losses, therefore the conditions required for droplet erosion are unlikely to occur in correctly designed production pipework systems. They define an acceptable velocity limit to avoid significant liquid impingement erosion to be[104]:

$$V = \frac{300}{\sqrt{\rho}} \quad (3.13)$$

In which

V: The maximum acceptable velocity (ft/s)

ρ : The liquid density (lb/ft³)

3.6.3 Cavitation Erosion

Cavitation corrosion is often encountered in metals and ceramics. Especially cooling water pump impellers, wicket gates, stay vanes, turbines, ship propellers, kurt nozzles, pipe parts, valves, shafts, valves, and filters can cause serious problems. When liquid goes through a constraint, such as a sharp elbow, low-pressure zones can form. Bubbles develop when the pressure is dropped below the liquid's vapor pressure. The bubbles then burst, causing shock waves. The amplitude of these shock waves can be large enough to destroy piping. Cavitation is uncommon in oil and gas production systems because operating pressures are often significantly greater than liquid vaporization pressures. Cavitation can be found in chokes, control valves, and pump impellers, but it is uncommon to be found in other components. Cavitation erosion is unlikely to develop in an elbow under normal operating circumstances unless it is directly downstream of a substantial flow restriction[105].

Calculating a cavitation number (K) as follows may forecast the start of cavitation in equipment or components with flow constrictions[108].

$$K = \frac{2(P_{min} - P_{vap})}{\rho v^2} \quad (3.14)$$

P_{min} : The minimum pressure occurring in the vicinity of the restriction (Pa)

P_{vap} : The vapor pressure of the liquid (Pa)

ρ : The density of the liquid (kg/m³)

v : The flow velocity through the restriction (m/s)

Cavitation is possible if the cavitation value is less than 1.5[108].

3.6.4 Erosion-Corrosion

Erosion-corrosion is a kind of tribocorrosion comprising mechanical and chemical reactions in which impacting particles or fluids erode a solid surface by abrasion, chipping, or fatigue while the surface corrodes at the same time. Inspection of the damaged equipment and consideration of the operating circumstances can typically distinguish between erosion and corrosion damage. Localized grooves,

pits, or other characteristic patterns are frequently caused by erosion in high-velocity areas. Corrosion is generally more distributed, and it produces scale, rust, or accumulation on the surface making it easy to spot[109].

The combined particulate erosion and corrosion is known as erosion-corrosion. The balance between the erosion and corrosion processes determines the advancement of the erosion-corrosion process[109].

Fresh equipment put in a purely corrosive flow corrode fast without particles until a brittle scale or gel forms on the surfaces exposed to the fluid. After the gel or scale has formed, it sets a barrier between the part and the fluid, reducing the rate of penetration significantly. This is also true when extremely low-level erosion is occurring at the same time as corrosion.

The erosion process predominates in strongly erosive flows when corrosion is also present, and gel/scale is scoured off exposed surfaces before it may affect the penetration rate. As a result, corrosion has little role in material penetration.

Erosion and corrosion processes can interact in intermediate circumstances. In this situation, scale/gel can develop and then be eliminated by the erosive particles on a regular basis. This results in a pitted surface, which allows for penetration rates that are orders of magnitude higher than those induced by pure erosion or corrosion.

Erosion-corrosion mechanisms may be extremely complicated since they combine two mechanisms that might be highly situation-specific. As a result, predicting erosion-corrosion penetration rates for a specific field setting is extremely challenging. It is possible to avoid erosion-corrosion by ensuring that the operating circumstances do not allow for either erosion or corrosion[104].

Chokes and other extremely susceptible components frequently employ special materials such as tungsten carbides, coatings, and ceramics. These materials are often brittle and hard.

Brittle materials corrode in a unique way. Impacts on brittle materials fracture the surface, and erosion rises linearly with impact angle, with perpendicular impacts

having the highest rate of erosion. The form of the erosion scar and the position of maximal wear will be altered as a result of this.

Most of these materials are more resistant to erosion than steel. Some coated materials, however, are prone to erosion. They may appear to have high resistance at first, but if the coating or substrate breaks, their resistance may rapidly deteriorate[104].

To control erosion on the material surface, the parameters of three components must be controlled: corrosive liquid, erosive particles, and target material. The microstructure, toughness, and hardness of the working part's surface are also the most important factors[110].

In ductile and brittle materials, the methods of material removal in erosion were distinct, with plastic flow playing a prominent role in the former and microfracture in the latter[111]. Many researchers have examined the mechanics of erosion in many ductile and brittle materials since then. Material loss during airborne erosion by hard particles in brittle materials like ceramics has been demonstrated to be caused by quasi-static development and chipping of lateral fractures that originate at sharp particle impact sites. During contact, a zone of plastic deformation occurs, and residual stresses associated with this zone provide the driving force for the expansion of the lateral fractures[112].

Solid particle erosion was also examined as a function of microstructure in a brittle material. Ritter et al. argued that erodent kinetic energy is predominantly utilized for grain boundary cracking in polycrystalline alumina, based on the finding that material removal occurs by individual grain ejections from the surface rather than lateral cracking[113]. Their model included a term for the material's grain size, resulting in an inverse relationship between toughness and grain size. With the creation of a new breed of toughened monolithic ceramics and ceramic composites, it has been shown that the toughness of these materials is not uniform, but rises with crack extension—a phenomenon known as the T-curve (Rcurve)[114].

3.7 Advanced Ceramics as Erosion / Corrosion Inhibitors

The use of advanced ceramics to prevent corrosion is not a new method. However, obtaining the advanced performances continue to be obtained by creating composites with these materials or combining these materials with other similar materials by methods such as mechanical activation. In recent years, researches on corrosion, boride, carbide, and nitride applications of metals have been the subject of researches due to their superior corrosion performance[115][116][117][118]. Because of their inherent high hardness, resistance to corrosion, high-temperature oxidation and wear, high diffusion-barrier properties, and low friction coefficient, transitional metal borides are potential candidates for protective coatings for machining tools, heavy-duty friction couplings, fuel cells, aerospace vehicles, and other applications. Among transition metal compounds, Zirconium-Based oxides, borides, and nitrides have seemed like the right candidate for anticorrosive material which can withstand harsh media for a longer time[8]. Especially Zirconium Diboride is standing out in corrosion researches because of its anticorrosive nature[119][120][121]. The other superior properties of this material will be explained in detail. On the other hand, due to its resistance to corrosion, chemical inertness, and being a healthy oxide, zirconia is preferred in many applications from the medical sector to the kitchenware sector, from furnace refractories to bearings. It is used as a nucleating agent in glass-ceramic technologies[122]. In frit production, it is entered as a raw material to increase the durability of the glass structure[25].

3.7.1 Zirconium Dioxide (ZrO_2)

The metallic zirconium (Zr) has the atomic number 40. Martin Klaproth first found it in 1789[123]. The hexagonal crystal structure of Zr is the most common. Zr doesn't exist in its metallic form in nature. There are four zirconium minerals that may be classified as follows[124]:

- 1) Zirconium orthosilicates: Zircon and metamict variants of zircon are orthosilicates of zirconium.

- 2) Baddeleyite and its changed variants of zirconium dioxide
- 3) Zirconsilicates including sodium, calcium, iron, and other elements, such as eudialyte, eucolite, gittinsite, and others: eudialyte, eucolite, gittinsite, and others
- 4) Weloganite and other zirconium carbonates with sodium, calcium, and other components
- 5) Other minerals, such as zirconolite ($\text{CaZrTi}_2\text{O}_7$)

After a series of complicated operations, effective separation of Zr components is required to generate pure zirconia powders. Zirconia nanopowder might be used to make a ceramic biomaterial. ZrO_2 is a polymorphic mineral that comes in three crystallographic structures: Monoclinic, Tetragonal, and Cubic.

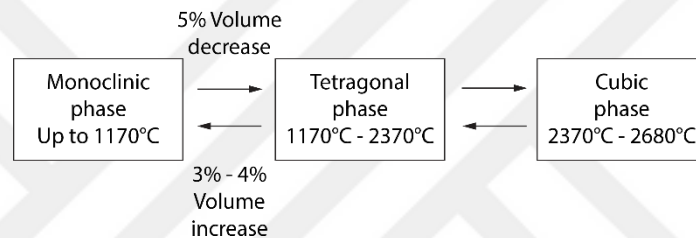


Figure 3.11 Phase transformations of ZrO_2

The monoclinic phase is stable up to 1170°C in room temperature (Figure 3.11), the tetragonal phase is stable between 1170°C and 2370°C, and the cubic phase is stable from 2370 °C to melting point. At around 1050°C, the monoclinic phase transforms to the tetragonal phase, which takes around 1170°C to complete[125]. The change is accompanied by a 5% reduction in volume. The transition exhibits a thermal hysteresis: the tetragonal phase is stable to over 1000°C when gradually cooled, but only converts to monoclinic at around 800°C. The tetragonal phase is metastable to room temperature after fast quenching. Changes in the form of 4% volumetric expansion and 0.16 (7%) shear strain occur during the changeover from the tetragonal to the monoclinic lattice structure[124]. The material breaks apart because the amount of strain and volumetric change exceeds the maximum stress limit (due to high internal stresses). Internal stresses (σ) are proportional

to the volumetric change amount and elastic modulus, but inversely proportional to the Poisson ratio.

Pure zirconia's "monoclinic" structure, which is stable at ambient temperature, transforms into tetragonal and cubic structures as temperature rises. Monoclinic, tetragonal, and cubic unit cells have structural similarities. When changing from a monoclinic to a tetragonal structure, for example, just one of the axis angles shifts to 90°. Because of the intimate unit cell interaction, zirconia polymorphic phase changes are quick (athermal, time-independent) and reversible (since they do not need atomic diffusion) (called diffusionless transformation or martensitic transformation). In the transitions between the phases, the strains change the phase structure of the material. Structural stabilizers are used to keep the structure, which is in the monoclinic phase at room temperature in its pure form, in the tetragonal and cubic phases during cooling.

• **Stabilization**

In order to stabilize the tetragonal or cubic phases, several oxides are added to zirconia. ZrO_2 is an oxidized version of the metallic zirconium. Depending on the presence of minor components like Ytria (Y_2O_3), Calcia (CaO), and Magnesia (MgO), zirconia can exist in tetragonal or cubic phases. With the correct quantity of components, a completely stable cubic phase may be created. When "x" moles of metal oxides with a cation valence of +4 are added to zirconia, not only are "x" moles of Zr^{4+} ions reduced but the positive and negative electrical charge balance is also disrupted[126]. As a result, when "x" moles of metal oxide is doped into zirconia, the number of oxygen ions with a negative electrical charge decreases in the crystal. In other words, the chemicals used to maintain zirconia's cubic structure cause the crystal lattice to produce "anion gaps". Y_2O_3 cubic oxides can be used to stabilize zirconia. In contrast to the same amount of CaO or MgO additions, when x mol Y_2O_3 is added to zirconia, x/2 mol oxygen vacancies appear in the zirconia crystal. Figure 3.12 depicts the zirconia-yttrium oxide phase diagram[127].



This phase shift diverts energy away from the fracture, perhaps halting development. This process is known as "transformation toughening." Furthermore, the change in volume causes compressive stress surrounding the particle, which leads to fracture propagation. Zirconia has outstanding mechanical qualities thanks to transformation toughening: high flexural strength—900 MPa to 1.2 GPa—and toughness—7 to 8 MPa $\sqrt{\text{m}}$ —0.5[123].

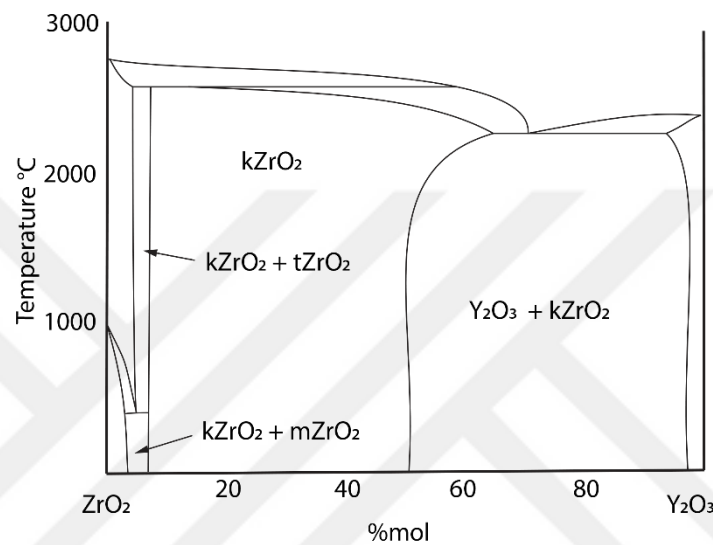


Figure 3.12 Phases between the ZrO₂ and Y₂O₃

- **Physical and Mechanical Properties**

The mechanical characteristics of zirconia are comparable to those of stainless steel. It has a traction resistance of 900-1200 MPa (Table 3.2) and a compression resistance of around 2000 MPa[128]. This material can also withstand cyclical load strains[129].

Table 3.2 Properties of ZrO₂ ceramic

Properties	Value
Molecular Weight	123.22
Coefficient of Thermal Expansion	$108 \times 10^{-7} \text{K}^{-1}$
Elastic Modulus	100 – 250 GPa at 20°C
Flexural Strength	180 – 1000 MPa at 20°C
Tensile Strength	330 MPa at 20°C
Fracture Toughness	10 MPa·√m at 20 °C
Hardness	12GPa(Vickers), 8–8.5(Mohs)
Thermal Conductivity	2-3 W/(m·K)
Refractive Index	n _{20/D} 2.13
Specific Heat Capacity	0.46 J/g.K
Melting Point	2.715°C
Boiling Point	4.300°C

When researchers applied a 28 kN intermittent force on zirconia substrates, they discovered that it took 50 billion cycles to break the samples, but when the force was more than 90 kN, a structural collapse occurred after just 15 cycles[124]. Surface treatments can also change zirconia's physical characteristics. The phenomena of low-temperature deterioration, or "aging," is a characteristic of zirconia that has received little attention. Water and nonaqueous solvents can cause zirconia hydroxides to develop along a fracture. This mechanism causes the fracture to expand faster, resulting in decreased strength, hardness, and density, which can contribute to restoration failure[125].

- **Chemical Properties**

Zirconia is acid and alkali-resistant, however, in concentrated hydrofluoric acid or hot concentrated sulfuric acid, it dissolves slowly. Fluoride and alkaline melt attack zirconia, although it is resistant to numerous fluxes, molten glasses, or melts, silicate, phosphate, or borate. Solid-solution oxides, zirconate compounds, or a combination of both can be made by firing zirconium oxide with alkaline oxides or caustics. At around 600°C, zirconium oxide is reduced by carbon. In a vacuum furnace with excess carbon, the process quickly converts to zirconium carbide at 1500°C. Carbon reduction produces zirconium tetrachloride and carbon dioxide in the presence of chlorine[130].

- **Health Effect**

The systemic toxicity of zirconium and zirconium salts is usually low. The dietary intake is estimated to be around 50 micrograms[130]. The majority of it goes through the stomach undigested, and what is absorbed accumulates significantly more in the skeleton than in tissue. Zirconium 95 is one of the long-lived radionuclides that has elevated cancer risk and will continue to do so for decades and centuries to come. [5]

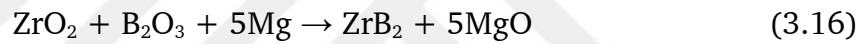
Zirconia's biocompatibility has been thoroughly investigated. With the use of highly pure zirconia powders that have been purged of their radioactive components, in vitro and in vivo experiments have shown the exceptional biocompatibility of Y-TZP[128]. There have been no reports of local (cellular) or systemic adverse effects to the substance. Recent research has found that bacteria accumulate less around Y-TZP than around titanium[128]. This might be due to differences in protein adsorption characteristics. None of the options are good for periodontal health. In terms of periodontal health, none of the studies found any differences or observed any alterations in the soft and hard tissues around zirconia-based restorations. Although several studies evaluated and investigated variations in zirconia biocompatibility, no evidence of gingival inflammation or periodontitis was found[123]. Based on these findings, zirconium oxide has been

suggested as a possible material for implant abutments with limited bacterial colonization potential[130].

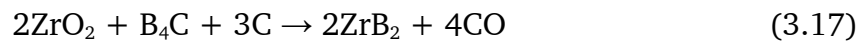
3.7.2 Zirconium Diboride (ZrB₂)

ZrB₂ is a high-temperature ceramic with a high amount of covalent bonds. Its melting point is 3246°C and such a strong material has a relatively low density (approx. 6.09g/cm³)[131]. The stable crystal structure at room temperature is hexagonal. It has relatively high thermal and electrical conductivity, high resistance to oxidation and chemicals. Because of these properties, they are used in aerospace fields such as hypersonic aircraft, rocket propulsion, and atmospheric re-entry.

ZrB₂ is a chemically synthesized ceramic. ZrB₂ can be obtained from ZrO₂ and B₂O₃ oxides by a metallothermic method by adding some Mg according to the following reaction[132]:



MgO formed as a result of the reaction is removed from ZrB₂ by acid leaching method[132]. Another common method for the production of ZrB₂ is the boron carbide reduction method[133]. If approximately 20% extra boron carbide is added to the system started according to the following reaction at temperatures above 1600C, ZrB₂ is obtained at the end of a sufficient time[134].



To eliminate oxides and enhance densification of ZrB₂, B₄C or carbon additions have been utilized[135]. However, as shown in Figure 3.13, these additions lower the composite's melting temperature owing to the eutectic formation, which is several hundred degrees lower than that of ZrB₂: 2220°C for ZrB₂-B₄C and 2390°C for ZrB₂-C[136]. At the eutectic temperature, a little quantity of B₄C or carbon (up to 2 mol percent) gets into a solid solution in ZrB₂[135]. A second phase with higher levels of additives exists, however, there are no further thermodynamically stable phases save the end members. The addition of B₄C as a second phase has been proven to improve hardness and flexure strength in ZrB₂, whilst carbon has

been found to reduce flexure strength. The impact of these additives on thermal, electrical, and oxidative behavior, on the other hand, have not been well explored.

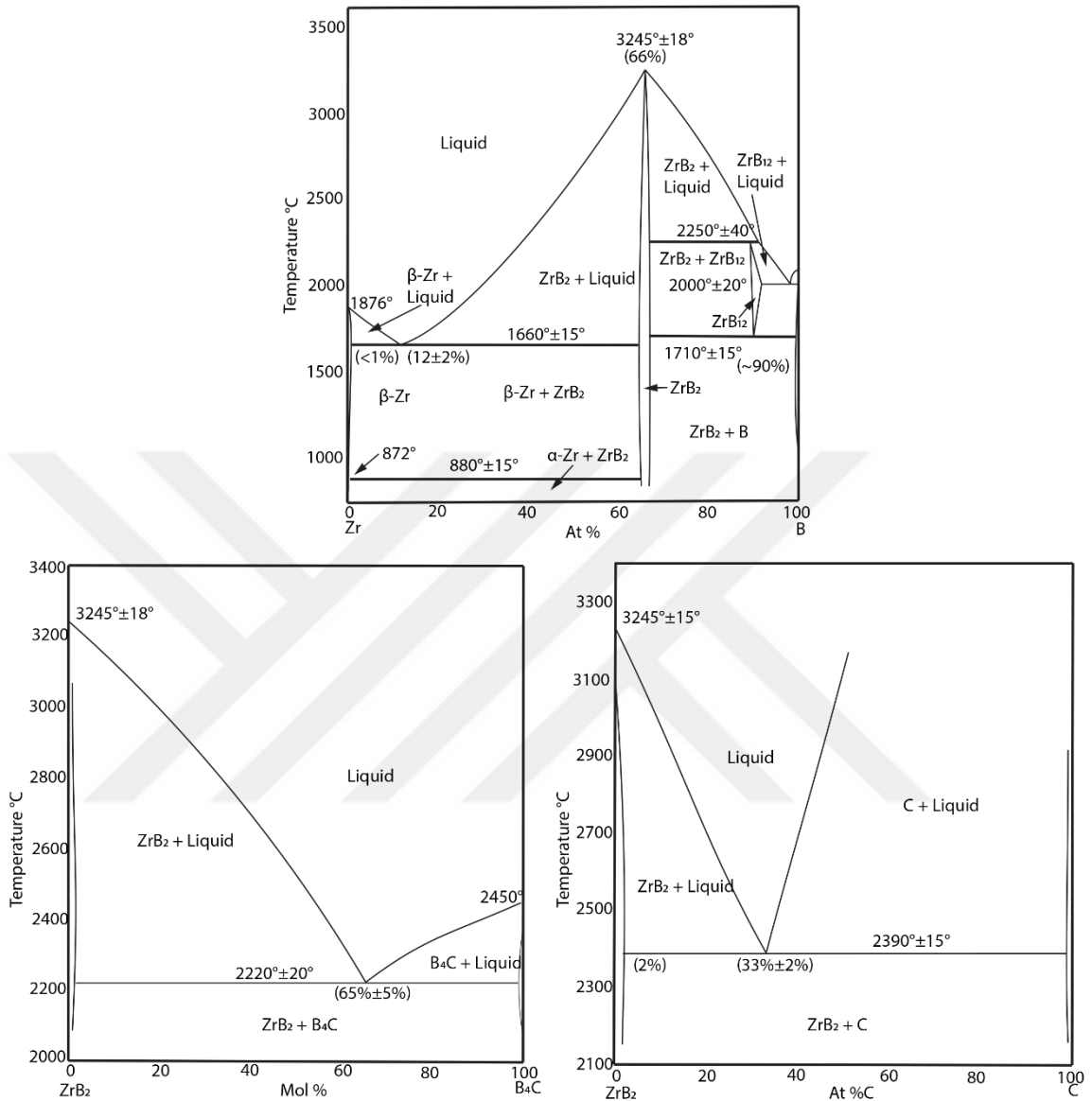


Figure 3.13 Phase diagrams of ZrB_2 with (a) B_4C and (b) carbon addition.

Along with all these methods, ZrB_2 can be produced by chemical vapor deposition, solid-state reaction, and sol-gel methods [137][138][139].

Mechanical and physical properties of this material in hexagonal form with a density of 6.10g/cm^3 are given in Table 3.3[140][131]. The melting temperature

of this material is 3200°C and its expansion coefficient is $60 \times 10^{-7} \text{K}^{-1}$ on average, its hardness is 13-23GPa, and its thermal conductivity is 23-24W/m.K.

Table 3.3 Properties of ZrB_2 ceramic

Properties	Value
Molecular Weight	112.85 g/mol
Density	6.10g/cm^3
Coefficient of Thermal Expansion	$59\text{-}62 \times 10^{-7} \text{K}^{-1}$
Elastic Modulus	420-490 GPa at 20°C
Hardness	13-23Gpa(Vickers)
Thermal Conductivity	23-24 W/m·K
Electrical Resistivity at 25 °C	6-9 $\Omega\text{W-cm}$
Specific Heat Capacity at 25 °C	$48.2 \text{ (J. (mol.K)}^{-1}$
Melting Point	3245°C

Figure 3.13 shows the primitive hexagonal crystal structure of metal diboride structures, MB_2 [131][141]. The AlB_2 prototype is defined by alternating layers of zirconium and boron atoms. The zirconium atom plane comprises seven atoms in a hexagonal densely packed form, while the base unit has a six member ring of boron atoms (sp^2 hybridized). The unit cell contains one formula unit in total. Each zirconium atom is surrounded by six other zirconium atoms in a plane and has 12 boron atom companions in neighboring planes[142]. Three boron atoms in plane and six zirconium closest neighbors in neighboring planes surround each boron atom[136].

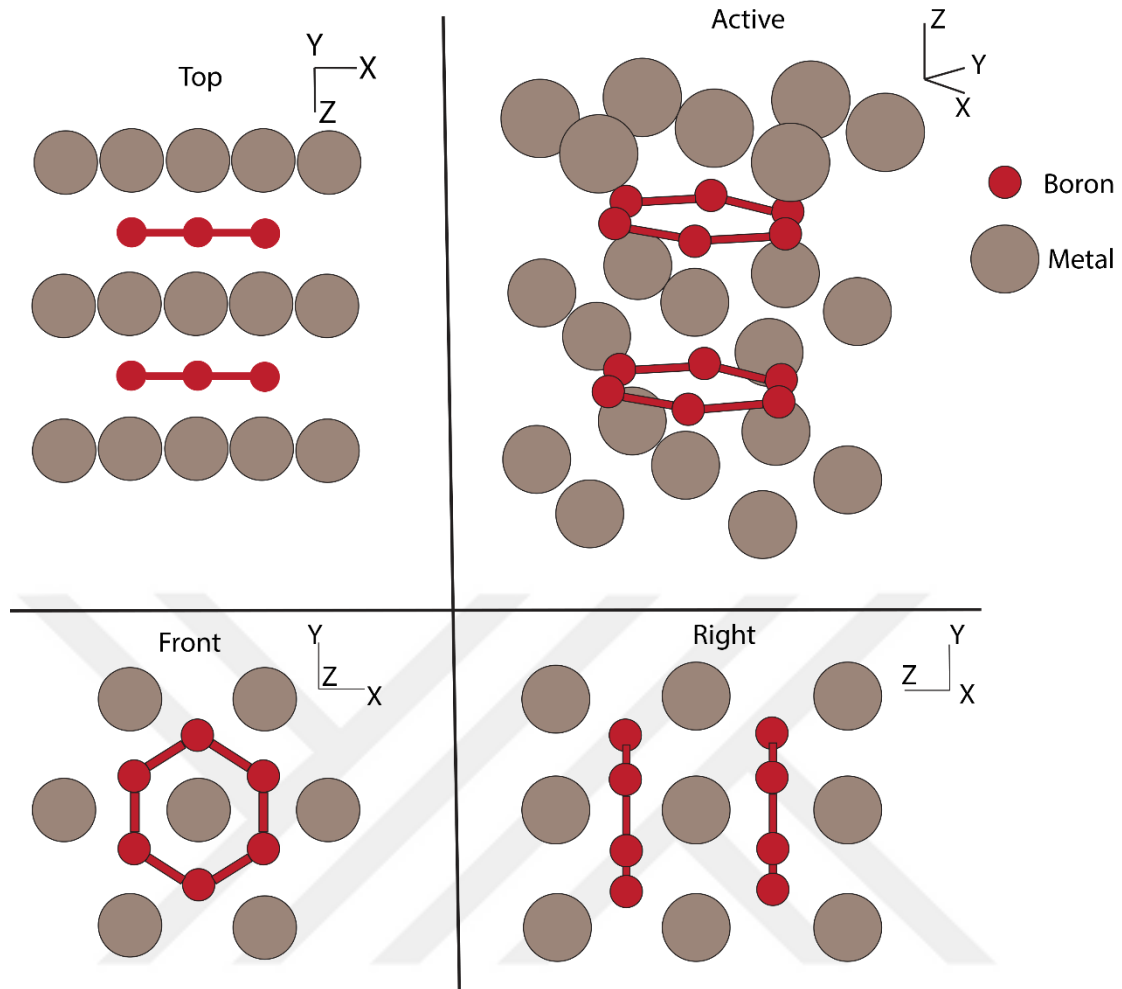


Figure 3.14 AlB_2 crystals structure that shows the symmetry of $P6/mmm$

The AlB_2 type crystal structure is unique in that it has a variety of distinct bonding environments. The boron sub-lattice, which often supports sp^2 bonding, is where the first form of bonding occurs (graphite-like structure). This form of link has been demonstrated to be covalent in nature[142]. The stiffness of the overall structure is increased by the strength of the B-B bonds inside the sub-lattice, resulting in the high melting temperature, hardness, strength, and chemical stability of transition metal diborides. The second form of bonding, M-B, is equally covalent in nature with a little bit of ionic character (8% for ZrB_2)[143]

When ZrB_2 is used as a bulk material, it is generally used with ceramics such as SiC , B_4C , WC . This is because if oxidation starts on the surface of the material, a

protective oxide layer such as SiO_2 forms on the surface, and this slows down the progress of oxidation by reducing oxygen diffusion.

Compared to the method used during the sintering of the ZrB_2 material, the smaller grain size and the higher pressure to be applied together with the higher temperature will increase the mechanical strength of the bulk product. Techniques such as spark plasma and hot isostatic press are used efficiently in the sintering of such advanced ceramics.



INTER-METALLIC ADHERENCE BEHAVIORS OF ENAMEL COATINGS

No matter how superior the coating materials have, if they cannot provide good adherence with the substrate, they are of no value. The first of the basic features that the coating materials should have been that they must be compatible with the substrate. From polymeric paints to surface nitriding, from chemical vapor deposition to sol-gel coatings, the common feature of all of them is having a good bond with the substrate material. The type and character of these bonds may vary, but they protect the substrate for a desired time during the service life.

Glass-ceramic materials show good performance against corrosion and erosion due to their high chemical resistance and hardness. For this reason, they are used to protect unstable metals with lower resistance. To protect the metal from erosion/corrosion, the porosity of the glass-ceramic coatings must be as low as possible and at the same time, there should be no discontinuities such as cracks, fractures, or ruptures on the surface. If the glass-ceramic coating doesn't show good adherence with the metal, all these errors are likely to occur. While the coated part is exposed to various impacts during use, if the coating on the metal surface does not adhere well, it may break and leave the metal vulnerable to the corrosive environment. The metal can be exposed to various forces such as abrasion, hitting, bending, tensile, and compression, and it is normal for the glass-ceramic coating, which is not as flexible as metal, to suffer cracks, ruptures, and chip-offs. In such cases, there are big differences between the well-adhering glass-ceramic coating and the non-adhesive coating in terms of protection from corrosion and aesthetics.

4.1 Bonding in Solids

The bonding of solid materials can occur in three ways: mechanical bonding, chemical bonding, and secondary bonding like van der Waals' forces[66]. Among these bonds, van der Waals' forces are generally the weakest and these kinds are frequently encountered in polymeric materials. The bonds formed as a result of the chemical reaction can be up to 100 times stronger than van der Waals' bonds[66]. In chemical bonds, it is also divided into three: ionic, covalent, and metallic[144]. While it's easier to explain the four basic forms of bonding separately, it's important to remember that while metallic bonding may be the most common, other types of bonding, especially covalent bonding, may also be present.

By describing metals as a combination of atomic cores (positive nuclei + inner shell of electrons) and valence electrons in the early 1900s, Paul Drüde developed the "sea of electrons" metallic bonding hypothesis[145]. When each of the metal's atoms contributes their valence electrons to the development of an electron cloud that surrounds the positively charged metal ions, this is known as metallic bonding[146]. All the atoms share the valence electrons in a metallic structure. The positively charged ions repulse each other consistently in this bond, causing them to organize themselves into a regular pattern held together by the negatively charged electron cloud. Strong electrical attraction binds the metal together because the negatively charged electron cloud surrounds each of the positive ions that make up the ordered 3D crystal structure. Every positive ion is equivalent is a feature of metallic bonding[146].

Alloys are one of the systems where metallic bonds are found most intensely[147]. An alloy is a mostly metallic system consisting of at least two elements, one of which is metal.

4.2 Inter-Metallic Bonding and Compounds

Intermetallic compounds are a kind of alloy with a certain stoichiometric formula with limited solubility, containing metallic bonds and partially ionic or covalent

bonds [148]. The bonding takes on an ionic nature when the electronegativity gap between the two metals grows. Because the electronegativity of aluminum and vanadium is 1.5 and the difference is zero, the compound Al_3V is predominantly metallic. The electronegativity of lithium is 1.0, it has an electronegativity difference of 0.5 with aluminum, resulting in a metallic-ionic bonding when they form the compound AlLi [146]. Intermetallic compounds normally have close-packed structures with high coordination numbers, however low coordination arrangements can emerge in exceptional instances[148]. When one atom is substantially smaller than the other and fits into the octahedral or tetrahedral interstice of a close-packed structure, low coordination number metallic formations are most prevalent. Metal nitrides and carbides, such as Fe_3C and ZrN , are examples of intermetallic compounds. The melting temperature of the compounds formed by intermetallic bonds is generally higher than the melting temperatures of the metals forming the compound. For example, Mg_2Sn melts at 780°C , while metallic Mg at 650°C and metallic Sn at 230°C which demonstrate the strength of intermetallic bonding. Since they contain ionic or covalent bonds, they can exhibit low electrical and thermal conductivity compared to metals. They may even exhibit ceramic material behaviors such as brittleness[149]. Examples of compounds containing covalent bonds are Mn_2Sn , Fe_3Sn , and Cu_6Sn_5 . Examples of ionic bonding compounds are Mg_2Si , Mg_2Sn . Due to their high internal order and mixed (metallic and covalent/ionic) bonding, they can also exhibit advantageous magnetic, superconducting, and chemical characteristics[148]. Some of the uses of intermetallic compounds include hydrogen storage materials in nickel-metal hydride batteries, turbine blade applications, barrier and contact layers in microelectronics, magnetics, super conductors, shape memory alloys, and dental amalgams[150].

4.3 Nature of Enamel Adherence

Good adherence between enamel coatings and steel plays an important role in the effective performance of enamel over a long period of time. In multi-layer and firing techniques, the first layer is a ground coat and provides adherence to the

steel with the help of metal oxides it contains, while the upper layer exhibits aesthetic, chemical, and mechanical performance on the surface. In the industrial sense, there is a demand for single coat single firing enamel compositions, which both adhere very well to the metal and perform good aesthetic and chemical inertness on the surface. Thus, maximum efficiency is achieved with less process, time, material, and energy. However, products such as white enamel can't be applied directly to the naked steel sheet. First, the steel is either Ni-deposition or a primer coat is applied.

Enamel coatings make a metal-to-metal bond with atoms in steel thanks to metallic ions that enamel contains. Four basic theories have been suggested to explain enamel adherence: chemical bond theory, dendritic theory, electrolytic theory, and the mechanical keying theory[66][151].

Chemical or oxide layer theory has different kinds of reactions such as dissolution, redox, interdiffusion, and precipitation. These reactions change the enamel-steel interface. Chemical reactions are essentially bonding occurrences involving electron exchange or connection between enamel atoms and a metallic surface in the presence of an electronic structure[152][153]. According to the theory, chemical bonding occurs depends on the lowest valence oxide the metal has. When the threshold energy for a chemical reaction is exceeded at the metal-enamel interface, a chemical reaction takes place according to the chemical potentials and activities of the oxides and metals. As a result of the reactions, a metal oxide layer is formed at the interface, and then bonding develops between the glass saturated with metal oxides and the metal[154].

According to the **mechanical keying theory**, it is assumed that there is a direct proportionality between the adherence of the enamel to the metal and the roughness at the enamel-metal interface. As a result of the experiments, strong and clear findings supporting this theory were obtained[151][68]. However, some researchers reject the judgment that adherence is only dependent on roughness. While very poor adherence can be observed on some very rough metallic surfaces, excellent adherence has been observed on smooth and flat surfaces under similar

conditions[154][66]. Glassy enamel penetrates the cavities on the metallic surface while it melts and becomes a viscous liquid, and after it cools, it locks itself into the leaked cavities and so a mechanical holding occurs[151]. Two types of measurement are proposed to measure this roughness at the metal-enamel interface: anchor points and interface ratio. If the rough ceramic-metal contact is responsible for adherence, the optimum correlation should be between adherence and anchor points per centimeter[155][151].

According to the **electrolytic theory**, when cobalt (Co) or nickel (Ni) in vitreous enamel comes into contact with iron base, it precipitates and forms a short-circuited local cell with iron as the anode[66]. Positive energy (current) travels through the melt from iron to nickel[154]. As a result of these reactions, iron is dissolved from the metallic surface and transported to the interface solution area, roughening the surface and causing enamel oxides to attach to the holes[156]. Because anodic iron is abundant and diffusing ambient oxygen exerts a depolarizing effect on the cathode side, these local cells are not depleted during firing. As a result, the iron leaves the metal and goes into solution indefinitely, the surface becomes roughened, and the glass fixes itself into the holes. As a result, this hypothesis is built on anchor points[66].

In the **dendritic theory**, the main mechanism responsible for adherence originates from the dendrite arms formed during cooling. Dendrites are the form in which metal crystallizes from molten metal, aqueous solutions, or any nonmetallic liquid in which metal compounds dissolve. After cooling, the dendrites develop from the base metal to the enamel, tending to mechanically adhere the enamel to the metal base[154][157][158].

These theories can work in support of each other. In this way, different theories are formed. In another interpretation of these theories, mechanical adherence can be mentioned at the interface where surface roughness increases with electrolytic or galvanic corrosion[66]. The existence of these theories does not exclude the chemical theory. Because oxidation-reduction reaction must take place for the corrosion increasing the roughness at the interface to take place[152].

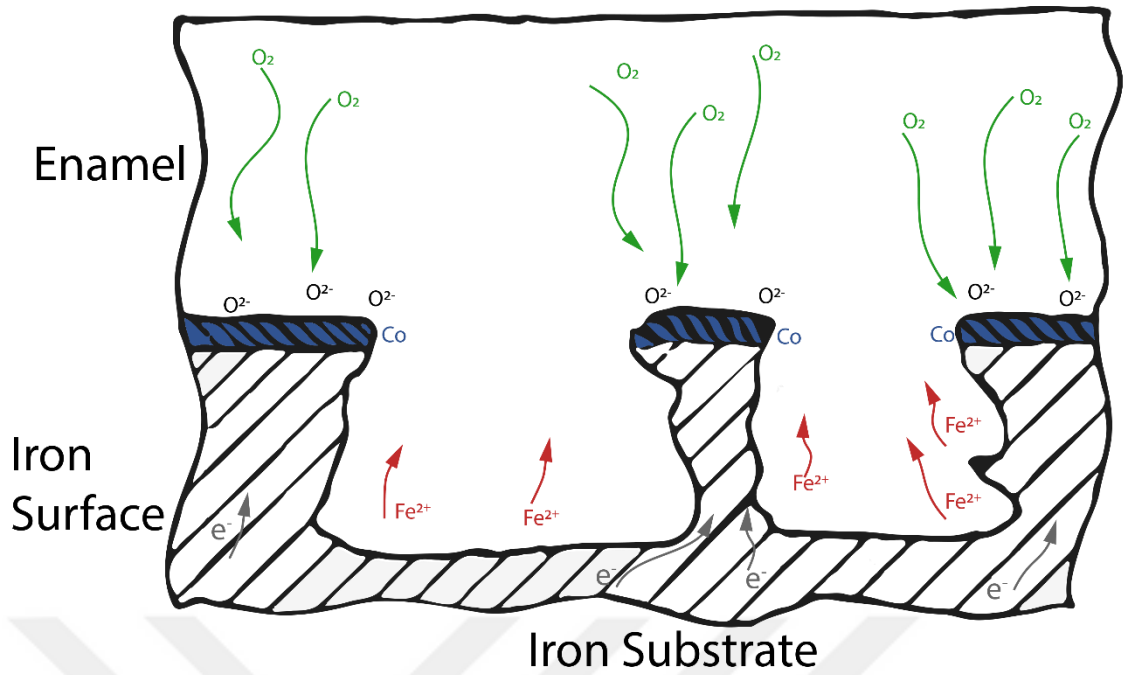
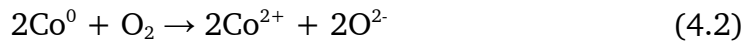
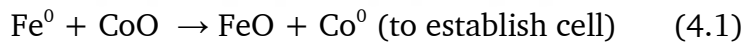


Figure 4.1 Schematic representation of galvanic corrosion in cobalt oxide bearing ground coat.

In Figure 4.1, galvanic corrosion at the interface of cobalt-containing enamel is represented by Dietzel[152]. According to Dietzel, the reactions at interface must be like below:



For these reactions to take place, it is assumed that the electrical neutrality in the enamel exists. Dietzel admits that in addition to the 1st and 2nd reactions, there may be a $2\text{FeO} + \text{CoO} \rightarrow \text{Fe}_2\text{O}_3 + \text{Co}$ reaction between the oxide layer and the enamel and that this reaction will not benefit the adherence.

5.1 Materials & Preparation

Frit and enamel quality mill additives were supplied from Akcoat Advanced Chemical Coating Company. ZrO_2 ceramic additive was also supplied from Akcoat Company, ZrB_2 additive was supplied from Nanografi CO. in 99.5% purity. The average particle size of ZrO_2 and ZrB_2 ceramics are $5\mu\text{m}$. The chemical composition of frit and the batch (mill) of reference (STD) enamel experiment analysed and calculated by Bruker S8 Tiger X-ray fluorescence (XRF) device are listed in Table 5.1. Also, mill additive ratios are given in Table 5.2.

Table 5.1 The chemical composition of frit analysed by XRF

Formula	% in Frit	% in STD Batch
SiO_2	50.29	71.79
Na_2O	17.66	9.29
Al_2O_3	2.09	4.74
B_2O_3	11.90	2.78
ZrO_2	3.66	2.43
TiO_2	3.63	2.22
CaO	2.67	1.56
F	3.32	1.46

Table 5.1 The chemical composition of frit analysed by XRF (continued)

Li ₂ O*	1.02	0.72
CuO	0.26	0.82
K ₂ O	1.26	0.77
MnO	0.78	0.47
CoO	0.71	0.45
Fe ₂ O ₃	0.28	0.26
P ₂ O ₅	0.15	0.12
NiO	0.20	0.12
BaO	0.12	-
Total	100	100

*Measured by Atomic Absorption Spectroscopy

Table 5.2 Batch (mill) recipe of the reference (STD) experiment.

Material	Weight (g)
Frit	100
Quartz	35
Clay	6.5
Sodium Nitride	0.13

Table 5.2 Batch (mill) recipe of the reference (STD) experiment (continued)

Magnesium Sulphate	0.08
Borax	0.3
Water	40

The experimental procedure was chosen as in Table 5.3. According to the plan, ZrO_2 and ZrB_2 additives were entered into the mill before grinding as 2%, 6%, and 10% by weight according to the frit weight. For example, in the ZO6 experiment batch, there are 100g of frit, other mill additives listed in table 5.2, and 6g of ZrO_2 .

Table 5.3 Code of Samples

	ZrO_2	ZrB_2
2wt.%	ZO2	ZB2
6wt.%	ZO6	ZB6
10wt.%	ZO10	ZB10
STD		

An alumina ball mill with a capacity of 300 grams was used for milling. The amount remaining above 150 mesh sieve of the slurry was adjusted to be 13 ± 1 on the bayer scale. The particle size distribution graph of the milled batch and ceramic raw materials is shown in figure 5.1. According to the graph, 90% of the total volume of sample has a size of $204\mu\text{m}$ or smaller, 50% of the total volume of sample has a size of $45\mu\text{m}$ or smaller, 10% of the total volume of sample has a size of $4\mu\text{m}$ or smaller. The final density of enamel slips was around 1.91 g/cm^3 .

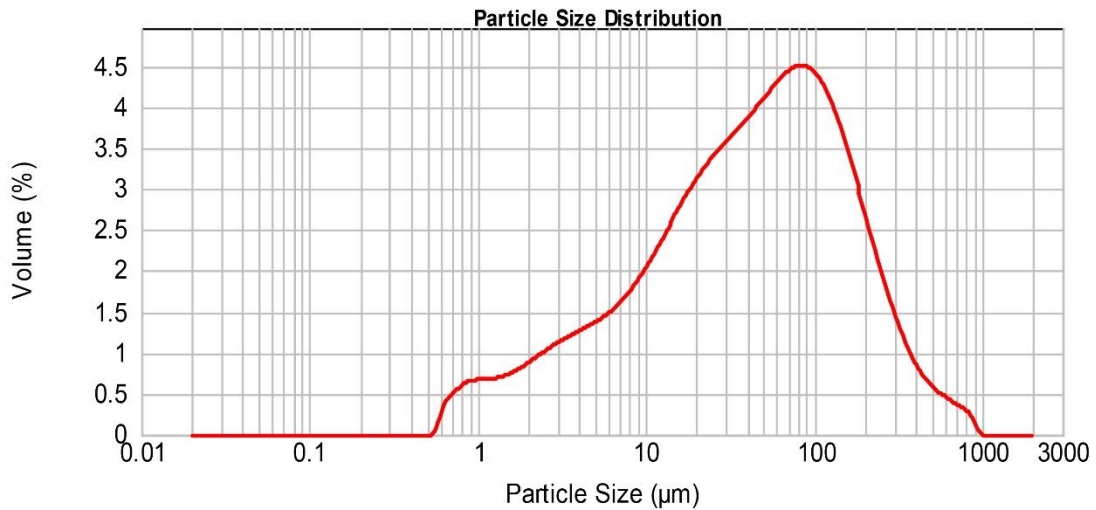


Figure 5.1 Particle size distribution of reference sample.

A standard steel plate is supplied with 105X105X2 mm dimensions. Steel was chosen as S300EK quality steel. The specimens were prepared in accordance with **ISO 28764**. Firstly, 10-20μm ground coat enamel is applied on one side and fired at 790°C for 2 minutes. After firing, the uncoated surface is sandblasted with silica sand at 6 bar pressure for 1-2 minutes. The sandblasted surface becomes ready for enamel application. The purpose of ground coating on one surface of the plate is to ensure that eliminates the weight loss due to the scale chip-off that can affect the corrosion test result. The purpose of sandblasting is to clean the scale-carbon mixture formed on the surface during back groundcoat firing.

The enamel slurry applied to the steel surface by the Dip Coating method is dried in an oven at 220°C for 10 minutes and then fired in a box furnace at 860°C for 10 minutes. The fired sample is taken out of the furnace, put on hold at room conditions to cool down. The final cover coat thickness was arranged as 250μm ± 50μm

5.2 Erosion/Corrosion Tests

Hot basic solutions can quickly corrode the enamel surfaces. Especially in water heaters, the high amount of alkali ions contained in tap water creates a corrosive environment for the enamel surface. As the temperature of the environment

increases, the corrosion rate also increases. Such environments can cause serious damage in a short time, especially in water heaters, chemical reactors, and pipes. There are special alkali-resistant enamel coatings developed to prevent this. In this study, two kinds of test solution were used to inspect the corrosion resistance of the enamel coating,

Enamel coated steel samples were prepared and tested in accordance with **ISO 28706-4:2016, Clause 11** — Other test solutions to the determination of resistance to chemical corrosion by alkaline liquids using a cylindrical vessel. %5wt. Sodium Hydroxide (NaOH) test solution is prepared using lab-grade NaOH supplied from Merck Co. and Water conforming to the requirements of **grade 3 of ISO 3696**. Solution temperature was kept at $100^{\circ}\text{C} \pm 1$ and the duration of the test was 6 hours for each sample. Every experiment was tested three times using the different plate specimens of the sample. Before the corrosion test, the surface of the specimens was cleaned with water, dried at 110°C for 2 hours, and kept in a desiccator for 2 hours. Then first weigh of each specimen was taken with the nearest $0,2 \times 10^{-3}$ g sensitive scale and recorded the starting mass, M_s . Liquid phase test was performed, so specimens were placed at bottom of the cylindrical vessel as face-up position. The upper side of the cylindrical vessel was covered with **borosilicate glass 3.3 supplied according to the ISO 3585:1998**. The wing nuts were screwed down and the vessel was fastened. The vessel was filled with 450ml of the test solution and the heating system was turned on. It takes approximately 10 min to reach the desired temperature. 6 hours later, the heating system was shutted down. Some of the solution specimens in the vessels were taken for ICP measurements and enamel specimens were detached after that. The enamel specimens were washed with an acetic acid solution (50 ml/L), exposed to the same rinsing, drying, and held in desiccator procedure as in the beginning. The final weight of each specimen was taken, M_f . All safety rules were followed during these operations.

Total loss in mass per unit area (ΔW_A) is calculated for the total duration of the test as below formulation:

$$\Delta W_A = \frac{(M_s - M_f)}{A} \quad (5.1)$$

Where A is the area exposed to attack, in m².

The enamel corrosion in the NaOH test progresses linearly with time (ISO 28706-4:2016). The corrosion rate, v , is computed as the rate of mass loss per unit area, g·m⁻²·h⁻¹, using the formula below:

$$v = \frac{\Delta W_A}{t} \quad (5.2)$$

where t is the test duration, in hour.

Also, it is possible to calculate the corrosion rate in mm per year, w , as below:

$$w = 3,504v \quad (5.3)$$

NOTE: Enamel is considered to be a homogenous substance (without gas bubbles) with a density of 2,5 g/cm³ in this formula.

Acid resistance of the same enamel surfaces was tested and evaluated in accordance with **Clause 11 of ISO 28706-1:2011** — other acids at room temperature. %10 by vol. Hydrochloric Acid (HCl) solution was prepared for acid resistance test using the %36 HCl and Water conforming to the requirements of **grade 3 of ISO 3696**. A few drops of the prepared solution were placed on the enamel coating and covered with a cap. After 1 hour, the samples were rinsed under tap water and dried with a soft filter paper. The test was performed at around room temperature (23°C ± 3). The classification scale is as in figure 5.2.

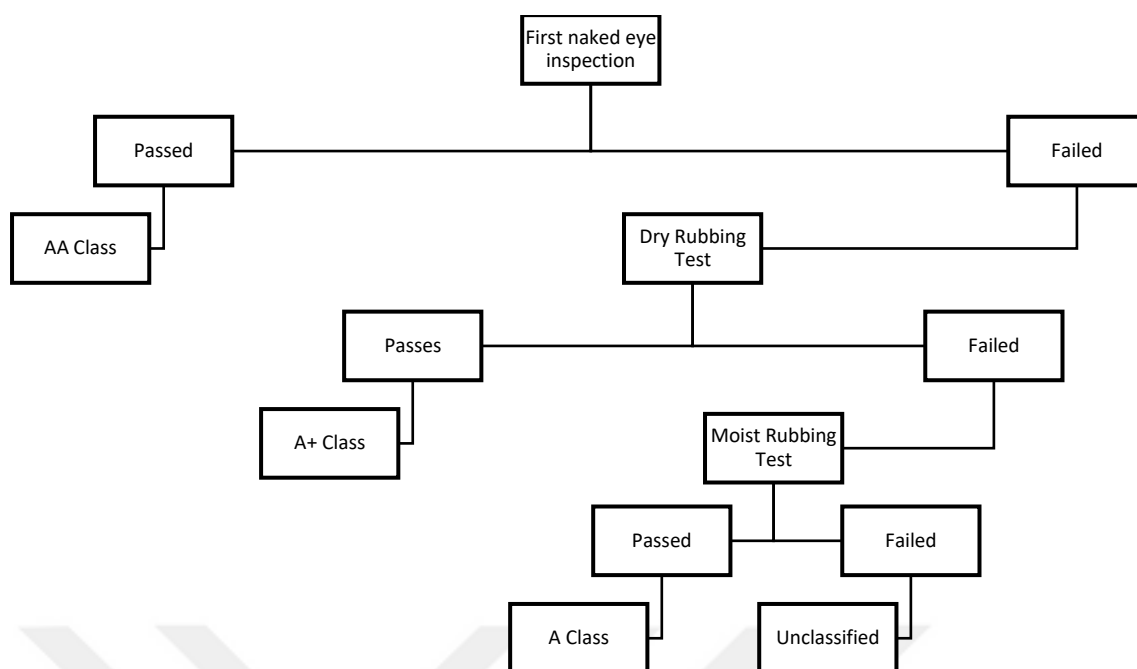


Figure 5.2 Test scheme according to ISO 28706-1:2011

5.3 Characterizations

Differential Scanning Calorimetry / Thermogravimetric Analysis (DSC / TGA) analyses were made simultaneously using the Netzsch STA 449F1 device in air environment with 10°C/min heating rate up to 1000°C.

The sintering behavior of the samples was inspected using Misura 3 HSML **heating microscope** equipment with 10°C/min heating rate.

X-ray Diffraction (XRD) analysis was employed using Bruker D8 Eco to investigate the crystallographic structure of fired and unfired enamel compositions.

Microstructures are investigated by JEOL JSM 6060LV **Scanning Electron Microscope (SEM)** with the acceleration voltage of 15 kV and the working distance of 14 mm. **Energy Dispersive X-Ray Spectroscopy (EDS)** was also used for the compositional analysis using the Mapping and direct techniques.

Cross-section inspections were made by FEI Quanta FEG-450 **Field Emission Scanning Electron Microscope (FESEM)** with an acceleration voltage of 15

kV, the working distance of 10 mm, and the spot size 3.0 Also, **EDS** equipment was used for compositional investigation. Line analyses and Mapping techniques were also used for cross-sectional inspection.

Inductively Coupled Plasma (ICP) measurements were made using Perkin Elmer Avio 200 ICP-OEs and Thermo Scientific X series II ICP-MS equipments. Test solution taken from the cylindrical vessel just after the basic tests completed.

To evaluate the practical adherence level between enamel coating and steel, the **BS EN 10209:2013 Impact Test** equipment and Scale were used where 1 refers to best and 5 refers to worst adherence.



6.1 Thermal Analyses

DSC/TGA analysis and heat microscopy analysis were used for thermal analyses of the trials. When the DSC/TGA curves of the standard enamel were examined, there was a mass loss of approximately 6.7wt.% in the TGA values of STD as shown in Figure 6.1. These enamels were tested after drying, that is, without physically bound water, there is a mass loss caused by volatile materials such as crystal bound water and other organic residues in clay, F, S, C, N, B in the whole structure. The only endothermic peak at around 575°C corresponds to dihydroxylation of clays phases like kaolinite and illite[159].

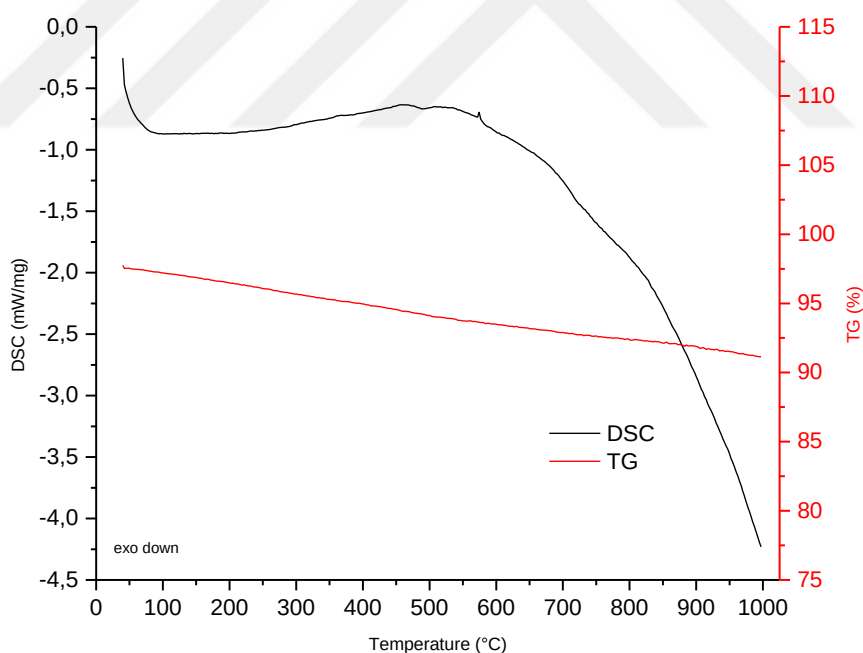


Figure 6.1 DSC/TGA Curves of enamel sample of STD specimen.

When the DSC/TGA curve of ZrO_2 doped ZO2, ZO6, and ZO10 samples was examined (Figure 6.2), the mass loss decreased compared to the standard sample.

The mass loss of ZO2 is around 2wt.%, ZO6 has lost around 4wt.% and ZO10 has lost around 2wt.%. There is no theoretical explanation for the mass loss in ZO6 to lose twice as much mass as in ZO2 and ZO10, but it may be due to insufficient drying of the sample or contamination during packaging, transportation. When the data is examined in detail, the exothermic peak in the range of 470-500°C is present in STD and all other samples if looked carefully. This peak is more prominent especially in ZrB₂ added samples due to drying differences of samples. This peak shows the thermal effect of endothermic organic decomposition combined with the much stronger exothermal effect induced by the combustion of the evolved gases, which occurs at higher temperatures[160].

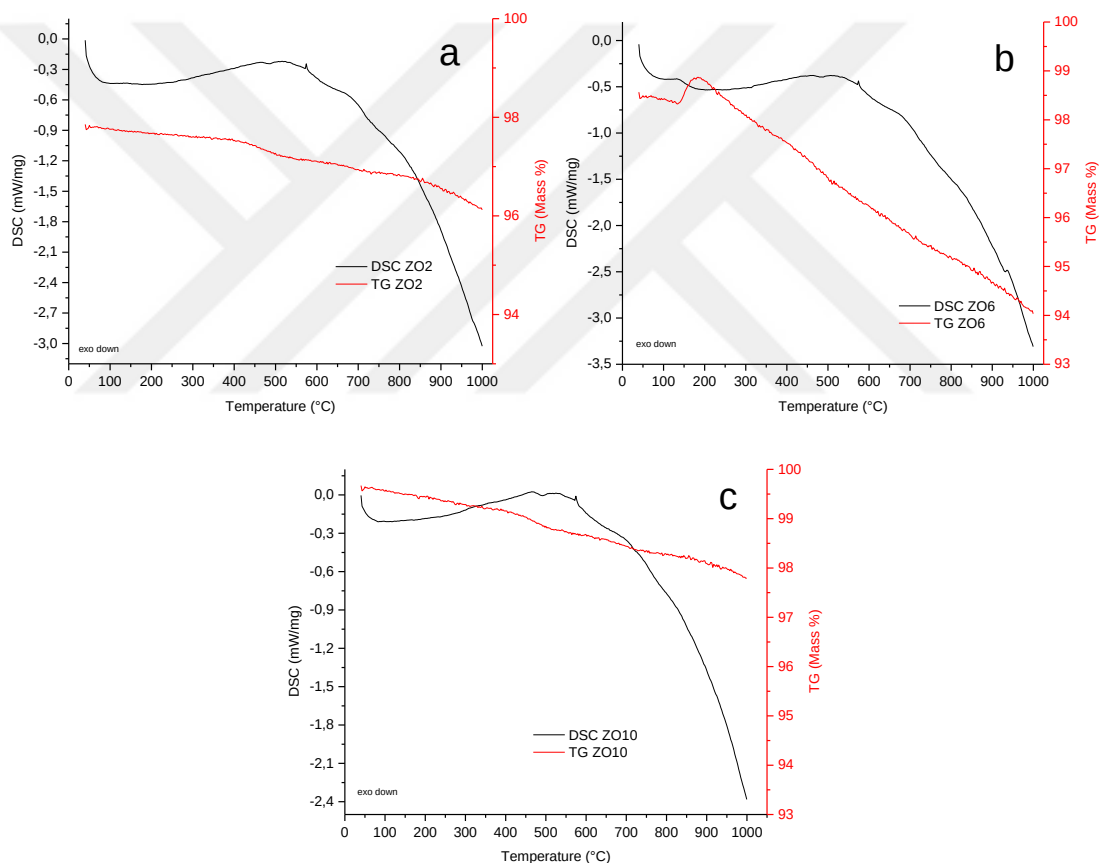


Figure 6.2 DSC/TGA curves of ZO2(a), ZO6(b), and ZO10(c) samples.

The fluctuation of the DSC curve around 150°C and the positive deterioration of the mass loss slope at that temperature also support the organic nature of the contamination. As in the standard sample, a small endothermic peak around

575°C is present in all ZrO₂ added samples. When we look at the thermal curves of ZrO₂ added samples in general, the low mass loss compared to the standard indicates that there is less gas output from these samples (Figure 6.2). The positive or negative effects of this situation on corrosion resistance will be examined by looking at the results of the analyses in the following sections.

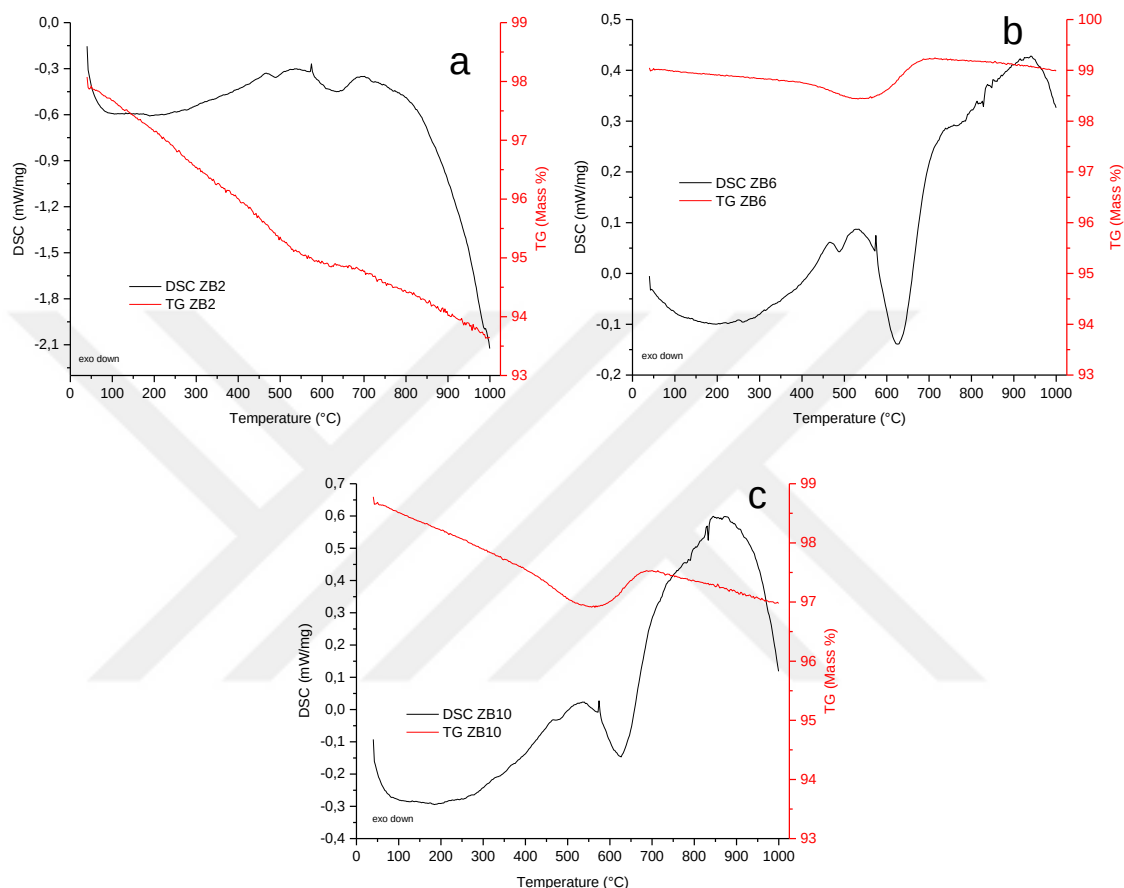


Figure 6.3 DSC/TGA curves of ZB2(a), ZB6(b), and ZB10(c) samples

DSC/TGA curves of samples containing ZrB₂ are shown in figure 6.3. When these curves are looked at superficially, it is striking that there are radical slopes different from those of the other STD and ZrO₂ doped samples. A wide exothermic peak in the 575-630°C range in the ZrB₂ doped (ZB coded) samples is not present in the STD and ZrO₂ doped samples. The intensity of this peak increases from ZB2 to ZB10. that is, as the amount of ZrB₂ increases, the intensity of the peak increases. This indicates that the exothermic peak is related to ZrB₂ material.

When the literature and the DSC result of the ZrB_2 material are examined, it can be said that this is a proof of the decomposition of ZrB_2 in the air as ZrO_2 and B_2O_3 according to the following reaction[131][161]. Additionally, the DSC/TGA curve of the ZrB_2 raw material is shown in figure 6.4.

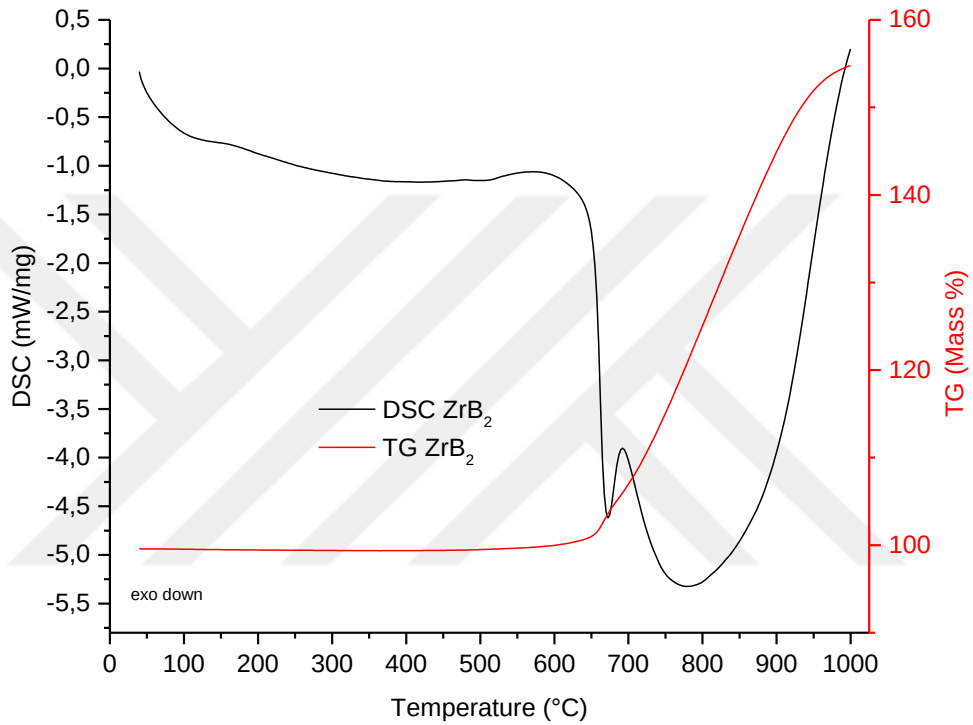
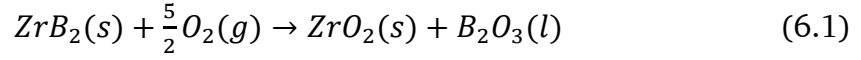


Figure 6.4 DSC/TGA result of ZrB_2 raw material.

According to the TGA result in Figure 6.4, the mass of the material as a result of oxidation that starts around 660-670°C is approximately 54%wt. has increased as much. Around 780°C, the exo peak reached its max point. On the other hand, in ZB2, ZB6 and ZB10 samples, mass increase and indirectly exothermic peak take shape around 600°C. When TGA results are examined in detail, it is seen that the increase in mass remains at a limited level and does not increase continuously. Even in the ZB10 sample with the highest amount of ZrB_2 , the mass loss trend continued after an increase of 0.6wt.% in the temperature range where the mass

increase occurred. This suggests that the oxidation in the structure is restricted at one point, which will be confirmed in XRD analyzes. While the total mass loss of the ZB2 sample remains around 4%, the mass loss of the ZB6 sample is almost zero. ZB10 has lost about 1% mass.

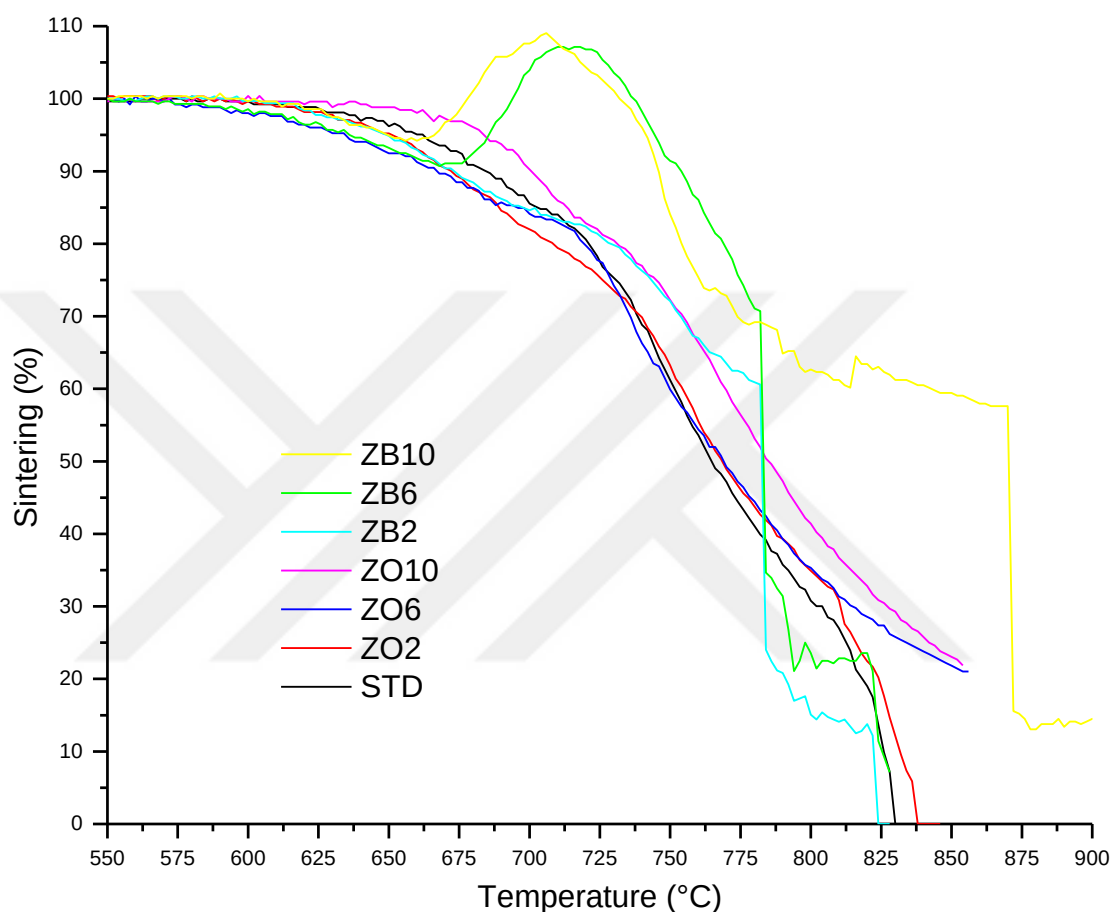


Figure 6.5 Heat microscopy results.

The graphic given by the heat microscope, which is the other part of the thermal examination, is shown in 6.5. According to the graph, the melting point of the ZrB_2 -doped samples could not be determined due to the increased volume of the samples due to the outgassing. STD sample starts to sinter around 660°C, softens around 725°C, and melts around 810°C. The thermal resistance of the ZO2 sample lagged behind the STD sample up to 730°C. After that, it remained 5-6°C ahead of

the STD sample in terms of thermal resistance. ZO6 sample lagged behind STD until 725°C just like ZO2, exhibited a heat resistance parallel to STD between 725-755°C. Then separated from STD after 755°C and made parallel progress to ZO2 after this temperature. The ZO10 sample, that is, the sample containing the most ZrO_2 , starts to sinter at around 680°C and exhibits melting behavior at around 820°C. Heat microscopy results of ZrB_2 doped samples show a misleading appearance after a certain level. The gas that emerges with the decomposition of ZrB_2 starting around 660-670°C, which is also confirmed in the DSC/TG results, affects the measurement by swelling the structure. The gas permeability increases with the decrease of viscosity of the sample that swells up to a certain point. When the sample reaches the softening temperature, that is, around 715°C, the structure starts to release gas and at one point, leaves all the gas in its structure. For the ZB2 and ZB6 samples, this point can be said to be around 780°C, for the ZB10 sample it can be said to be around 870°C.

6.2 Crystallographic Analyses

Two types of XRD examinations of 7 samples were made: before firing (milled and dried batch) and after firing. Milled batch pellets were fired at the same temperatures as enamel-applied plates were, at 860°C to simulate firing on the steel plate. Fired samples are named as adding an 'F' at the end of the specimens' codes. For example, the milled and dried sample had been named ZO2, the fired sample of this specimen was named 'ZO2-F'.

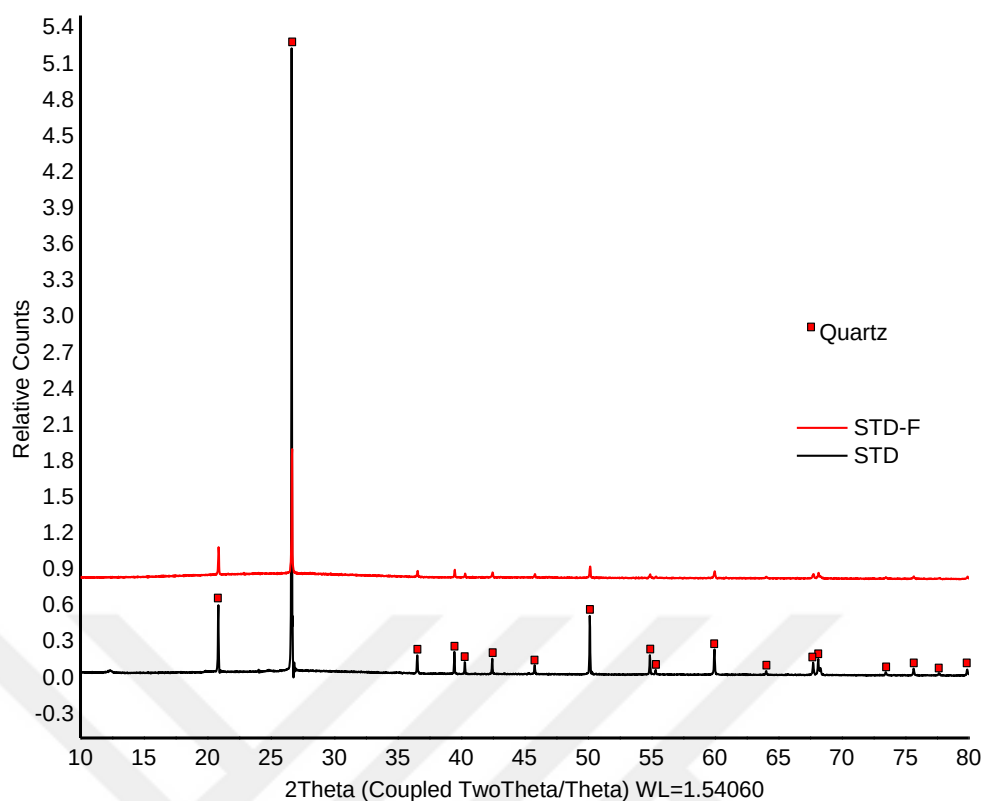


Figure 6.6 XRD results of milled (STD) and fired (STD-F) reference samples.

When the XRD analysis of the standard sample was examined, Quartz, which was added as 35%, dominated all other materials and showed itself in the structure as in figure 6.6. In the XRD pattern of the sample, which became enamel by firing, some amorphization in the range of 15°- 35° angles is noticeable. The quartz in the structure continues to exist even after firing. The amorphous region is considered to have formed as a result of the partial vitrification of quartz. Because the frit, which is currently in glass form, could not show itself in the XRD pattern.

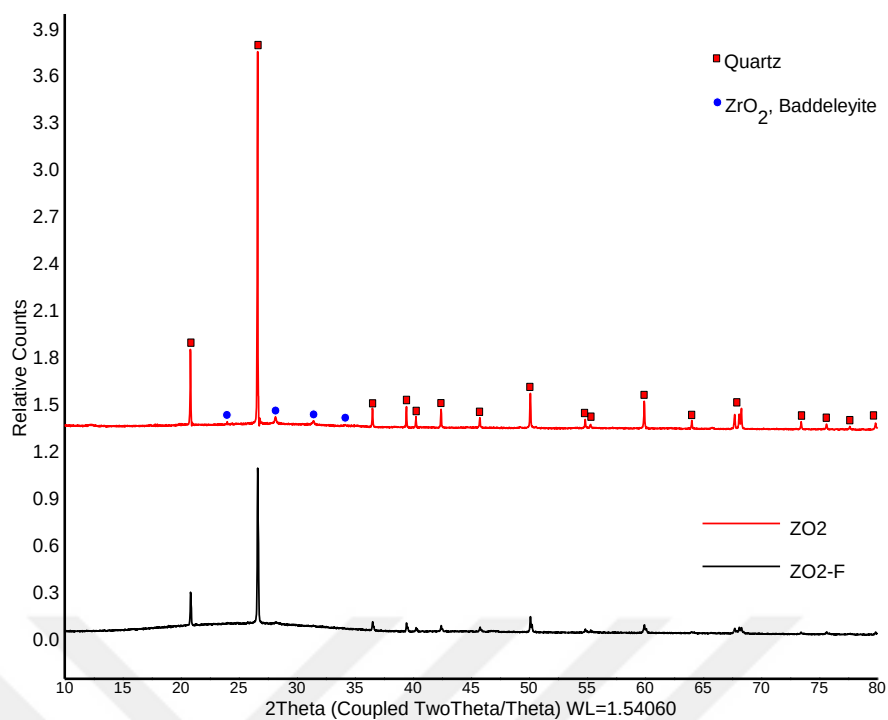


Figure 6.7 XRD pattern of ZO2 sample

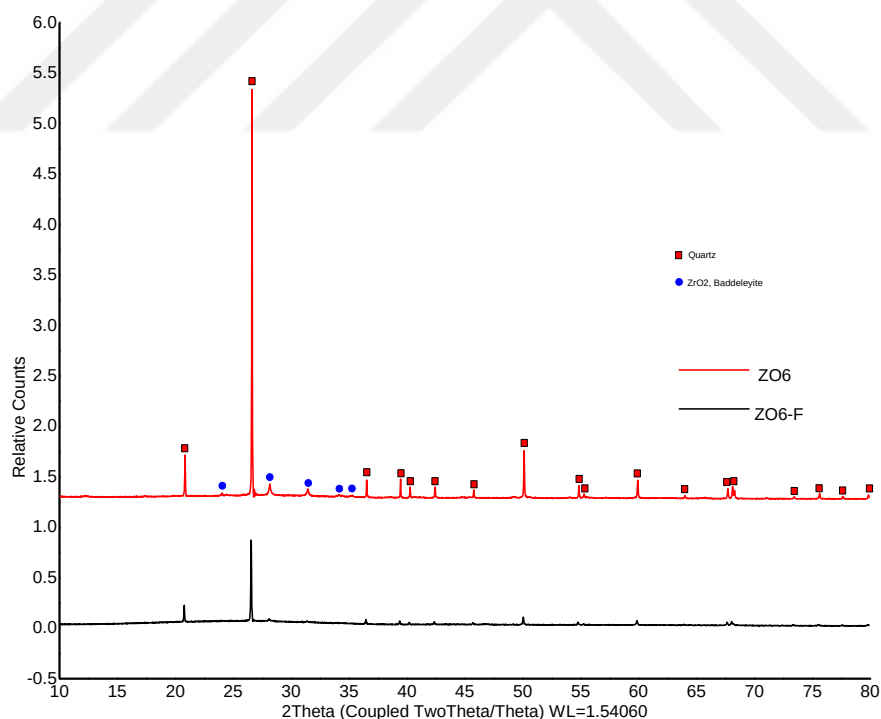


Figure 6.8 XRD pattern of ZO6 sample.

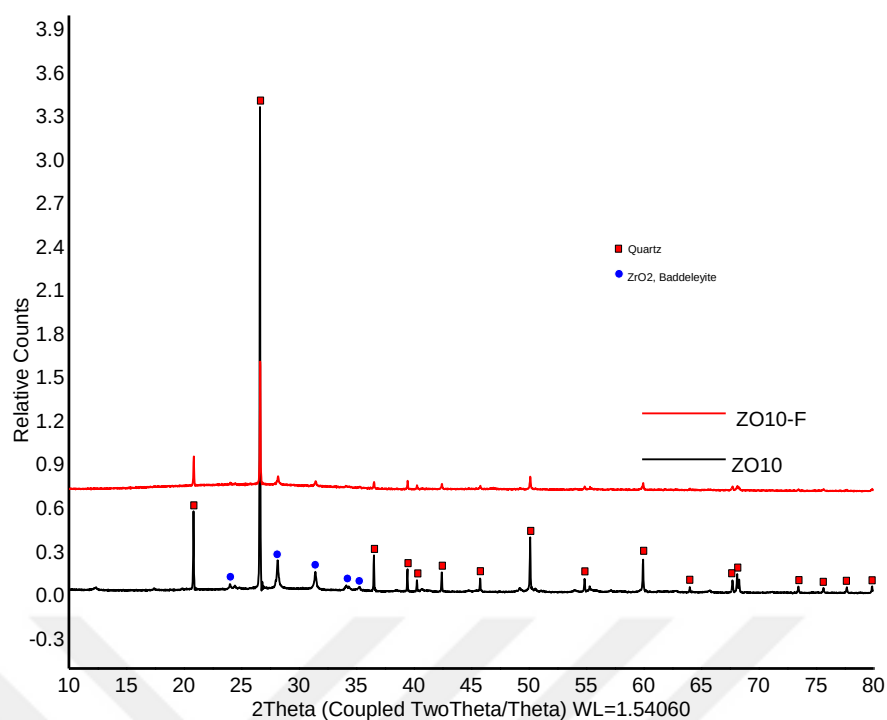


Figure 6.9 XRD Pattern of ZO10 sample

The XRD pattern of the ZO2 sample is also largely the same as the STD sample as shown in figure 6.7. However, the added ZrO_2 showed low intensity in the 28° and 31° bands. In Figure 6.8 and Figure 6.9, the milled and fired data of ZO6 and ZO10 samples are shown separately, and as expected, ZrO_2 peaks are seen in all. This indicates the presence of quartz and zirconia ceramics after firing the samples. While vitrification was observed in the pattern after firing, there was a decrease in the count number of the peaks in the fired XRD patterns of all samples. It can also be said that some crystals overlapped and join into a glassy structure.

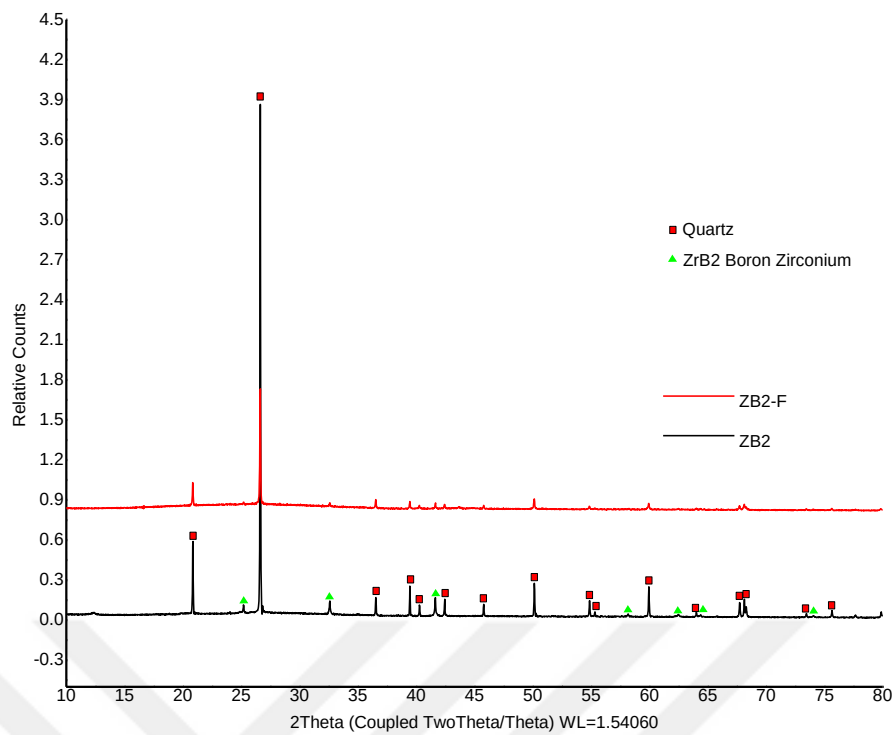


Figure 6.10 XRD pattern of ZB2 sample

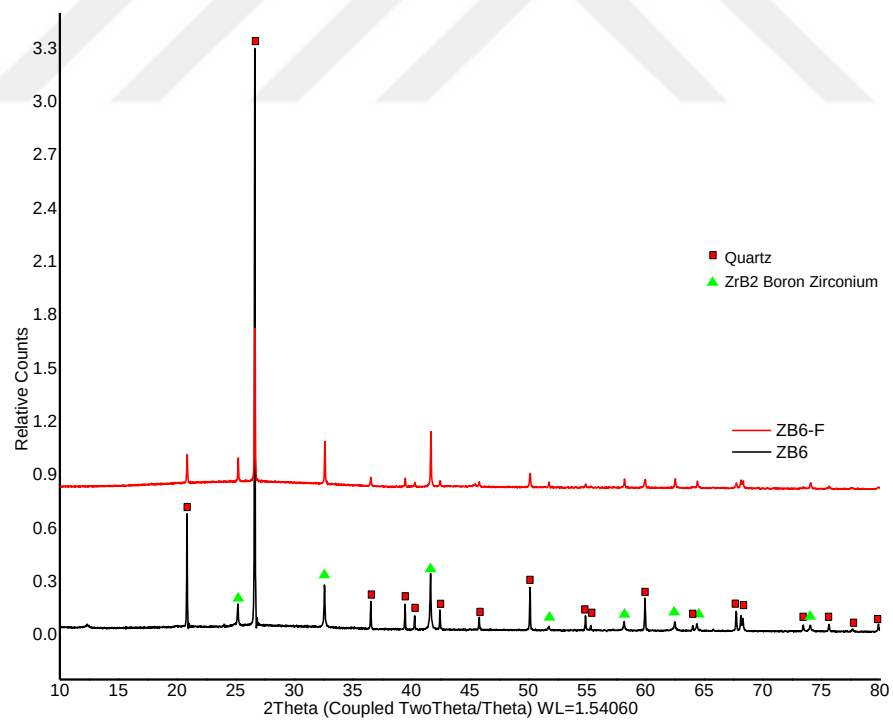


Figure 6.11 XRD pattern of ZB6 sample

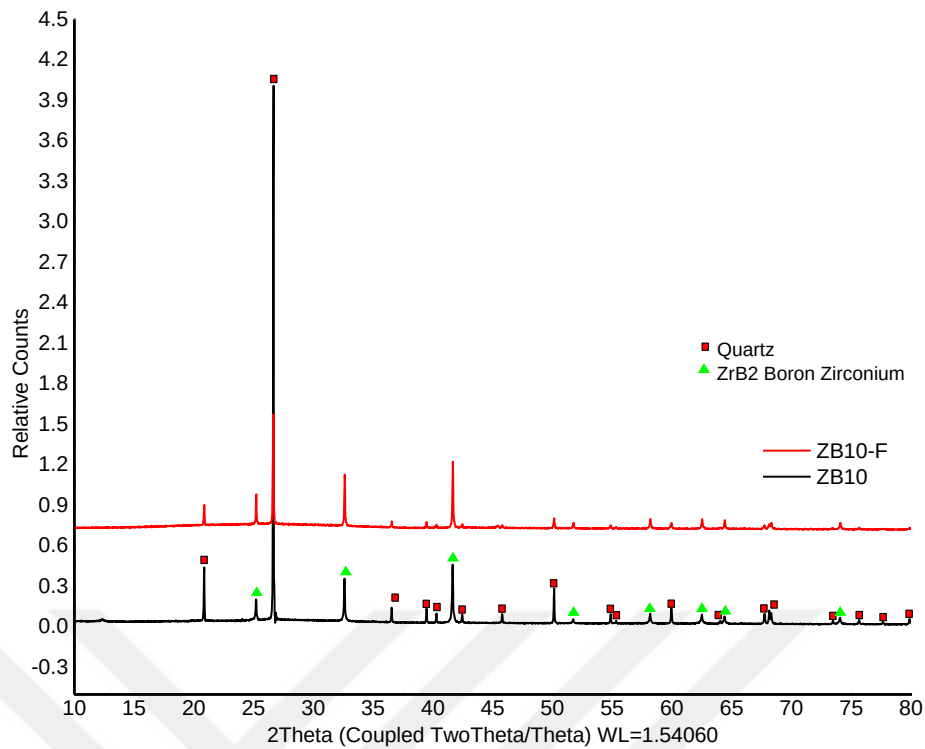


Figure 6.12 XRD pattern of ZB10 sample

In ZB trials, it can be thought that ZrB_2 crystals will not remain in the enamel structure after seeing the thermal curve of ZrB_2 . However, according to the XRD results, most of the ZrB_2 in ZB trials seems to have remained intact. In the ZB2 sample seen in figure 6.10, the intensity of the ZrB_2 peak becomes very low after firing. However, in the ZB6 and ZB10 trials in figure 11 and figure 12, the intensity of the ZrB_2 peak seems to be preserved with a small decrease. For the ZrB_2 ceramic to remain largely intact within the enamel structure, another structure that prevents oxidation must be formed on its surface. According to the DSC/TGA results, B_2O_3 emerging in the liquid phase with the decomposition of ZrB_2 and other stable oxides in the enamel surround these grains and prevent more oxygen diffusing inside[131]. For this reason, it is possible to say that certain amounts of ZrB_2 advanced ceramic grains exist without decomposition in the structure. Also, SEM/FESEM results, which will be examined in the following sections, also presented images that support this evidence.

6.3 Base Erosion / Corrosion Analyses

6.3.1 Basic Solution Test Results

The data obtained as a result of the experiments performed against alkaline basic solution attacks were calculated in three ways: the amount of mass loss per unit area, rate of mass loss per unit area, and mm per year. To remind once again, all samples (STD, ZO2, ZO6, ZO10, ZB2, ZB6, ZB10) were tested three times with different plates of specimens against to NaOH solution and made an average result as stated in the graphs.

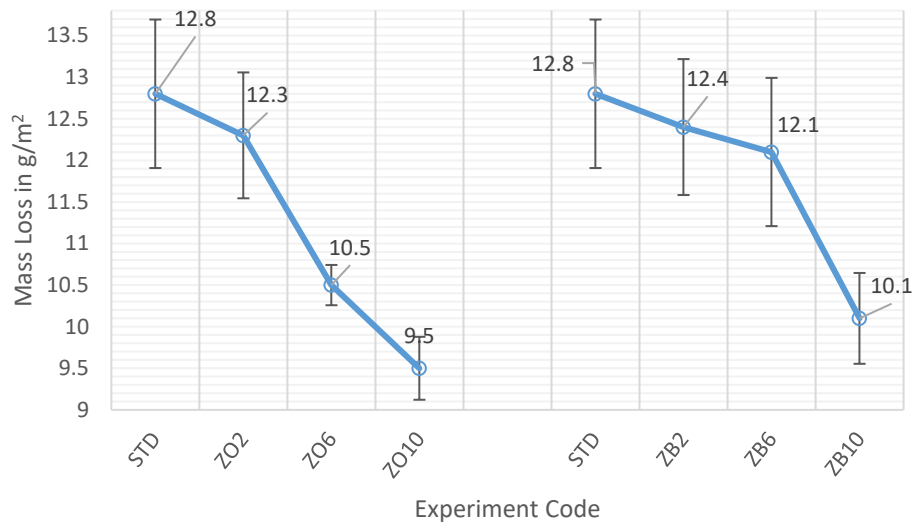


Figure 6.13 Total loss in mass of specimens per unit area against to NaOH solution

The results in terms of mass loss per unit area of erosions caused by the attack of the basic solution are shown in figure 6.13. According to the results, the standard sample lost 12.8 g/m² mass after 6 hours, while ZO2 12.3, ZO6 10.5, and ZO10 9.5 g/m² eroded. Also, ZrB₂ addition increased the resistance against corrosion. ZB2 sample 12.4, ZB6 sample 12.1, and ZB10 sample 10.5 g/m² eroded. In both ZrO₂ and ZrB₂ additives, the resistance to corrosion increases as the additive percentage increases. When 2% of both advanced ceramic additives are added into the enamel batch, the resistance to corrosion increases compared to the standard,

but there is no radical difference between these samples in terms of erosion/corrosion amounts. When 6% of both additives were entered, the ZrB_2 additive increased slightly the corrosion resistance, but the ZrO_2 additive increased more at this percentage from 12.8 to 10.5 g/m^2 . When it comes to the 10% addition of advanced ceramics, both of them provide good resistance to erosion/corrosion. Especially addition of 10% ZrO_2 to the standard sample reduced the corrosion resistance by approximately 25%. This reduction rate is up to 21% when 10% ZrB_2 is added. While the slope of the increase in corrosion resistance rises after 2% in the trials with ZrO_2 , it increases radically after 6% in the trials with ZrB_2 .

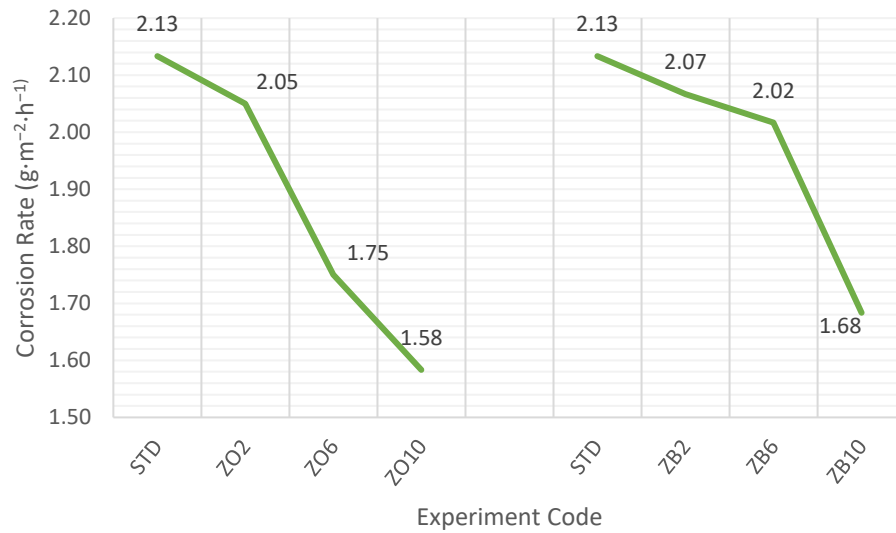


Figure 6.14 Hourly rate of mass loss per unit area

These two ratios, which are above 20%, can be considered as efficient values. When the results are analyzed on an hourly basis, the criticality of these decline rates becomes even more prominent. In figure 6.14, STD sample was eroded 2.13 g/m^2 per hour. This rate decreases below 2 when the ZrO_2 rates increased over 2% or ZrB_2 increased over 6%. According to the calculations stated in figure 6.15, STD sample corrodes 7.48mm per year in a heavy basic environment (NaOH). One by one, ZO2 corrodes 7.18mm, ZO6 6.13mm, ZO10 5.5mm corrodes per year. ZB2 corrodes 7.24mm, ZB6 corrodes 6.13mm, and ZB10 corrodes 5.9mm per year.

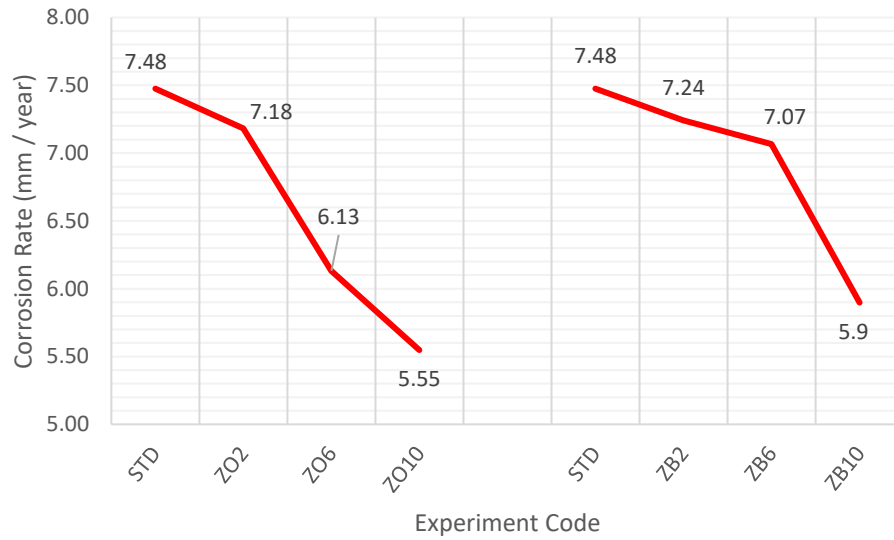


Figure 6.15 Erosion / corrosion rate in terms of millimeter per year.

6.3.2 SEM / EDS Results of STD And ZrO₂ Doped Experiments

When the SEM images of the reference sample are examined, there are light and dark areas before the wear, which can be seen in figure 6.16. It was determined by EDS analysis that this lightness and darkness were caused by compositional differences (figure 6.16). The light and dark areas continued to exist after the erosion and the elevation difference is visible from the images.

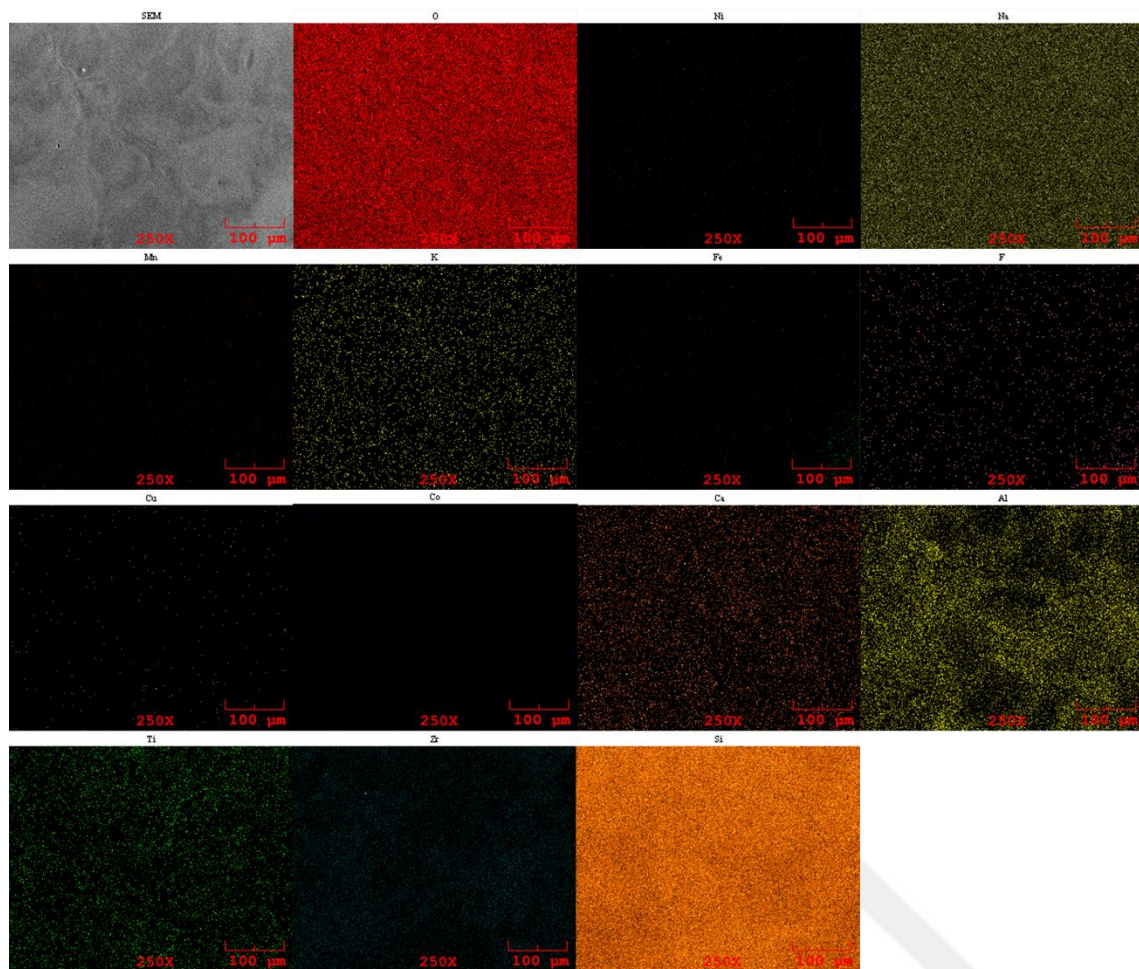


Figure 6.16 X-Ray Dot of STD surface

It can be said that, the general distribution of elements is homogeneous except for a few elements in figure 6.16. Al and Si elements appear to be clearly phased in the structure. We can consider these phases as Al dense phases and Si dense phases. Although these changes between the phases are not radical, especially on the Si basis, the color intensities confirm that there is a difference. In addition, Zr and Ti elements also show slight fluctuations, although not as much as Al. Also, this phase fluctuations could come from different frit particles with different compositions. The count density of metals such as Mn, Ni, Co, Fe, Cu is low because they are less in composition and concentrate towards the lower side of the enamel rather than the surface.

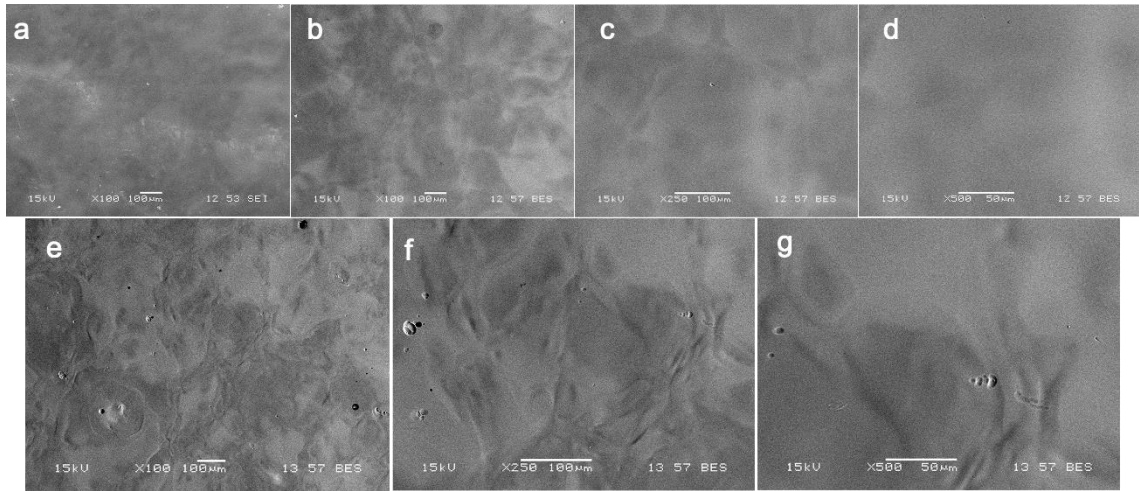


Figure 6.17 SEM images of STD sample. a, b, c, and d surfaces of samples before base corrosion. e, f, and g are the images of base corroded surfaces. a-100x magnification secondary electron mode (SEI), b-100x magnification backscatter electron mode (BES), c-250x BES mode, d-500x BES mode, e-100x BES mode, f-250x BES mode, g-500x BES.

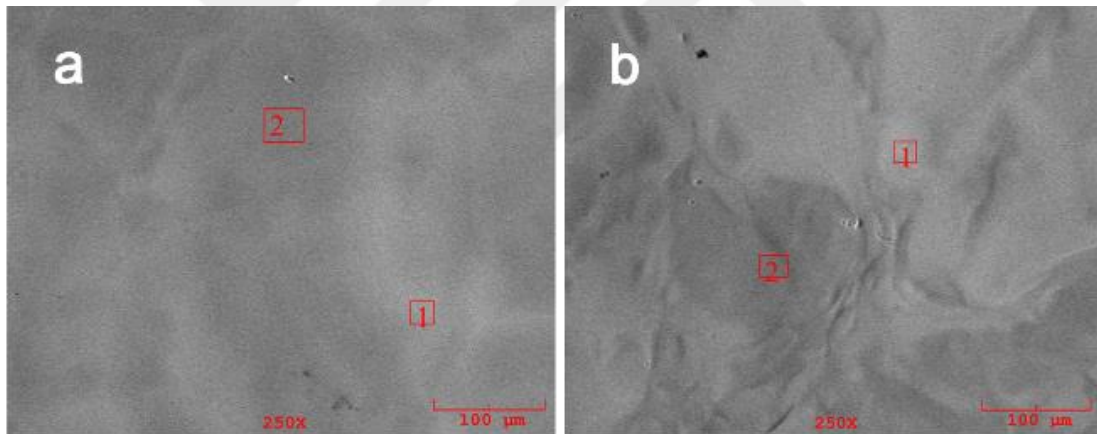


Figure 6.18 EDS image results of eroded(b) and uneroded(a) surface of STD with NaOH solution.

EDS measurements of eroded and uneroded surfaces are shown in figure 6.18 and Table 6.1. According to the results, the amount of Aluminum element varied significantly between the dark and light regions. The amount of Al in the dark areas is less than in the light areas. The amount is almost halved. In addition, it is remarkable that the amount of Ca and Mn in the dark areas on the eroded surface has decreased by half.

Table 6.1 EDS compositions of figure 6.18

Elt.	a-1	a-2	b-1	b-2
O	31.358	33.813	32.867	35.559
F	0.000	0.130	0.000	0.088
Na	13.152	11.949	12.582	11.565
Al	2.527	1.601	3.344	1.712
Si	34.633	36.870	33.772	38.128
K	0.709	0.723	0.796	0.780
Ca	2.136	2.198	2.541	1.286
Ti	2.440	2.401	2.018	2.607
Mn	0.725	0.935	0.757	0.450
Fe	0.143	0.363	0.319	0.472
Co	0.976	1.034	0.677	0.998
Ni	0.473	0.186	0.345	0.354
Cu	1.197	0.985	0.854	0.300
Zr	9.532	6.812	9.127	5.700

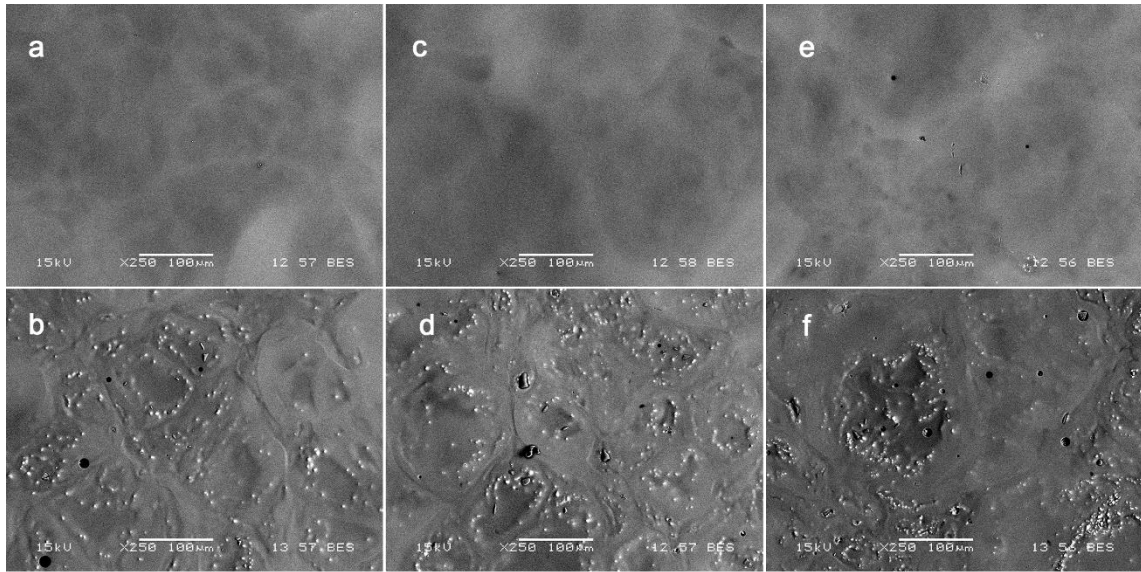


Figure 6.19 SEM images of surfaces of ZO experiments. a-Uneroded ZO2, b-ZO2 Eroded with Basic solution, c-Uneroded ZO6, d-ZO6 Eroded with Basic solution, e-Uneroded ZO10, f-ZO10 Eroded with the basic solution

Figure 6.19 shows the states of ZO2, ZO6, and ZO10 before and after corrosion. The pre-corrosion images are similar in all three samples, and the black and white areas present in the standard sample are also present in these samples. In the eroded images of these samples, different from the standard, clusters of white dots take attention. When we approach the white dots and do their analysis, we get a high amount of zirconium signals from them, as seen in figure 6.20(b)(c). Therefore, it can be said that these particles are ZrO_2 grains added as mill additives. As expected, the population of these particles increased from ZO2 to ZO10. The presence of white spots is not visible on uneroded surfaces. While the Si-dominated structure around the ZrO_2 grains dissolved in the presence of the aggressive solution with erosion, the ZrO_2 grains resisted corrosion and continued to exist in the structure.

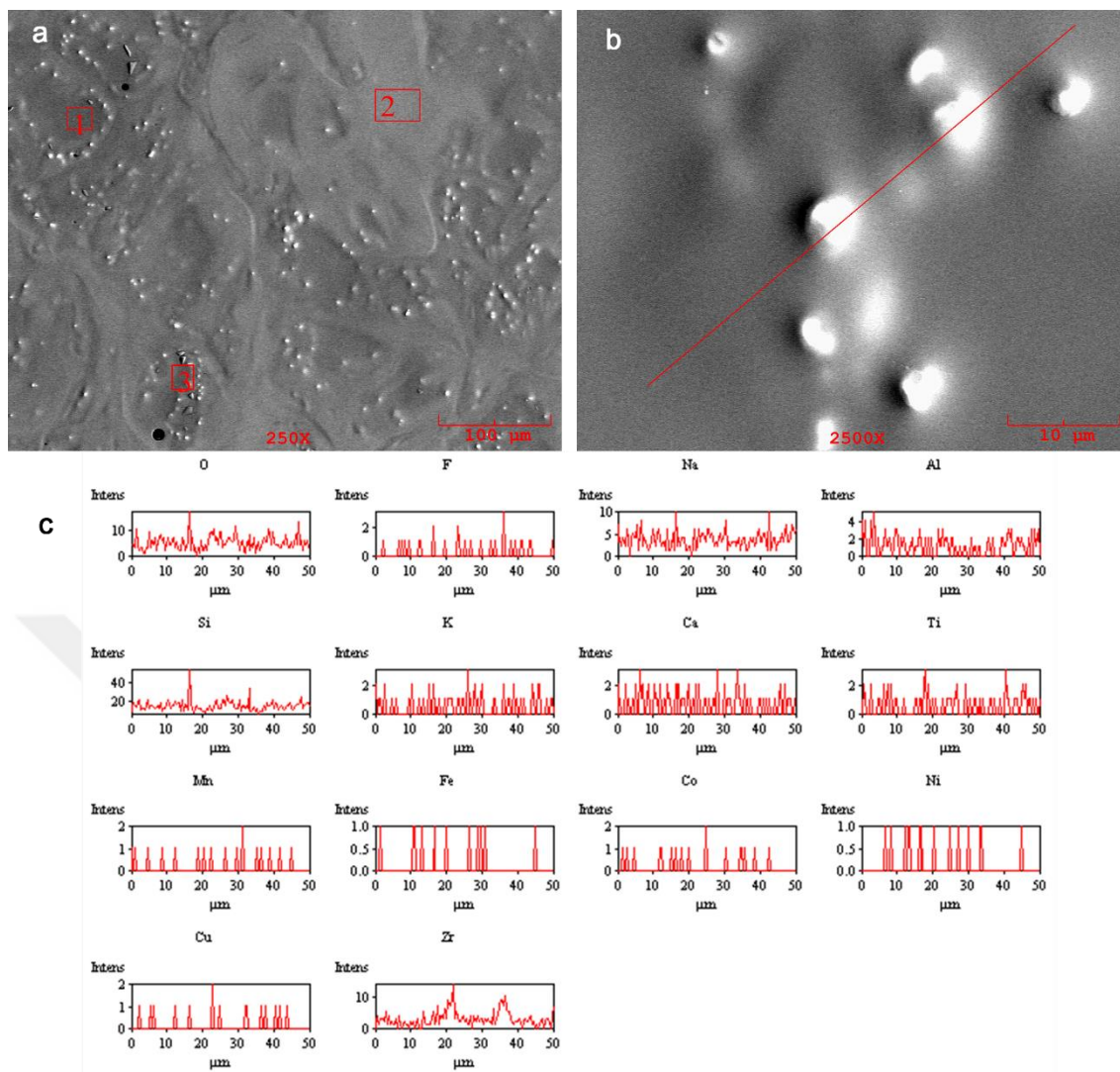


Figure 6.20 EDS and Line analyses of corroded ZO2 sample. a-EDS areas, b-white zirconia particles, c-line analyses of zirconia particles.

Table 6.2 wt.% composition of areas stated in figure 6.20.

Elt.	a-1	a-2	a-3
O	34.534	34.923	33.072
F	0.000	0.000	0.040
Na	11.732	12.933	10.843
Al	0.581	2.714	2.629

Table 6.2 wt.% composition of areas stated in figure 6.20 (continued)

Si	40.440	32.606	38.429
K	0.648	0.012	1.013
Ca	2.192	0.996	1.810
Ti	2.370	1.943	1.285
Mn	0.165	2.121	0.290
Fe	0.263	0.703	0.383
Co	0.859	0.276	0.992
Ni	0.770	0.555	0.514
Cu	0.430	0.023	0.375
Zr	5.017	0.422	8.324

When the EDS analyses in Figure 6.20 and Table 6.2 are examined, it can be said that the corrosion is more in the first dark region, and the corrosion is less in the second light region than in the first. It can be inference due to both the elevation difference and the absence of ZrO_2 grains. The amount of Al in the 1st region is about 4 times less than in the 2nd region. In the 1st region, the amount of K and Ca is high. Mn and Fe are more in the second region. Region 3 is the region with the highest amount of Zr as expected. Zirconium clusters around the dark islands can be seen in the mapping result of the ZO10 sample in figure 6.21. Al intensity difference between the dark and light areas can also be seen in the map. Some Si particles show themselves in the structure come from quartz addition.

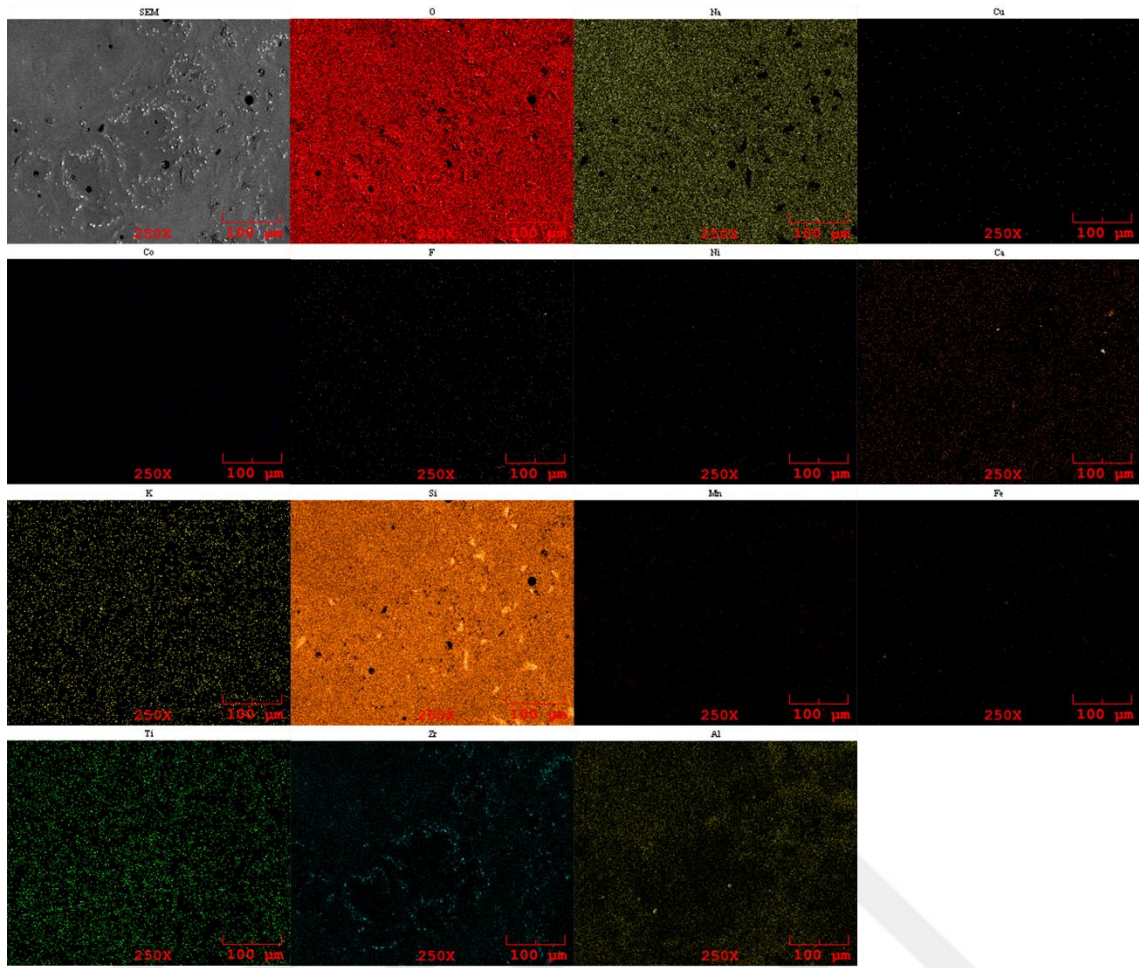


Figure 6.21 Map Analysis of corroded ZO10 sample

6.3.3 SEM / EDS Results of ZrB_2 Doped Experiments

SEM images of ZrB_2 doped samples are shown in figure 6.22. When the images are examined, uneroded surfaces, holes, and bright white grains attract attention. Counts couldn't be taken from the holes, and it can be said that these holes were formed as a result of gas escaping. In the first thermal analysis, we also mentioned the gas output in the ZrB_2 doped samples. Gas bubbles are formed as a result of the evaporation of the B_2O_3 liquid resulting from the decomposition of ZrB_2 . Gas bubbles that are trapped just under the surfaces and couldn't escape also appear as a result of erosion. These bubbles around $25\mu\text{m}$ are visible in the eroded surface images.

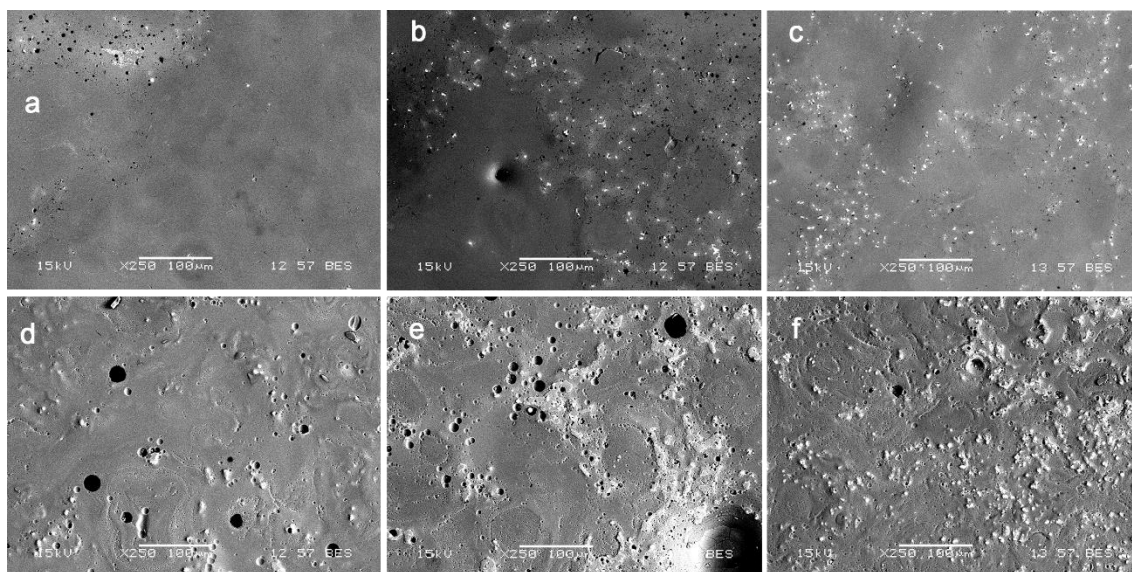


Figure 6.22 SEM images of ZB experiments. a-uncorroded surface of ZB2, b-uncorroded surface of ZB6, c-Uncorroded surface of ZB10, d-corroded surface of ZB2 with basic solution, e-corroded surface of ZB6 with basic solution, f-corroded surface of ZB10 with basic solution.

As the white grains contain a high amount of Zr and O elements as seen in figure 6.23. During the EDS, measurements, B count was not taken from the surface. However, XRD studies and Cross-Sectional FESEM studies confirm that these samples have a high amount of ZrB_2 crystals. Nevertheless, grains just under the surface could be ZrO_2 crystals according to the SEM/EDS results. The grains inside the structure and on the surface have different conditions. The grains on the surface are exposed to air during the firing, but the grains embedded in the enamel structure are all covered with oxidic and glassy materials during the firing. So the existence of two different crystals in the fired final enamel structure is possible.

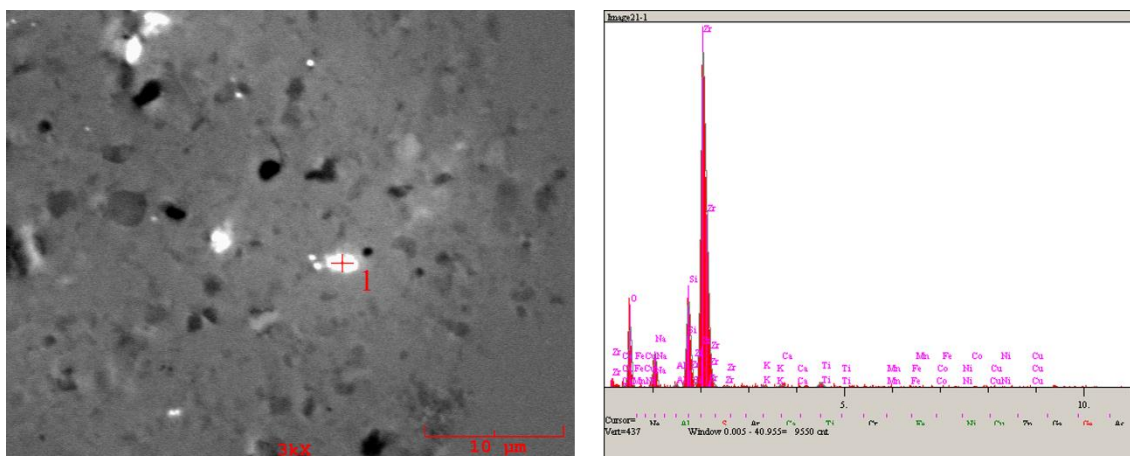


Figure 6.23 Dotted EDS Analysis of crystal on the surface of uneroded ZB2 sample.

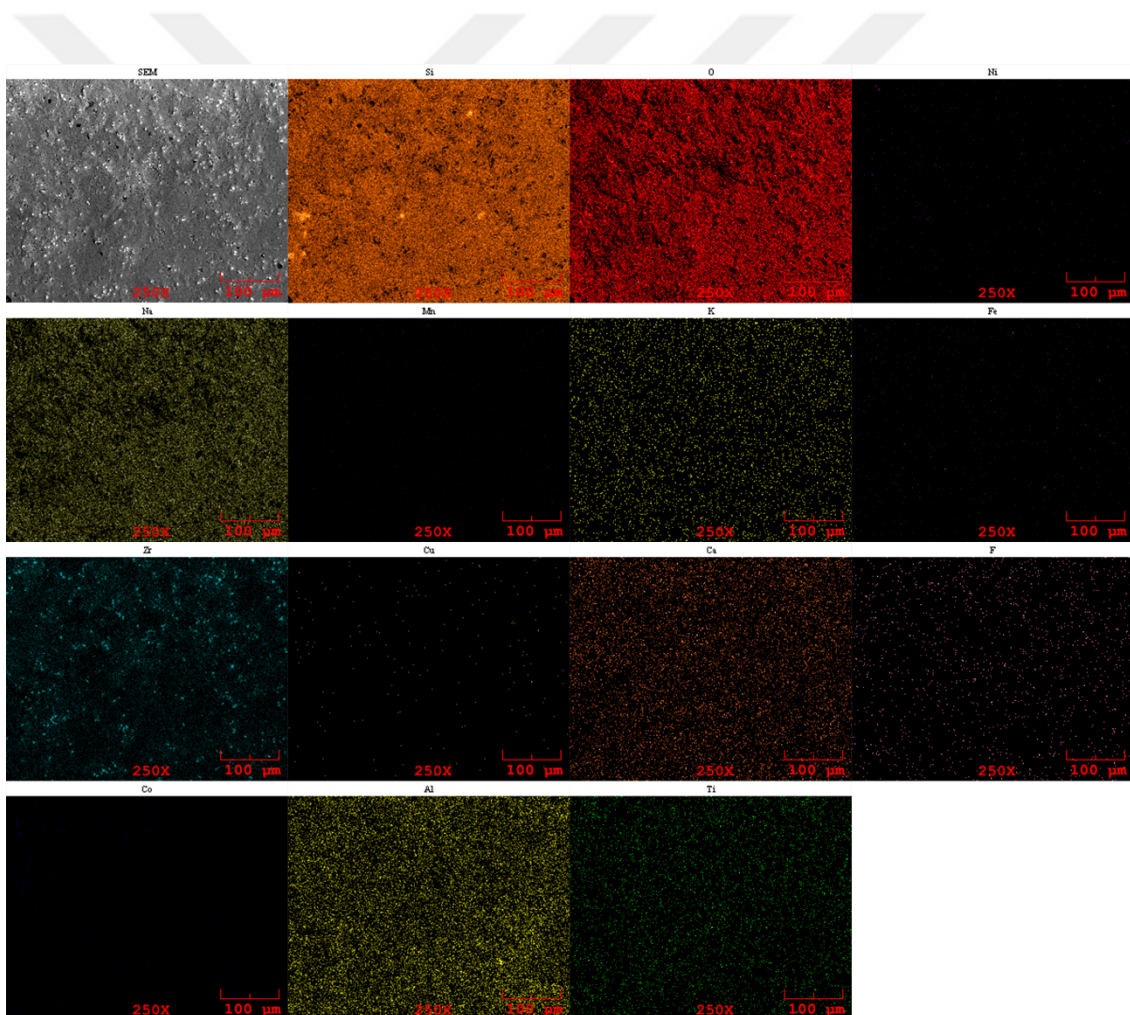


Figure 6.24 Map images of eroded ZB10 sample.

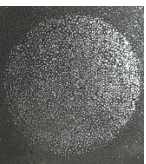
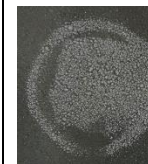
In Figure 6.24 the surface mapping of the corroded ZB10 trial is exhibited. It is also shown in the map result that the bright spots are Zr intense regions. In addition, while a decrease was observed in the amount of Na, Ca, Al, F in the eroded regions, the amount of Si was concentrated in those regions.

6.4 Acid Erosion / Corrosion Analyses

6.4.1 Acidic Solution Test Results

When it comes to acid resistance, results are more qualitative. HCl acid resistance of advanced ceramics added samples were evaluated relatively according to ISO 28706-1. After 1 hour exposing 10%Vol. HCl, the resistance levels and the pictures of enamel surfaces are listed in table 6.3.

Table 6.3 Acid resistance levels of samples according to classification scale given in fig 5.2.

STD	ZO2	ZO6	ZO10	ZB2	ZB6	ZB10
AA	AA	A+	A+	Unclassified	Unclassified	Unclassified
						

ZrO₂ and ZrB₂ mill additives are not providing extra protection against to harsh acidic environment according to the results.

6.4.2 SEM / EDS Results of STD and ZrO₂ Doped Experiments

SEM images of STD and ZrO₂ doped surfaces etched with 10% HCl are in figure 6.25. When the images were examined, a different image from NaOH corrosion was encountered. While the reference sample shows very little topographic change, regional peeling off is seen on the surfaces of other ZrO₂ added samples. The sizes of the peeled areas vary from 125µm to 260µm.

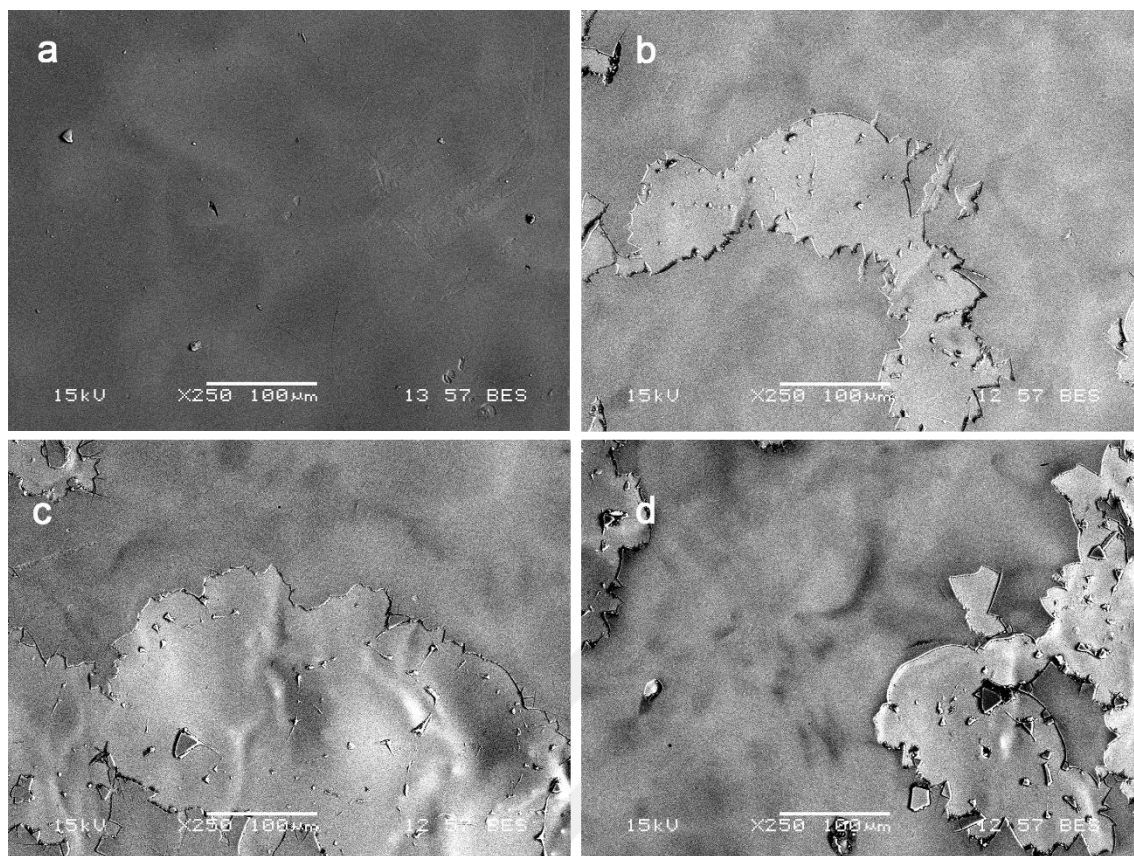


Figure 6.25 SEM images of eroded areas with HCl acid. a-STD, b-ZO2, c-ZO6, d-ZO10

The SEM image showing the peeled and unpeeled areas together of ZO2 is shown in figure 6.26. EDS analysis was obtained from three areas (Table 6.4): Peeled ground, unpeeled ground, and white spot on the peeled ground. When the EDS analyzes are examined, it can be said that the white spot has a similar composition to the other regions, that is, ZrO_2 crystals were not found in the acid-eroded regions. When the uneroded and eroded regions are compared with each other, the excess of Si amount in the 3rd region draws attention at first. The uneroded zone contains 12wt.% more Si than the eroded zone. In addition, a decrease in the amount of K, Ti, and Fe was detected in the uneroded zone. It should be noted that, although the presence of elements, below 1% in EDS analysis, is possible, their percentage accuracy is debatable. For this reason, it is not possible for elements such as Ni, Co, Mn, Cu to be in these percentages, especially on the surface. The percentages of the oxides of these elements are specified in the

preparation section and the percentage of each of them is below 1wt.% in the whole structure.

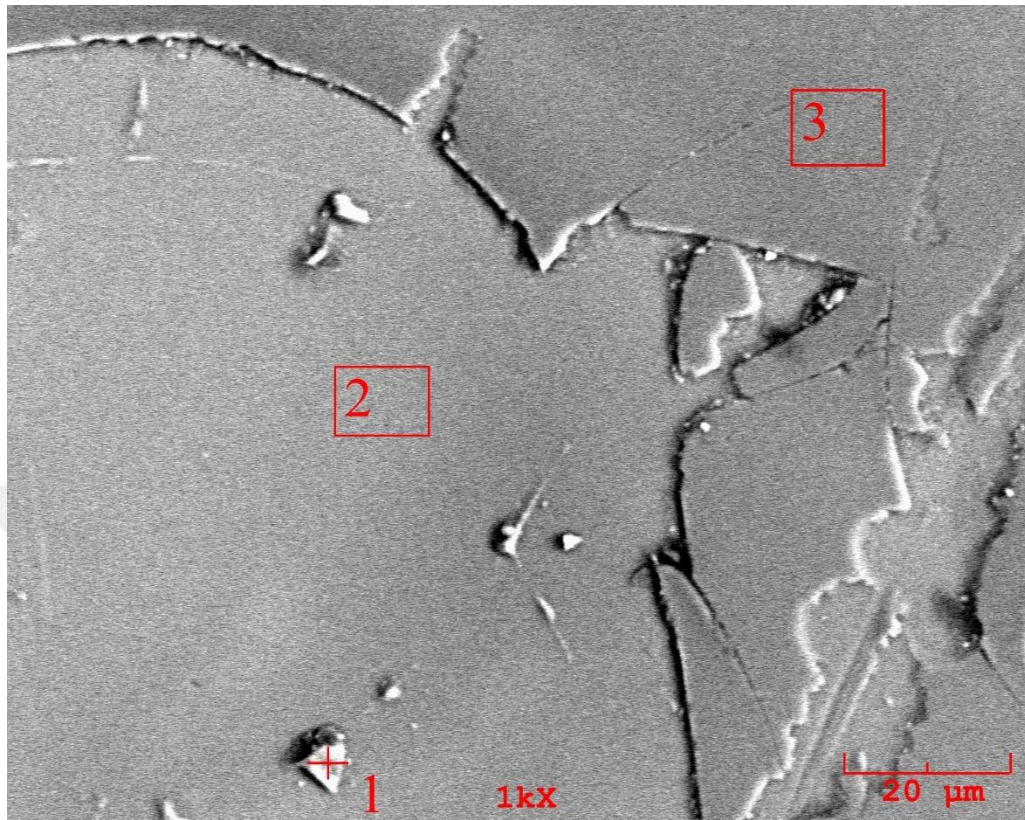


Figure 6.26 SEM / EDS analysis of a peeled-off area on ZO2 sample eroded with acidic solution. X1000 magnification

Table 6.4 EDS results of stated areas in figure 6.26 by %wt.

Elt.	1	2	3
O	33.378	34.117	34.238
F	0.000	0.129	0.000
Na	7.202	12.119	10.465
Al	2.093	2.401	2.480
Si	39.714	33.632	38.274

Table 6.4 EDS results of stated areas in figure 6.26 by %wt (continued)

K	1.388	1.205	0.883
Ca	2.093	2.230	2.391
Ti	1.533	2.002	0.989
Mn	0.657	0.440	0.369
Fe	0.566	0.735	0.425
Co	0.289	0.797	1.020
Ni	1.175	0.372	0.269
Cu	0.000	0.287	0.620
Zr	9.913	9.536	7.577

When the EDS / Map images of the HCl etched surface of the ZO10 sample are examined (Figure 6.27), the difference in Si density between the peeled region and the unpeeled region draws attention at first glance. In addition, there is fluctuation in the amount of Na and Al. Al fluctuation on the surface is known to exist on uncorroded standard surfaces. There is also some fluctuation in the element Ca, but a clear inference cannot be made because the count density is low.

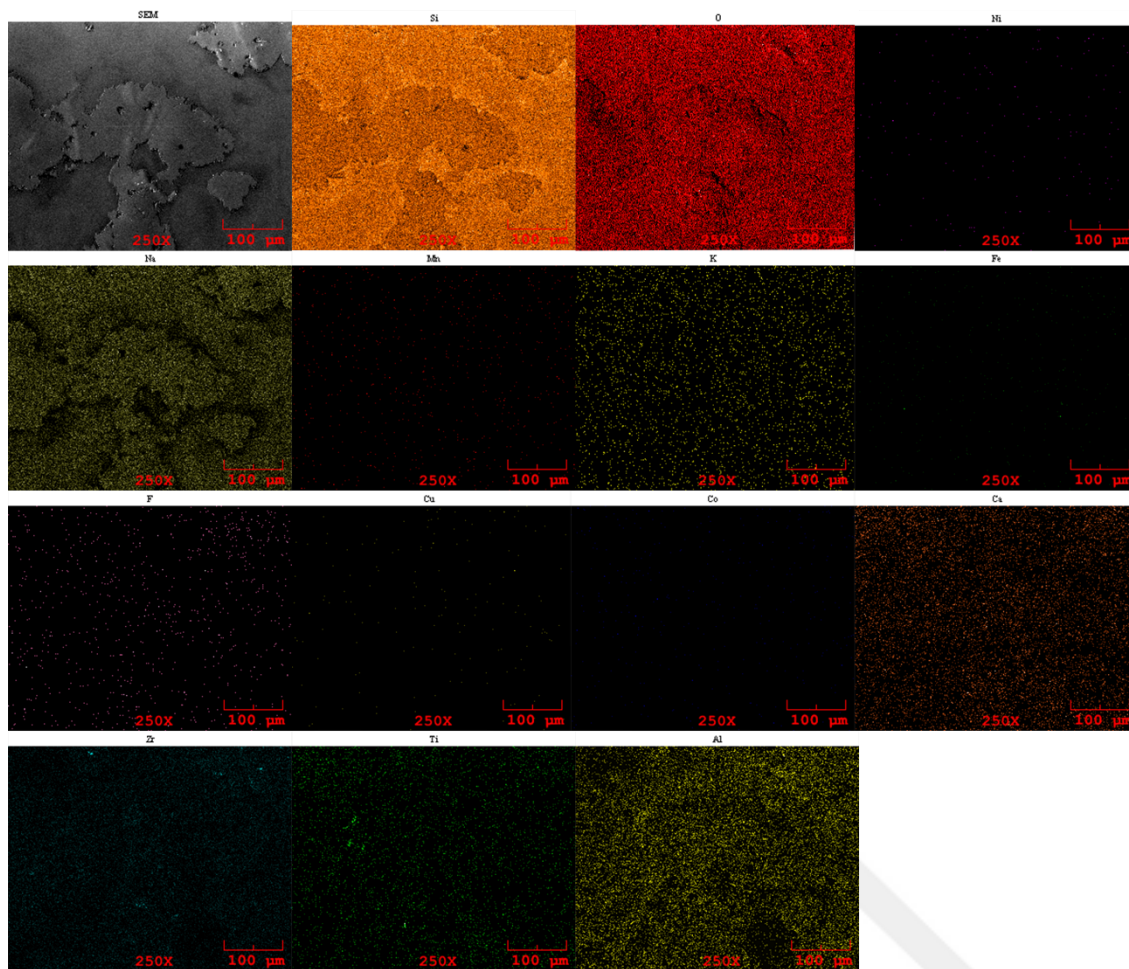


Figure 6.27 EDS / Map images of peeled off area on ZO10 sample eroded with HCl

6.4.3 SEM / EDS Results of ZrB₂ Doped Experiments

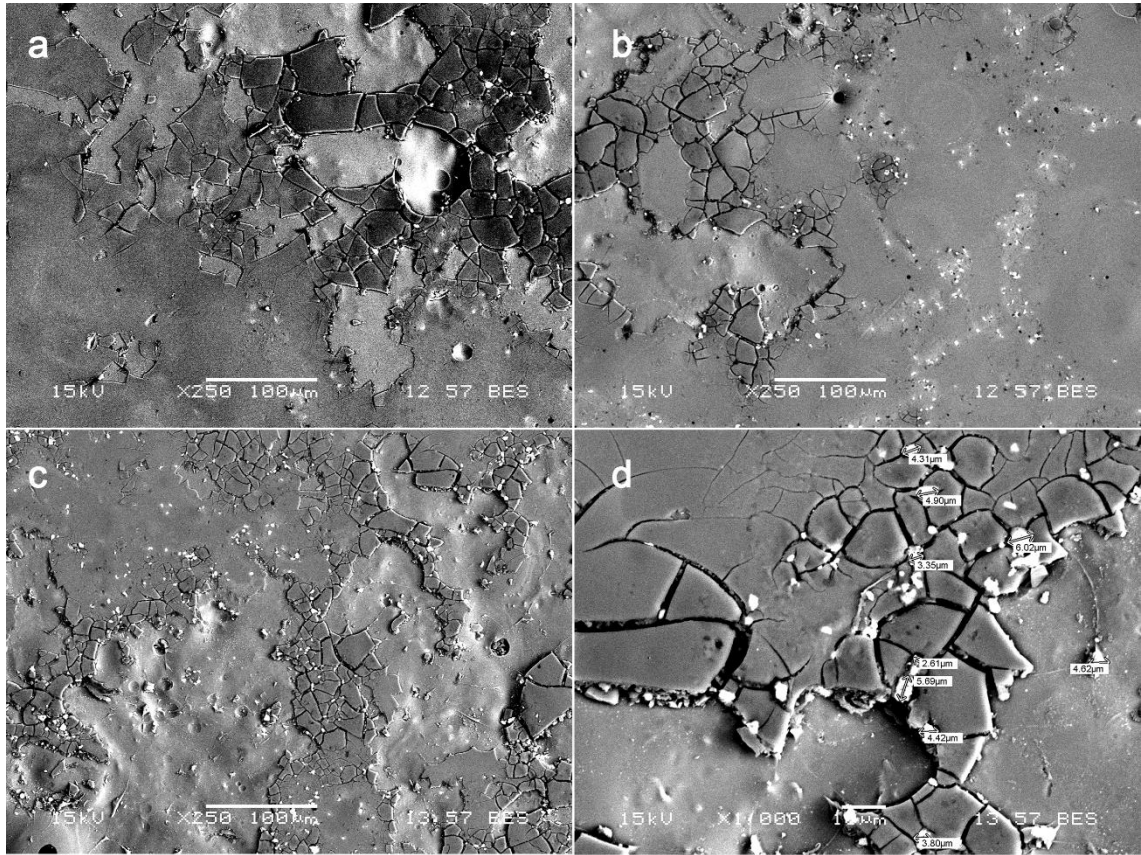


Figure 6.28 SEM photos of HCl acid corroded ZB samples. a-ZB2, b-ZB6, c-ZB10 x250 mag., d-ZB10 x1000 mag.

Figure 6.28 shows the surface of samples ZB2, ZB6 and ZB10 attacked with HCl. The image is very different from the region attacked by hot NaOH. Erosion occurred in the form of layers from the surface. Erosion first developed by forming cracks on the surface and as the cracks progressed, the layers started to peel off. As the amount of ZrB₂ increased from ZB2 to ZB10, the dimensions of the eroded layer seem to increase. While the peeled-off regions of ZB2 are in the 50-100μm size range, the regions on the ZB10 are around 200μm. It can be seen from figure 6.28(d) that there are homogeneous shiny crystals on the surfaces of these samples, unlike the ZrO₂ doped samples. The size of these crystals varies between 3-6 microns and is in the size range of the added ZrB₂ additive.

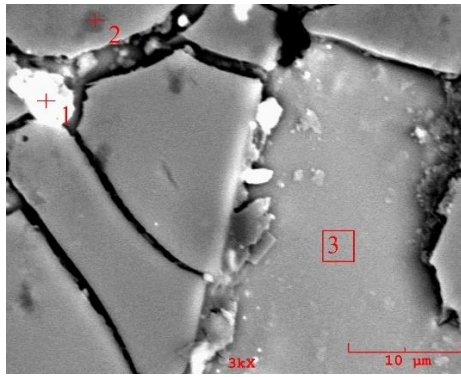


Figure 6.29 EDS measurements of HCl eroded ZB2 sample.

Table 6.5 Compositional EDS results of areas in Figure 6.29

Elt.	1	2	3
O	21.544	28.362	36.046
F	0.000	0.000	0.000
Na	0.912	0.412	15.216
Al	0.231	0.205	3.507
Si	3.794	49.433	36.355
K	0.333	0.263	0.725
Ca	0.412	0.300	1.886
Ti	0.592	1.408	2.956
Mn	0.037	0.119	0.958
Fe	0.239	0.252	0.554
Co	0.122	0.518	0.912
Ni	0.327	0.177	0.680
Cu	0.859	0.969	0.447
Zr	70.599	8.837	1.372

In Figure 6.29, three different EDS measurements were taken from the HCl-attacked region of the ZB2 sample. The numerical values of the measurement are also given in Table 6.5. According to the measurements, it has been determined that the region number 1, bright crystal, is the ZrO_2 crystal. As mentioned before, there are ZrB_2 crystals in the structure, but oxidation is normal since the atmospheric conditions of the surface side are different from the inner of the enamel. When the general distribution of the crystals is examined, it can be seen that there is a similar distribution in the eroded and non-eroded regions. When the 2nd (unpeeled) and 3rd (peeled) regions are compared, Na, Al, Ca, K, Ti seem to increase in the peeled region. Especially Al and Na elements showed an increase of around 20-30 times. However, the high amount of Si and Zr elements in the unpeeled region (2) is remarkable according to region 3. In addition, the distribution of the mentioned elements is also seen in the acid attack region of the ZB10 sample (Figure 6.30).

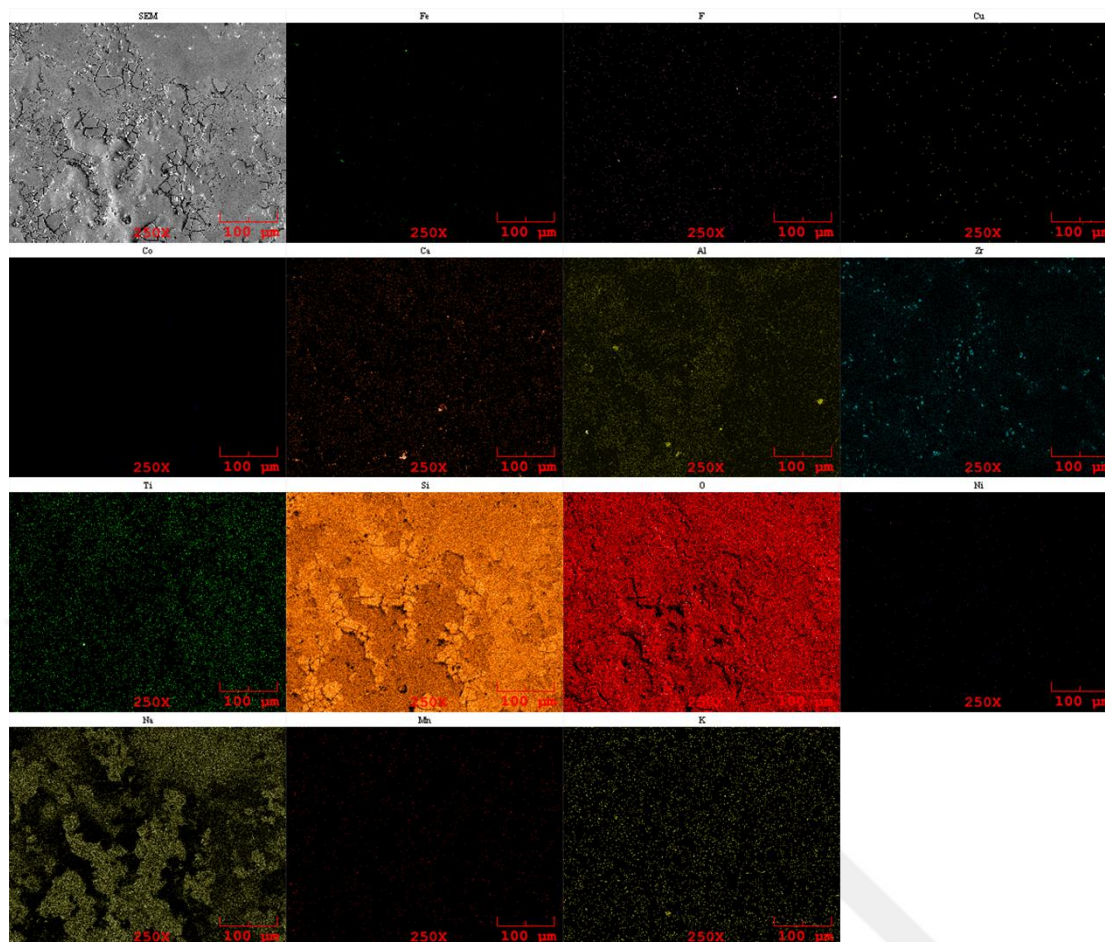


Figure 6.30 EDS / Map images of HCl attached ZB10 sample.

Most of the enamel coatings are complex alkali metal borosilicates that look like a network of SiO_4 tetrahedra and BO_3 triangular configurations with alkali metals like lithium, sodium, and potassium or alkaline earth metals like calcium and barium in the network interstices. Although fused silica is the pinnacle in terms of acid resistance, it cannot be applied to metals in the traditional way due to its high softening point and poor thermal expansion. The structure becomes more fluid by rupturing or distorting this normal SiO_4 lattice. As a result, B_2O_3 is injected to lower the softening point by breaking part of the Si-O links and forming an uneven network. Alkali and alkaline earth metals are introduced into the lattice to further disrupt the network. More bonds are broken when fluorine is added to the frit; an oxygen atom ($-\text{O}-$) that links two silicon or boron atoms is replaced by a fluorine atom ($\text{F}-$), which is monovalent and hence cannot unite two Si or B atoms,

triggering bond rupture. Silica, titania, and zirconia cause a reduction in acid resistance of enamel surface. The HCl acid cause an exchange between metal ions in the network modifier of the glassy structure and hydrogen ions from the acid. This happens naturally on the enamel surface, but as the process progresses, a thin layer of silica-rich material forms, which prevents the further attack of acid. The evidence of this Si-rich thin layers obtained by SEM/EDS in the following sections. Acid attack is thus influenced by enamel batch and pH of solution, as well as time and temperature of exposure. B_2O_3 is also leached off, and it has been discovered that the ratio of Na_2O to B_2O_3 is consistent for each enamel and is determined by the composition of the enamel.

Acid resistance is required to be at the highest level (AA Class), especially in fields such as household ovens, cookwares such as pots and trays, and reactors. These tests are performed with weak acids such as citric acid for short periods. For this reason, it would be best to determine the acid resistance of the enamel according to the type of environment in which the enamel is used. When you apply one of the strongest acids such as HCl acid on an acid-resistant primer coat, it will render the surface unusable within 1 hour. However, this acid can damage alkali-resistant enamel compositions up to certain levels. Strong mineral acids destroy enamel more aggressively than weak organic acids in general. The intensity of organic acid action on enamel rises as the acid's dissociation constant increases. Temperature has a very important role in acid resistance; when the temperature of the solution increased to the boiling point, the faster surface will be attacked. The temperature has a greater impact than acid concentration. Acid resistance is affected by the enamel mill addition, the degree of firing, and the furnace environment. Increased clay and alkaline electrolytes detract from this characteristic, and underfiring has a negative impact as well. From this perspective, organic suspending agents are superior to clays, although other criteria must also be considered. Similarly, replacing one percent milling clay with one percent more colloidal bentonite is advantageous. Large additions of quartz at the mill improve heat resistance, and acid resistance is improved if the firing

temperature is raised enough to dissolve a significant amount of this silica in the glass.

6.4.4 ICP / MS-OEs Analyses

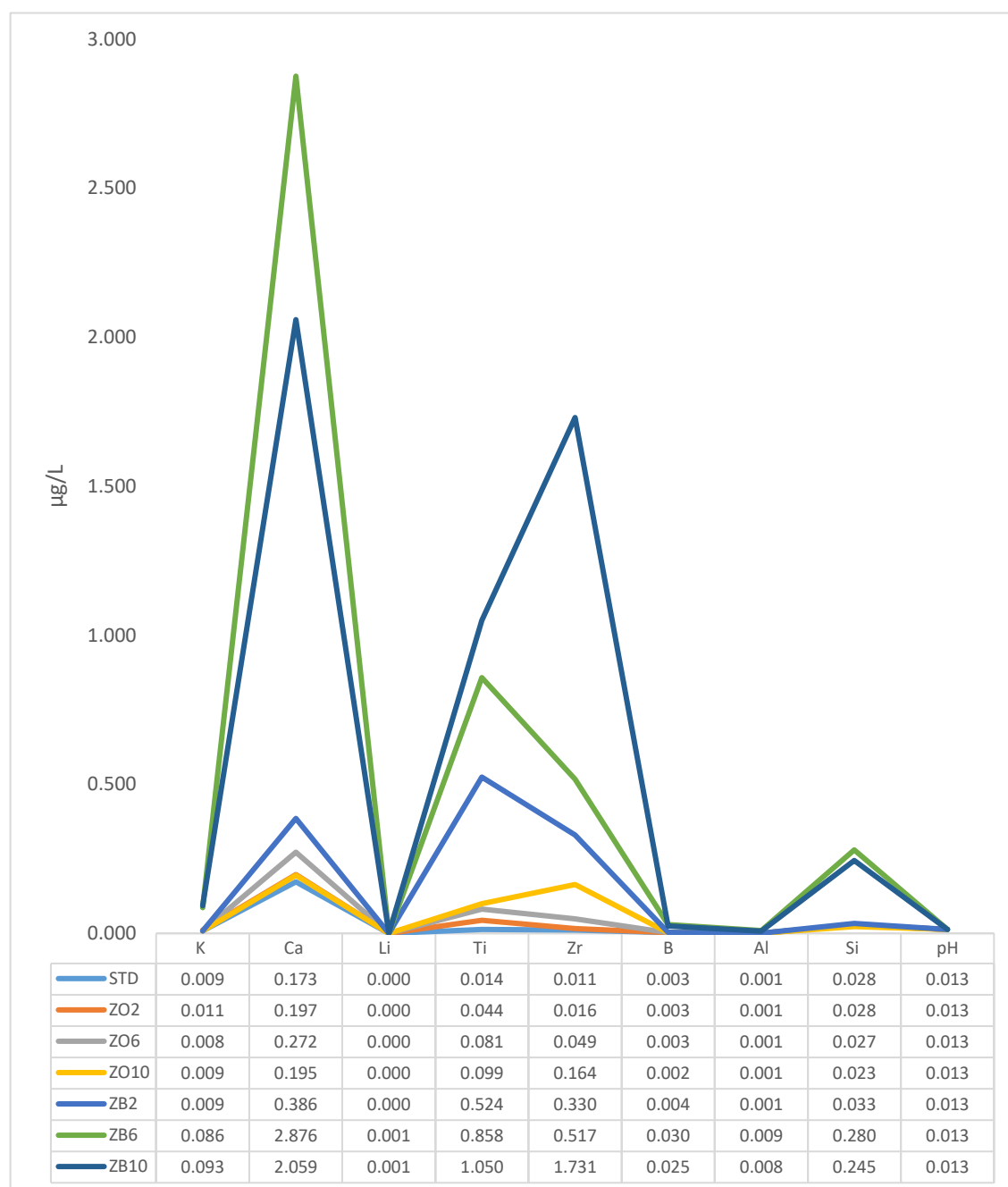


Figure 6.31 ICP / MS-OEs and pH measurements of basic test solutions

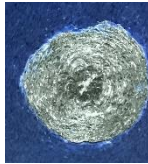
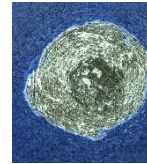
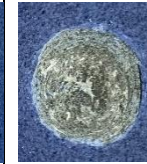
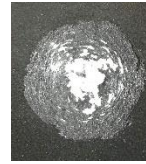
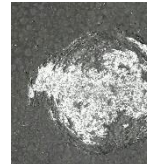
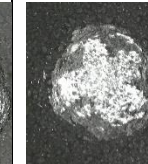
Before examining the results of ICP, it should be noted that proportionality cannot be established between the amount of solute in ICP and mass loss tests, and no study or finding on this subject has been found in the literature. When the results are examined (Figure 6.31), the amount of elements released to the solution of the ZrB_2 doped samples is generally higher than the other experiments. In particular, the amount of Ca, Zr, and Ti increased to thousands. It can be said that these results are not surprising considering that the aggressive solution is the highly corrosive hot NaOH solution. The amount of K was at similar levels in the other trials, except for ZB6 and ZB10 (approx. $8\mu\text{g/L}$). In Ca release, the STD sample showed the best performance (approx. $173\mu\text{g/L}$). Li exhibited the lowest solubility. The ZB2 sample oscillated similar to the STD sample. Ti and Zr elements were also able to stand in the STD structure, and the doping had a negative effect on the release of these elements. The release of element B was resolved at a similar level (approx. $3\mu\text{g/L}$) in the STD and ZO trials, but as expected, the solubility of this element increased in the ZB trials. The solubility of the Al element did not differ much from $1\mu\text{g/L}$ except for ZB6 and ZB10. The solubility of Si element was also dissolved between $280\text{-}240\mu\text{g/L}$ in ZB6 and ZB10 samples. The pH level of the solutions did not move away from 13.

6.5 Inter-Metallic Adherence Behavior of Glass-Ceramics to Steel

6.5.1 Impact Test Results

Adherence between the GC enamel and the steel surface is evaluated according to the international impact test standard. Results are exhibited in table 6.6. The adherence level of the standard sample is at the best level, that is, number 1. ZrO_2 doping did not have a negative effect on adherence compared to the standard sample. However, the same cannot be said for ZrB_2 doping. Adherence level decreased by 1 point in the ZB2 trial compared to the STD, and by 2 points in the ZB6 and ZB10 trials.

Table 6.6 Impact test evaluations of samples according to BS EN 10209

STD	ZO2	ZO6	ZO10	ZB2	ZB6	ZB10
1	1	1	1	2	3	3
						

6.5.2 FESEM / EDS / Line Analyses of Cross-Sections

When the interface of the standard sample is examined (Figure 6.32), bubbles of various sizes up to 36 μm and corroded metal arms in the 1-2 micron range can be seen. The lateral morphology of these corroded steel arms appears as in figure 6.32(c) at 50000 magnification.

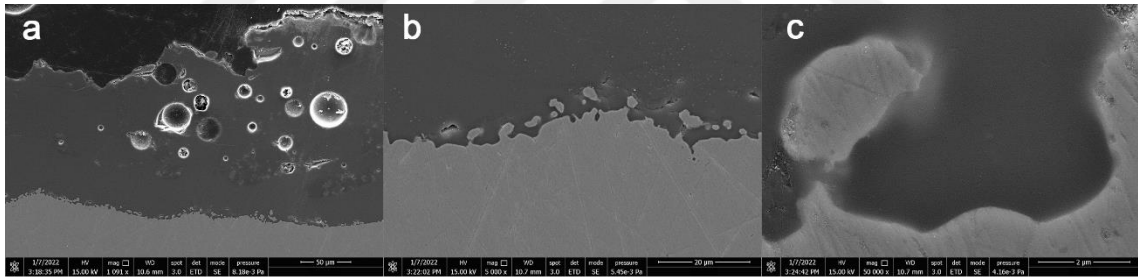


Figure 6.32 FESEM cross-section images of STD sample. a-X1000 magnification, b-X5000 mag., c-X50000 mag.

In the line analysis made from the steel to the enamel (Figure 6.33), it is seen that the Si, O, and Na elements, the enamel composition, have increased significantly. Fe element decreases as expected, but no radical changes are observed in Co and Ni elements. In fact, when the graph is carefully examined, the amount of Co decreases from the steel to the enamel structure. When the compositions are compared, it can be said that the Co element is higher in steel than in enamel by looking at the results.

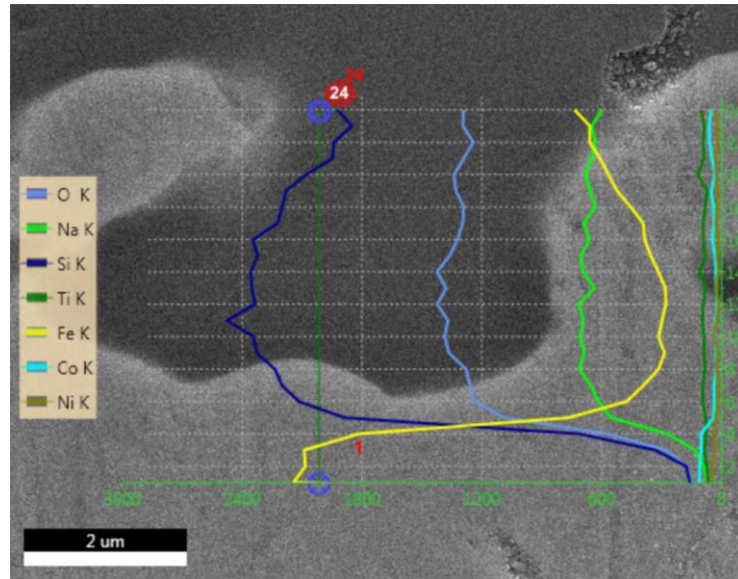


Figure 6.33 Line Analysis of intersection from metal to enamel (STD).

Interface images of ZO2, ZO6, and ZO10 samples are given in figure 6.34. The topography of the transition zone appears similar in the images. When the bubble structures are compared, it can be said that there are more gas bubbles in the ZO10 sample compared to the other samples. The melt viscosity of the structure increased as a result of ZrO_2 addition. For this reason, the gas bubbles remained in the structure without having enough time to leave the structure.

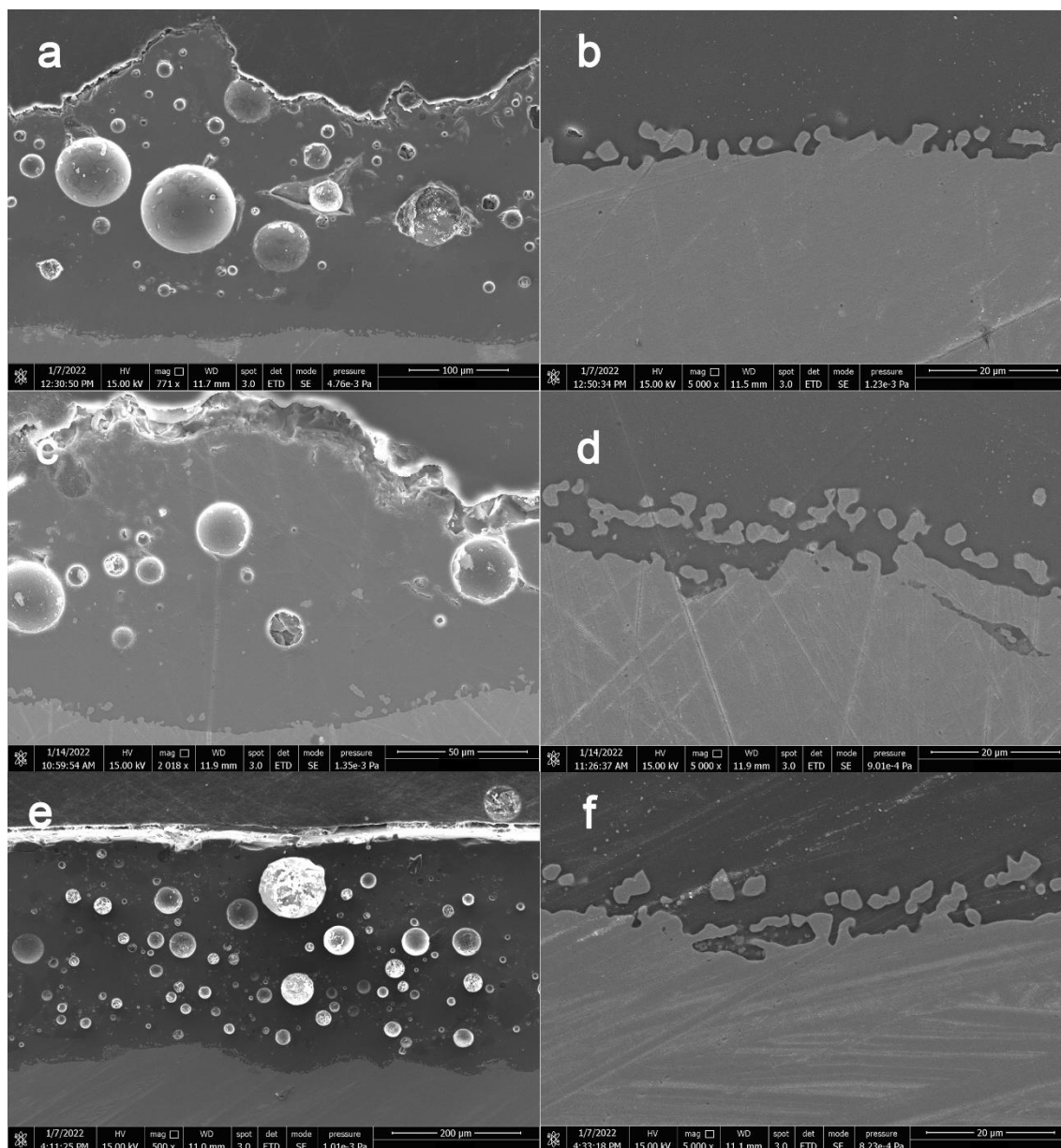


Figure 6.34 Cross-section images of ZO2, ZO6, ZO10 samples. a- ZO2, b- intersection of ZO2, c-ZO6, d-intersection of ZO6, e-ZO10, d-intersection of ZO10

A mapping of the transition between the corroded metallic arm and the enamel is given in Figure 6.35. In the map analysis performed at 50000 magnification, it was determined that Ni and Co elements, which are expected to be concentrated in the transition region, are present in the region. While Co and Fe exhibit a gradient transition from steel to enamel structure, Ni seems to be homogeneously dispersed in both structures.

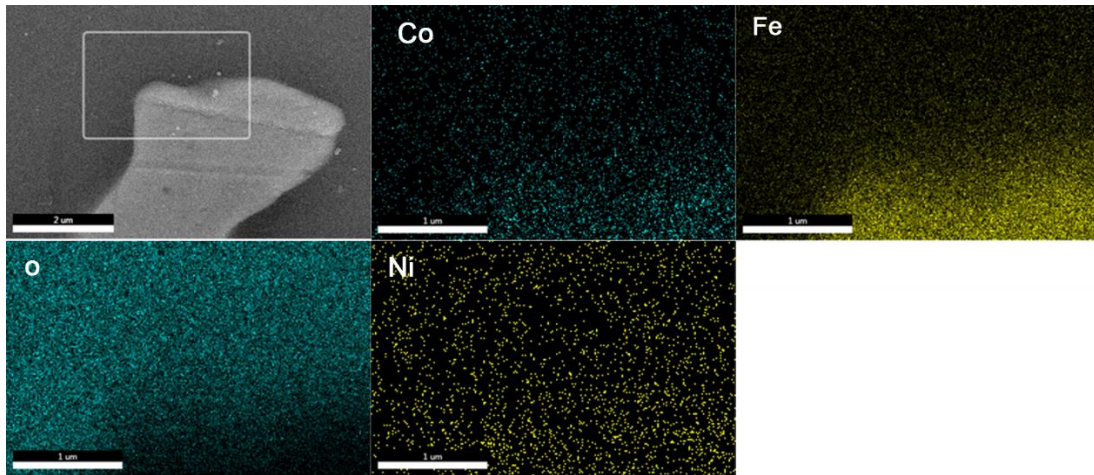


Figure 6.35 Map images of the metallic dendritic arm in the enamel structure of ZB2 sample.

The elemental distribution in the ZO2 sample is given in Figure 6.36. It has been confirmed that ZrO_2 grains in the structure are also found in regions close to the metal surface. The place seen as a red Al grain is the contamination that settled on the surface during metallographic preparation.

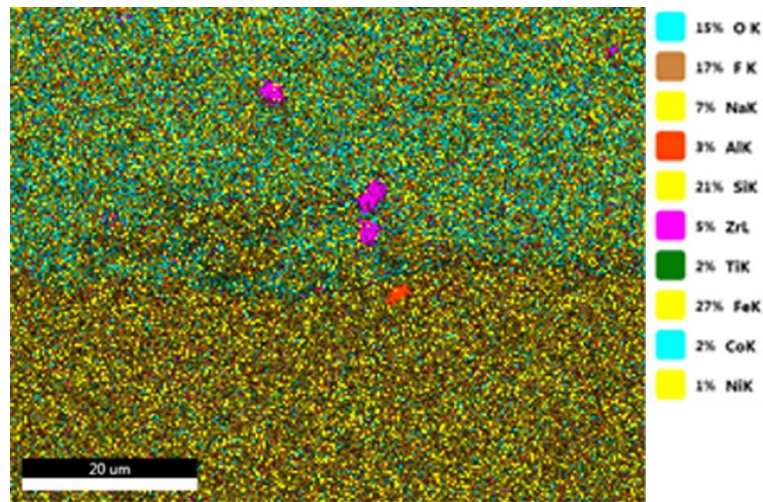


Figure 6.36 Cross-sectional Map image of ZO2 sample.

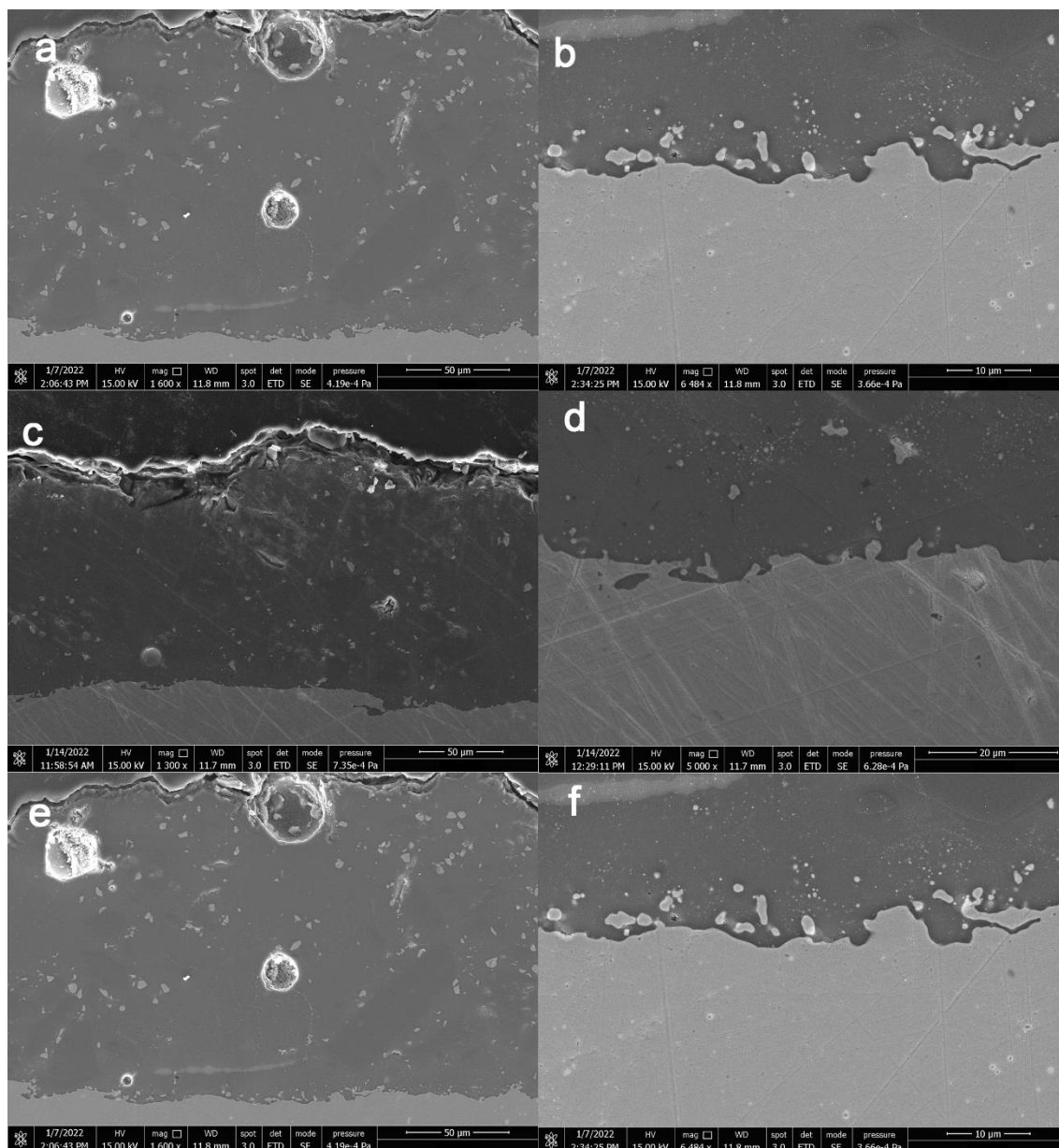


Figure 6.37 Cross-sectional images of ZB experiments. a-ZB2, b-intersection of ZB2, c-ZB6, d-intersection of ZB6, e-ZB10, f-intersection of ZB10

When the cross-sections of the ZB samples were examined (Figure 6.37), it was determined that the ZrB_2 particles were homogeneously distributed in the structures. Line analysis on one of these grains (Figure 6.38) confirms that the grain is a ZrB_2 crystal. When the metal-enamel interfaces are examined, metal corrosion is present in the ZB samples, as in the STD sample, and the metallic arms have passed into the enamel structure. However, it has been confirmed in

the examinations that the metallic arms in these samples tend to move away from the metal surface.

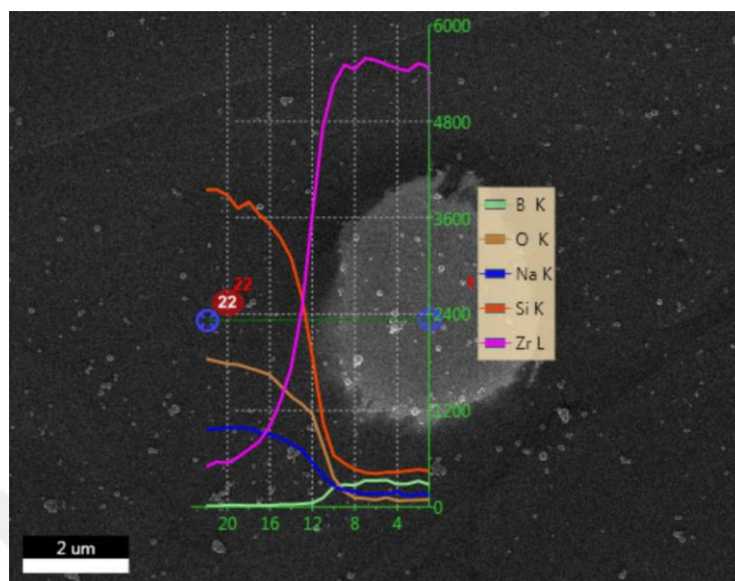


Figure 6.38 ZrB₂ particle in the ZB2 sample.

The elemental transition between these arms and the enamel was confirmed by performing Line analysis (figure 6.39) on the ZB6 sample, and the distribution of Ni, Co, Fe metals responsible for corrosion during the transition is the same as in the STD sample.

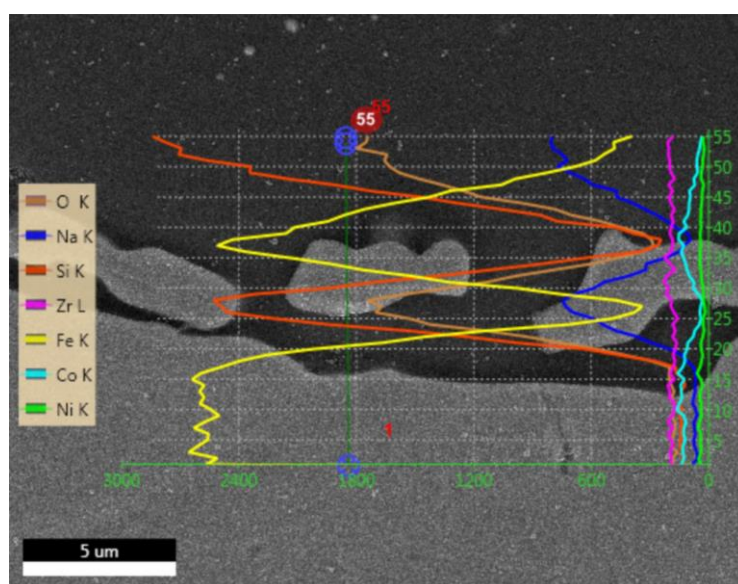


Figure 6.39 Line analyses from intersection of ZB6 sample.

When the map images of the microstructures are examined, one of the important elements noticed is the formation of Si dense phase regions within the cross-sectional structure. In figure 6.40, it can be said that the 5 μm -sized ZrB_2 crystals together with the Si-condensed phase regions, which are approximately 50 μm in size, are the quartz minerals found in the structure.

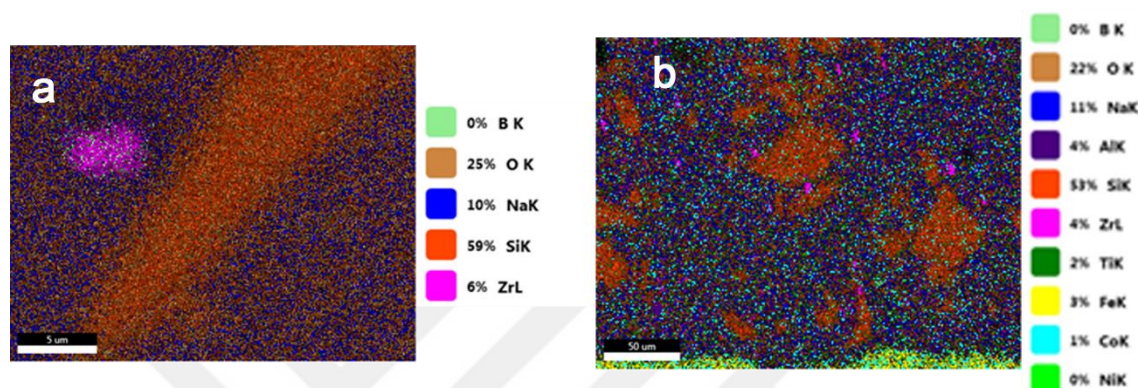


Figure 6.40 Cross-section mapping of ZB6 (a) and ZB10 (b) sample.

For adherence to occur between enamel and steel, the environment where diffusion can take place at the interface must have sufficient energy and fluidity. When the thermal graphs of the samples are examined, advanced ceramics reduce the diffusion ability of the entire structure at the same temperatures compared to the standard sample. This directly affects the rate of corrosion at the interface, thus the amount of dendrite to be formed[162].

Because various chemical reactions occur at different temperatures, the oxygen supply is critical during the thermal process. Water can serve as a useful source of oxygen for iron oxidation.

6.6 Conclusion and Future Work

In studies with two advanced ceramic additives, ZrO_2 and ZrB_2 , which were selected as candidates in the preliminary studies to understand and improve the corrosion mechanism of enamels, the rate and amount of corrosion were slowed down. The thermal behavior of the structures has an important place in the

adjustment of the erosion and corrosion mechanism. The diffusion of the elements in the structure during firing, the efficiency of the reactions, and the size and amount of the gas bubbles also affect the corrosion rate. As a result of etching the enamel surface with a basic solution, OH ions attack the Si matrix, and it forms a gel-like Si-OH structure on the surface, reducing the diffusion (corrosion) rate on the surface. However, with the Liquid Droplet and Particulate Erosion mechanisms that occur during boiling, all gel-like structures that slow down the rate of corrosion on the surface are swept away and corrosion progression becomes unstoppable. During the acid attack, according to the ion exchange rule, H^+ ions settle in the structure, while alkali metal ions are concentrated and move away from the structure. Regions with low Si density and high alkaline density dissolve away from the structure. Advanced ceramic particles resist erosion in the structure, but if the alkali-intensive regions around the particle dissolve as a result of acid attack and the bubbles reduce the bonding density at the crystal-enamel interface, erosion of the crystals is inevitable.

The effect of macro-scale interventions such as sandblasting provide good adherence between the enamel and steel, but the adherence is basically provided at the micro-level, not the macro level. Ni and Co metals form a galvanic corrosion cell on the steel surface with activation energy provided during the firing. While some metal dissolves, the + and - poles formed in these corrosion cells, the enamel fills into the cavities. In this way, a key-lock binding takes place on a micro-scale. Fe and Co metals precipitated after corrosion form an intermetallic phase at the interface[66].

ZrO₂ advanced ceramic is stable at the melting temperatures of enamel does not transform into any compound and does not release gas. However, when a large amount is added to the structure, it makes the structure more thermally stable, decreases the diffusion ability of the enamel structure, and increases its viscosity. For this reason, it can increase the amount of porosity by slowing the gas release in the structure. The ZrB₂ crystal maintains its form in the structure to some extent, but it decomposes as B₂O₃ and ZrO₂ in the regions that receive enough heat, causing swelling in the structure due to the vapor phase of the B₂O₃ liquid. Since

the ZrB_2 crystal is surrounded by oxides with a higher oxygen affinity than Zr in the enamel and the O diffusion is limited in the structure, it cannot be oxidized with full efficiency. To prevent the oxidation of this crystal, using it together with a material such as SiC, B_4C that will take oxygen before ZrB_2 or covering the ZrB_2 with a material that will prevent oxidation during firing will play a more effective role against corrosion in the enamel structure and other anticorrosive structures. In addition to all these, electrochemical measurement methods (Potentiodynamic polarization, linear sweep voltammetry, Mott–Schottky curves, etc.) frequently used in metals and metallic coatings can be useful in understanding corrosion resistance of enamel on metal, and there are current studies on this subject. (see the Literature Review section). In addition to all these, studies on cathodic protection could be useful to increase the service life of water heater systems, in addition to compositional studies (see section 3.5.4).

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PUBLICATIONS FROM THE THESIS

International Conference Papers

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