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STUDY OF INTERFACE BETWEEN GLASS AND STEEL FOR CORROSION RESISTANCE APPLICATION

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Abstract:
A protective glass- based coating of N-15 and N-25 glass was deposited on the Crofer steel by slurry method and its effect on 7500C-8500C has been studied. Oxidation behavior of steel at high temperature of 12500C was also investigated. Interface study of N-25 glass &Crofer steel and N-15 glass &Crofer steel has been done and found that coating of N-15 glass on the steel is more smooth and effective to prevent the surface of steel from corrosion. Structural study of different type of glass has also been done. Bare steel sample as well as coated steel sample was taken for the study of their isothermal oxidation which shows that the glass coating could prevent the corrosion and improve the quality of steel surface for practical application. This corrosion resistant effect takes place because a thin layer of molten glass is formed on the surface of steel at high temperature. This layer then acts as a diffusion barrier. This coating of glass and steel is cost effective, hence have wide application in many infrastructural construction where corrosion is a big challenge. It is also very useful in marine conditions where steel is most likely to be corroded be sea water.

Keywords: Chlorinity; Silanol; Glass Coating; Corrosion; Crofer Steel; Diffusion.

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1. Introduction

Glass is generally defined as the solid which possess a non-crystalline or amorphous crystal structure and when its temperature rises towards its melting point, it shows the transformation region of glass. These are formed by solidification of the melt and shows the atomic structure similar to the liquid phase which is supercooled and displays various mechanical properties of a solid. Since structure of glass is independent of temperature it can be distinguished from that of liquids. This can be clearly understood on the basis of variation when we take the specific volume of crystal liquid at different temperature and also specific volume of glass at different temperature. Figure 1,[1]. T_g represents intersection point of temperature between the curve for the glassy state and that for supercooled liquid. In this region where bend in the curve appears, the material has got more viscous (Viscosity was raised up to 10^{12} to 10^{13}P). In the crystallite model of glass it is found from the observation that glasses are consists of assembly of very large number of small crystals and are called crystallite. Random-network model emphasis that glasses are composed in

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the array of three dimensional network. In this pattern, structural unit is repeated on regular interval basis with symmetry and periodicity in the crystal are not present. In the formation of oxide glass with random network some conditions and rules must be followed which are given as under:[2]

1) Every ion of oxygen must be linked to 2 or less cations.
2) The oxygen ion should have coordination number 4 or less than 4.
3) Oxygen polyhedral should share corners only.
4) The minimum number of shared corners of every polyhedron must be three.

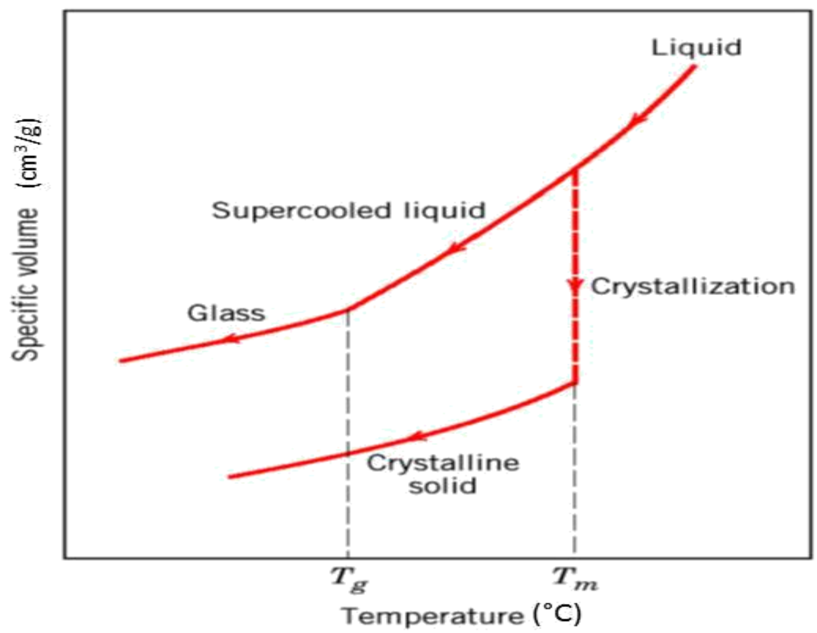

Figure 1: Specific volume-temperature relations for Liquid, Glass and Crystal [21].

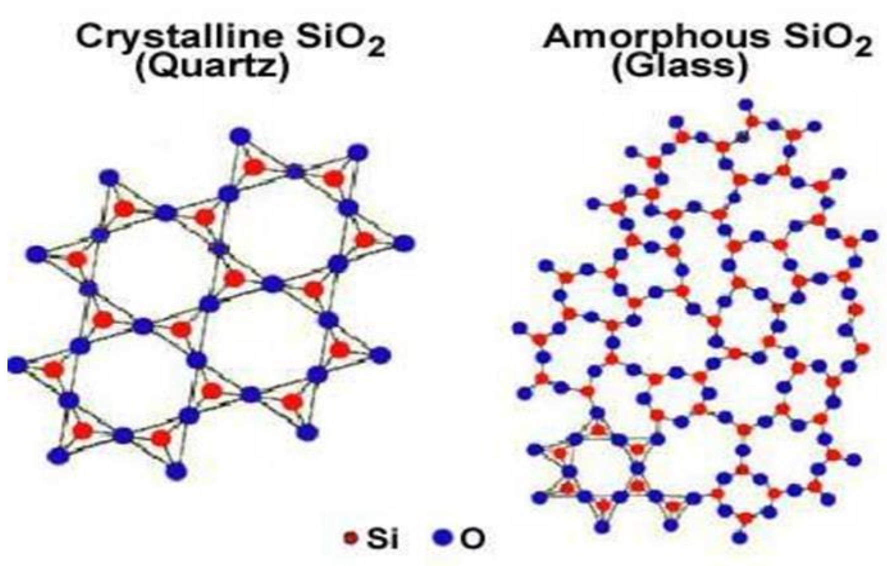

Figure 2: (a) Ordered crystalline form and (b) Random- network of the same composition [21].

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This model can be considered as the best possible presentation of various silicate glasses and can be generated as a model based on random-array concept where units of structure are arranged randomly. Fig:2,[2].

2. Structure of Oxide Glasses

Oxide glasses have three major class of components namely- network formers, intermediates and modifiers. Si, B, Ge, P etc. are network formers which forms a chemical bond which is based on cross-linked network. Ti, Al, Zr, Mg, Zn etc. which are intermediates acts as a network former and modifier depending upon composition of glass. Ca, Pb, Li, Na, K etc. are known as modifiers which can alter the network structure. The presence of small and mobile alkali metal ions in the glass causes some amount of electrical conductivity specially at the high temperature or when the glass is in the state of molten phase.Due to their low mobility, alkaline earth ions limits the diffusion of various ions specially the alkali ions. Alkali and alkaline earth ions both are present in a general commercial glass for the purpose of easy processing and satisfying corrosion resistance [3]. If alkali ions are dealkalized and removed from the glass surface, it can be made corrosion resistant. This can be done by reaction of glass surface with other cations like S or F compounds.

1) **Silicate Glasses:** The melting point of pure silica (SiO2) is 1710^0C, which has the properties like low thermal expansion, high softening temperature and good chemical and electrical resistance. It is relatively transparent over a wide range of wavelengths from visible and U.V. to Ultrasonic waves. If $SiO_2$is mixed with alkali oxides or alkaline earth oxides to the ratio of oxygen to silicon to a value of more than 2, then it causes in breaking up of three dimensional network and single bond of oxygen is formed. This singly bonded oxygen does not provide any contribution to the network [4].
2) **Borate Glasses:** If B_2O_3 is added either with alkali oxides or alkaline earth oxides the BO4 tetrahedra is formed. In this formation, two triangles are converted into a tetrahedral by every oxygen which was added along with alkali oxide ions. All the modifier oxides converts BO_3 triangles into BO_4 tetrahedra provided concentration of oxides have the maximum value of 30 mole%. If the arrangements of crystal is triangular requirement for local charge compensation caused by modifying cation is simplest, then singly bonded oxygens are associated with BO_3 triangles not with BO_4 tetrahedra, [5].

2.1. Corrosion of Glass

Corrosion is a natural impact of atmospheric environment which affects the structural stability of the components. The overall loss due to corrosion is estimated around 4% of GNP and at least 25% of this loss could be avoided by using appropriate corrosion control technology[6].As compared to other materials, glass is the better corrosion resistant material and is considered as the corrosion-proof material. But inspite of this, glass may also corrode and even get dissolved under some specific conditions. This phenomena necessitate to select proper kind of glass, because different types of glasses have varied degree of corrosion resistance. After testing the intensity of attack in the laboratory it is found that such corrosions are most significant for phosphoric acids and hydrofluoric acids.[7]. Glass is attacked by solutions of alkali and acids in different ways. The silica is directly attacked by alkali, whereas the alkali which is present in the glass is attacked by

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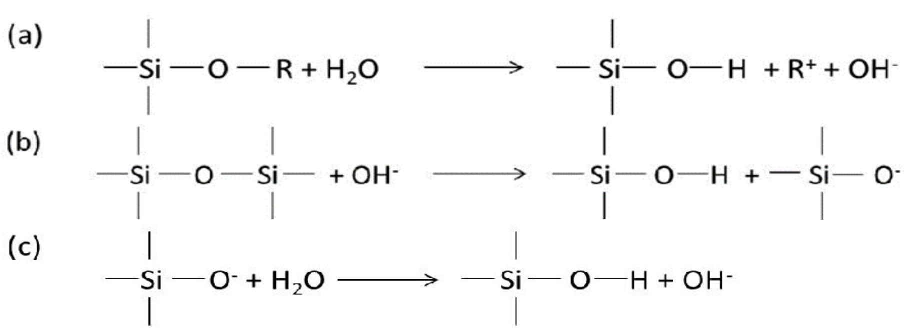
acids. The surface of the glass simply dissolves when it is attacked by alkali solution which causes to expose a new surface of glass and subsequently it get dissolves . When it is attacked by acid, the alkali present in the glass is removed and the glass is corroded. Water corrosion and acid corrosion are more or less similar in nature, which becomes significant at high temperatures. After the study of different types of glasses it is found that fused or silica glass has the highest resistance against the corrosion which is followed by low alkali aluminosilicate and borosilicate glasses. Sodium is more harmful to the corrosion resistance of the glass [8].

1) **Atmospheric Corrosion:** Atmospheric corrosion of glass can be classified in two types called dynamic corrosion and static corrosion. During dynamic weathering, water from atmosphere adhere to the surface of the glass and extract the alkali ion but it is supplied again which restrict the pH value to rise towards the high alkaline range. In static type of corrosion a very less volume of water is in contact with a larger surface area of the glass for a long duration and when pH attains the value >8.5 alkaline attack causes severe structural surface damage.
2) **Marrine Corrosion:** Seawater is a conductive electrolyte which contains salts, gases, suspended organic and inorganic matters and live organisms. Apart from these, variables like temperature, pressure, hydrodynamic conditions and oxygen concentration also has considerable affects. Steel is most common construction material used in marine conditions. It is used for ships, drilling platforms, offshore structure, underwater pipelines and cables because of its excellent mechanical properties and weldability. It has another advantage that it is abundant and cheaper to produce relatively at low cost as compared to other materials. However, its corrosion resistance is not ideal in corrosive medium such as sea water which contains 3-3.5% NaCl [9]. Chlorinity, conductivity and salinity are three major terms which helps us to measure the degree of corrosive seawater [10]. Generally, salinity of seawater lies between 33 to 37 parts per thousand, while local conditions may affect the value of salinity. Conductivity of sea water strongly depends on temperature, moderately depends on salinity and weakly depends on pressure. Chlorinity is defined as the weight in grams of chloride ion content per thousand grams of water, which can be calculated by taking total content of halogen as being chloride.
3) **Aqueous Corrosion:** Reaction between aqueous solution and glass leads to surface deterioration of glass. Various factors such as temperature of solution, impurities present in the solution, content of salts in solution and pH value of solution also affects the corrosion mechanism of glass. Corrosion mechanism can be understood in following three steps.



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In first step OH- is formed which leads to dissociation of glass. In subsequent steps very strong Si-O-Si bond is broken and silanol is formed which may either go into solution or form a film on the glass surface.[21]

3. Glass Coating

Most common treatment against the corrosion are application of enamel, painting and plating. All these methods forms a barrier between the material and the external environment which prevents the corrosion of material. Out of these, enamel coating or glass coating is extremely corrosion resistant which permanently protects the steel [11]. When the glass is fused on the surface of the metal at high temperature, it is called vitreous enamel. It has variety of excellent properties like: it is hard, it is resistant to chemicals, it is durable, it is resistant to scratches, it is smooth, it is easy to clean and it is fire resistant. It does not fad even with UV light. For synthesis of this material, powder of the glass is fired on the substrate within the range of 750^0C and 850^0C and the glass is fused on the material. Due to such high temperature, glass powder gets melts and flows on the surface of metals which subsequently becomes hard. This results into a durable and smooth vitreous coating on the metal. This enamelware is basically a combined layer of metal and glass. The thin layer of glass is applied on to the surface of steel sheet either as electrostatically- applied powder or water-based slurry method [12]. Coating can be done in two ways. One is known as two-coat system in which ground-coat frits contain oxides which are present in the thin layer of ground-coat which is responsible for adhesion between enamel coating and steel surface. Another is single-coat achieved by single-fire coating in which coating requires the use of more selectively processed steel. Steel materials which are selected for coating should have specific properties so that it should be coated effectively and excellent quality of adhesion could be achieved between the steel and glass surface[13].

COMPOSITION OF GLASS (mol%)

SAMPLE	SiO_2	CaO	Al_2O_3	Na_2O	TiO_2
N-25	45	15	10	25	5
N-15	55	15	10	15	5

CHEMICAL COMPOSITION OF STEEL (wt%)

ELEMENT	Fe	Mn	Si	Ti	Cr
CROFER STEEL	76.6	0.4	0.017	0.06	22.6

Slurry method using fine Zinc glass is used to apply coating of glass on to the cleaned surface of steel. This slurry of glass is prepared in various liquids. It is then heated and dryed in a furnace at 900^0C in air for 1 hour. During this heat treatment some constituents of glass and steel diffuses to each other which form an adherent bond of glass layer on the surface of steel and forms coating. Glass coating attracts lots of attention for protecting metals from oxidation at high temperature [14]. This feature of glass can be considered to protect steel from corrosion by apply glass-coating on it. Its process is also simple and low-cost which includes spraying of glass powder on the metal surface. In this coating, the slurry prepared was applied on the hot specimen for protection by air-sprayed method. When high temperature is provided to the sample, the slurry sprayed got melts and becomes thick. This results in the decrease of porosity and increase in density which causes the formation of compact coating layer on the surface of steel very quickly. The layer formed due

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to melting is free of pores and overlay the steel sample completely. Due to formation of this layer as a barrier, the inward diffusion of oxygen is prohibited. Subsequently, at the interface between sample and coating, the partial pressure of oxygen is reduced. Therefore, steel metal is protected from corrosion with the help of glass coating on the surface of steel which is an effective measure.

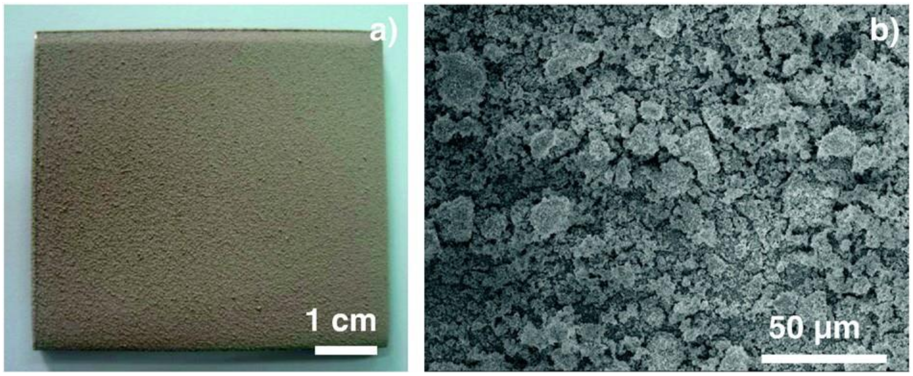

Figure 3: (a) Macroscopic Image and (b) SEM Image of Coating [20]

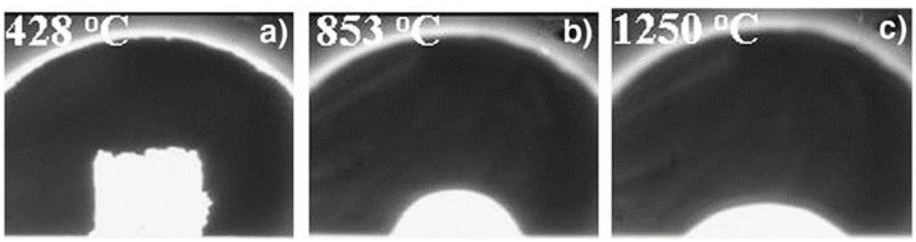

Figure 4: Hot Image Macroscopic Images of glass powder at different temp. [20]

4. Corrosion Testing

Corrosion can be treated as an electrochemical process of redox reaction in which flow of electrons or flow of current occurs and therefore it can be measured and controlled electronically [15]. Corrosion properties of metals as well as of metal components along with the different electrolyte solutions can be characterized by using a method which is based on controlled electrochemical process. These characteristics of corrosion are unique to every metal or every solution.

5. Interaction Study Between Steel and Glass

Glass coating on metallic substance is useful in manufacturing industries because it leads to the development of heat and corrosion resistant material. A strong binding of two materials depends on chemical and physical factors of interface. High chemical resistance of glass provides good corrosion resistance on the surface of steel. In addition to this density of the glass is less compared to the metallic coating which has additional advantage.

1) N-25 Glass and Crofer steel: Coating of N-25 glass on Crofer steel is done at 900^0C by heating for 1 hour. After the micrographic visualization, two types of morphological features of crystalline phases were found. One is staircase like structure trying to form a hexagonal shape means $NaAlSiO_4$ phase which is a sodium rich phase. Second type is granules type of structure and grows between the lines which is $Na_4Ca_4(Si_6O_{18})$ phase. It is seen that both the

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phases have sodium content which proves the presence of sodium in the structure after heat treatment [16]. Out of these, N-25 glass has maximum sodium content as compared to others. After analysis it is found that Chromium and Iron from the steel are diffused into the glass. X-ray dot mapping gives the confirmation that diffusion of Cr and Fe is required for good bonding between Crofer steel and glass. The diffusion of Cr is more prominent than other elements. After the cross-sectional study of interface between N-25 glass and Crofer steel it is found that interfacial layer seems to be weak at some places. Cr and O elements are main constituents at the interface. Since elements like Carbon and Titanium are smaller in size, they easily gets path to diffuse and hence their diffusion takes place. It is also reported in literature that the Cr diffuses more vigorously than other species [17].

2) N-15 Glass and Crofer steel: From X-ray study of heattreated N-15 glass-ceramic, no indication of crystalline phase was found and uniform and smooth coating of N-15 glass on Crofer was observed. In this process of coating, Fe and Mn elements have diffused from steel into smooth coated glass area and Cr is not present in this coated area. Analysis revealed that diffusion of Cr from steel into glass leads to formation of flowery pattern which might have occurred due to presence of defect structure as this pattern is not observed in other areas.Observations shows that Si, Ca, Al, Ti, Na, O, Cr and Fe elements are uniformly distributed in the selected area. After analysis of cross-sectional microstructure of the interface between N-15 and Crofer steel, it is found that glass coating was highly bounded with base steel but some pores were visible across the surface which was unexpected [18]. This glass was poorly densified because of the crystallization of glass at temperature of coating. A glass powder compact is composed of small spheres which are densely packed. These sphere would densify initially due to its viscous flow satisfying frankelequation [19]. Moreover, when the temperature is increased it causes the coalescene and expansion of small pores and led to formation of pores. As the temperature is further increased, the pores would be vented out from the glasses and the final glass coating were densified. At the interface between N-15 glass and Crofer steel. Cr and O elements are main constituents. Study of line profile spectrum shows that diffusion of Fe , Mn and Cr into the glass is more prominent than other elements. However, the interface is very strong and mainly Cr and O elements are present at the interface. Apart from this, diffusion of Ti, Al and Na from glass side into steel also occurs. After the X-ray dot mapping of the area of interface it was revealed that all elements are uniformly distributed in the selected area. In addition to this diffusion of Al and Na from glass into steel and diffusion of Cr and Fe from steel into glass takes place, and the interface is free from porosity.

6. Result and Conclusion

After careful observation, it is found that steel can be protected effectively from oxidation even at temperature of 1250^0C with the help of glass coating. At this temperature, to keep the growth rate of Cr_2O_3 slower proper supply of Cr from steel is required which can be achieved at this temperature by reducing the diffusion of oxygen from air which is ultimately possible because of presence of glass coating [20].

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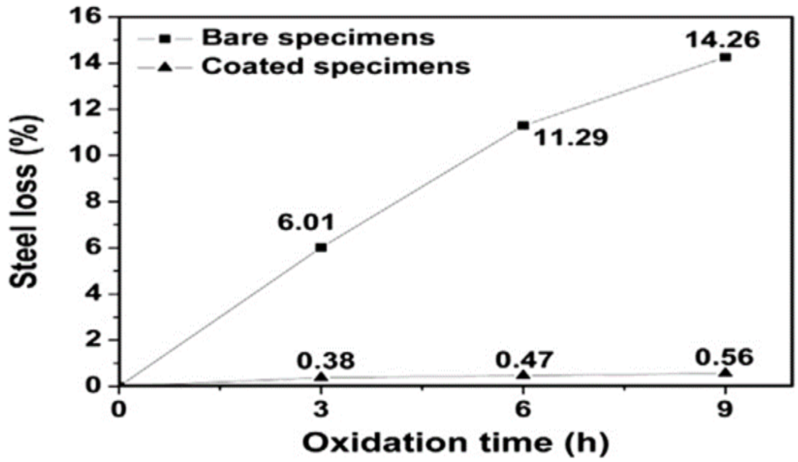

Figure 5: Steel loss of sample after oxidation at 1250^{0}C in air.[20]

At such a high temperature the layer of Cr_2O_3 got cracked and pores are formed. In such condition, a new protective film or healing layer is formed and therefore in case of molten glass coating, the coated steel sample will maintain a protective film of Cr_2O_3 [20].

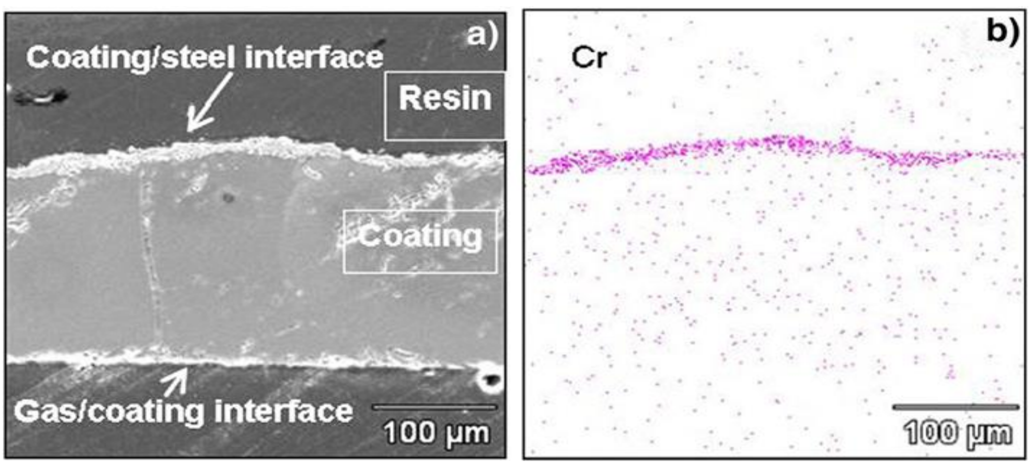

Figure 6: (a) Cross-section Microstructure, (b) Cr Element mapping of glass coating.[20]

After study of theoretical calculation it was found that thermal stability of N-15 glass as compared to the other glasses is highest. Dilatometer data indicates that with increase in SiO_2 content, softening temperature (Ts) of the glass increases which is due to the decrease in Na_2O content that lead to formation of Si-O network. N-15 glass shows low crystallization even at higher temperature which makes it most suitable glass for coating on steels. The presence of non-bridging oxygen causes to the change in physical properties of glasses like electrical conductivity, density and refractive index. UV- visible and refractive index results confirmed that the N-15 glass is most suitable for coating. During heat treatment, initially in silica- glass matrix nucleation of silica phase takes place and later on diffusion causes cations such as Na^+ and $Al3^+$ to enter in SiO_2 matrix which results in formation of other crystalline phases. $Fe3^+$ ion is the main factor which is responsible for binding the glass coating with the steel sample because it is diffused to the glass side. The corrosion shows that N-15 glass is most corrosion resistive and formed smooth coating layer on Crofer steel.

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