A Study of the effect of adding antimony oxide to the coating surfaces of steel and cast Iron by glass

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Abstract

The study included adding antimony oxide to mixtures of coating metal surfaces (Enameling), after it was selected ceramic materials used in the coating metal pieces of the type of steel and cast iron in two layers. The first is called a ground coat and the second is a cover coat.

Ceramic materials layer for ground coat have been melted down in platinum crucible at a temperature of 1200^{o}C to prepare the glass mixture (Frit). It was coated on metals at a temperature of 780^{o}C for two minutes, while the second layer was prepared glass mixture (Frit) at a temperature of 1200^{o}C, but was coated at a temperature of 760^{o}C for two minutes.

Underwent tests crystalline state of powders (Frits) and enameled samples using X-ray diffraction technique and found that the process of powders and ground coat layer is random, while the cover layer included having developed a silicon oxide and titanium oxide phases. It was measured density, coating thickness and Knoop hardness for each layer. As well as practical tests conducted dipping enameled samples in diluted and concentrated sulfuric acid, as well as diluted and concentrated hydrochloric acid for three days at a temperature of 100^{o}C. The samples showed good resistance against these acids. The addition of antimony oxide reduced the presence of bubbles in the coated cast iron and enhancement physical and mechanical properties.

Key words

Metal coating, physical adhesion, chemical adhesion, resistance to acids.

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دراسة تأثير اضافة اوكسيد الأنتيموني في طلاء سطوح الفولاذ وحديد الزهر بالزجاج

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الخلاصة

تضمنت الدراسة اضافة أوكسيد الأنتيموني الى خلطات لتزجيج سطوح المعادن (Enameling) بعد أن تم اختيار المواد السيراميكية التي تدخل في تزجيج قطع معدنية من نوع فولاذ وحديد الزهر بشكل طبقتين، الأولى تسمى بطبقة الأساس (ground coat) والثانية تسمى بطبقة الغطاء (cover coat).

المواد السيراميكية لطبقة الأساس تم صهرها في بودقة بلاتين عند درجة حرارة 1200^{o}C لتحضير الخليط الزجاجي (Frit). وتم تزجيجها على المعادن عند درجة حرارة 780^{o}C لمدة دقيقتين، في حين الطبقة الثانية تم تحضير الخليط الزجاجي (Frit) الخاص بها عند درجة حرارة 1200^{o}C ولكن تم تزجيجها عند درجة حرارة 760^{o}C لمدة دقيقتين.

اجريت فحوصات الحالة البلورية للمساحيق (Frits) والنماذج المزججة باستخدام منظومة حيود الأشعة السينية (XRD) ووجد ان طور المساحيق وطبقة الأساس هو عشوائي في حين طبقة الغطاء تضمنت وجود اطوار أوكسيد السيلكون وأوكسيد التيتانيوم. وتم قياس الكثافة وسمك الطلاء وصلادة نوب لكل طبقة. كذلك اجريت فحوصات عملية بتغطيس النماذج المزججة بالطبقتين في حامض الكبريتيك المخفف والمركز، وكذلك حامض

الهيدروليك المخفف والمركز لمدة ثلاثة ايام عند درجة حرارة 100^oC. واثبتت النماذج مقاومة عالية ضد هذه الحوامض. ان اضافة أوكسيد الأنتيموني قلل من وجود الفقاعات في طلاء حديد الزهر وحسن الخواص الفيزيائية والميكانيكية.

Introduction

The coated of metal surfaces of a process called enamel by adding more than one layer of glass on metal surfaces (Steel, cast iron, aluminum ....), to improve the performance of those parts and make them work in conditions of air, thermal or chemical severe. The enamel was many important uses which protect metals against corrosion, resistance to acids and alkalines, protection from the heat, protection from weather conditions and improve the external appearance of the surfaces of metals. This process have many advantages and make it a technology method for use of cheap metals price works in difficult conditions, especially in the production units of chemicals. The color of the ground coat layer was often blue or black or gray, while the cover coat layer was a white or blue, depending on the type of oxides used in the enameling process [1, 2]. The coated of metal parts in multiple ways, including immersion (Dipping), spraying and foundry (Flow coat) [3, 4]. There are many factors which must be taken into consideration when coated any metal part in the forefront of thermal expansion, as it must have thermal expansion of the glass material required equal or convergence to thermal expansion of metal surface required. So when thermal expansion coefficient of the material glass larger than the thermal expansion coefficient of the metal it will be got small cracks called crazing, and if happened the opposite meaning that the thermal expansion of the glass lower coefficient of thermal expansion of the metal coefficient it will be got gouge layer glass from the metal surface, called peeling. Other important factor in processes is called thermal shock resistance, which is a direct function of the thickness of the material coated on the surface of the metal, and little thickness provides resistance to thermal shock conveniently, also coatings must not exceed a thickness of 400 μm, and can be added one or more layers [5]. The adhesion of layer glass surface to the metal is generally done in two ways of physical adhesion and chemical adhesion. The physical adhesion happened through the dendritic adhesion for the glass material to the rough surface, while the chemical adhesion includes formation chemicals bonds between the metal surface and metal oxides through glass surface materials. The metal oxides used such as cobalt oxide, nickel oxide and manganese oxide [1]. There are many studies and research on the subject for large importance in various industrial applications, a researcher Shieu et al. 1999, studied the adhesion of porcelain coat on the metal type stainless steel 316L, they found that the adhesion depends on the morphology of surface, and rough surface much better than the smooth surface. The surfaces that have the same roughness not affected the process of thermal oxidation treatment prior to coated processes [6]. Baydaa in 2007 studied the properties of different types of enamel for the coated metal surfaces as well as open and closed porosity in the enamel layer [7]. Donkmenk et al. in 2008 studied the subject of the influence of the presence of carbon ratio (C) and titanium ratio (Ti) in sheet steel on glass coating of steel operations, and found that those two elements have a very important in the hot operation for sheet steel before enameling and reflected on coated operations processes. The best ratio of titanium to carbon (Ti / C) is greater than 2.5 in order to be more stabilizing steel [8]. Bodagi and Dafarbana in 2011 studied the effect of adding cobalt oxide (CoO) in the adhesion of the glass surface on the steel process, and found that cobalt oxide have been a large force in the adhesion process, but without the presence of cobalt oxide is sticking weak, and the time period for thermal treatment increases[9]. Ghazi et al. in 2014 studied the effect of added different ratios of titanium dioxide on the properties of the enamel for the protection of steel. Through the study shows that this type of coated ceramic provides high corrosion resistance in acidic media with high temperature. In addition to the large hardness and high reflectivity. This type of coated was very useful to protect carbon-steel [10].

Experimental work

A. Preparation of raw materials for the ground coat

First: It was chosen as the appropriate oxides in Table 1, and weight of each of the ingredients accurately, then mixed and milled in a ceramic ball mill for 24 hours in order to homogenize. Second: Melting ingredients blended using platinum crucible in an electric furnace at a temperature of 1200^{o}C for 30 minutes to ensure the fusion and homogeneity well. Third: Pouring molten glass into a container filled with water at laboratory degree to get a glass mixture called frit. Fourth: Grinding the glass mixture (frit) in a ceramic ball mill used porcelain balls for 24 hours to obtain a glass powder with high softness. Fifth: Sieved the powder for particulate size ≤ 50μm. Sixth: Add auxiliary materials to the powder as in Table 2 to get a glass slurry and this a glass slurry placed in ceramic ball mill for 24 hours to homogenized.

Table 1: Materials used in the preparation of the ground coat and cover coat [1].

Materials	Ground Coat (wt %)	Cover Coat (wt %)
SiO_2	56.43	41.56
B_2O_3	14.9	12.85
Na_2O	16.6	7.18
K_2O	0.51	7.96
Li_2O	0.72	0.59
CaO	3.06	0
ZnO	0	1.13
Al_2O_3	0.27	0
TiO_2	3.1	21.3
CuO	0.39	0
MnO_2	1.12	0
NiO	0.03	0
P_2O_5	0	3.03
CoO	1.24	0
F_2	1.63	4.4

Table 2: Glass slurry for ground coat and cover coat [1].

Materials	Ground Coat (wt %)	Cover Coat (wt %)
Frit	65.5	63.5
Kaolin	4.58	4.44
Borax	0.34	0.32
Magnesium Carbonate	0.08	-
Water	29.5	31.74

B. Preparation of metal surfaces

First: It was selected pieces of low carbon steel and grey cast iron with dimensions 5cm×5cm×1cm, was subjected chemical analysis of the elements involved in their formation using spectrometer instrument device, the results shown in Table 3 and Table 4. The pieces were mechanically cleaned through bombarding by silicon carbide (SiC) particles. Second: Chemically treatments of metal pieces for the purpose of good chemical cleaning and preparation of surfaces, using different materials as shown in Table 5. This process gives the cleanup and activation of the surface for good adhesion of glass layer to the surface of the metal. Third: Drying metal pieces at 75^{o}C for 30 minutes.

Table 3: Chemical components of steel (low carbon steel).

Composition	Wt %
C	0.12
Si	1.21
Mn	1.29
P	<0.01
S	0.022
Cr	0.021
Ni	0.37
Mo	0.019
Cu	0.061
Al	0.055
Ti	0.069
V	0.12
Nb	0.085
Co	0.068
W	0.017
Pb	<0.007
Fe	96.456

Table 4: Chemical components of cast iron (grey cast iron).

Composition	Wt %
C	3.15
Si	2.8
Mn	0.295
P	0.021
S	0.009
Cr	0.048
Ni	3.75
Mo	0.026
Cu	0.078
Al	0.003
Mg	0.031
Fe	89.789

Table 5: Materials and chemical cleaning solutions used [1].

Step	Solution	Composition	Temperature (^oC)	Time (min)	
				Dipping	Spraying
1	Alkaline solution	34g/l Na_2CO_3 with 4g/l NaOH	100	6-12	1-3
2	Rinse with hot water	Water	49-60	2-4	0.5-1
3	Rinse with cold water	Water	25	2-4	0.5-1
4	acidic solution	H_2SO_4 with concentration 5-10%	71-65	5-10	5-10
5	Rinse with cold water	Water & H_2SO_4 with pH3.5	25	2-4	2-4
6	Solution $NiSO_46H_2O$	5.2-7.4 g/l with PH3.5	60-82	5-10	5-10
7	Rinse with cold water	Water & H_2SO_4 with pH3.5	25	2-4	2-4
8	Neutral Solution 2/3$NaCO_3$ & 1/3 Borax	0.6-2.09 g/l	49-54	3-6	3-6

C. Coated the pieces by ground coat

First: Using dipping process to coated pieces of metals (steel and cast iron) by ground coat glass slurry. Second: Drying the pieces that have been dipped at 50^{o}C for 60 mutes. Third: Heat treatment of dried pieces with a glass of ground coat in an electric furnace at a rate of increasing and decreasing with 15^{o}C / min and stay at a temperature of 780^{o}C for two minutes. After making sure of landing the furnace temperature was take out the pieces from the furnace to evaluate the enamel layer.

D. Add the cover coat

First: Prepared a glass mixture (Frit) of cover coat layer as in Table 1, with the same way to prepare a glass mixture for ground coat layer, at temperature 1200^{o}C for 30 minutes, and after that grinding glass and sieved to ≤50μm, follow was added auxiliary materials to get glass slurry as in Table 2. Second: When ensure success of the ground coat layer, was immersion pieces with glass slurry of cover coat, to acquire certain regular thickness, followed by drying at a temperature 50^{o}C for 60 minutes. Third: Heat treatment of dried pieces with a glass of cover coat in an electric furnace at a rate of increasing with 15^{o}C / min, then its stay at a temperature of 760^{o}C for two minutes. and then, decreasing with 15^{o}C / min.

E. Add antimony oxide (Sb_2O_3)

It was to follow the same steps as the previous work preparing also, coated ground layer and cover layer materials in Table 1, but the addition of antimony oxide by 1% wt at the absence of the proportion of silica SiO_2 with the same percentage (it means replacing of 1%wt of the silica and adding instead of antimony oxide Sb_2O_3 for both coated ground layer and cover layer) and follow the same steps.

Results and discussion

First: XRD- tests: Examinations of glass mixture (powder of frit) for the ground and cover showed that broadening shape as in Fig. 1, as well as ground coat enamel layer extremes random. But cover coat enamel layer developed a silicon oxide and titanium oxide phases clearly has emerged in addition to the random-phase and results are shown in Fig. 2. The same results obtained were added antimony oxide Sb_2O_3. The appearance of phases for silicon oxide and titanium oxide in the cover coat enamel layer has a very important role in the resistance to acids [10].

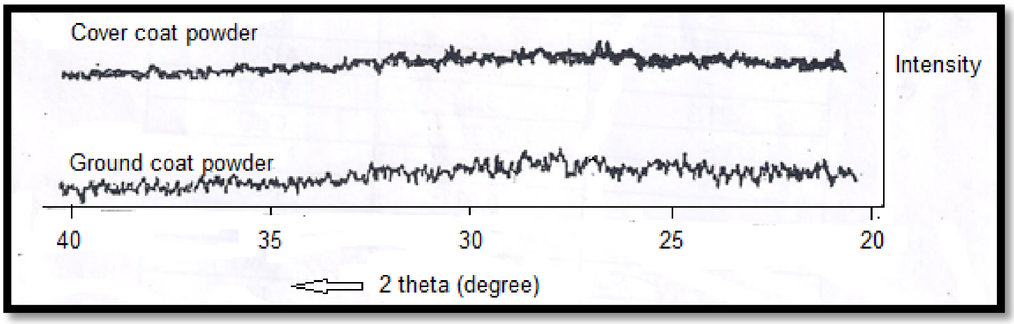


Fig.1: X-ray diffraction spectrum for ground coat and cover coat powder.

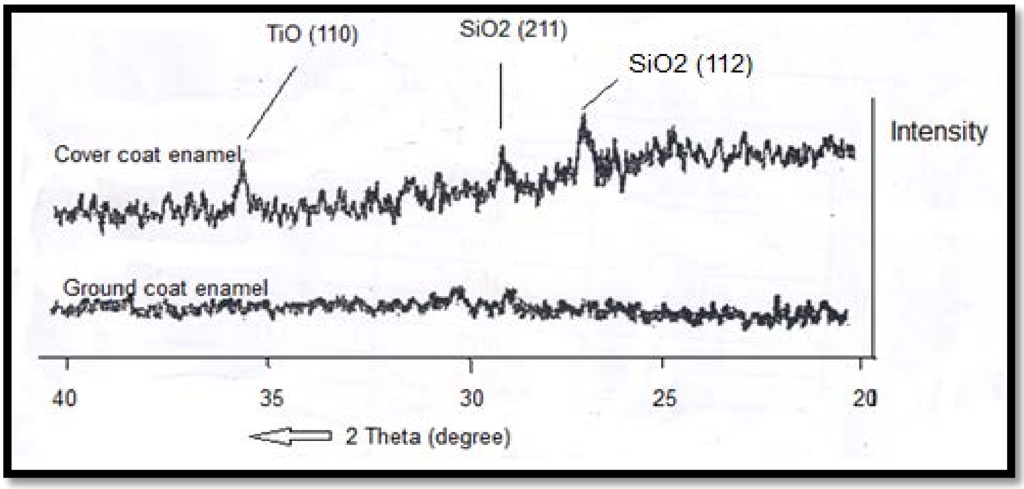


Fig. 2: X-ray diffraction spectrum for ground coat and cover coat enamel.

Second: measurements of density, hardness and thickness

The density was measured by Archimedes method for the samples have been prepared for this purpose. Microscopic hardness measurement by Knoop Hardness. The thickness of the ground coat enamel layer and cover coat enamel layer were measured using thickness gauge measurement (Coating Thickness Meter / CM-8822), the results were shown in Table 6 and Table 7, without and with addition of antimony oxide respectively.

Table 6: Density, hardness and thickness of the coating enamel layer on the steel and cast iron without the addition of antimony oxide.

Measurement Type	Ground coat		Cover coat	
	Steel	Cast Iron	Steel	Cast Iron
Density (gm/cm^3)	2.50	2.50	2.62	2.62
Knoop Hardness(kg/m^2)	1200×10^6	1100×10^6	1270×10^6	1210×10^6
Thickness (μm)	310	315	360	372

Table 7: Density, hardness and thickness of the coating enamel layer on the steel and cast iron with the addition of antimony oxide.

Measurement Type	Ground coat		Cover coat	
	Steel	Cast Iron	Steel	Cast Iron
Density (gm/cm^3)	2.58	2.58	2.74	2.74
Knoop Hardness(kg/m^2)	1260×10^6	1220×10^6	1310×10^6	1290×10^6
Thickness (μm)	300	310	350	365

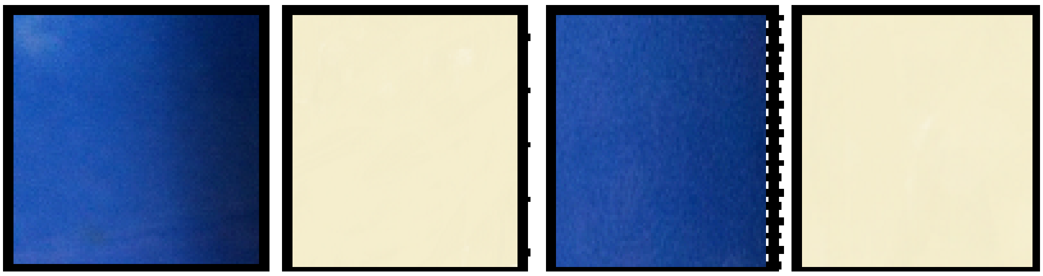
Table 5 and Table 6 show that the presence of antimony oxide, has enhancement the amount of density, hardness and the possibility of obtaining coatings with less thickness, and this truth was very useful for thermal shock resistance. Since when not addition antimony oxide popped visible bubbles on the surface of the ground coat enamel and cover coat enamel, especially in the case of cast iron coated. The reason for this phenomena was due to the high percentage of carbon in cast iron and released from the metal surface by reacting with the oxygen component to formation carbon dioxide (CO_2), which creates bubbles in the surface of the glass layer. The presence of antimony oxide in the glass mixture layers have an important role in reducing the viscosity of the glass layer, and thus allow the bubbles to leave through the glass layer. Thus, make the surface of the coated layer with a smooth, glossy and excellent hardness. As the amount of hardness which range (1260×10^6-1310×10^6 kg/m^2) of the steel and (1220×10^6-1290×10^6 kg/m^2) for the cast iron and the results agree with the published data [5]. Thickness for all cases were compatible with reference[1].

Third: chemical tests

Weight of coated samples in the sensitive balance, and create a framework of teflon material and paste it on the coated layer, then poured the amount of sulfuric acid H_2SO_4 diluted by 50% and the center by 90%, and put it in the oven at a temperature of 100°C for three days. After that measured the weights of the coated samples. The same tests as well as measurements were conducted using hydrochloric acid HCl center and diluted in the same proportions. Chemical tests to cover coat layer pointed to no decrease in weight, as well as to no decrease of the disappearance of gloss surfaces coated, for both types of acid (sulfuric acid, hydrochloric), to coated on the steel surface and cast iron in the case of addition antimony oxide. While in the absence of antimony oxide some decreases obtained by weight as well as to the disappearance of gloss to the surface in the case of coated cast iron, this indication to the penetration of acid between the pores coated samples.

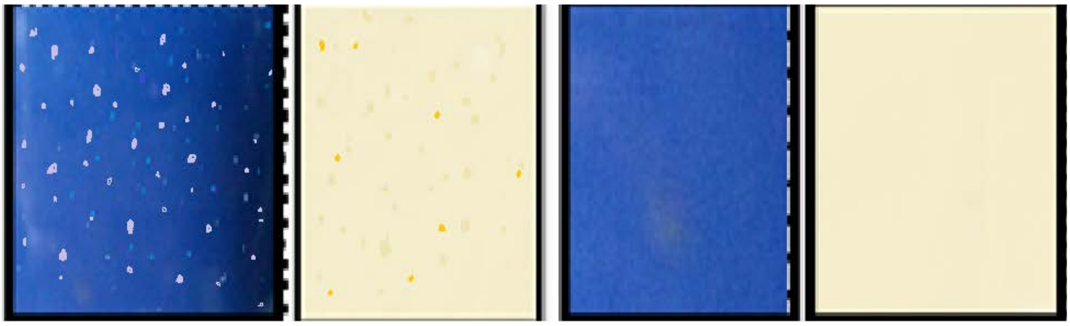
Fourth: microscopic examination

Optical tests were done using optical microscope to see the cracks or bubbles, in addition to gloss surfaces. It was shown that the coated surfaces of the steel in the absence and the presence of antimony oxide is free of defects such as cracks and bubbles as shown in Fig. 3. While the cast iron for both classes ground coat and cover coat have defects in the form of bubbles, when does not enter antimony oxide, but when enter antimony oxide free surfaces of these bubbles appeared as shown in Fig. 4.



(a)ground coat **(b)cover coat** **(c)ground coat** **(d)cover coat**

Fig. 3: Steel enameling (X200); (a, b) without addition antimony oxide, (c, d) by addition antimony oxide.



(a)ground coat (b)cover coat (c)ground coat (d)cover coat

Fig.4: Cast iron enameling (X200); (a, b) without addition antimony oxide, (c, d) by addition antimony oxide.

Conclusions

Non-introduction of antimony oxide in the coated mixtures for the ground coat enamel and the cover coat enamel has led to the possibility of coated steel surfaces well, and there are so many bubbles in the coated layers of cast iron. But when addition antimony oxide was found that possibility of coated the ground coat enamel and the cover coat enamel for steel and cast iron without cracks or bubbles approximately. Coated the cover coat enamel was resistant to acids and difficult weather conditions. Addition antimony oxide enhanced the density, hardness and reduced thickness of the coating.

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