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Analysis of Fe_3O_4 Protective Coatings Thermally Grown on Color Picture TV Tube Structural Steel Components

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This article concentrates on the analysis of formation of Fe oxides grown on different treated steel and relation of macroscopic properties of oxides with the structure, composition of layers formed in the color picture (CP) TV tube blackening furnace. Samples subjected to the blackening presented shadow mask, frames and inner shields used in the constructing of CP TV tubes. The chemical composition of the working gas was 100 ppm of O_2, 1 % of the volume – CO and 2 % of the volume -H_2. The CO_2 / CO ratio varied from 5.4 in the introduction part of the furnace to 6.3 at the maximum temperature point of the furnace. The H_2O/ H_2 ratio varied from 0.19 in the vestibule zone of the furnace to 0.38 in the middle part of the furnace. Inside of the heating zone, the mask temperature was 580 ±10 °C and the whole time of exposure of substrates in the maximum heating zone of steel blackening zone was 5 – 7 minutes. It is shown that blacking treatment of the shadow masks, frames and inner shields structural components of CRT made of A51EKE brings to the formation of iron oxide layer composed of magnetite (Fe_3O_4) and hematite (α-Fe_2O_3) where phase composition can vary from 1 : 1 to 1 : 1.5 depending on the surface treatment and subsequent thermal exposure.

Keywords: iron oxides, oxidation process, magnetite, hematite.

INTRODUCTION

The 16 iron oxides (including hydroxides and oxide hydroxides) have numerous applications and there are of continuing importance for research and technology. More sophisticated applications, including their use as ferrofluids for hermetic seals, exploit the unique magnetic properties of iron oxides, particularly magnetite Fe_3O_4, hematite, α-Fe_2O_3 and maghemite, γ-Fe_2O_3 [1, 2].

The magnetite Fe_3O_4 is the dominant phase whatever the oxidation time, and its proportion increases continuously during oxidation at 400 °C, in artificial air.

Usually the initial etching of the metallic surface leads to a complex oxide film constituted of iron hydroxides that is transformed during oxidation into α-Fe_2O_3 [3].

XPS data [4] indicated that depending on the environments used for the oxidation, products of pure iron oxidation were composed mainly of Fe_2O_3, FeOOH and/or Fe_3O_4. These compounds belong to the common products of the atmospheric corrosion of steel, which include $Fe(OH)_2$, $Fe(OH)_3$, α-, β-, γ–, δ-FeOOH, α-, β-, Fe_2O_3 and Fe_3O_4. The oxide morphology was highly diversified and dependent on the environment when it was formed on a thin iron film. Oxides in the form of small columns were observed after exposure to wet air.

If the bulk iron was used, oxides grew at random on separated spots in the form of irregulars hills [4]. It was found that oxide formed during the oxidation at room temperature consists of Fe^{2+} mainly, corresponding to FeO. For larger coverage (after longer oxygen exposure) Fe^{3+} is also found. The amount of Fe^{3+} decreases with the oxidation temperature.

During oxidation, Fe^0 is displaced from lattice positions and possibly incorporated in the oxide layer, but more probably at the Fe / oxide interface [5].

Knowledge of the morphology and composition of oxides on iron is important for characterizing the corrosion processes, and also in connection with application of thin iron oxide films, such as FeO, Fe_3O_4 and Fe_2O_3 in recording media. The structure of thin films depends on the surface morphology of the substrate, and it can be expected that the morphology of the substrate and of oxides will affect many properties of the substrate / oxide systems.

Despite that formation of Fe_3O_4 on shadow masks, frames and inner shields of color picture TV tubes, known as a blackening treatment, is employed widely in the technology of color picture (CP) TV tubes, temperature, atmosphere (gas content) and dew point control defining properties of the final product should be analyzed to obtain the macroscopically uniform layers.

This article concentrates on the analysis of formation of Fe oxides grown on different treated steel and relation of macroscopic properties of oxides with the structure, composition of layers formed in the CP furnace.

EXPERIMENTAL

A blackening furnace was employed in AB "Ekranas" for the blackening treatment (forming Fe_3O_4) of shadow masks, frames, and inner shields controlling the temperature, oxidation atmosphere (D gas), and dew point.

Composition of the steel A51EKE used in the experiment was as following: Fe (97.7 – 98.3 %), Ni (0.25 %), Cr (0.25 %), S (0.05 %), P (0.004 %), Mn (0.5 –0.8 %), Si (0.17 – 0.37 %), C (0.47 – 00.55 %), and surface roughness $R_a \cong 120$ μm. Samples subjected to the blackening presented shadow masks, frames and inner

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Table 1. Steel surface preparation and oxidation process details

No	Substrate preparation	Oxidation process		Other successive processes
		T, °C	*t*, min	
1 – 3*	I cleaning method	580 ±15	5	
4	I treatment method	580 ±15	5	1. Annealing in lehr (300 °C) 2. Sticking process in the sticking lehr (400 °C), t = 40 min.
5	II cleaning	580 ±15	5	1. Annealing in lerh 300 °C) 2. ticking process in the sticking lehr (400 °C)
6	II cleaning	580 ±15	5	

shields used in the constructions of CP TV tubes. The chemical composition of the working gas was 100 ppm of O_2, 1 % of the volume – CO and 2 % of the volume – H_2. The CO_2/CO ratio varied from 5.4 in the introduction part of the furnace to 6.3 at the maximum temperature point of the furnace. The H_2O/H_2 ratio varied from 0.19 in the vestibule zone of the furnace to 0.38 in the middle part of the furnace. The values of oxidation gas ratios were comparable with the recommended ones for the iron oxidation process ($CO_2/CO > 0.9$, $H_2O/H_2 > 0.25$) [6 – 7]. D gas supply pressure was (7.0 ±0.5) kPa, dew point was +60 °C and D gas temperature was 200 °C. D gas input flow rate was 370 to 450 m^3 per hour. The temperature increase rate from the vestibule blackening furnace to the maximum heating zone was ≤ 60 °C/min. Inside the heating zone, the mask temperature was 580 ±10 °C and the whole time of exposure of substrates in the maximum heating zone of steel blackening zone was 5 – 7 minutes. The cooling down from 580 to 250 °C temperature was performed with the rate 0.6 – 0.9 °C/min. The cooling zone temperature was 70 – 80 °C. The net conveyor belt speed carrying the blackening objects was 0.6 – 0.9 m/min.

Before the blackening, different cleaning process and heat treatment were applied for the CP TV tube steel constructions. The cleaning included exposure in "SurTec" alkaline concentrates (SurTec 138 recyclable Soak in combination with "SurTec" 089 2.13:1) and 0.3 – 0.4 % volume concentration "SurTec" 533 Aqueous Corrosion Inhibitor for corrosion protection) (I cleaning method) or alcohol cleaning (II cleaning method).

The oxide formation was analyzed for the temperatures 580 – 593 °C corresponding to the temperature field range in the lehr (blackening furnace). More details on the steel cleaning and treatment processes are presented in Table 1. The iron oxide surface morphology was investigated by Intel Play optical microscope and scanning electron microscope (SEM) Joel SM-IC25S. The roughness of iron oxide was measured by Hommel Tester 500 (the precision class 1by DIN4775, diamond radii – 5 μm, pressure 1.6 mN) in two perpendicular directions. The surface porosity of grown oxide was estimated exploring product of $K_3Fe(CN)_6$ that appears on the steel surface as blue color salts – result of Fe and hexacyanoferrimetry chemical reaction. Phase composition and crystal structure of the iron oxide on the steel substrate was analyzed by X-ray diffractometer DRON-3,0 (Cu K_α ($\lambda = 0.154$ nm, $U = 30$ kV, $I = 20$ mA). All specimens were analyzed in a Kratos X-ray analytical photoelectron spectrometer equipped with the nonmonochromatic Al K_α, ($h\nu = 1486.6$ eV) X-ray radiation source. Photoelectron peaks from the surface associated with carbon (C1s), oxygen (O1s) and iron (Fe2p) were registered. C1s emission from hydrocarbon contamination (binding energy 285.0 eV) was used as an internal standard to estimate the amount of homogeneous shift. The sheet resistance measurements of iron oxide layers were done by four-probe method. Adsorbed gas emission from the iron oxide surface was analyzed in vacuum system "A700Q ("Leybold Heraeus"). The gas composition and kinetics of gas desorption from the samples with linear dimensions 2×2 cm^2 covered by oxides was measured by quadruple mass-spectrometer "Anavac-2" within 2 – 200 a.m.u. region. Three samples corresponding to the different positions in the blacking furnace (or temperature range 565 – 595 °C) were analysed.

RESULTS AND DISCUSSIONS

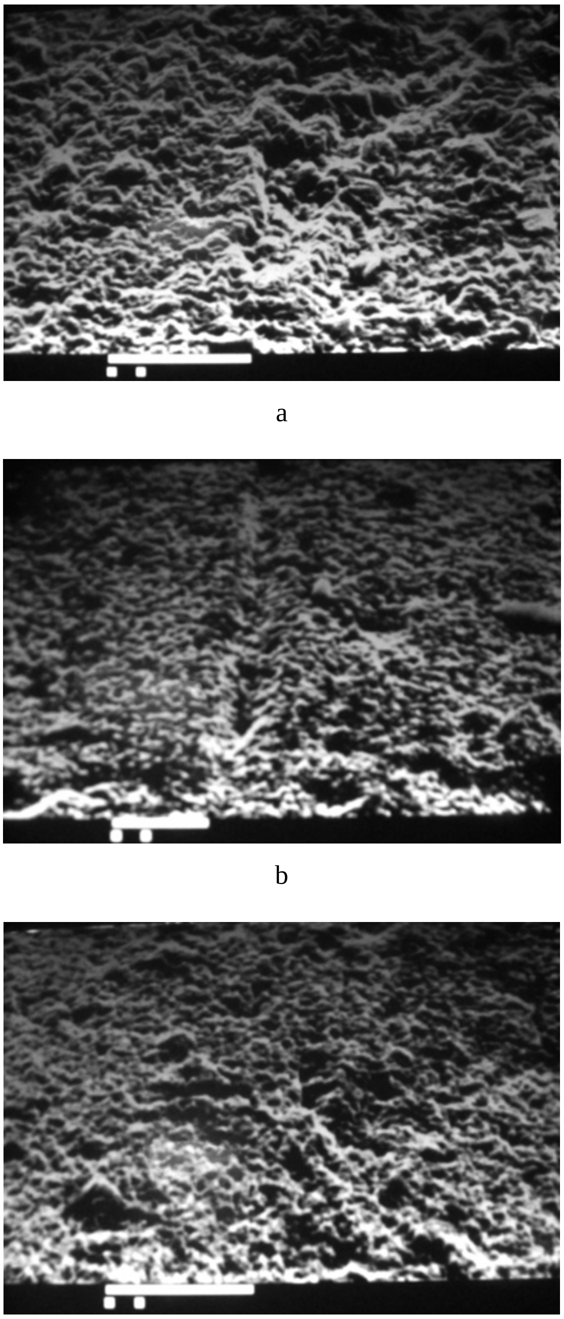
The iron oxide thin film thickness (defined by SEM), porosity and resistance are presented in Table 2 One can see that iron oxide thickness is not influenced by cleaning method, but homogeneity of the film is very sensitive to the surface treatment. The maximum value of iron oxide porosity was observed for the "alcohol treatment". On the other hand, it decreased after heating at higher temperatures (extra heating in lehr or sticking procedures). The iron oxide sheet resistance varied from 0.1 to 2 Ω and it was independent of the oxidation temperature.

Table 2. Thickness, resistance and film homogeneity of iron oxide dependent on the oxidation process

Sample number	Thickness, μm	Homogeneity, %	Sheet resistance, Ohm
3	5.6	0.30	0.1 – 0.2
4	4.85	0.89	2.0
5	4.85	0.40	1.5 – 2.0
6	4.8	4.30	0.1-0.2

The maximum resistance value was found for the annealed samples and samples annealed in the lehr. The typical iron oxide film morphology is presented in Fig. 1. Typical values of the oxide roughness varied in the range 3.4 – 2.02 μm.

The XRD results of iron oxide on steel surface are presented in Fig. 2 and corresponding phase composition in Table 3. From comparison H-α-Fe_2O_3 and α-Fe peaks intensities ratio it was found that the main components of these peaks were H-α-Fe_2O_3.



a

b

c

Fig. 1. Typical surface morphology of the Fe_3O_4 samples: a – No3, b – No4, c – No 6 (marker size 10 µm)

One can see that the iron oxide phase composition was dependent on the steel surface treatment and following substrate heating.

The X-ray patterns present iron oxide on the steel substrate after the first treatment method before and after heating. It was found that magnetite peak M(422) disappeared after extra annealing and intensity of the peak H(104) decreased. These two peaks weren't observed only for the oxides grown using alcohol treatment and not applying any heating procedures. Fe_2O_3 content changed from 53 to 42 % and from 47 to 60 %. The extra sample heating contributed to the phase changes preferably to the formation of Fe_2O_3. These changes were detected for both cleaning methods of the substrate.

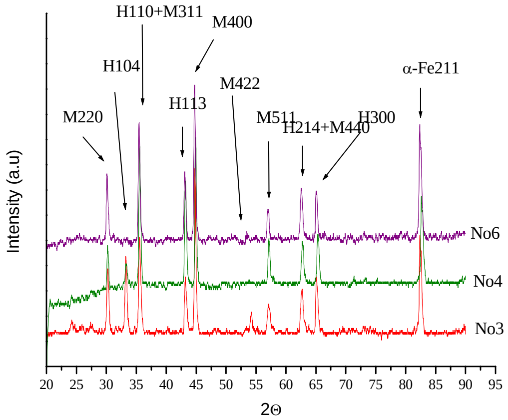
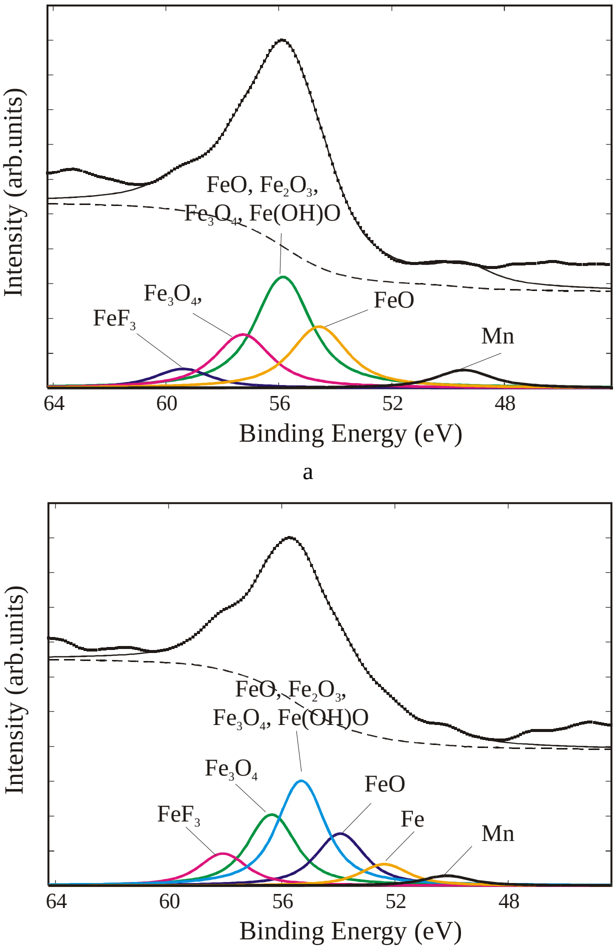


Fig. 2. X-ray diffraction patterns (Cu K_α radiation) showing the magnetite (M:Fe_3O_4) and hematite (H-α–Fe_2O_3) phases for the different treated samples (No 3, 4, 6)

Table 3. Results of the iron oxide phase analysis (XRD)

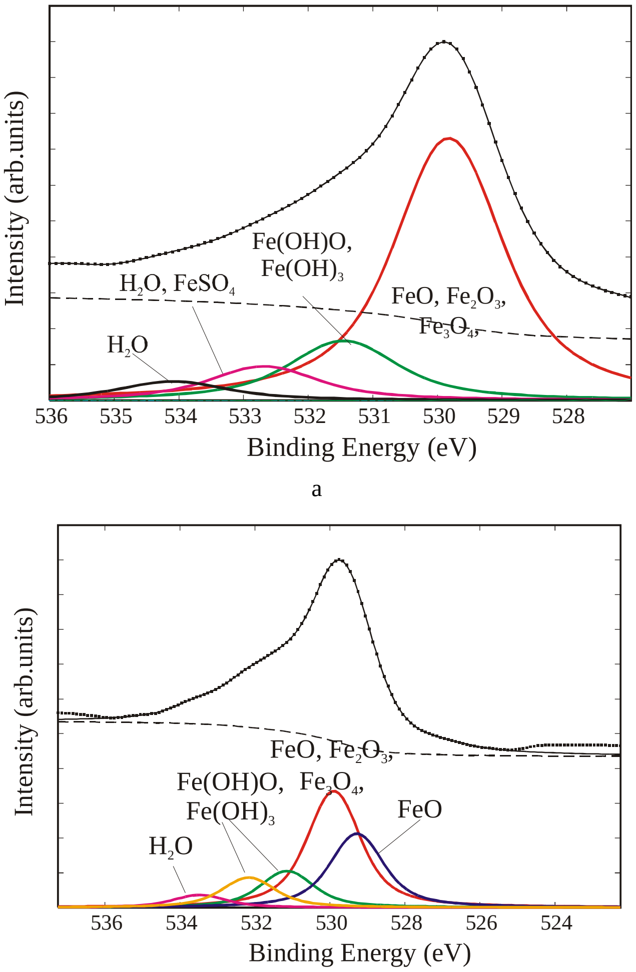
Sample number	Fe_3O_4	Fe_2O_3
3	50	50
4	42	58
5	40	60
6	51	49



a

b

Fig. 3. XPS fitting of Fe3p: a – No 3; b – No 4



a

b

Fig. 4. XPS fitting of O1s: a – No 3; b – No 4

The iron oxide surface composition measured by XPS is presented in the Table 4. The XPS results (Fe3p and O1s peak intensities and fitting results) for the typical samples No 3 and No 4 are presented in Fig. 3 and Fig. 4. According to these results the carbon, oxygen and iron content in the iron oxide surface varied from 39.30 % – 54.91 %, 21.94 % – 46.83 %, 2.32 % – 6.40 % correspondingly and were dependent on the sample treatment and subsequent thermal exposure.

One can see that the composition of iron oxide was dependent on the surface preparation and successive annealing process, except the sample, which was cleaned only in alcohol. Fe amount in the surface layer was only 2.32 % in this sample.

After Fe2p, Fe3p, O1s and C1s peak fitting it was found that the main chemical bonds between iron, oxygen and hydrogen atoms were Fe_2O_3, Fe_3O_4, FeO and Fe(OH)O, $Fe(OH)_3$ (Table 5). The Fe-C bonds were not observed in the Fe2p and Fe3p peaks. This means that the highest concentration of C defined from the C1s peak was due to C-H bonds that arise from organic components on the iron oxide. The next fact that follows from the XPS analysis is that water and organic impurity amount increases after extra heating of oxides in lehr.

Table 4. Distribution of chemical components on the iron oxide surface (the XPS results)

Sample number	Fe, %	O, %	C, %
3	6.40	38.68	54.92
4	11.12	21.94	66.93
5	19.18	41.51	39.30
6	2.32	46.83	50.84

Table 5. Chemical bonds concentration of iron oxide surface from the (Fe2p peak fitting analysis)

Peak	Sample number			
	3	4	5	6
Fe3p				
Fe		7.67		
FeS, FeS_2		18.76		3.06
Fe_3O_4, Fe_2O_3, FeO,Fe(OH)O	93.55	63.44	81.09	83.91
Fe2$(SO_4)_3$		10.13	9.10	26.92
O1s				
Fe_2O_3,Fe_3O_4, FeO	88.11	70.82	89.33	
Fe(OH)O, $Fe(OH)_3$,	15.85	13.55	8.89	11.4
Fe2$(SO_4)_3$, $FeSO_4$		11.08		
H_2O		4.55	1.77	3.55
C1s				
Fe(C–H), _C–H	43.19	97.45	66.08	62.75
Fe(C–H–O). _C–O, $Ni(CO)_4$	31.24	0.48	16.22	
$Fe(CO)_5$, Me_C=0	22.45	1.32	2.07	26.67
C–F	3.13	0.75	5.12	10.58

Table 6. Adsorbed gas emission from the iron oxide samples in dependence on the surface treatment and successive technology

Gas compo-nents	a.m.u.	Residual gas background of peak intensities (a.m.u)	Residual gas peak intensities (a.m.u) for the vacuum chamber with the samples		
			No.4	No.5	No.6
H_2O	18	65.0	75.7	79.4	80.3
N_2	28	22.0	16.10	13.5	13.0
O_2	32	7.5	5.10	4.0	3.3
CO_2	44	5.5	3.1	3.1	3.4

Adsorbed gas emission results from the different iron oxide samples in dependence on the surface treatment and successive technology are presented in the Table 6. It was found that during exposure of the samples in the vacuum (degasation of the samples), water was the main adsorbed gas component, that contributed mainly to the residual gas spectra. This is in good agreement with the XPS fitting results.

CONCLUSIONS

Blackening treatment of the shadow masks, frames and inner shields structural components of CRT made of A51EKE brings to the formation of iron oxide layer composed of magnetite (Fe_3O_4) and hematite (α-Fe_2O_3) where phase composition can change from 1:1 to 1:1.5 depending on the surface treatment and subsequent thermal exposure.

Formation of the magnetite phase takes place within the range (580 ±15) °C corresponding to the temperature range of a blackening furnace.

Cleaning of the samples in the alkaline solutions is an effective way of surface preparation as compared to the alcohol treatment.

All following technological procedures (extra annealing in lehr, annealing in thermal sticking process) brings to the increase water and organic impurities concentration in the oxide layers.

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