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The influence of corrosion process on spectral properties of glassy coatings

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Glassy enamels are characterized by high chemical durability. Their chemical resistance properties, however, differ from those observed for conventional oxide glasses. This is because of their specific chemical composition and microstructure determined by enamel technology. In longer periods of exploitation in corroding conditions glassy coatings deteriorate continuously, the most significant changes taking place in the near-surface region. The main goal of this work was to establish the influence of chemical corrosion on spectral properties of glassy coatings. Changes in microstructure, gloss and reflectance were studied using electron microscopy and reflectance spectroscopy. It was confirmed that enamels based on pigments have higher durability than enamels coloured by ion dyes.

Keywords: glass, enamel, corrosion, optical properties.

1. Introduction

Corrosion of glassy materials is a very complicated process. It is influenced by several external and internal parameters. Chemical composition, internal stress and inhomogeneity of the glass are the main parameters determining behaviour of the material in corrosion environment. Application of the glass as a coating on the metal (enamel) draws attention other parameters characteristic of this technology [1–3]:

– oxides promoting adherence to the metal substrate must be present (usually CoO, NiO, MnO),

– some components are introduced due to application technology (clay, some electrolytes),

– surface active oxides are usually added (MoO_3),

– pigments and fillers are also present.

Moreover, crystalline phases or gas bubbles are usually observed in the glassy coatings. Because of this complicated chemical and phase composition, interaction with corrosion medium is also very complicated and usually unpredictable on the basis of theoretical consideration.

The main subject of this study was to establish the influence of corrosion process on spectral properties of selected glassy coatings. Studies concentrated on enamels having high absorption properties in the range of solar spectrum as this coatings were intended to be used as a solar collector absorber [4–6].

2. Experimental procedure

Glassy coatings with high absorption properties can be obtained by introducing colouring oxides into the glass batch or by introducing pigments into the enamel slurry [1, 4]. Both types of the methods of coating preparation were used in this study. In our study, we used based on the glass with composition as shown in the Table.

In the case of coating having pigments base glass was colorless and black pigment (8%) was introduced. Coatings were prepared by means of enamel technology and applied on a 1 mm thick steel substrate. Coatings were fired at 850 °C for 6 min in isothermal conditions. The samples obtained were subject to corrosion tests in controlled conditions in the following solutions:

– 1% sulfur acid (H_2SO_4),
– 1% citric acid ($HOC(CH_2COOH)_2COOH$),
– 0.5% sodium alkaline (NaOH).

T a b l e. Chemical composition of the base glass.

	Mass content [%]			
Component	G106	G102	G205	G78
SiO_2	58.43	55.43	60.64	34.14
B_2O_3	9.70	9.7	9.58	17.24
Na_2O	7.05	7.05	11.7	13.54
K_2O	1.88	1.88	2.13	3.43
CaO	2.51	2.51	3.19	—
BaO	0.56	0.56	3.19	4.47
TiO_2	6.38	4.38	6.38	1.16
ZrO_2	—	5.00	—	—
Li_2O	2.68	2.68	3.19	0.87
CaF_2	—	—	—	11.37
Al_2O_3	—	—	—	2.97
CoO	1.64	1.64	—	1.64
NiO	1.63	1.63	—	1.63
CuO	2.32	2.32	—	2.32
MnO	1.55	1.55	—	1.55
MoO_3	1.05	1.05	—	1.05
FeO	2.62	2.62	—	2.62

Tests were carried out for 30 to 180 min at 40 °C in isothermal conditions. The fluid flew through the measuring cell continuously. The flow was forced by follicular pump, Garmon-Rupp Industries – 200 l/min. Spectral properties were measured in reflected light mode using Konica-Minolta CM-2600d spectrometer with spherical geometry d/8. Electron microscope Joel 5400 with EDS Oxford Instruments Link 300 with energy disperse X-ray analysis (SEM, EDX) was used for microstructure observation.

3. Results and discussion

Different ways of absorption coating preparation (using pigments or by ion dye) give materials with different spectral characteristics. The most representative results are shown in Figs. 1–4. Ion coloured coatings are characterized by reflectance varying with wavelength. This is due to colour balancing by the ion dyes used. Changes in the surface region due to acid corrosion environment are only slightly seen in the reflectance, Fig. 1**b**, but appear to influence much more the gloss, Fig. 1**c**. The changes observed decrease with wavelength. Reflectance and gloss spectra have similar character for 1% sulfur acid and 1% citric acid.

a

	L*(D65)	a*(D65)	b*(D65)
0 min	22.64	-1.86	6.20
30 min	22.88	-1.96	6.17
120 min	22.77	-1.87	6.19

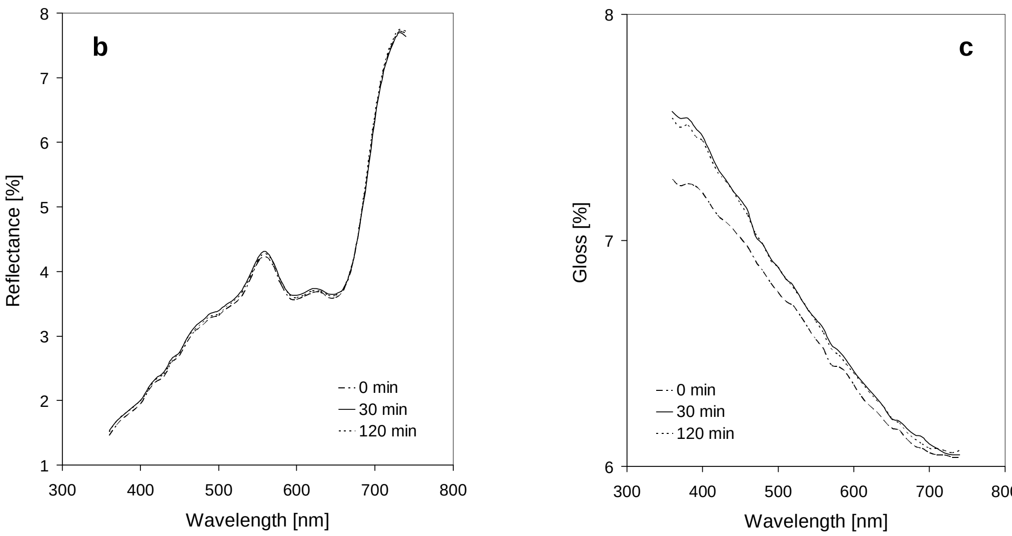

Fig. 1. Spectral characteristic of G102 coating (ion pigmented) after corrosion in 1% sulfur acid; **a** – colour parameters, **b** – reflectance, **c** – gloss.

	L*(D65)	a*(D65)	b*(D65)
0 min	5.77	0.74	0.06
30 min	6.97	0.76	0.19
120 min	6.93	0.74	0.18

a

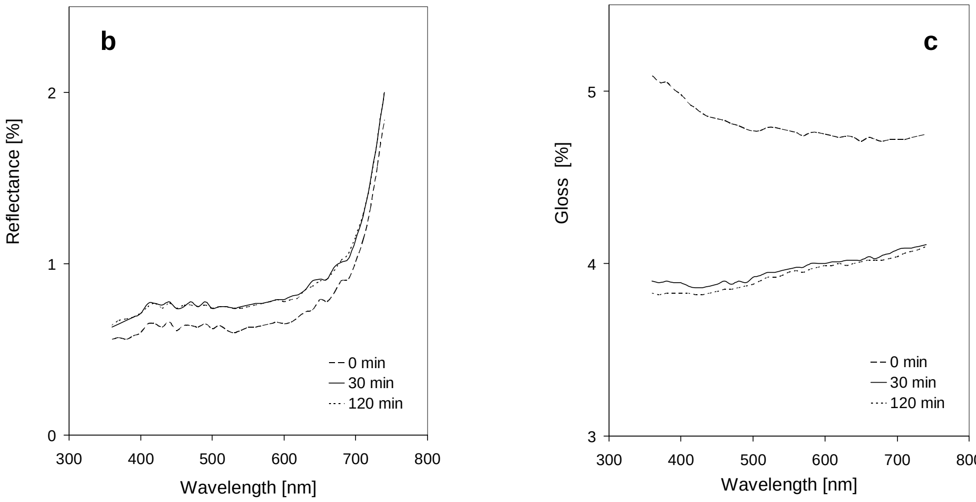

Fig. 2. Spectral characteristic of G205 coating coloured by pigment after corrosion in 1% sulfur acid; **a** – colour parameters, **b** – reflectance, **c** – gloss.

	L*(D65)	a*(D65)	b*(D65)
0 min	15.46	-2.50	-3.41
30 min	14.40	-2.57	-2.88
120 min	14.16	-2.55	-2.90

a

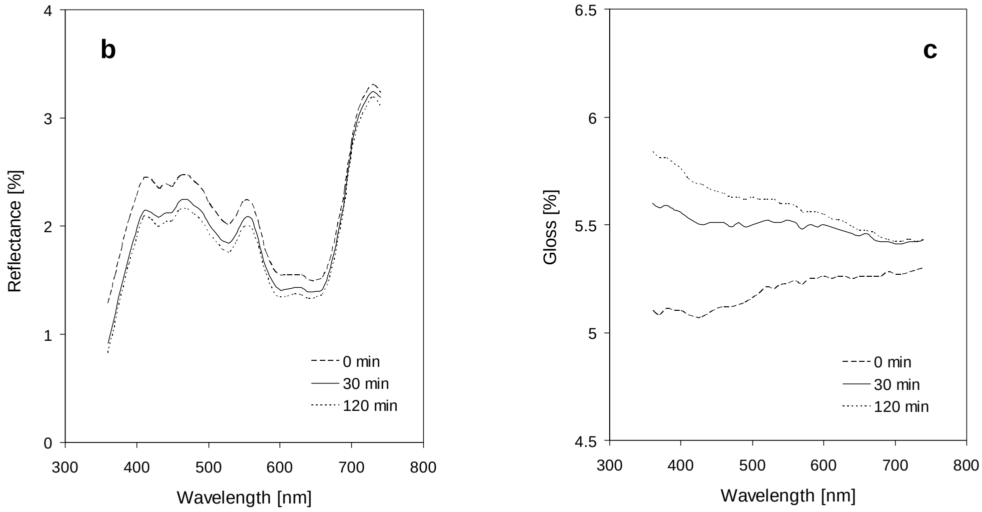

Fig. 3. Spectral characteristic of G107 coating (ion pigmented) after corrosion in 1% NaOH; **a** – colour parameters, **b** – reflectance, **c** – gloss.

Alkaline solution leads to the lowering of reflectance in all wavelength, Fig. 3**b**, and greater changes in gloss, Fig. 3**c**, this tendency decreasing with wavelength.

Enamels coloured with pigments have shown less differences in reflectance, Figs. 2 and 4. Interaction with acid solutions leads to an increase in reflectance, Fig. 2**b**, and greater decrease in gloss, Fig. 2**c**. In the case of alkaline solutions (0.5% NaOH) it leads to an increase in reflectance in the measured range and only slight loss in gloss, Fig. 4**b**. The characteristic features of interactions under study are acceleration of changes at the beginning of the test (0–30 min) and stabilization of the parameters with time (30–120 min). These changes a especially seen in the colour parameters: L^*, a^*, b^*, Figs. 1**a**, 3**a** and Figs. 2**a**, 4**a**. The values of these parameters compared at the beginning of the corrosion test and after 20 and 120 min show the most significant changes to be observed during the first 30 min. Parameters a^* and b^* are rather stable but luminance L^* changes most significantly.

The relations observed are due to the different chemical composition of the near surface and top layers of the coatings. The chemical changes are connected with the coating application technique, *i.e.*, wet spraying. In this technique, some milling additives (mainly clay) form non-continuous thin layers on the top of the coating, as one can see in Fig. 5**a**. This can by avoided using different application technique like electrostatic powder spraying.

The surface of fired enamel shows some amount of pin holes which are remnants of gas bubbles migrating to the surface during firing. The presence of gas bubbles is

a

	L*(D65)	a*(D65)	b*(D65)
0 min	5.42	0.88	0.4
30 min	6.53	0.81	-0.02
120 min	6.82	0.82	0.2

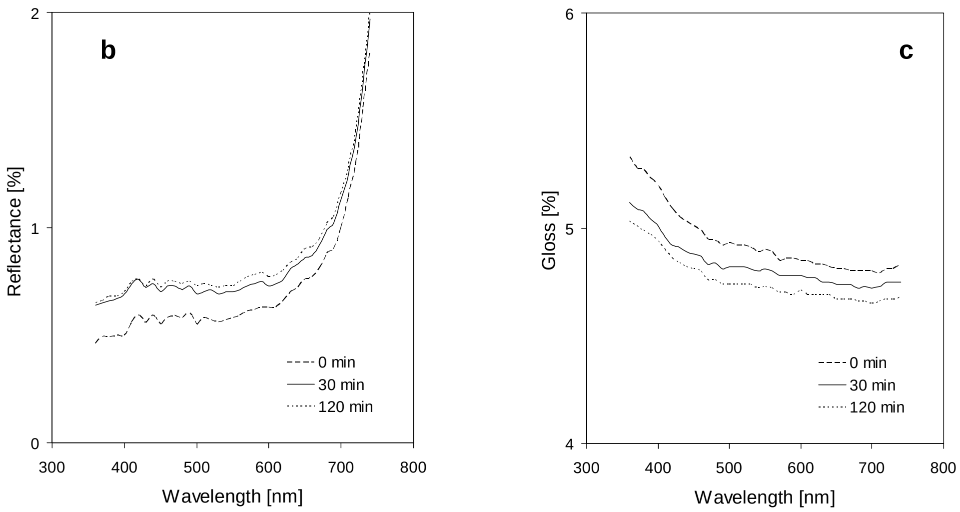

Fig. 4. Spectral characteristic of G205 coating coloured by pigment after corrosion in 0.5% NaOH; **a** – colour parameters, **b** – reflectance, **c** – gloss.

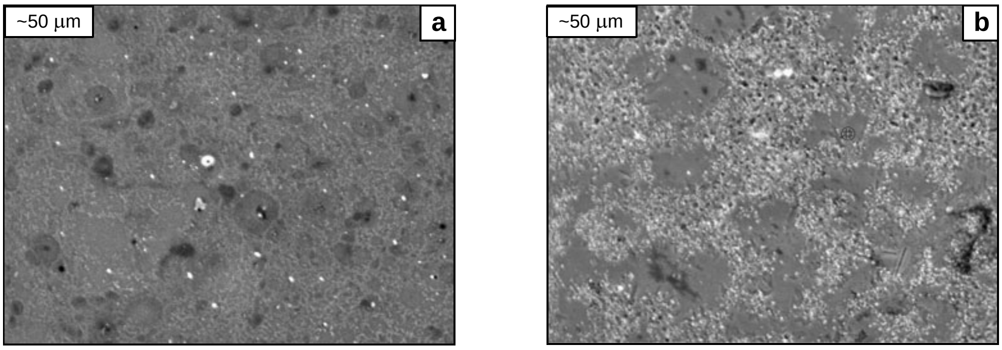

Fig. 5. Microstructure of G78 sample; **a** – after firing, **b** – after corrosion in 1% citric acid.

a characteristic property of the enamel coating (bubbling structure). The bubbles are closed and isolated. They enhance the elasticity of enamel and in this sense they play a positive role, however the corrosion process can lead to the opening of the bubbles and this process speeds up the degradation of the coating, Fig. 5**b**. In this figure, results of strong corrosion of G78 direct enamel are shown. Homogeneous regions are the fused parts of solid glass. Highly defective regions containing open pores and bubbles are due to the leaching of near surface region of grains containing clays, bentonite and quartz. Such high degradation is usually not observed in normal exploitation conditions and means low chemical resistance of the coating.

4. Conclusions

The following conclusions can be derived from conducted studies:

– Coatings with similar spectral properties can be obtained when glass frit is coloured by metal ions or pigments are introduced into the enamel slurry.

– Changes in the spectral properties have a decaying character and stabilize with corrosion time. The most significant changes are observed in the case of luminance L^* while colour parameters a^* and b^* are stable.

– It is more efficient to use pigments in high absorption coating preparation as optical parameters are more stable and higher chemical resistance can be achieved.

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