Influence of deposition technique on the protective properties of epoxy films

Einfluss der Abscheidetechnik auf die Schutzeigenschaften von Epoxidfilmen

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The electrochemical impedance spectra, the anodic polarization curves and the time dependence of paint capacitance and paint resistance have been used in this paper to evaluate the protective properties of epoxy films on carbon steel substrate. The coatings were formed using four deposition techniques (brushing, immersion, cathodic and anodic electrodeposition) with the aim to determine the effect of deposition type on the anticorrosive performances of epoxy paint. Interpretation of Nyquist and Bode impedance spectra with the immitance analysis Equivcrt. programme has established an electrical equivalent circuit with two time constants fitted to describe the electrodeposited epoxy/carbon steel system in the 3 % sodium chloride solution and an electrical equivalent circuit with four time constants fitted in case of epoxy films applied by brush or immersion. The anodic polarisation measurements show nobler corrosion potentials and smaller dissolution current densities for the carbon steel in the presence of the electrodeposited films in comparison with epoxy coatings applied by brush or with the immersion technique. The values of the porosity, water uptake, and ionic transport through the film emphasize the higher performances of the electrodeposited films, characterized by uniformity, porosity absence, low water permeability and few conductive pathways.

Elektrochemische Impedanzspektren, anodische Polarisationskurven und die Zeitabhängigkeit der Beschichtungskapazität und des Beschichtungswiderstandes wurden in dieser Arbeit benutzt, um die Schutzeigenschaften von Epoxidfilmen auf Kohlenstoffstahlsubstraten zu beurteilen. Die Beschichtungen wurden mittels vier verschiedener Abscheidetechniken hergestellt (Streichen, Tauchen, kathodische und anodische elektrolytische Abscheidung). Ziel war es, den Einfluss des Abscheidetyps auf das korrosionsverhindernde Verhalten der Epoxidbeschichtung zu ermitteln. Die Interpretation der Nyquist- und Bode-Impedanzspektren mit dem Analyseprogramm Equivcrt. ergab einen elektrischen Analogieschaltkreis mit zwei Zeitkonstanten für das System elektrolytisch abgeschiedenes Epoxid/Kohlenstoffstahl in 3 % Natriumchloridlösung und einen elektrischen Analogieschaltkreis mit vier Zeitkonstanten für Epoxidfilme, die durch Streichen oder Tauchen aufgebracht wurden. Die anodischen Polarisationsmessungen zeigten edlere Korrosionspotentiale und geringere Auflösungsstromdichten für den Kohlenstoffstahl bei Anwesenheit von elektrolytisch abgeschiedenen Filmen im Vergleich zu Epoxidbeschichtungen, die durch Streichen oder Tauchen appliziert waren. Die Werte für die Porosität, Wasseraufnahme und Ionentransport durch den Film heben das bessere Verhalten der elektrolytisch abgeschiedenen Filme hervor, die durch Gleichmäßigkeit, Abwesenheit von Porosität, geringer Wasserpermeabilität und geringen leitfähigen Pfaden gekennzeichnet sind.

1 Introduction

The deposition technique of the paints is a decisive factor to obtain good anticorrosive performances of the protective films. This influences the coatings porosity and consequently their permeability to water and corrosive species as well as the adhesion to metal surfaces. These properties are very important, because only a low permeability and a good adhesion can ensure the protection of the metal surface in a corrosive environment and prevent the starting of the corrosion process. An accurate evaluation of these parameters could be provided by electrochemical measurements and therefore their application to study paint films had received a great attention in the last years [1–5].

The electrochemical impedance spectra (EIS), the anodic polarization curves and the time dependence of the paint capacitance and paint resistance have been used in this paper to evaluate the protective properties of the epoxy films deposited on carbon steel substrate using various deposition techniques.

2 Experimental

The protective epoxy films were applied on carbon steel samples (disks) previously polished and degreased (no primer was used). Table 1 presents the paint films, which were tested in this paper. All coatings were stabilized for 14 days before testing.

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Table 1. The paint films
Tabelle 1. Beschichtungsfilme

Film symbol	Expoxy resin type*	Deposition technique	Curing	Coating thickness (μm)
A	anionic-modified (carboxylate groups)	anaphoresis	30 minutes at 180 °C	18–20
C	cationic-modified (secondary amine)	cataphoresis	30 minutes at 180 °C	18–20
B	epoxy-polyamide	brushing	room temp.	20–25
I	epoxy-polyamide	immersion	room temp.	25–30

* without pigments

The experiments were conducted in stagnant, naturally aerated 3 % sodium chloride solution under ambient conditions during a 60 days period.

The electrochemical impedance measurements were performed at open circuit potential, in a $10^{-1}-10^{5}$ Hz frequency range, after different immersion periods. The experimental impedance spectra were analysed on the basis of the electrical equivalent circuits using the fitting software developed by *Boukamp* [6].

The physical properties obtained from the principal elements of the electrical equivalent circuits were used for the characterization of the epoxy coatings. So, the paint capacitance and paint resistance were monitored with the immersion time and their time dependence has permitted to establish the water permeability of the paint films and the movement of the ions through films [7].

The anodic polarization curves have been recorded for bare and painted electrodes by potentiostatic polarization (50 mV/5 min. step), after various immersion times; the efficiency of the protective films and their porosity were determined from the dissolution current densities [8].

3 Results and discussion

3.1 Electrical equivalent circuits for epoxy film/carbon steel systems

The variations in the dielectric properties of the films due to the water uptake and the ionic transport are reflected in the changes of their impedance characteristics. These changes accentuate in time and depend on the deposition technique as can be seen from Figs. 1 and 2, which present Nyquist and Bode diagrams after different immersion periods.

The interpretation of EIS data with the immitance analysis Equivcrt. programme in case of the electrodeposited epoxy films established the presence of two time constants (Fig. 3): one time constant concerning the paint film (paint film capacitance Q_{pf} and paint film resistance R_{pf}) describes the electrical and barrier properties of the paint film; the other time constant concerning the metal surface (charge transfer resistance R_{ct} and double layer capacitance Q_{dl}) describes the corrosion reactions at the paint/carbon steel interface.

But, in the case of the epoxy films applied by brush or with the immersion technique, the interpretation of the impedance spectra show the presence of four time constants (Fig. 4); in addition, one time constant for the existing pores in the paint film (pore capacitance Q_{por} and pore resistance R_{por}) and another time constant for the diffusion process through the paint film (diffusion capacitance Q_{dif} and diffusion resistance R_{dif}).

The fitting quality is good; the errors magnitude between the measured and the calculated results with these electrical equivalent circuits is satisfactory.

3.2 Water permeability and ionic transport through paint films

The evaluation of the time trends of the paint capacitance and paint resistance from the electrical equivalent circuits has permitted to determine the water permeability of the epoxy films and the ionic transport through these.

Supposing: the homogeneous water dispersion, the lack of water-polymer chemical interaction and the absence of swelling process, the volume fraction of water uptake (Φ_t) in the paint films was calculated from the time dependence of the paint capacitance with *Brasher* and *Kingsbury*'s formula [9]:

$$\Phi_t = (\log C_t/C_0)/\log 80, \quad (1)$$

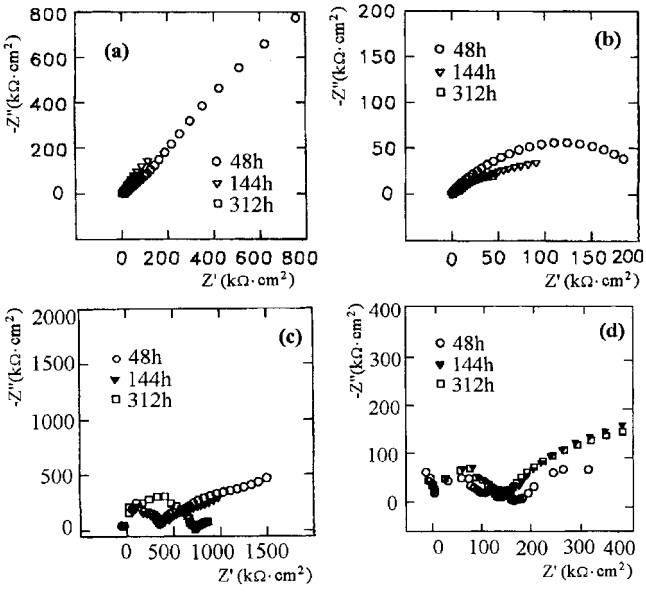

Fig. 1. Nyquist spectra for epoxy paint deposited on carbon steel after various exposure periods in 3 % sodium chloride solution: a) A; b) C; c) B; d) I

Abb. 1. Nyquist-Spektren für Epoxidbeschichtungen auf Kohlenstoffstahl nach verschiedenen Auslagerungszeiten in 3 % Natriumchloridlösungen: a) A; b) C; c) B; d) I

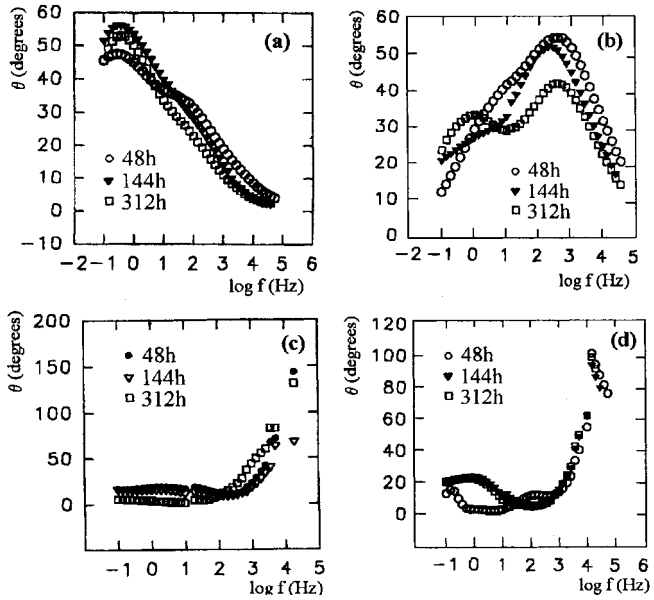

Fig. 2. Bode plots corresponding to spectra from Figure 1
Abb. 2. Bode-Plots entsprechend den Spektren aus Abb. 1

where C_t is the paint capacitance at time t, C_0 is the paint capacitance at time t = 0 and 80 is the relative permittivity of water.

The absorbtion diagrams were established; these emphasized that the water permeation into the epoxy paint films follows the model proposed by *Touhasent* and *Leidheiser* [10]. At first the water enters into the film defects (capillary water) and then the polymer is partially penetrated by the water (into polymer water).

The data presented in Table 2 show low permeability of the electrodeposited epoxy coatings (2.1 % in vol. for cataphoresis and 1.8 % in vol. for anaphoresis). The epoxy films applied by brush or with the immersion technique are more permeable to water (6.4 % in vol., respectively 8.1 % in vol.); the capillary water due to the existing pores in these films (confirmed by the microscopical assessment) represents 82 % and respectively 88 % from the total water uptake.

The movement of the ions through the epoxy paint films was estimated from the area of the conductive pathways (A_t), which develop in the films between the substrate and the bulk electrolyte. This was calculated with *Walter*'s formula [11]:

$$A_t = 1/(kR_t), \quad (2)$$

where l is the average distance of the pathways (≈ paint film thickness), k is the conductivity of the pathways (≈ conductivity of the bulk solution) and R_t is the resistance of the protective film at the time t.

The obtained data point out a reduced ionic transport in the electrodeposited epoxy films. As can be seen from Table 2 the conductive pathways represents $\approx 9 \times 10^{-6}$ % from total surface of the electrodeposited films, resulting in a decrease of the ion movement (≈ 50–70 times) in comparison with the films applied by brush or immersion.

The water penetration process is faster than the development of the conductive pathways for all tested epoxy films (Table 2). Therefore, the rate-controlling step of the substrate corrosion is the ionic transport through the paint films.

3.3 Electrochemical characteristics of the epoxy films and the carbon steel substrate

The polarization curves offered supplementary information about the corrosion behaviour of the painted specimens, but these depend on the exposure time in the electrolyte solution before the polarization.

Figure 5 illustrates the anodic polarization curves recorded after 5 hours of immersion in the test solution for bare and epoxy painted carbon steel.

The specimens coated with the electrodeposition techniques present similar behaviour, which is characterized by a marked tendency to limit the corrosion of the carbon steel substrate in comparison with those two deposition techniques (brushing and immersion). The corrosion potential is nobler and remains almost stable over time. The dissolution current

Table 2. Water uptake and ionic transport in epoxy paint films
Tabelle 2. Wasseraufnahme und Ionentransport von Epoxidfilmen

Parameter	Epoxy Paint Film			
	A	C	B	I
Total water uptake (% in vol.)	1.8	2.1	6.4	8.1
Capillary water (% in vol.)	1.4	1.8	5.3	7.2
Into polymer water (% in vol.)	0.4	0.3	1.1	0.9
Water saturation time (hours)	288	264	454	528
Total area of conductive pathways (cm^2/1 cm^2 coating)	9×10^{-8}	9.6×10^{-8}	7×10^{-6}	5×10^{-6}
Percentage of coating surface with conductive pathways (%)	9×10^{-6}	9.6×10^{-6}	7×10^{-4}	5×10^{-4}
Time for development conductive pathways (hours)	340	360	600	780

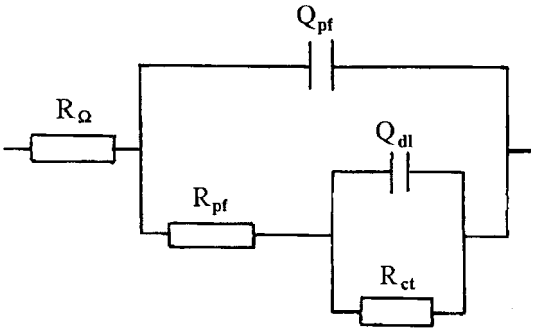

Fig. 3. Electrical equivalent circuit with two time constants
Abb. 3. Elektrischer Analogieschaltkreis mit zwei Zeitkonstanten

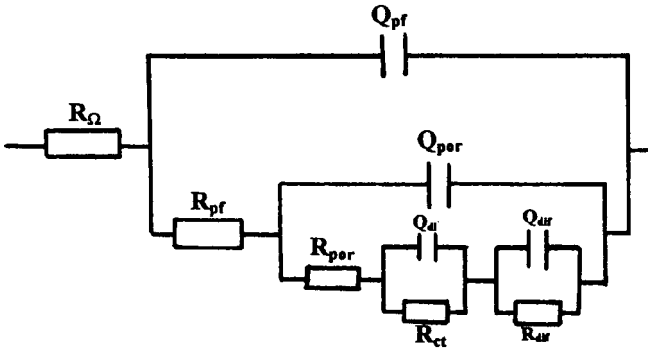

Fig. 4. Electrical equivalent circuit with four time constants
Abb. 4. Elektrischer Analogieschaltkreis mit vier Zeitkonstanten

densities of the electropainted carbon steel present an accentuate decrease in comparison with the carbon steel painted by brush and with the immersion technique (Table 3).

Comparing the dissolution current density of the painted carbon steel with that of the bare carbon steel, the porosity (P%) and the efficiency (E%) of the epoxy films tested were calculated [12]:

$$P\% = (i_p/i_b) \cdot 100, \quad (3)$$

$$E\% = [(i_b - i_p)/i_b] \cdot 100, \quad (4)$$

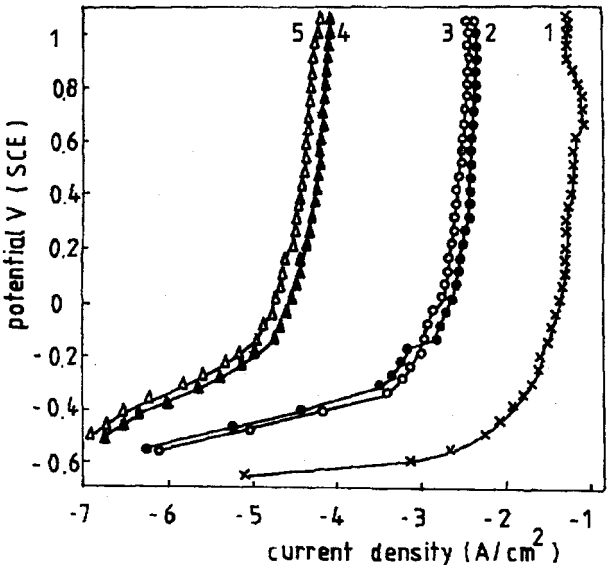

Fig. 5. Anodic polarization curves of bare (1) and epoxy painted carbon steel (2 – I; 3 – B; 4 – A; 5 – C) after 5 hours of immersion in 3 % sodium chloride solution
Abb. 5. Anodische Polarisationskurven von blankem (1) und epoxidbeschichtetem Kohlenstoffstahl (2 – I; 3 – B; 4 – A; 5 – C) nach 5 Stunden Tauchen in 3 % Natriumchloridlösung

where i_b is the dissolution current density for bare carbon steel and i_p is the dissolution current density for painted carbon steel.

It resulted a good performance of the electrodeposited films; their efficiency does not decrease in time below 99 % (Table 4). This is due to their uniformity and the porosity absence (Table 5).

Microscopical assessment confirmed the high performances of the electrodeposited films as well as the good adhesion to the carbon steel substrate during the immersion period (60 days) in 3 % sodium chloride solution.

4 Conclusion

1. By using the EIS measurements and polarization curves, the influence of the deposition techniques on the protective properties of the epoxy films has been investigated.

Table 3. Electrochemical characteristics of carbon steel after 1 and 60 days of immersion in 3 % sodium chloride solution
Tabelle 3. Elektrochemische Kennwerte von Kohlenstoffstahl nach 1 und 60 Tagen Tauchen in 3 % Natriumchloridlösung

Immersion period (days)	Painted carbon steel A	C	B	I	Bare carbon steel
			Corrosion potential (V vs. SCE)		
1	− 0.47	− 0.45	− 0.53	− 0.55	− 0.70
60	− 0.49	− 0.48	− 0.55	− 0.565	− 0.75
			Maximum dissolution current density (A/cm²)		
1	9.1×10^{-5}	7.8×10^{-5}	1.2×10^{-3}	1.7×10^{-3}	7.5×10^{-2}
60	2.7×10^{-5}	2.5×10^{-5}	1×10^{-2}	1.1×10^{-2}	9.8×10^{-2}

Table 4. Efficiency (%) of tested epoxy films
Tabelle 4. Wirkungsgrad (%) der untersuchten Epoxidfilme

Immersion period (days)	Epoxy paint film A	C	B	I
1	99.8	99.9	93.2	90.7
30	99.7	99.8	88.8	85.9
60	99.6	99.7	84.6	81.0

Table 5. Porosity (%) of tested epoxy films
Tabelle 5. Porosität (%) der untersuchten Epoxidfilme

Immersion period (days)	Epoxy paint film A	C	B	I
1	0.12	0.10	6.8	9.3
30	0.20	0.19	10.2	14.1
60	0.28	0.25	15.4	19

2. Analysis of the impedance spectra (Nyquist and Bode diagrams) has established that an electrical equivalent circuit with two time constants fits to describe the electrodeposited epoxy film/carbon steel systems in the 3 % natrium chloride solution. In case of the epoxy films applied by brush or immersion an electrical equivalent circuit with four time constants is fitted.
3. The saturation value of the water uptake in the tested epoxy films emphasizes a low water permeability of the electrodeposited films; the films deposited by brush or immersion are permeable to water, especially in the capillary phase.
4. The ionic transport is reduced in the epoxy coatings electrodeposited on carbon steel; the maximum area of the conductive pathways is lower in comparison with the epoxy films applied by brush or immersion ($\approx 50-70$ times).
5. The results of the polarization curves confirm the good performance of the electrodeposited epoxy coatings; their efficiency does not decrease in time below 99 %.
6. The deposition technique has a significant influence on the protective properties of the epoxy coatings; the films formed by electrodeposition techniques present high performances being characterized by uniformity, porosity absence, low water permeability and few conductive pathways.

5 References

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