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Surface morphology and corrosion behavior of zinc and zinc composite coatings with Cr(III) based conversion films

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The results concerning the obtaining of protective conversion films (CF) on zinc and zinc composite coatings from environmentally friendly solutions are demonstrated and commented. The newly obtained CF are based on the application of ammonium-Cr(III) salt with oxalic acid - ammonium tris (oxalato) chromate [III] –(ATOC).Depending on its concentration as well on the immersion time three types of CF can be obtained – transparent, light-green and gray-black colored which differ in their corrosion resistance and protective properties. The latter are estimated in a neutral corrosion medium of 3% NaCl containing chloride ions as corrosion activators and leading in general to appearance of local corrosion. The protective ability of CF is investigated by using of polarization resistance measurements and neutral salt spray chamber test. Their surface morphology is characterized with SEM.

The composite zinc coatings contain embedded core-shell type stabilized polymeric micelles (SPMs, based on poly-propylene oxide and poly-ethylene oxide). The influence of the SPMs incorporated in the metal matrix on the surface morphology and on the corrosion behavior of the obtained CF is commented on and discussed.

Key words: composite coatings, conversion films, corrosion, zinc, stabilized polymeric micelles

INTRODUCTION

Zinc is a metal that is not widespread in the earth crust and its content is about 0,007 wt.%. However, the electrogalvanized zinc coatings find significant application on an industrial scale for corrosion protection of different parts, components and structures of steel. Zinc coatings are relative stable at atmospheric conditions and their corrosion rate is the lowest in the pH range 7 – 12. Under the influence of environment and in the presence of moisture this metal is covered with a layer of the so called “white rust” the latter consisting of different corrosion products depending on the medium – for example zinc hydroxide chloride, zinc oxide, zinc hydroxide, zinc hydroxide sulfates. This layer has in general barrier properties and impedes the penetration of the corrosion agents deeply inside.

The electrodeposition of Zn coatings on steel substrates is applied since the zinc is a sacrificial coating due to its more negative potential compared to the iron or steel substrate. However, its safe exploitation is relative limited due to the aggressive nature of environment containing industrial pollutants which demonstrates the need of additional efforts to improve its protective properties[1-14].

One possible way is to electrodeposite zinc composite coatings the latter containing incorporated metallic, non-metallic, polymeric particles etc.,which method is often applied in the last decades in many industrial sectors[15-17]. In general, such coatings exhibit high corrosion resistance [15-19].Another method is the alloying of Zn with metals like Mn, Co, Ni etc., but the protective characteristics of these galvanic alloys also need additional improvement especially in aggressive media.

The lifetime of the galvanized steel is significantly prolonged by application of different post-treatment, for example, short-time immersion in special developed chemical solutions for obtaining of conversion films (CF) like chromite (Cr^{3+}) ones[20-22].They show lower susceptibility against aggressive corrosion solutions and can be a basis for further treatment with organic paints. Their color and thickness can be altered by variation of the solution composition, pH value, temperature, immersion time.

The aim of the present work is to obtain appropriate solutions for conversion films on zinc and composite Zn coatings, to characterize and evaluate their protective parameters in selected model corrosion medium and to estimate the surface peculiarities of these layers.

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EXPERIMENTAL

Sample preparation

The investigated samples are electrodeposited on a low carbon steel substrate with sizes 20 x 10 x 1 mm, whole surface area of 4 cm^2 and coating thickness of approximately 12 µm. Deposition conditions: current densityof 2 A/dm^2; room temperature – 22 °C; metallurgical zinc anodes.

Galvanic coatings

Zinc coatings are electrodeposited from electrolyte with a composition 150 g/l $ZnSO_4.7H_2O$, 30 g/l NH_4Cl, 30 g/l H_3BO_3, additivesAZ-1 (wetting agent) - 50 ml/l and AZ-2 (brightener) - 10 ml/l, pH value 4,5–5,0.

Composite zinc coatings

These coatings are electrodeposited from the same electrolytes and at the same electrodeposition conditions described above with an addition of 1g/l of powdered stabilized nano-sized polymeric micelles (SPMs) based on $PEO_{75}PPO_{30}PEO_{75}$ (poly-ethylene oxide – poly-propylene oxide – poly-ethylene oxide)tri-block copolymer. PPO is the hydrophobic core and the PEO is the hydrophilic shell of the SPMs.

Stabilized polymeric micelles (SPMs)

The procedure for preparation of the SPMs includes the formation of core–shell type micelles in aqueous media at 60 ºC followed by UV-induced polymerization leading to the formation of asemi-interpenetrating polymer network[23].

Solutions for chemical treatment/passivating

The additional surface treatment of Zn and composite coatings is carried out by usage of three solutions with different chemical composition based on the application of ammonium-Cr(III) salt with oxalic acid - ammonium tris (oxalato) chromate [III] –(ATOC) presented in Table 1.

The surface layer of the chromite films appeared on the metal surface after a short-time immersion of the sample is transparent-, gray-black- or light green-colored dependent on the ATOC concentration, pH value and immersion time. The latter varies from 30 seconds up to about 1 minute and the obtained CF has a thickness of about 200-300 nm. The concentration of the main components demonstrated in Table 1 is given in definite limits since the quality of the obtained films varies depending on some functional parameters like color, adhesion etc.

The obtained CF-s are ready for corrosion treatment after 24 h stay – the so called “time for ripening of the films”. During this period the latter become more hard, hydrophobic and wear-resistant.

Table 1. Composition of the passivating solutions for obtaining of CF-s

Chromite film	Components	Amounts
Transparent CF	ATOC Co^{2+} HNO_3 (50%)	5,0– 15.0 g/l 0 -1,2 g/l up to pH 1,6 – 2,0
Gray-black CF	ATOC $AgNO_3$ H_3PO_4 HNO_3 (50%)	10,0– 20,0 g/l 1,0 - 2 ,0 g/l 0 –10,0 ml/l up to pH 1,6 - 1,7
Light-green CF	ATOC $Na_2S_2O_5$ HNO_3 (50%)	10,0– 20,0 g/l 50,0 – 65,0g/l up to pH 1,7 – 2,0

In all cases the pH value of the solutions is corrected by using of different HNO_3 amounts in order to improve the adhesion of the conversion films to the zinc. The samples are also prior immersed for several seconds in a 0,2% HNO_3 solution for “activating” of the surface and thereafter rinsed with distilled water.

Corrosion medium and reproducibility

A model corrosion medium of 3% NaCl solution with pH 6.7 at ambient temperature of about 25ºC is used. The results from the electrochemical investigations are in average of 5 samples per type i.e. for each measurement 5 replicatesof Zn or its composites. Aiming at receiving of better reproducibility prior to the polarization resistance test all samples are temporized for a definite period in the model medium atconditions of open circuit potential (OCP).

Sample characterization

The sample characterization is realized by using of the following methods:

- Polarization resistance (Rp) – the measurements are carried out for a test period of about 300 hours with‘‘Corrovit’’equipment in the range of ±25 mVrelative the corrosion potential. From the Stern–Geary equation[24] it is known that higher Rp value (in Ω.cm^2) corresponds to highercorrosion resistance and to lower corrosion rate;

- Neutral salt spray (NSS) chamber – the investigations are conducted in compliance with the requirements of BDS EN ISO 9227: 2012 and ASTM B-117-03 by application of "Heraeus-Vötsch" corrosion chamber, Germany. Corrosion medium was pulverized NaCl solution at pH 6,5 – 7,2 and temperature of 35 ± 2 °C. During the testing the time for appearance of the so called "white rust" (corrosion of the coating – Zn or composite zinc with CF) or "red rust" (corrosion of the steel substrate and diffusion of iron ions as a result of the degradation process) as well as the change of the surface area damaged by the corrosion can be registered.

The evaluation of the conversion coatings is presented in estimation marks according to BDS 15258-81, method C (for cathodic coatings) in the case when the "white rust" is estimated. The degree of the surface damages(in %) is brought into relevant estimation mark. For example, mark 10 means that the coating is without damages; 8 means that the damaged surface area is between 0,25 - 0,5%; 6 – between 1 and 2%; 1 – between 32 and 64%; 0 - the coating does not fulfill its protective functions any more.

The "red rust" is estimated according to BDS 15258-81, method B (for anodic coatings) and also in estimation marks: mark 10 means without damages; 9 – damaged surface(red spots) occupy up to 1% from the sample surface; 8 – damaged surface is between 1and 2,5% from the whole surface; 6 – between 5 and 10%,; 4 – over 30%. It is assumed that bellow estimation mark 4 the substrate is so heavily damaged from the corrosion that it is practically unusable.

- Scanning electron microscopy – the surface morphology of the samples is investigated by using of INCA Energy 350unit.

All electrochemical measurements are performed in a common three-electrode cell (volume of 250 ml). The ohmic resistance of the corrosion medium is minimized by application of a Luggin-capillary. Platinum plate is taken for a counter electrode and the potentials are measured with respect to the saturated calomelelectrode (SCE).

RESULTS AND DISCUSSION

Obtaining of ammonium oxalate chromium (III) complex

The crystals of ammonium tris (oxalato) chromate are thin elongated prisms and have a monoclinic structure. Their color varies.The three oxalate groups of the complex ion are planar while the three inner oxygen atoms form octahedral surrounding with a central Cr atom – Figure 1.The crystals lose water in a dry atmosphere and absorb water in a humid air.

For obtaining of ATOC initially definite amounts of $H_2C_2O_4.2H_2O$ are mixed with $(NH_4)_2C_2O_4.H_2O$in a minimal water amount. The appearing suspension is slowly stirred with saturated solution of ammonium dichromate leading to the final product – violet crystals. The latter are dried at room temperature.

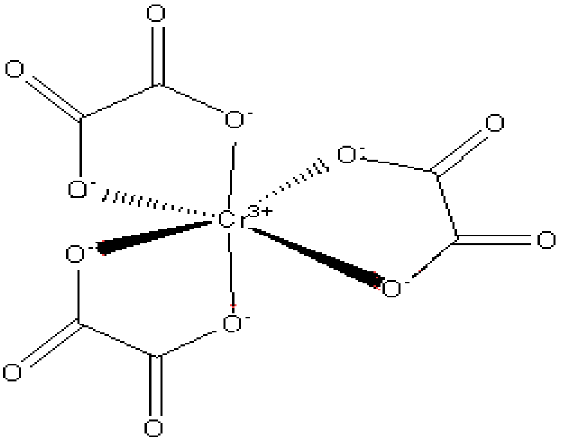


Fig. 1. Structure of ammonium tris (oxalato) chromate [III] anion.

The formal equation of the reaction can be presented as follows:

$$2(NH_4)_2C_2O_4 + (NH_4)_2Cr_2O_7 + 7\ H_2C_2O_4 \rightarrow 2(NH_4)_3[Cr(C_2O_4)_3] + 6CO_2 + 7H_2O$$

The preparation procedure must be realized very carefully in order to avoid in the possible appearance of Cr^{6+}-ions in the final product.

Polarization resistance (Rp) measurements

The data obtained from the polarization resistance measurements for zinc coatings with different CF after 300 hours of corrosion treatment in the model medium are demonstrated in Figure 2. At the beginning of the testing the samples with the transparent (TCF) and light-green CF (LGCF) show very high Rp values – curves 1 and 3, respectively. Thereafter the result for the transparent film decreases readily and it becomes the lowest one at the end of the experiment. The zinc coating with the light-green CF has relative close Rp values during the whole period. The sample with gray-black CF (GBCF) presents the lowest polarization resistance in the first 50 hours but thereafter its protective ability increases and at the end of the test period its Rp data is comparable with that of the sample with light-green CF – about 2700-2800 $\Omega.cm^2$.

The results for galvanic and composite zinc coatings (from bath containing 0,1wt% SPMs) with and without light-green CF are shown in Figure 3.

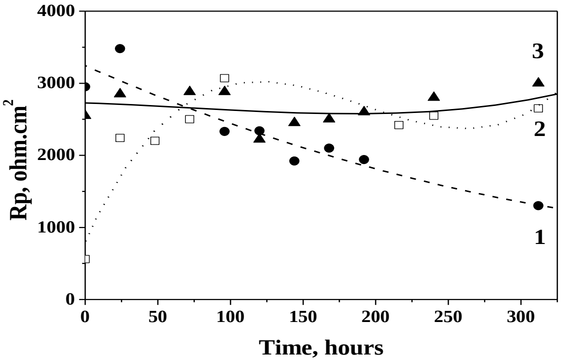


Fig. 2. Polarization resistance of zinc with different CF-s:1 – transparent; 2 – grey-black; 3 – light-green

The polarization resistance of the zinc is the lowest one with Rp values of about 1000-1500 Ω.cm^2. Contrary to this the Rp values of the composite zinc are greater and show an increasing tendency at the end of the period. These results qualitatively correlate to the data obtained for the same coating types in 5% NaCl solution although the Rp values in the latter are to a certain extent lower.

At the end of the testing both coatings with light-green CF do not have remarkable damages on the surface but the Rp values of the composite one are with about 500 Ω.cm^{2}greater than that of the non-composite zinc sample (curves 4 and 3, respectively). The reason for this can be explained with the formation of a mixed surface layer which consists of newly formed corrosion product – zinc hydroxide chloride (ZHC), registered previously by us with XRD method from one side - and of SPMs from another. As well known ZHC characterizes with a low product of solubility value (~ 10^{-14}) which has a barrier effect. In that case the hydrophobic part of the SPMs leaving in the mixed layer additionally increases the inhibiting of the penetration of the corrosion medium deeply inside.

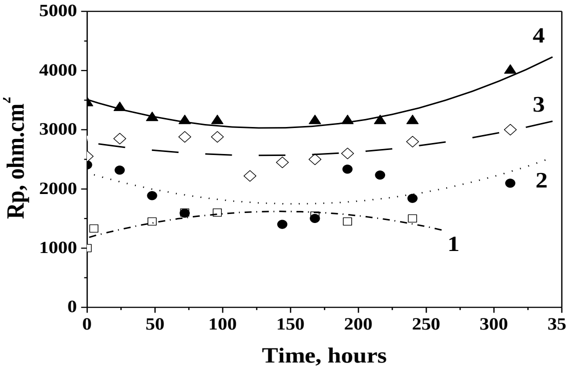


Fig. 3. Polarization resistance of zinc and composite zinc with different CF-s:1 – Zn; 2 – composite Zn;3 – Zn with light-green CF; 4 – composite Zn with light-green CF.

NSS method

The results obtained from the NSS method concerning electrodeposited non-composite zinc coatings with three different CF (transparent, gray-black and light-green) are demonstrated in Figure 4. The experimental data registered show best protective abilityof the light-green CF which does not have any damaged surface areas during the first 3 cycles. Thereafter the newly appeared zinc corrosion products begin to cover the coating and at the 4-th cycle the “white rust” occupies between 4 and 8 % of its surface. At the 9-th cycle the damaged surface of this sample is between 32 and 64%.

The other two CF-s demonstrate in general close tendencies ofdecreasing which is more strongly expressed for the transparent one the latter been almost totally covered by “white rust” after the 5-th cycle. Contrary to this, the gray-black CF lasts relative longer time – up to the 8-th cycle.

The results obtained about the appearance of “red rust” of zinc and composite zinc samples are presented in Figure 5.

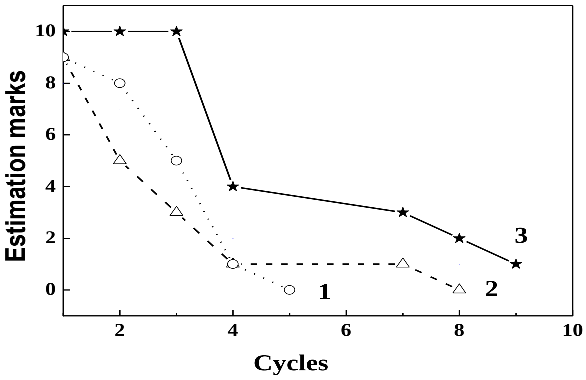


Fig. 4. NSS data about “white rust” registered on Zn with different CF-s:

1 – transparent (TCF); 2 – grey-black(GBCF); 3 – light-green(LGCF).

After 8 cycles the best results (without any damages) show both Zn (1) and composite Zn (2) with light-green CF as well as the composite zinc with transparent (4) and with gray-black CF (6). At the 15-th cycle the zinc and its composite with light-green CF are still without damages (1,2), both coatings with transparent CF (3,4) have “red rust” on about 1% of the surface and the Zn coating with gray-black CF (5) has between 10 and 30% damages on the surface. At the 22 cycle only the composite zinc with light-green CF (2) is without “red rust” on the surface which means this CF protects successfully the substrate. The galvanic Zn with LGCF (1) and the composite one with TCF (4) demonstrate estimation mark 9.

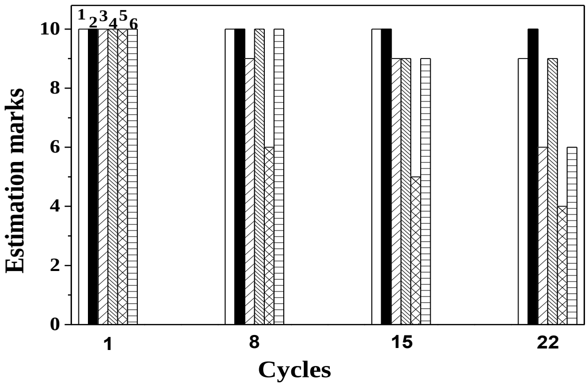
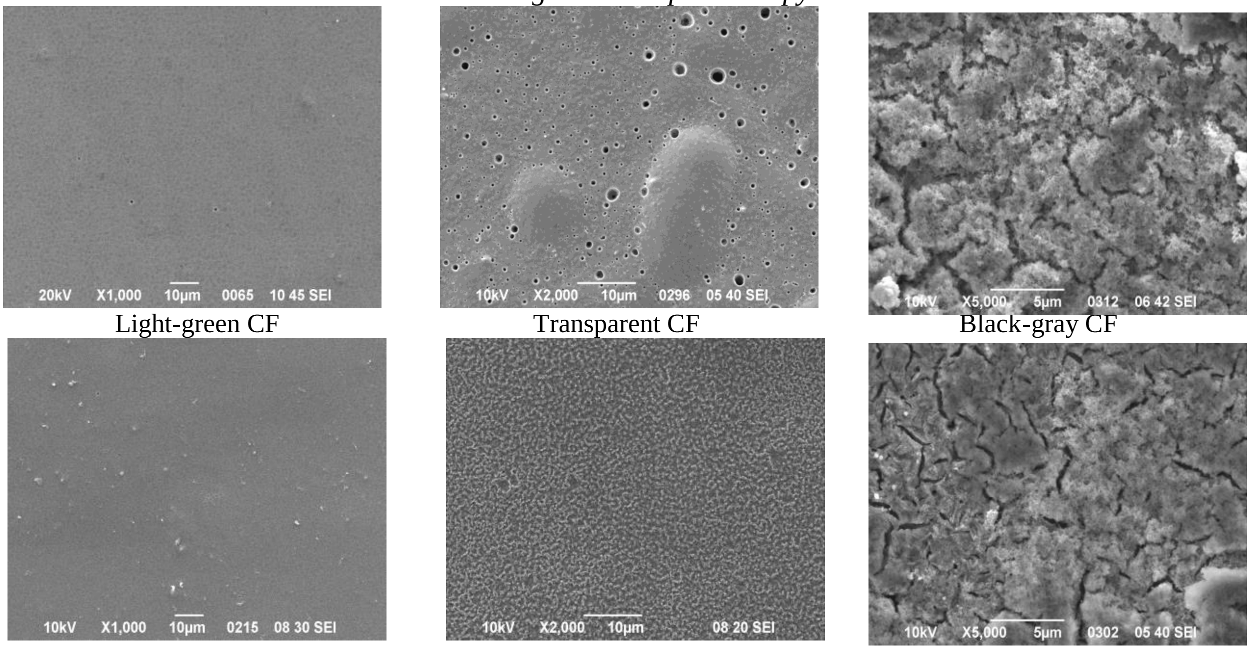


Fig. 5. NSS data about "red rust" registered on Zn and composite Zn with CF-s: 1 –Zn with LGCF; 2 – composite Zn with LGCF;3 – Zn with TCF; 4 – composite Zn with TCF;5 – Zn with GBCF; 6 – composite Zn with GBCF.

Scanning electron spectroscopy



Light-green CF Transparent CF Black-gray CF

Fig. 6. SEM images of Zn(up) and composite Zn(down) with different CF

Typical surface morphology of non-composite and composite zinc coatings are presented in Fig. 6. It is seen that the sample surfaces of the presented coatings exhibit marked differences. The surface of the non-composite with CF is more uneven and in some places also some holes or other inhomogeneity appear. Contrary to this the surface morphology of the composite zinc looks in general more even especially when light-green CF is applied.

DISCUSSION

As well known the corrosion resistance of the zinc depends on the formation of a protective layer of corrosion products with low product of solubility which distinguishes with barrier properties. When the electrodeposited coating (composite or non-composite) is chemically treated at low pH value in solutions containing for example Cr(III) based salts two parallel processes are appear - dissolution of zinc and evolution of hydrogen with following reactions presented below:

$$\text{Anodic: Zn} \rightarrow Zn^{2+} + 2e^-$$

$$\text{Cathodic: } 2H^+ + 2e^- \rightarrow H_2$$

The reduction of hydrogen ions leads to an increase of pH value in the vicinity of the Zn surface, which results in the precipitation of chromium hydroxide and zinc hydroxide from Cr(III) andZn(II) ions and formation of additional thin surface layer.

Finally, the simultaneously presence of conversion film, corrosion products as a result of the dissolution process and incorporated in the metal matrix SPMs(practically insoluble in the model corrosion medium) lead to better corrosion resistance of the chromited composites compared to the chromited non-composite zinc deposits.

CONCLUSIONS

The presented results demonstrated clearly the possible application of environmentally Cr(III) based solution for chemical treatment of composite and non-composite zinc coatings in order to increase their protective properties. Depending on the composition and on the content of the ATOC the protective action of the chromite layer can change providing protection to different extent. The presence of SPMs in the zinc matrix leads to increase of the corrosion resistance compared to the pure non-composite zinc.

It can be finally summarized that the presented coatings demonstrate high protective ability in the selected corrosion medium which could be viewed and comparable with some of the “smart” composite coatings with embedded nano-containers with inhibitor [25,26].

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ПОВЪРХНОСТНА МОРФОЛОГИЯ И КОРОЗИОННО ПОВЕДЕНИЕ НА ЦИНКОВИ И ЦИНКОВИ КОМПОЗИТНИ ПОКРИТИЯ С КОНВЕРСИОННИ ЗАЩИТНИ ФИЛМИ НА БАЗА ТРИВАЛЕНТЕН ХРОМ

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(Резюме)

Представени и коментирани са резултатитепо получаване на защитни конверсионни филми върху цинкови и цинкови композитни покритияот екологични разтвори. Новоразработените конверсионни филми съдържат амониево-хромена сол на тривалентния хром с оксалова киселина – амониево-три-оксалат-хроматенкомплекс. В зависимост от неговата концентрация и от времето на потапяне са получени три типа конверсионни филми върху цинкови и цинкови композитни покрития – прозрачен, светлозелен и сиво-черен – които се различават по своята корозионна устойчивост и защитни свойства. Последните са оценени в неутрална корозионна среда на 3% NaClс хлорни йони като корозионни активатори, които предизвикват локална корозия. Защитната способност на конверсионните филми е изследвана с методите на поляризационното съпротивление и камера „Солена мъгла". Повърхностната морфология е оценена със сканираща електронна микроскопия. Композитните цинкови покрития съдържат вградени стабилизирани полимерни мицели тип „ядро-обвивка"на база полипропилен оксид и полиетилен оксид. Дискутирано е влиянието на тези стабилизирани мицели върху повърхностната морфология и върху корозионното поведение на покритията.