

Sol-Gel derived Nanocomposite Materials for Corrosion Protection of Aluminium Alloys

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Abstract

Thermally curable nanocomposite coating materials have been developed to seal and protect copper-containing aluminium alloys against corrosion. The coating material was prepared via the sol-gel-process starting from epoxy functionalised silanes, nanoscaled silica and organic diole crosslinker. This coating matrix was additionally supplied with a varying content of cerium oxide (1-20 wt.%). The corrosion protective efficiency of these coatings was investigated on aluminium alloys Al 6013-T6 and AlCu4MgSi by salt spray test and electrochemical impedance spectroscopy (EIS), both on coatings with an artificial damage. Here, the pure coating matrix showed first corrosion attack by filiform corrosion and pitting after 10 days on Al 6013, and after 2 days on AlCu4MgSi. By additional incorporation of cerium oxide, on Al 6013 filiform corrosion and pitting could be effectively suppressed with a content of at least 20 wt.% CeO₂ (related to solid content of the coating) and no corrosion attack ($R_i=0$, $W_b=0$) was observed over a period of 60 days (1440 h) of salt spray test. For AlCu4MgSi, which has a higher copper content and thus a higher corrosion sensitivity, the addition of cerium oxide in the coating matrix provided efficient protection against filiform and pitting corrosion on the artificial damage during a salt spray exposition of 14 days (336 h). EIS studies on the damaged coatings confirmed these results.

Introduction

Aluminium and its alloys are in a widespread use as lightweight construction material in manifold application fields. For certain construction purposes in industry (e.g. automotive, aviation), copper containing aluminium alloys are of particular importance as for their special mechanical properties, e.g. dynamic strength.

Generally, aluminium is characterised by an effective self passivation caused by the spontaneous formation of a dense, protective oxide layer under air with good adhesion to the metal. This passivation layer is stable under atmospheric conditions in the pH-range of about 4.5 to 8.5, whereas it is attacked by stronger basic or acid media [1]. According to [2] coatings which hermetically seal the metal surface and through this prevent the contact to the corrosive medium would be the most favourable route to prevent corrosion. This requires completely dense inorganic coatings like enamels. The application of enamels or sputtered inorganic layers is limited for components not sensitive to high temperature treatment or simple geometries. For practical use, polymer based protection coatings in combination with passivation treatments (e.g. anodizing, chromatising, phosphatising) is widely established in the market [3]. Chromate conversion coatings show the far best results and are the standard process in the aviation industry. This is due to their ability to form a conversion layer with a strong passivation effect. In order to obtain a sufficient long term effect a primer layer is used on top of the conversion layer serving as a chromium reservoir [4, 5, 6], which then is covered with a top coat from design and mechanical protection

reasons. The mechanical protection of polymer coatings is limited due to their softness. The toxic properties of Chromium, especially the cancerogenic potential of Cr^{6+} is one of the main reasons for the search for alternative passivating agent or alternative processes [7], and a serious restriction for the use of chromium has to be anticipated by the European community. Several approaches are under investigation at present. In [5, 6, 7, 8, 9, 10, 11, 12] alternatives for chromates are investigated. It could be shown that cerium compounds are able to form conversion layers similar to these formed by chromium, but their performance has to be improved. First investigations were carried out concerning the application of sol-gel coatings as a replacement for chromate pretreatments, which showed, that an active corrosion protection can be achieved by additional incorporation of transition metal salts (e.g. CeCl_3 , $\text{Ce}(\text{NO}_3)_3$) into the coating [13]. The cerium salts have the disadvantage that anions are incorporated in the coating layer, which themselves are diffusible and therefore can act as corrosion promoters. Borates also have shown to be effective, but problems occur with the long term effects due to the high solubility of the majority of borates. Cobalt as a heavy metal is also restricted due to its toxic properties. In [11, 12], the effect of oxide conversion layers is investigated. This is an interesting concept, since no disturbing anions have to be used. The authors show that the formation of a remarkable conversion layer was observed. The corrosion inhibiting effect however is lower than with comparable chromate conversion layers.

Another approach was realized in [14, 15], where a thermodynamical approach for stabilising the interface between the metal surface and the polymer coating by formation of Al-phosphate type of layers. Since these layers are very thin, they need an efficient protection by a stable cover layer. The stabilisation of the interface also was used in the investigations described in [16, 17]. In opposition to [14, 15], the formation of silicates is used as a stabilising factor. In addition the stabilising compounds should be incorporated into the coating system to form a single layer coating system. For this reason, a sol-gel derived inorganic organic composite system was chosen [18]. It was shown, that this approach led to an efficient corrosion protection, which is improved by the high abrasion resistance of these coatings, but no passivation by diffusion of protective compounds can be obtained by these coatings. The protective effect is attributed to the low free energy of $\equiv\text{Si-O-Al}\equiv$ systems. The coatings described in [17] already show a reasonable protection which is of interest for many applications, especially due to their high abrasion resistance. With these coating materials good corrosion protection was obtained on aluminium (Al99,5) and aluminium alloys like AlMg3 and AlMgSi1. Yet, on copper containing alloys (AlCu4MgSi, Al 6013) no efficient protection against filiform corrosion could be obtained especially on coating damages, although adhesion on the metal substrate was still given.

In the present work it was investigated how far the addition of corrosion inhibitors to the systems described in [16, 17] can be used to obtain an improved corrosion protection, especially at the environment of a scribe, where the protective layer is cut down to the metal surface. The idea was to add corrosion inhibitors like CeO_2 to coating materials [18]. This again should lead to single layer systems. Oxides were chosen in order to avoid anions which, in case of sufficient diffusibility act as enhancers of local electrochemical elements. The basic system was based on epoxy group containing silanes, methyl group containing silanes, ortho ethylsilicate and bisphenoles. Due to the epoxy groups, the systems can be crosslinked by use of appropriate catalyst at elevated temperatures. By hydrolysis and condensation, a sol-gel backbone is built up besides the organic chains.

Experimental

a) Synthesis of the coating materials

Based on sol-gel derived coating materials have been described previously for corrosion protection of aluminium [16, 17, 18]. The synthesis of the coating materials was proceeded as follows:

In a first step 3-glycidioxypropyl-trimethoxysilane were pre-hydrolysed by addition of acidic water. Then a solution of bisphenole-A diluted in a 1/1-mixture by weight of ethanole/ethyl-isopropylether was added. Besides tetraethoxysilane and methyl-trimethoxysilane were mixed and hydrolysed by addition of a colloidal aqueous solution of SiO_2 and additional distilled water (pre-hydrolysis). This mixture was stirred for 1 hour at ambient temperature and then added to the above mixture of GPTS and bisphenole-A. Finally the synthesis was finished by addition of amino-base as initiator for the organic crosslinking reaction.

The synthesis of CeO_2 containing systems is described elsewhere [19, 18].

Cerium oxide was then added as colloidal nanoparticulate solution (20 wt.%) in acetic acid. The content of CeO_2 was varied between 1-20 wt.% related to the solid content of the coating matrix. In the following experiments, 1, 5, 10 and 20 wt.% of CeO_2 were adjusted. This mixture was stirred for 20 minutes at ambient temperature before the subsequent addition of the dissolved bisphenole-A. Afterwards, the synthesis was continued as described above.

b) Preparation of substrates and fabrication of coatings

Pre-cleaning and degreasing of the aluminium samples (alloys Al 6013 and AlCu4MgSi) was carried out at 60°C for 3 minutes in an ultrasonic bath using an aqueous commercial alkaline cleaning agent (3 wt.% of P3 Almeco 18[®] in deionized water). Immediately afterwards the samples were rinsed with running deionised water for 1 minute by slightly brushing and then dried for 10 minutes at 80°C in an electric oven.

The coating material was applied as prepared, with a solid content in the range of 44 wt.-% for the matrix system and 42-43,5 wt.-% for the systems containing additional cerium oxide colloidal solution. The coatings were applied on degreased aluminium substrates (10x15 cm) by spin coating at 400-600 rev./min. After coating, the wet films were left to dry for 10 min at ambient temperature and then cured in an electric oven for 2 h at 130°C.

c) Characterisation

The coating thickness was determined by eddy current method (Fischer-Permascope[®] D21 1D, Helmut Fischer GmbH + Co.). Abrasion resistance was measured on a Taber-Abraser test device of Taber Industries[®] (CS 10F wheels; 5.4 N) and quantified by weight loss after 1000 cycles. The viscosity of the coating materials was measured in a rotation viscometer (Haake, Germany) with a cylindrical test assembly. For microstructure analysis a high resolution scanning electron microscope (FEG, type 6400F, JOEL Inc.) was used. Corrosion resistance was tested in neutral salt spray climate (SS) corresponding to DIN 50021 on 10x15 cm plates and by impedance measurement (Zahner IM6 from Zahner[®] Messtechnik) during immersion in 0.1 M NaCl electrolyte solution, followed by visual and microscopic observation. Impedance measurements were carried out with an electrochemical cell consisting of a three electrode device with a 10 cm² exposed working area (coated plate), a SCE ($\text{Hg/HgCl}_2/\text{KCl}$) reference electrode and a platinated platinum counter electrode. The measurement was

performed at a constant amplitude of 20 mV in the frequency range $10^{-2} \leq f \leq 10^5$ Hz at a coated plate with an artificial scribe of min. 0.2 mm in width slightly beyond the pitting potential of the corresponding alloy.

Results and Discussion

The corrosion protection of copper containing aluminium alloys is of special interest, since these materials are important for light weight constructions because of their special mechanical properties (e.g. high dynamic strength) compared to other aluminium alloys. But, since aluminium and copper act as anodic and cathodic components which are in constant contact in the material, these alloys are especially sensitive to corrosion attack, since copper as a metal more noble than aluminium forms a galvanic cell in presence of an electrolyte. The requirement for a sufficient corrosion protection in addition to a barrier function and good adhesion in order to prevent the access of electrolyte to the metal surface, an active protecting component is desirable to provide an additional protection in the case of coating damage. Therefore an optimisation of the coating material was carried out, focusing on the incorporation of an active inhibiting agent. As test material, two aluminium alloys of practical use with different copper content, Al 6013-T6 and AlCu4MgSi, were chosen.

To obtain additional protection on these copper-containing alloys, e.g. at coating damages, Ce-compounds were taken into consideration. For the cerium compound a sufficient diffusibility of Ce^{4+} is indispensable for the transport to a surface damage. On the other side, no diffusible anions should be present in this process. CeO_2 was considered to have a to low solubility rate [20], and is anion-free. After the addition of CeO_2 the sol changed into a slightly translucent yellowish appearance. Thus a stable sol was obtained with a viscosity in the range of 9 to 11 mPa*s. In Fig. 1 a representative HTEM-micrograph of a coating sol containing 20 wt.% of CeO_2 is shown. The agglomeration shown this micrograph is considered to be responsible for the cloudy appearance of the sol but this should disturb the envisaged effect.

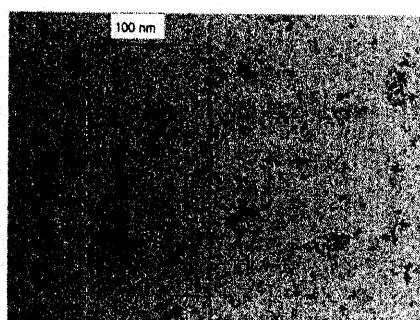


Fig. 1: HTEM-micrograph of the coating sol containing 20 wt.% of CeO_2 related to the solid content of the coating material.

As already mentioned, the surface properties such as abrasion resistance are of high importance for the practical use of coating materials. As shown elsewhere [18,19], these properties strongly depend on the thermal treatment and the densification parameters of the coating. Corresponding to previous investigations of the curing procedure by test of mechanical resistance a curing temperature of 130°C with a curing time of 2 h was found to be optimum [17]. Based on these results, a curing of 2 h at 130°C was employed on all coating materials in the following experiments, too. The abrasion resistance obtained for the thus cured coating materials was determined

by taber abrasion test (CS10F wheels, 5.4N) with a weight loss of 1.5-1.6 mg/1000 cycles (for comparison: polyvinylidenefluoride coatings on aluminium show 20-25 mg/1000 cycles).

The coating thickness applied in the following investigations was adjusted to be about 10 μm . This value is low compared to existing organic polymer coatings. The abrasion resistance of 1.5 is similar to layers obtained through anodizing aluminium. These layers, however, in general are thinner (3-4 μm). So, the 10 μm abrasion resistance coatings are considered to be a good compromise between anodized and organic polymeric layers. In view of the possible application as a primer system, the coating thickness should also not exceed 10 μm . Coatings have been fabricated on Al 6013-T6 by spin coating after thoroughly cleaning the surfaces as shown in the experimental, and cured at 130°C for two hours.

Examination of the cured coating material, applied on Al 6013-T6 by spin coating, with 20 wt.% of CeO_2 , by TEM showed, that the CeO_2 is very well dispersed in the coating, as shown in Fig. 2.

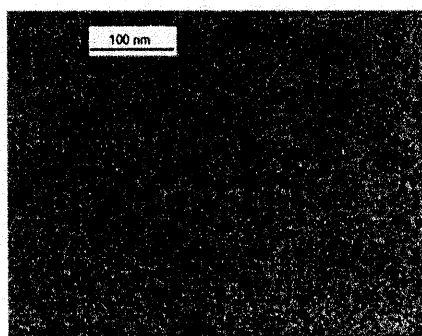


Fig 2: TEM-micrograph of the nanocomposite coating, containing 20 wt.% of CeO_2 related to the solid content of the coating material, thermally cured at $T=130^\circ\text{C}$ for 2 h on Al 6013-T6.

For the investigation of the active corrosion protective potential of CeO_2 dispersed in the sol-gel composite matrix filiform and pitting corrosion in salt spray atmosphere was observed. For this, substrates (10x15 cm) of aluminium alloys Al 6013-T6 and AlCu4MgSi were coated by spin coating and cured as described above. The coating thickness was determined to be in all cases $10\ \mu\text{m} \pm 0.5\ \mu\text{m}$. Corrosion testing was carried out after making an artificial scribe of about 0.2 mm in width in salt spray test. The coatings were checked regularly concerning infiltration and wash out (white residues) at the scribe and surface corrosion by pitting or filiform corrosion. For reasons of comparison, the CeO_2 -free coating matrix was tested on both aluminium alloys (Al 6013-T6 and AlCu4MgSi). CeO_2 concentrations of 1 and 20 wt.% were used.

Results obtained on Al 6013-Alloy

The aluminium alloy Al 6013 has a copper content of about 0.8 %. For this reasons a higher corrosion sensitivity can be anticipated compared to pure aluminium. The results of corrosion testing of the coated and uncoated alloy in salt spray climate after various times are shown in Fig. 3. The salt spray test was carried out for 240 and 1440 hrs.

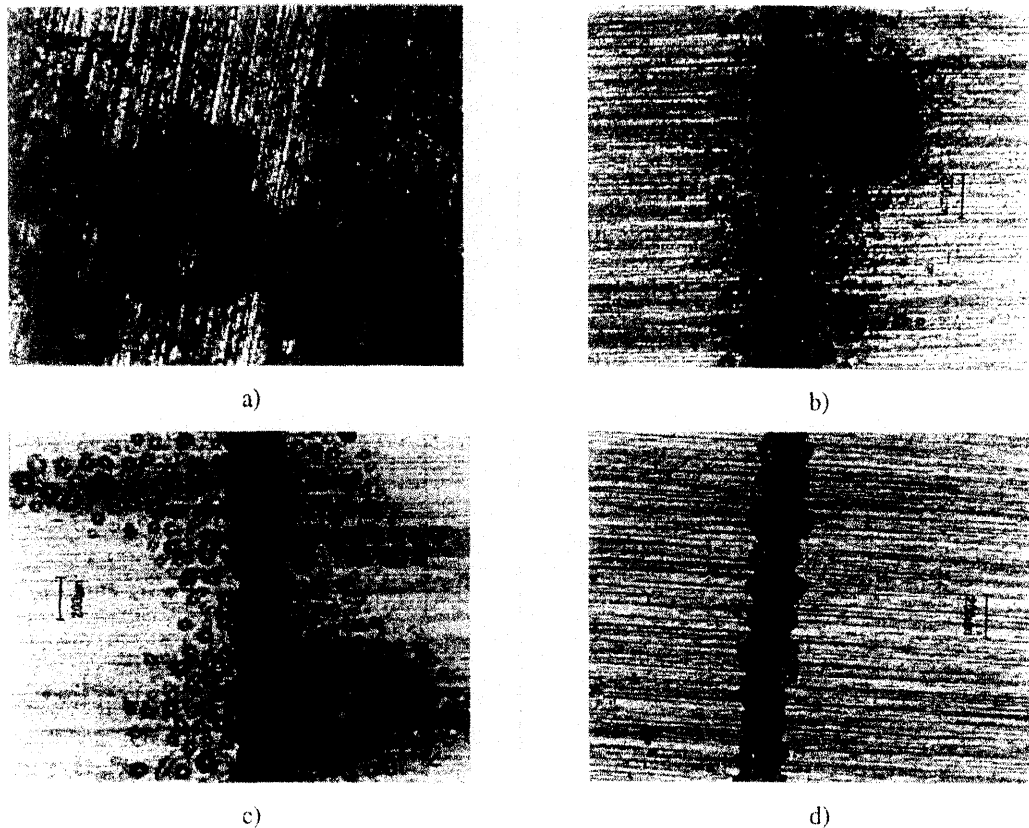


Fig. 3: Microscopic photographs of Al 6013-T6 substrates after salt spray test with different test periods: a) 240 h, uncoated, b) 240 h, CeO₂-free coating c) 1440 h, CeO₂-free coating d) 1440 h, with coating containing 20 wt.% CeO₂; the coating thickness was 10 μm.

The corrosion attack on the uncoated Al 6013-T6 plate is expectedly heavy, characterised by strong pitting corrosion after 240 hrs of exposure. The salt spray test results of the CeO₂-free coating also indicates a fast corrosion attack. After 240 hrs of exposure plates coated with these coatings already showed the first fine lines of filiform corrosion and starting pitting corrosion localised in the surroundings of the test scribe, whereas the undamaged surface was still intact (Fig. 3b). The corrosion attack increases within 1440 hrs of exposure, after which additionally to the pitting corrosion an infiltration of the coating close to the test scribe is observed (Fig. 3c). For a coating material containing 1 wt.% of CeO₂ corrosion attack by filiform corrosion in the scribe surroundings first appears after 360 hrs, whilst a coating material with 5 wt.% CeO₂ shows first pitting close to the artificial scribe only after 360 hrs, but still no filiform corrosion was observed. In contrast to these findings, coatings containing 10 wt.% or 20 wt.% of CeO₂ did not show any corrosion and no delamination ($W_b=0$) in the investigated interval of 1440 hrs (Fig. 3d). In Fig. 3, the W_b values as a function of the CeO₂ content is shown.

These results suggest, that CeO₂ plays an active role to inhibit corrosion even at coating damages and thus suppresses the formation of filiform and pitting corrosion and, later, also delamination of the coating in the corroded area. The optimum content of CeO₂ for Al 6013-T6, seems to be in the range of 10-20 wt.%. The results show that the CeO₂ actually shows a passivation effect by an assumed diffusion of Ce⁴⁺ to the interface. Since diffusion of Ce⁴⁺ does not appear in organic polymers, the inorganic organic matrix seems to be enhancing this process. To clear this, more investigations have to be carried out.

Results obtained for AlCu4MgSi-Alloy

Copper content for AlCu4MgSi is about 4 %. The same experimental procedure was carried out with AlCu4MgSi . Due to the higher sensibility of this alloy, the corrosion attack was expected to be heavier. The results are shown in Fig. 4.

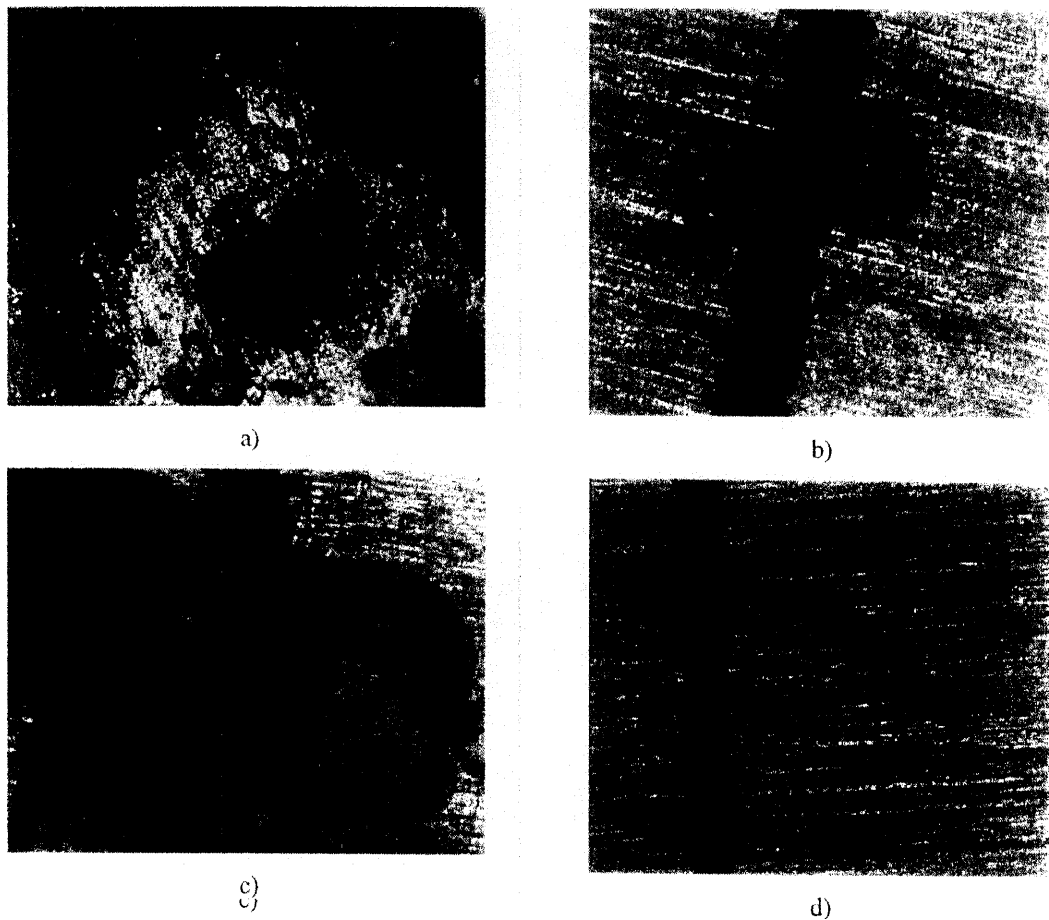


Fig. 4: Microscopic photographs of AlCu4MgSi-substrates after SS-test with different test periods: a) 48 h, uncoated, b) 48 h, with pure coating matrix c) 336 h, with pure coating matrix d) 336 h, with coating containing 20 wt.% CeO₂. The coating thickness was about 10 μm.

The tests showed, that the uncoated metal is strongly attacked by corrosion already after 48 hrs of salt spray exposure (Fig. 4a). The CeO₂-free coating showed first pitting starting from the artificial scribe already after 48 hrs (Fig. 4b), which increased with increasing test time. After 240 hrs besides pitting heavy filiform corrosion appeared (Fig. 4c). In contrast to that, the coating containing 1 wt.% and 5 wt.% of CeO₂ showed first pitting only after 3-4 days. The coating containing 10 wt.% of CeO₂ could be observed first corrosion attacked after 6 days of salt spray test by pitting and slight filiform corrosion. The coating with a content of 20 wt.% of CeO₂ was not attacked by pitting or filiform corrosion in the test period and no wash out at the low end of the scribe could be observed (Fig. 4d). First damage by slight pitting in the artificial scribe appeared visibly after 480 hrs of salt spray test. For this reasons the tests with 1440 hrs were not carried out. At this time, still no surface attack could be observed.

Resuming it can be said, that these first results indicate, that the corrosion protective performance of the hybrid sol-gel coating on both copper containing aluminium alloys could be significantly increased by the incorporation of CeO_2 . The inhibiting activity was especially effective at the interface between the coating and the metal surface at the scribe area, where filiform corrosion as well as pitting corrosion and therefore the delamination of the coating could be effectively suppressed. The effect was stronger on the aluminium alloy Al 6013-T6 with the lower copper content, where no corrosive attack appeared within the testing period of 1440 hrs was observed. These results were furthermore confirmed by impedance measurements, as depicted for the alloy Al 6013-T6 in Fig. 5 and for AlCu4MgSi in Fig. 6. All plates were measured with an artificial scribe of 0.2 mm width with an exposed working electrode area of 10 cm².

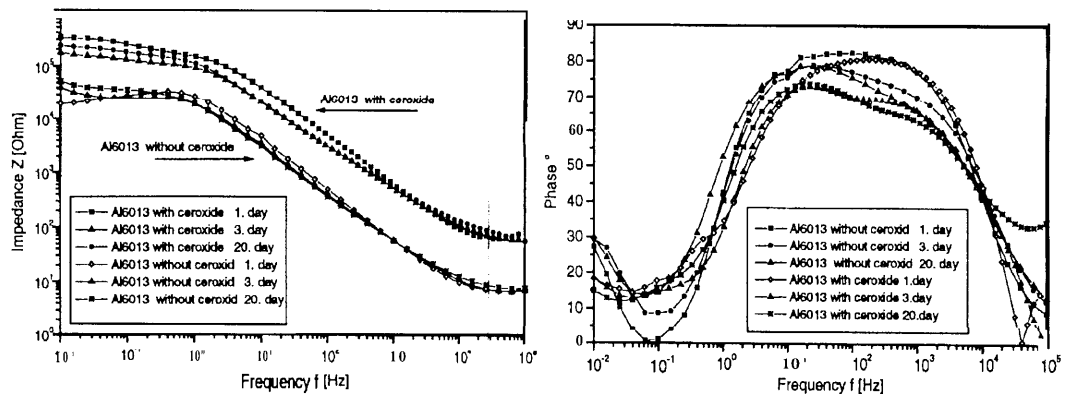


Fig. 5: Bode plots for aluminium Al 6013-T6 with coating containing 20 wt.% of CeO_2 (upper curves) in 0.1 M NaCl solution. The measurement was carried out at an artificial scribe of 0,2 mm in width under applied pitting potential.

The impedance spectra of coated alloy Al 6013-T6 show a capacitive behaviour for the CeO_2 -free and the CeO_2 coating materials with practically no change over a period of 20 days (Fig. 5, left). On the other hand, the results of the impedance measurements show a clear difference between the pure nanocomposite coating behaviour and the performance of the coating containing 20 wt.% cerium oxide. Thus, for the CeO_2 -free coating, already on the first day of measurement, a polarisation resistance of only $4.5 \cdot 10^4 \Omega$ was found, which nearly corresponds to the value of the pure aluminium alloy Al 6013-T6. The result might indicate, that no additional inhibiting effect seems to be provided by this coating type on the test scribe. In contrast to this, it could be observed in the salt spray test that the uncoated alloy shows strong corrosion after 240 hrs whereas for the alloy with CeO_2 -free coating significantly less corrosion could be detected in the same test. From this result it can be concluded that the CeO_2 -free coating has a corrosion protecting effect. An explanation for the observed difference could be as follows: At the beginning of the experiment the uncoated aluminium alloy has a passivating alumina layer on top of the surface which gave the same impedance value compared to the alloy with CeO_2 -free coating on the first day of measurement because of probably some diffusibility in the CeO_2 -free coating. This alumina layer is destroyed during the following corrosion test whereas the alloy with the protective CeO_2 -free layer remains more stable (only pits after 15-20 days) because of the formation of thermodynamically stable $\equiv\text{Si-O-Al}\equiv$ bonds built up at the interface between coating and alloy. Yet, for the cerium oxide containing coating on Al 6013-T6

(20 wt.% CeO_2 related to the solid content of the coating matrix) a distinctly higher polarisation resistance of about $2.5 \cdot 10^5$ to $3 \cdot 10^5 \Omega$ could be detected, which nearly remained constant for the whole measuring period of 20 days. This indicates, that the coating provides an additional protective activity even at the scribed surface, thus hindering a corrosion attack on the bare scribe, on which no visible corrosion attack by pitting was visible during the whole test period of 20 days. The curves of the phases (Fig. 5, right) show a wide maximum in middle frequency range, which can be related to contact of electrolyte to the aluminium alloy in the artificial damage. The appearance of only one maximum in the curves indicate that there is no corrosive attack. The differences between CeO_2 -free and CeO_2 coating materials can not be detected in these curves.

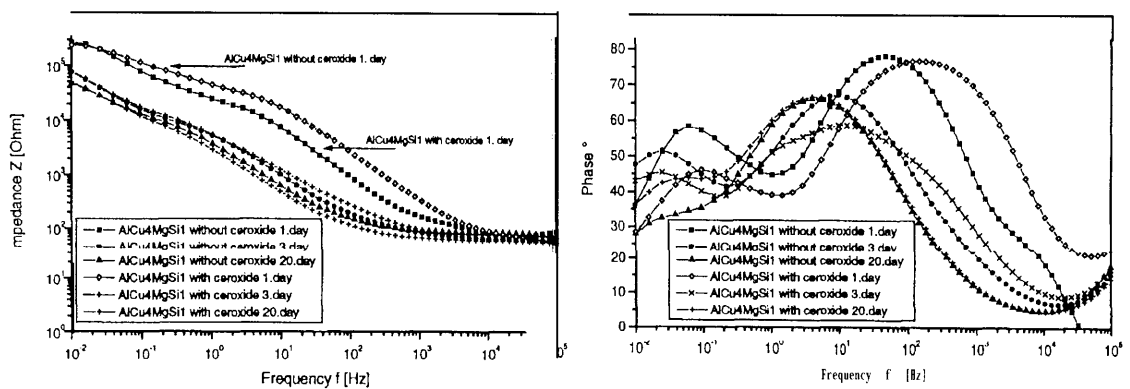


Fig. 6: Bode plots for aluminium AlCu4MgSi with coating without CeO_2 and with coating containing 20 wt.% of CeO_2 in 0.1 M NaCl solution. The measurement was carried out at an artificial scribe of 0,2 mm in width under applied pitting potential.

The impedance spectra of the coated alloy AlCu4MgSi (Fig. 6, left) show no significant differences between the CeO_2 -free and the CeO_2 coating materials. The course of the curves indicates the beginning of corrosion. The curves of the phases (Fig. 6, right) show the appearance of a second maximum in the lower frequency range, which can be related to the beginning of local corrosion of the alloy. Due to the higher sensibility of this alloy, the corrosion attack starts earlier. The results of the EIS confirm principally to those of the salt spray tests. Higher Cu content in the alloy leads to earlier appearance of corrosion attack. The results also show that EIS can be used as method more sensible for corrosion detection especially when the behaviour is followed by impedance and phase degree.

Summary and Conclusion

An inorganic-organic nanocomposite coating material has been supplied with CeO_2 as corrosion inhibitor, which could be homogeneously dispersed in the coating matrix, thus resulting in a homogeneous, transparent single layer coating after application and curing on aluminium substrates.

The investigations of the corrosion resistance show, that by incorporation of CeO_2 , the corrosion protective effect of the coating under salt spray conditions on copper containing aluminium alloys could be significantly increased. Especially effective suppression of filiform corrosion and thus increasing the surface corrosion protection could be observed. On both copper containing alloys, Al 6013-T6 and AlCu4MgSi , 20 wt.% of cerium oxide in the

coating provided best protection. These first results point out, that cerium oxide incorporated in a coating system can provide an active corrosion inhibiting effect on aluminium alloys. Thus, cerium oxide containing coatings could become a potential replacement for the toxic and hazardous chromate inhibitors. In this direction further investigations based on these first promising results are foreseen, focusing on the action of cerium oxide as an active corrosion inhibitor and also on the role of the inorganic organic matrix in enhancing the diffusion of the Ce^{4+} . The following questions will be of special importance:

- Composition and structure of the metal-coating interface in the case of inhibitor containing coating
- Distribution of cerium oxide in the metal-coating interface, investigation of possible secondary phases
- Clarification of mechanism of corrosion inhibition activity of nanoscaled cerium oxide in a damaged coating

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