

# A new corrosion protection coating system for pressure-cast aluminium automotive parts

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A simple to employ corrosion protecting coating based on sol-gel derived new nanocomposites for Al alloys has been developed. This composite coating reacts to the Al surface by formation of a thermodynamically stabilized interface. Moreover, for pressure cast Al, the coating process can be used for sealing the pores at the same time. © 1998 Published by Elsevier Science Ltd. All rights reserved.

**Keywords:** corrosion protecting coating; sol-gel derived nanocomposites; al alloys

## Introduction

Corrosion, in general, is an undesired reaction and affects various materials, such as metals, glasses or ceramics. Whereas in metals, corrosion is mainly combined with an oxidation reaction, on glasses corrosion takes the form of a dissolution of the glassy network. The initial reaction in this case, in general, is an ion exchange where alkaline ions are exchanged against protons<sup>1</sup>. In ceramics, the corrosion mainly takes place in the grain boundaries as a first step followed by a degradation of the microstructure dissolution of the ceramic materials, especially in hotmelts. A simple way for preventing any corrosion would be a hermetic sealing of the surface by an appropriate coating with materials completely stable against diffusion of corrosive molecules, such as water, oxygen, acids or bases or a combination of these. Only these properties can be provided by purely inorganic materials like metals, glasses or ceramics or a combination of them. However, two difficulties appear. First, these coatings have to be brought onto the surface in a pinhole-free way, for example, by liquid metal coating (such as zinc plating) or dip coating into glass melts. Coatings grown upon the surface by electrochemical processes or anodizing, in general, do not have completely pinhole-free surfaces. On the other hand, the cited coating techniques cannot be employed in many cases due to the temperature sensitivity of the substrate or the properties of the coating, for example, the brittleness in the case of ceramic or glass coatings.

So the idea came up to combine inorganic and organic properties, as shown by Dow Corning in 1992<sup>2</sup>, the principle of which is shown in *Figure 1*.

The results show that aluminum does not show any corrosion even after 1000 h of salt spray test but as clearly can be seen from *Figure 1*, this process is costly

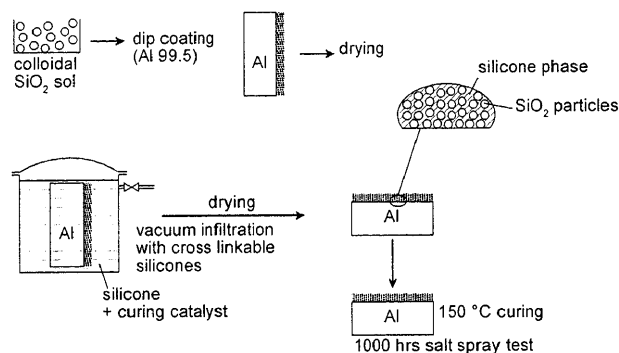


Figure 1 Schematics of a nanocomposite coating on aluminum

since it provides a series of different steps. So it never had a breakthrough on the market, but the basic idea to use inorganic-organic composite materials to combine both diffusion barrier and, as a result from the inorganic network, the required flexibility, for example, on coatings on metals, is worthy of investigation. In this paper, the development on an inorganic-organic composite materials for corrosion protection of aluminium alloy surfaces is shown. Inorganic-organic composite materials, meanwhile, have an interesting history and are employed in many other areas<sup>3-5</sup>.

## Basic principle and thermodynamical consideration

The synthesis of materials by the so-called sol-gel process<sup>6</sup> opens up the possibility of the fabrication of inorganic-organic polymers, which are multifunctional materials. This allows the incorporation of different functions, which is of interest for making tailored materials for protective coatings. The basic principles of such structures are shown in *Figure 2*.

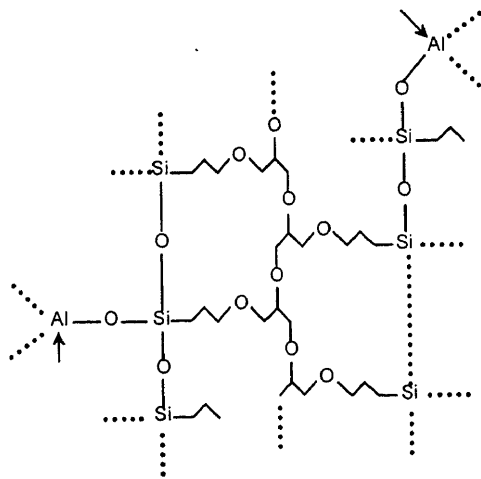


Figure 2 Structural principles of inorganic-organic composite materials

Due to the fact that the described network in Figure 2 can be modified by additional components, for example, components reactive to aluminum surfaces in the form of SiOH or SiOR groups, which then form stable bonds to the surface, these composite systems can be used as an approach for corrosion protection. It is postulated that the formation of Si-O-Al links should be thermodynamically favored. In Table 1, data for the free energy for several Si-O-Al containing compounds are given.

The interesting fact is that the alumina silica mixed compounds altogether show much lower free energy values than the boehmite, which is one first step of the oxidation of an aluminum surface in the presence of moisture. This leads to the concept that if it is possible to form alumina/SiO<sub>2</sub> interfaces, they should be stable against corrosion.

The resulting concept of this approach is shown in Figure 3.

The dashed areas represent nanoparticles. These nanoparticles seem to be suitable to be incorporated into the inorganic-organic backbone in order to provide mechanical stability, as already shown elsewhere<sup>7</sup>. In combination with the thermodynamical stabilization of the surface, another thermodynamical effect also can be taken into consideration, which is closely linked to the structure of these inorganic-organic composite materials. As depicted in Figure 4, if organic polymers only are used as a coating, in the case that water is penetrating into the interface and oxidizes the

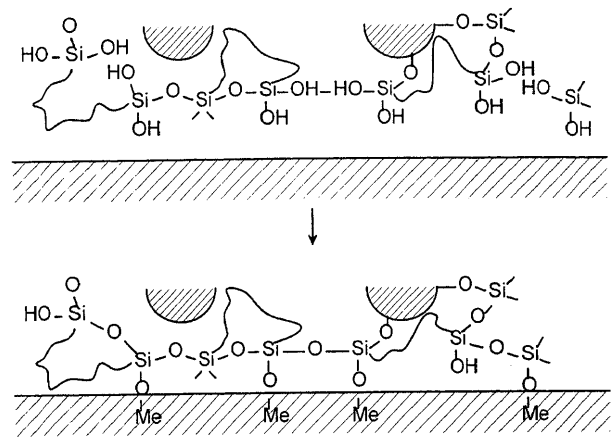


Figure 3 Concept of the interface design for corrosion-protective coatings on aluminium

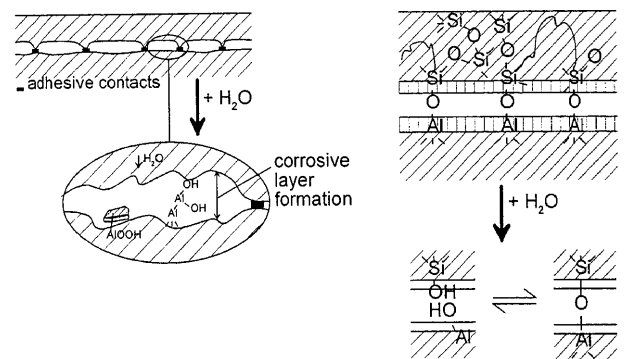
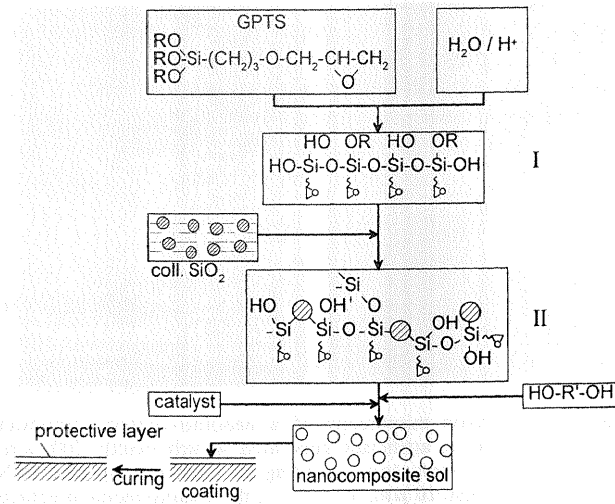


Figure 4 Differences in the interfacial behavior of a 'flexible' metal-to-polymer interface and an 'immobilized' composite interface

aluminium, due to the flexibility of the organic coating, an interfacial corrosion layer can be formed in the voids created by the organic network flexibility. In opposition to this (right side of the drawing), if an inorganic backbone is formed, which creates much more inflexibility, even in the case that one of the Si-O-Al bonds is hydrolysed, the 'corrosion product', in this case OH groups, cannot be transported away and according to the law of mass actions an equilibrium is produced between a hydrolyzed and an unhydrolysed bond. So the interface is 'immobilized' and the corrosion cannot propagate.

Table 1 Free energy values of several alumina and silica compounds

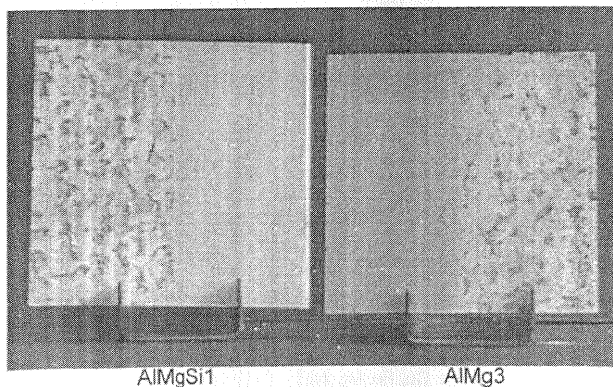
Thermodynamics Gibbs free energy of alumina and silica modifications and alumo-silicates		
Type		213Δ <sub>Gf</sub> (kJ mol <sup>-1</sup> )
Mullite	3Al <sub>2</sub> O <sub>3</sub> · 2SiO <sub>2</sub>	-6901
Sillimanite	Al <sub>2</sub> O <sub>3</sub> · SiO <sub>2</sub>	-2616
Cormierite	α-Al <sub>2</sub> O <sub>3</sub>	-1675
Boehmite	AlOOH	-985
Quartz	SiO <sub>2</sub>	-910
AlOH + HOAl → Al-O-Al + H <sub>2</sub> O     ΔH = -48 kJ mol <sup>-1</sup>		
AlOH + HOSi → Al-O-Si + H <sub>2</sub> O     ΔH = -462 kJ mol <sup>-1</sup>		



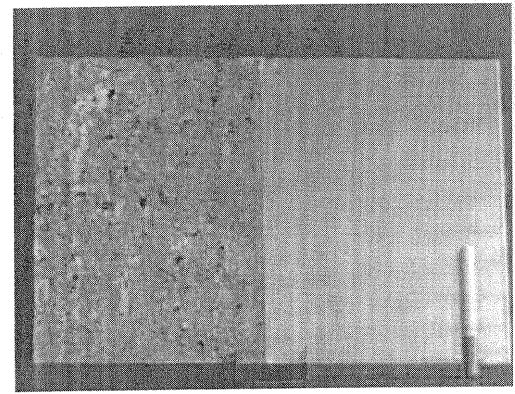
**Figure 5** Schematics of the synthesis of a nanocomposite sol based upon GPTS, nano-scaled SiO<sub>2</sub> particles and sols, application process of these liquid sols onto metal surfaces and curing to protective layers

### Experimental

The schematics of the experimental is shown in *Figure 5*. At first, the pre-hydrolyzation of 3-glycidyloxypropyltrimethoxysilane (GPTS) was started by adding acidic water (1–3 mol of water for every mol of silane). This mixture was stirred for 2–24 h at room temperature. A colloidal solution of SiO<sub>2</sub> particles (5–15 wt.% SiO<sub>2</sub> related to the amount of silane) either in 2-propanole or in water was added to the solution. After 10–60 min of continued stirring, a solution of a diolic compound (e.g. bisphenol-A, bisphenol-S) either in ethanol or in ethyl-isopropyl-ether was added. The molar ratios of diol: GPTS were varied between 20–40 mol%. Finally the synthesis was finished by addition of an alkaline catalyst (e.g. *N*-methylimidazole; 2–5 wt.% related to the amount of GPTS) as initiator for the organic crosslinking reaction. Pre-cleaning, i.e. degreasing, of the aluminum samples was carried out at 60°C for 2 min in an ultrasonic bath using a commercially available alkaline solution (0.8 wt.% of Metax R-1570 in deionized water). Immediately afterwards the samples



**Figure 6** Comparison of uncoated and nanomer-coated aluminum alloys after 120 h CASS test (salt spray, copper chloride, acetic acid, pH 3); AlMgSi1 (left) is half-coated on the right; AlMg3 (right) is half-coated on the left; coating thickness: 15 μm; corrosion can only be noticed in the uncoated area

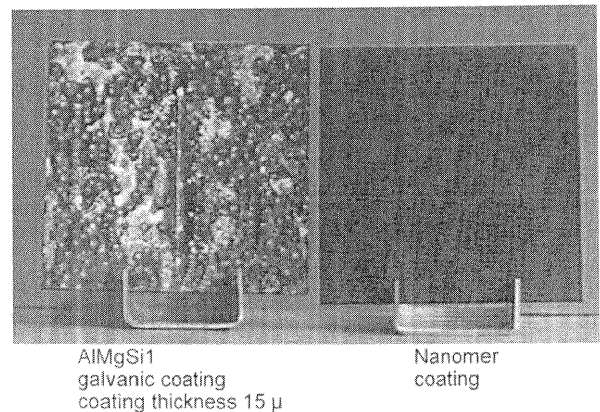


**Figure 7** Comparison of uncoated (left) and nanomer-coated (right) Al 99.5 after 120 h CASS test (salt spray, copper chloride, acetic acid, pH 3); film thickness: 12 μm; to demonstrate the proportion, a cigarette was placed on the right

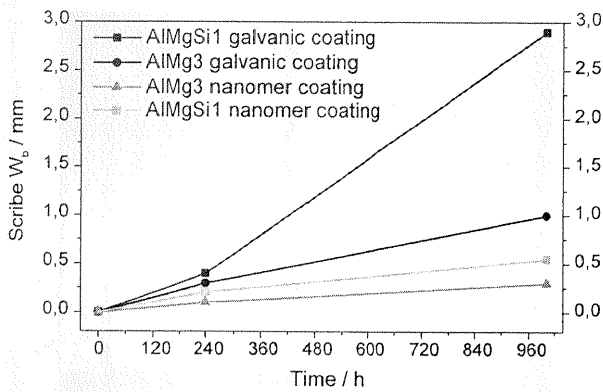
were rinsed with deionized water for 1 min and dried at 80°C for 10 min in an electric oven. The process is carried out in a way that an organoalkoxysilane (GPTS) is reacted to an oligomeric compound (I) and filled with SiO<sub>2</sub> nanoparticles to obtain a ligand nanocomposite (II). A catalyst to crosslink the epoxy grouping is added, and, after coating, the crosslinking process takes place at  $T = 100\text{--}150^\circ\text{C}$ .

### Results

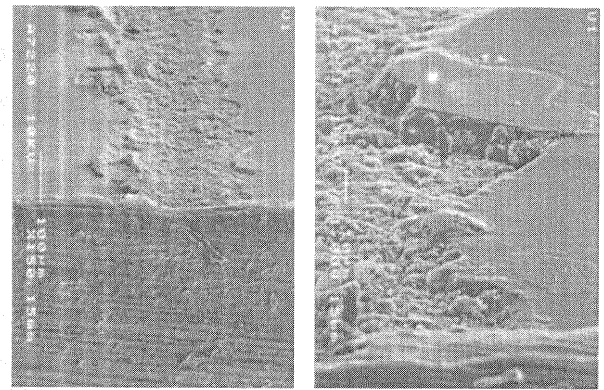
Systems prepared according to the experimental procedure can be as so-called nanocomposite sols and used for coating techniques on aluminum. The coating thicknesses used in these cases are in the range of several μm (5–10 μm). This is a very thin coating compared to organic polymer coating, but due to the high scratch-resistance, the mechanical stability of these coatings is in the range of the best numbers known from anodizing processes, and it is expected that, due to the thermodynamical stabilization of the interface, even this thin type of coatings provides sufficient corrosion protection. After coating and curing, the effect of the coatings has been tested by CASS tests. In *Figure 6*, two



**Figure 8** Comparison of commercial protective coatings (left: galvanic coating; coating thickness: 15 μm) and nanomer-coatings (right: film thickness: 10 μm) on AlMgSi1 after 240 h CASS test (salt spray, copper chloride, acetic acid, pH 3)



**Figure 9** Comparison of commercial protective coatings (galvanic coatings; thickness: 15  $\mu\text{m}$ ) and nanomer-coatings (thickness: 10  $\mu\text{m}$ ) on different aluminum alloys (AlMgSi1, AlMg3) concerning scribe expansion versus time after salt spray test according to German standard DIN 50021



**Figure 10** Electron microscopy of a nanomer-coated aluminum sheet (Al 99.5) at an artificially generated scratch (width: 200  $\mu\text{m}$ ) after 1000 h salt spray test according to German standard DIN 50021; film thickness: 10  $\mu\text{m}$ ; no scribe at the coating-metal-interface can be noticed

different aluminum alloys are compared after 120 h CASS test.

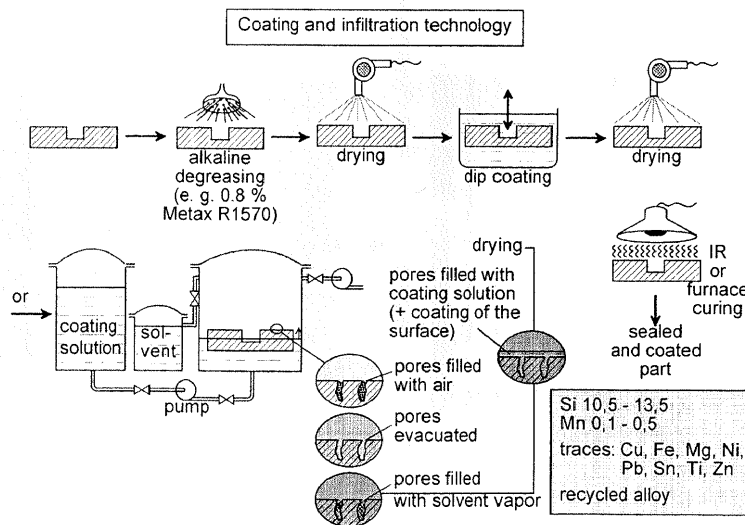
The experiments clearly show the high protective power in this type of coating. In Figure 7, 99.5 aluminum is shown also in the 120-h CASS test, and no corrosion is observed. In Figure 8, the 240-h CASS test is shown, and it also clearly depicts the good corrosion resistance.

In Figure 9, different coatings are compared by the scribe expansion vs. time. The coatings are compared to galvanic coatings (anodizing processes), and it clearly shows the much better corrosion protection. In Figure 10, it is shown that even after a 1000-h salt spray test (DIN 50 021), no scribe expansion can be observed. This is consistent with the hypothesis that due to the thermodynamic stabilization, no damage of the interface, even if the scribe goes through to the substrate, occurs. Based on these investigations and results, a process has been developed to coat pressure-cast aluminum alloys from recycling aluminum with traces of manganese, copper, iron, magnesium, nickel, lead, tin, titanium and zinc with a silicon content between 10.5 and 13.5%. These type of alloys, in general, show

an undesired porosity after casting. The developed process is shown in Figure 11. It shows that it is possible to seal and coat the aluminum parts in one and the same step by vacuum infiltration. The obtained corrosion-protective properties are the same as described above. So, summarizing, one can say that this new type of corrosion-protective system, which easily can be employed, shows overall properties equal or superior to anodizing processes. The advantage is that, as also shown in the last figure, no chromating or phosphating processes are required. In addition to this, the coatings show excellent abrasion-resistant properties. For example, the Taber abrader test (1000 cycles, 500 g,  $\text{Al}_2\text{O}_3$  rubber wheel) leads to hardly visible damage.

### Conclusion

The investigations show that it is possible by using a thermodynamical concept of stabilized interfaces to employ highly effective corrosion-protective coatings



**Figure 11** Schematics of cleaning, coating, sealing and curing of porous pressure-cast aluminum parts; cleaning was carried out easily only by alkaline degreasing; coating and sealing can be achieved by an one-step vacuum infiltration process

on aluminum alloys by simple wet-coating techniques. Due to the fact that the required coating thicknesses are rather low, it is possible to end up with low-cost highly effective coating techniques. The concept is not only restricted to aluminum, but has the potential to be employed to various other metals.

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