High temperature protection

Novel pigments in sol-gel coatings inhibit corrosion at up to 1300°C

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A range of sol-gel anticorrosive coatings has been developed using active pigments consisting of metal particles coated with a very thin layer of semiconducting titanium dioxide. By appropriate pigment selection, protection can be provided at service temperatures up to 600 °C and for short-term exposure in metal processing operations at up to 1300 °C.

Today's thin film nanotechnology-based coatings can provide remarkably effective protection for metals. The novel pigments discussed below provide ways to extend this protection to very high temperatures.

One special procedure for the synthesis of nano coating materials is the sol-gel process. Sol-gel materials can obtain very good adhesion to an oil-free metal surface such as steel, without special pretreatment. This good adhesion combined with a high level of impermeability against water and contaminants leads to good corrosion protection even in very thin layers between 0.5 and 3 µm.

This in turn permits their use in applications such as chromate-free primers, anti-fingerprint coatings and generally in thin and transparent corrosion protection for special applications on steel. If a nanotechnology approach is combined with the principles of sophisticated varnish technology and suitable compounds such as inorganic or metal particles in the 0.5-100 µm size range between are integrated into the matrix, the potential for tailoring properties such as corrosion protection, formability and temperature resistance are very greatly increased.

For example, the integration of zinc particles in the micrometre size range coated with an electrically conductive nano TiO_2 layer in an inorganic matrix ("NXACP" technology) leads to a coating material with excellent active cathodic corrosion protection, much more resistant to corrosion than a coating containing the usual uncoated zinc pigments.

After more than 2000 h in the ISO 9227 neutral salt spray test, a coating of this type less than 10 µm thick shows no red rust and almost no "white rust" on a mild steel sheet, not even in a scratch exposing the uncoated steel surface.

Higher temperatures require different active pigments

The use of zinc particles, is, however, restricted to applications in a temperature range of up to 250 °C. For corrosion protection at higher temperatures the use of an active element with higher temperature resistance is needed.

Magnesium has significantly higher melting and boiling points than zinc of 650 °C and 110 0°C respectively. When magnesium pigments are coated with a nano TiO_2 layer and are integrated into a suitable inorganic matrix, coating materials are obtained which offer active corrosion protection even after long-term thermal loading at 600 °C, or in combination with aluminium pigments after short-term loading up to 950 °C.

This may allow for the creation of a completely new class of corrosion-resistant coatings for applications in exhaust pipes, tubing, industrial plants etc. The integration of aluminium components into an organic-inorganic matrix even allows steel to be protected from scale formation in processes such as hot stamping, heat treatment and forging between 900 °C and 1300 °C.

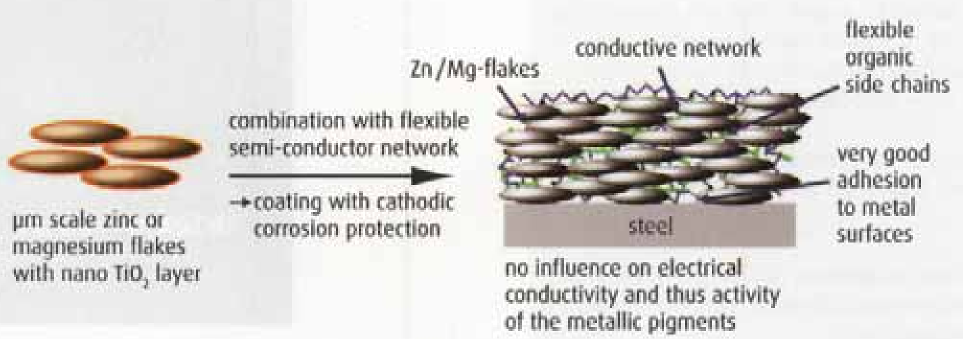

Figure 1: Schematic representation of an active corrosion protection coating based on zinc or magnesium pigments embedded in an inorganic semi-conducting material

Semiconductor pigment coating enhances performance

When zinc pigments are mixed into siloxane coatings, the very surface-active and non-conductive nature of SiO_2 poses a problem. One can easily apply such systems as coatings for metal, but the active corrosion protection is largely lost due to the loss of electrical conductivity of the pigment particles between themselves or in relation to the substrate.

Zinc dust paints are a well-known example of conductive anti-corrosive coatings that have been used for several decades. These are based on TEOS (tetraethoxysilane)-hydrolysates with a high loading of zinc dust. The new approach to retaining conductivity is to bond the metallic pigments into a conductive matrix.

The nanotechnology approach to the production of active zinc or magnesium coatings is to replace the non-conductive SiO_2 as a pigment bonding agent with the semiconductor TiO_2 in a matrix based on TiO_2 and flexible organic side-chains as shown in *Figure 1*.

This figure shows the formation of an active corrosion protection coating containing zinc or magnesium. The semiconductor (in most cases TiO_2) has several functions. During synthesis the titanium oxide is adsorbed on the surface of the zinc particles and immediately protects them in the coating solution. The layer thickness on each zinc or magnesium particle is only a very few nanometers.

After application and curing, the reactive Ti-OH groups are bonded in these coatings to form a dense network. Since every particle is covered with a layer of TiO_2, the formation of white rust is drastically reduced, while the semi-conducting properties of the TiO_2 mean that sufficient contact is maintained by the individual metallic pigments amongst themselves and to the substrate. *Figure 2* shows the corrosion protection of an "NXACP-Zn" system compared with a galvanised steel and an uncoated steel sheet.

The outstanding properties of a 6 µm zinc-titanium-dioxide-coating can be seen in *Figure 2*, compared to zinc-coated plate with approximately 7 µm galvanising, that showed very severe white-rust formation after 1,000 h salt spray test (ISO 9227). An uncoated plate is completely rusted after this exposure.

The object of this development is to substitute for the use of multilayer coatings by increasing the corrosion protective effect of the thin zinc-titanium-dioxide-coatings. An interesting special use for nanocoatings on steel based on this concept exists in the field of high-temperature corrosion protection.

Magnesium gives active protection up to 600 °C

Zinc is a powerful corrosion protection pigment for coatings on steel. One limitation already referred to is temperature. Zinc has a melting point of 415 °C and a boiling point of 907 °C under normal atmospheric pressure. For applications in the range up to 600 °C one could use chromated aluminium pigments in coatings (though these are no longer permissible due to ecological aspects) or the expensive stainless steel.

Figure 2: Comparison of coated steel plates after 1000 h salt spray test according to ISO 9227; left: without coating, middle: zinc-titanium-dioxide-coating, right: galvanized zinc-coated steel after 150 h salt spray test

Aluminium pigments have higher temperature stability but show no cathodic protection on steel due to passivation of aluminium. Magnesium could be a useful alternative because it has the lowest electrochemical potential at -2.38 V and a temperature stability close to that of aluminium with a melting point of 650 °C and a boiling point of 1100 °C.

Magnesium metal coatings on steel show a strong cathodic activity. The problem is the high sensitivity of magnesium to corrosion. A 7 µm magnesium metal film on steel shows extreme corrosion in the salt spray test. A white powder over a red rusty steel is formed in only a few hours.

The solution uses the same concept as before. Magnesium pigments coated with a thin titania film used as a 7 µm coating on steel can survive more than 250 h in a salt spray test without red rust. To demonstrate the temperature stability of these coatings, a 7 µm "NXACP-Mg" coating on 22MnB5 steel was pretreated for 200 h at 600 °C.

After this, the coating was subjected to 100 h in the salt spray test. *Figure 3* shows the results. After the 200 h treatment at 600 °C and 100 h in salt spray test, the zinc-

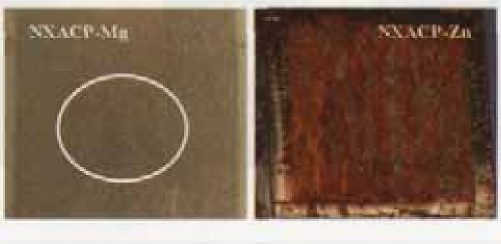

Figure 3: Comparison of 22MnB5 steel plates with 7 µm coating after treatment for 200 h at 600 °C and 100 hr salt spray test; left: NXACP-Mg; right: NXACP-Zn

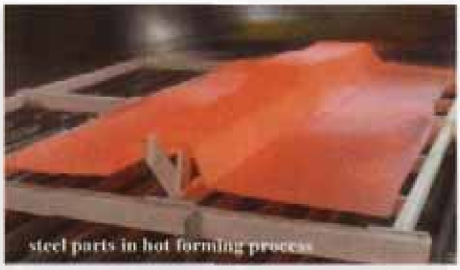

Figure 4: Coated 22MnB5 steel sheet after cold preforming and heating up to 950°C

based coating shows high levels of corrosion. The long exposure at a temperature higher than the melting point of zinc meant that the pigment oxidised very rapidly and lost its active anticorrosion properties.

The magnesium-based version of the coating is stable under the same conditions and can be used as a cathodic protection coating up to 600 °C. This leads to many possible applications.

Apart from general use as a low-cost alternative to zinc pigments, treated magnesium pigments could be used in coatings for screws, tubes etc in high temperature applications and even to provide a low-cost alternative to stainless steel exhaust systems with service temperatures of 500-600 °C.

The next step to consider are processes where for a short time the temperature is higher than 800 °C and possibly up to 950 °C. The problem at these temperatures resembles protection against corrosion, as well as protection against the formation of scale by oxidation.

Scale and active corrosion protection up to 950 °C

A special application for coating systems based on chemical nanotechnology is the protection of steel against formation of scale. The hot forming of steel at 950 °C is a new production process in the automotive industry. The strength of steel is enhanced by this process, hence the same mechanical stability can be achieved with lower sheet thickness, and in this way the weight of the car is reduced.

The problem has been surface scaling at this high processing temperature, which leads to unprofitable downtime due to cleaning of the pressing tools from flaked off oxide layers. A new nanotechnology development called "x-tec+" protects steel against scaling for use in the whole process chain including direct and indirect hot stamping, spot welding, cataphoretic painting as well as general corrosion protection [1].

The protective particles are aluminium pigments in combination with magnesium pigments [2-8]. The basic idea was *to integrate organic compounds into the coating material*, which should protect the aluminium particles from oxidation, combined with "NXACP-Mg" in an inorganic-organic matrix. Active corrosion protection can be achieved, and after 48 h almost no formation of rust, not even in the scratch, was observed. An application is shown in *Figure 4*.

The system can be used for automotive parts in direct and indirect press hardening. Inductive and conductive heating is also possible. This process is an interesting alternative to AlSi coatings with cathodic corrosion protection. The scale protection principle can also be used for processes at higher temperatures such as forging or hardening of steel.

Protection against scaling obtained at up to 1300 °C

Temperatures higher than 1000 °C and up to 1300 °C are normally used for the forging and hardening of steel. Scale formation during the heating procedures in ovens or with conductive or inductive heating results in surface defects from stamping in scale on the forging press, and a subsequent loss of material.

Aluminium pigments in a water-based sol-gel inorganic-organic nanocomposite binder offer good scale protection during the heating process and have good adhesion to the steel during the forging or heating process (*Figure 5*).

This figure shows a coated steel part before and after heating at 1250 °C for 6 minutes, compared with an uncoated part subjected to the same conditions. The uncoated part shows a lot of scale, while the coated part is well protected. These coating materials are available as water-based dip coating solutions which can be applied very easily before the forging process. The same materials can also be used for hardening processes, and also during conductive or inductive heating procedures up to 1300 °C for a few seconds.

Protection must be matched to temperature conditions

This paper provides an overview of the general principles and actual as well as possible future applications of corrosion protection coatings by chemical nanotechnology between room temperature and 1300 °C.

The nanotechnology approach described in this paper has a wide field of application for corrosion protection, as shown in *Figure 6*. At room temperature the zinc-based

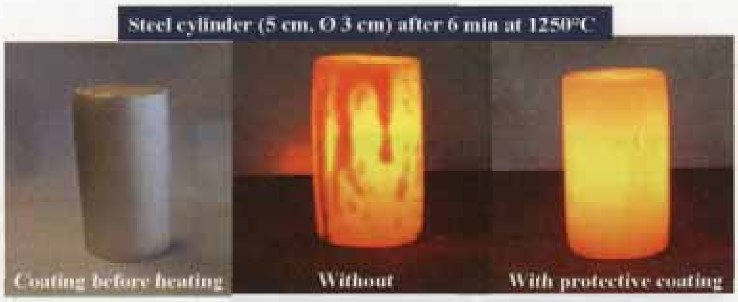

Figure 5: Scale protection of steel during forging processes

coating system described here provides active corrosion protection for steel with ten times better corrosion endurance in the salt spray test than a zinc coated steel with the same thickness of galvanising.

The magnesium-based concept provides stable active corrosion protection at temperatures up to 600 °C. Up to 950 °C, these coatings can be used in combination with aluminium pigments for scale protection, coupled with active corrosion protection for press hardening or other metal forming processes.

For forging and hardening processes at temperatures up to 1300 °C for a few minutes, water based nanocomposite binders in combination with aluminium pigments offer durable and effective scale protection.

New concepts for thinner coatings in combination with more effective and multifunctional corrosion protection are under development.

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Results at a glance

››› Sol-gel coatings can provide effective protection of steel at very low film thicknesses. However, the non-conductive silicon matrix interferes with the action of conductive protective pigments such as zinc.

››› A range of novel active anticorrosive pigments has been developed. These consist of protective metal particles coated with a very thin layer of semiconducting titanium dioxide to protect the pigment surface while enhancing the conductivity of the coatings and their electrical contact with the surface.

››› Sol-gel type coatings using zinc-based pigments of this type are effective at normal temperatures. At service temperatures approaching 600 °C, magnesium (with a higher melting point) is far more effective. At still higher temperatures, short-term protection against surface oxidation or scale formation can be provided by mixtures of treated magnesium and aluminium or aluminium alone.