November/December 2008
Volume 20 No.6

dmg world media

THE JOURNAL OF ALUMINIUM PRODUCTION AND PROCESSING

ALUMINIUM INTERNATIONAL TODAY

• *ENVIRONMENT* • *SECONDARY* • *INDEX 2008* •

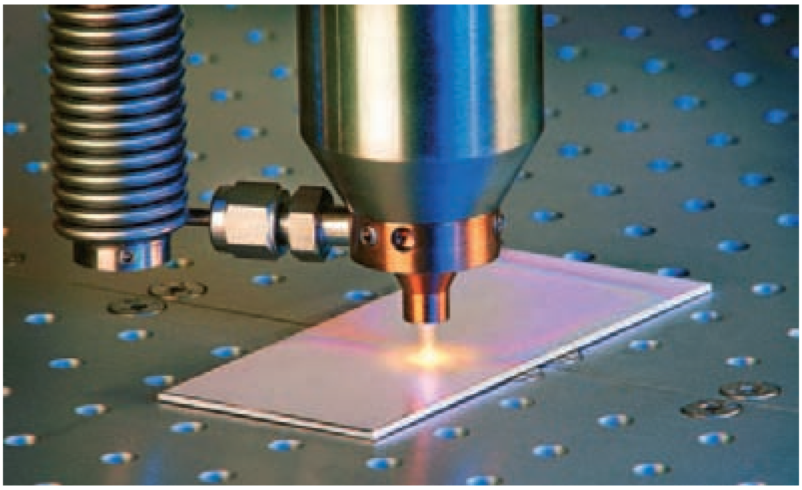
Pioneering corrosion protection by new plasma technology

The development of plasma treatment at atmospheric pressure has enabled ultra-fine cleaning and coating of mating surfaces in preparation for adhesive bonding as well as the ability to coat adjacent surfaces with a thicker layer of organosilicon to greatly improve corrosion resistance.

A major supplier to the automotive sector has recently started using plasma technology for pretreating motor pump housings. With the new process the surfaces of metallic components are selectively coated in-line at atmospheric pressure to prevent bond line corrosion.

Whether the aim is to provide protection against corrosion or to facilitate cleaning of a surface, the *PlasmaPlus* technology newly developed by Plasmatreat GmbH based in Steinhagen, Germany in collaboration with the Fraunhofer IFAM, Bremen, offers an abundance of different layers for selective coating.

The basis of the new process is the Open-Air Atmospheric-Pressure Plasma technology that is already used throughout the world. A large supplier to the automotive sector has been using this technology since early in 2008 to protect steering system components against corrosion.



Right: Open-air-PlasmaPlus for nanocoating of surfaces

Glass-like passive layer

To produce a protective layer an organosilicon compound is admixed with the plasma applied at atmospheric pressure. Due to the high-energy excitation in the plasma this compound is fragmented and deposits on the target surface in the form of a glass-like layer. The chemical composition can be varied according to application to achieve the best results for different materials (eg metal, plastic, glass or ceramics). The deposited coating is similar chemically and in thickness to that as a coating applied under vacuum (**Fig 1**).

To evaluate the film thicknesses scanning electron microscope (SEM) studies have been carried out. At a magnification of x50 000 the micrographs of cross sections of coated samples reveal an homogeneous layered structure free of pores (**Fig 2**). This is very important in corrosion protection because it identifies a passive protective layer, ie the attack of corrosive media is prevented by a barrier. The material in the layer itself is not sacrificed during corrosion attack as is the case in a galvanised steel surface (which exhibits sacrificial corrosion protection).

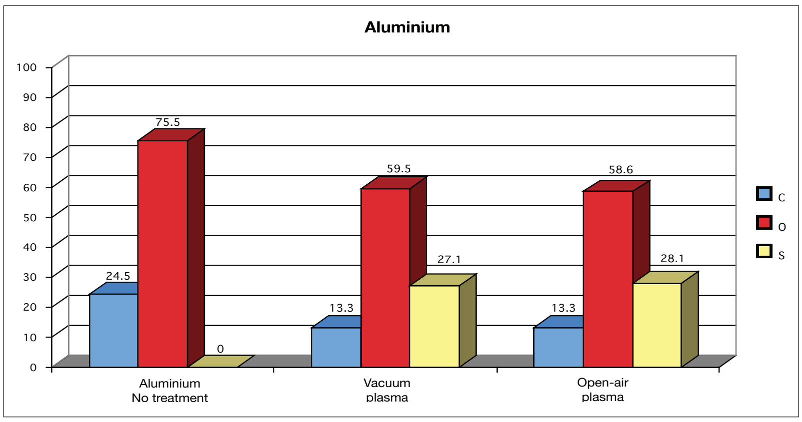


Fig 1: XPS analysis comparing in-line atmospheric PlasmaPlus coating treatment to low pressure plasma (vacuum chamber) treatment.

Particularly effective for Al

Apart from its ability to be used in a production line, the great advantages of PlasmaPlus technology with respect to other coating techniques arise in its ability of selective coating. The anticorrosive action is particularly effective for aluminium alloys. The layer can protect the aluminium for several days against direct salt spray mist (DIN 50021) without the visual appearance of the metal being affected.

To demonstrate the mode of action an aluminium plate (Al 99.5%) was partly coated while the rest of the surface remained in the unprotected initial state. After 96 hours exposure to the salt spray test the uncoated aluminium surface proved to be highly corroded (dark surface) while the coated area still exhibited its original lustre. The transition between the corroded and uncorroded region is clearly discernible in the photomicrograph at x100 magnification (**Fig 3**).

If the plasma coating is to be used for corrosion protection a thick layer (several hundred nanometres) is advisable since this is more resistant to corrosive media such as electrolyte solutions, acids and alkalis. In contract, for preparation for an adhesive layer just a few nanometres suffice. A thin layer already possesses all the important functional groups with which the adhesive can react and undergo strong bonding. The resulting very good adhesion of the coating to the base material effectively prevents any infiltration at the bond line so preventing bond line corrosion. In the case of an adhesively bonded component such as a motor housing or printed circuit board housing, infiltration is particularly harmful since power transmission in structural joints is no longer ensured, or in the case of housings, leaks around the sealing adhesive can occur.

Improved leak-proofing with plasma

At TRW Automotive, a world major for vehicle safety systems, the motor pump housings for steering units have been coated by means of Open-air PlasmaPlus technology. Coating is carried out in-line and ensures best possible protection against the penetration of moisture. Even microscopically small leaks arising from corrosion can result in a short circuit and in failure of steering assistance. Coating by means of atmospheric-pressure plasma plays a key role here.

The parts fed in via a rotary table are first subjected to an identification check by bar code scanner using robots and then checked for dimensional accuracy. The flange surfaces to be bonded are then intensively cleaned by plasma from any organic contaminants, for example minute residues of milling and drilling emulsions, so that the organosilicon layer applied later can bond in an optimum way to the aluminium housing (**Fig 4a**).

After a thin coating is applied (**Fig 4b**) the housing parts are deposited on the rotary table and can be removed by the operator. In a second production sequence the adhesive is metered out and the housing cover is fixed in place. As a result of this process sequence the bonded joint is ideally protected against infiltration and the housing material against corrosive attack in the flange region.

The mechanical, but above all the corrosive stresses to which the part is subjected during its life must not result in failure of the adhesive joint as otherwise the electric motor together with the electronics would no longer be protected. These environmental effects are simulated by weathering in the SWAAT test (sea water acetic acid test) for which the results are presented in **Table 1**.

By comparison with the original process in which, after bonding, an anticorrosion agent based on a fluoropolymer was manually sprayed onto the outside along the bond line, substantially better leak-proofing has been achieved with the plasma-polymerised layer. In the weathering tests, duration until breakthrough, ie the appearance of the first signs of corrosion in the interior of the housing, was increased by about 50% to over 750 hours.

Thus, coating using the new plasma technology affords not only the optimum preconditions for an enduringly stable adhesive bond but also simultaneously ensures a long service life for the part

Safe & environmentally friendly

The patented Open-air Plasma system, a robust, high throughput processing system – is characterised by a threefold action:

- it activates a surface by selective oxidation;
- it eliminates static charge; and
- brings about micro fine cleaning.

When an appropriate precursor material is added, selective nanocoating of surfaces can be accomplished.

The system is capable of implementation in-line and is compatible with robots, offering extraordinary cost-effective solutions.

Due to the small quantities of coating used and its non-toxicity the process is very environmentally friendly. No solvents are required. There is no need to remove a coating prior to recycling the component at end of life as it contains no harmful compounds.

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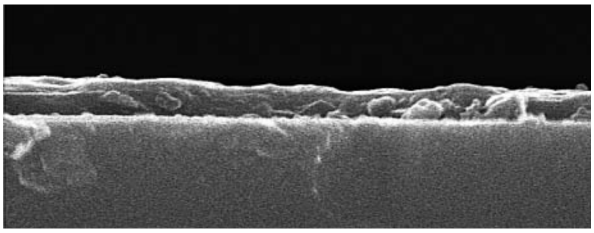
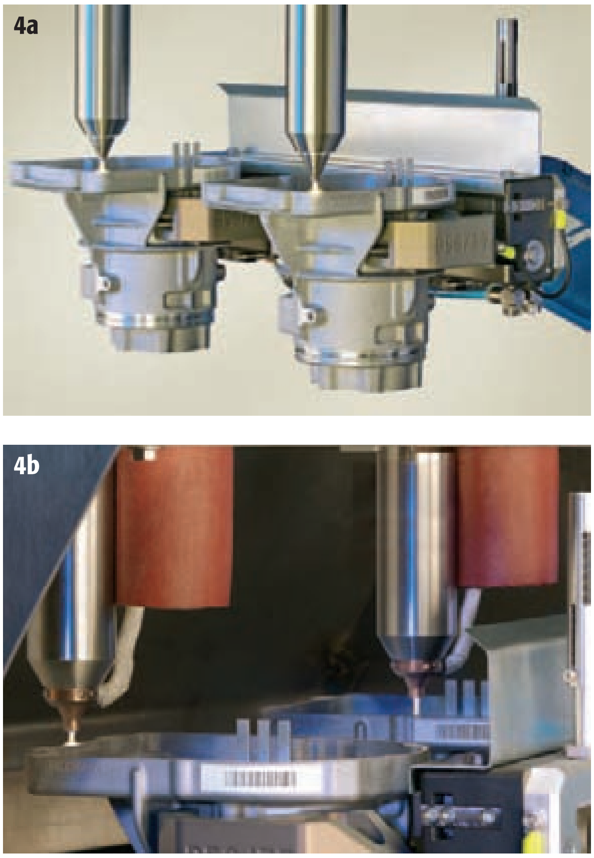


Fig 2: **Section through a plasma layer approximately 100µm thick (SEM at x50000).**

Fig 3: **Under the microscope at x100 the region protected by the plasma layer (left) exhibits no sign of corrosion even after direct exposure to the salt spray test for 96 hours.**



Figs 4a & b: **Prior to plasma coating the motor housings are precleaned with the atmospheric-pressure plasma (4a) after which they are coated with a monolayer film by adding a precursor material to the plasma (4b)**

SWAAT-Test	Test duration [hours]			
	50	250	500	750
Without corrosion protection	leak-free	leak	leak	leak
Anticorrosion fluoropolymer sprayed on	leak-free	leak-free	leak-free	leak
Coating with open-air plasma	leak-free	leak-free	leak-free	leak-free

Table 1 **Leak-proof check by the salt spray test**