

Combustion chemical vapor deposition

A technology to improve adhesion on surfaces to be coated

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Introduction

Combustion chemical vapor deposition is a technique to deposit thin functional layers. It is part of the group of chemical vapor depositions (CVD) [1]. When using combustion-CVD a precursor will be mixed into the combustional gases. As precursors mainly metalorganic compounds like silanes or siloxanes are used (e.g. Tetramethylsilane TMS and Hexamethyldisiloxane HMDSO). Initiated through the combustion energy the precursors are forming very reactive compounds which are deposited on the surface forming firmly bonded silicate coatings with a thickness of 5–50 nm (see SEM-micrographs 6–8).

The aforementioned technique is comparable with the vacuum based CVD, LPCVD (Low-pressure CVD) and PECVD-Systems (Plasma-enhanced CVD). A schematic presentation of the general sequences of the CVD process is given in Fig. 1.

The combustion treatment by itself in order to activate surfaces of metals and plastic materials was already developed in the years 1950 and following [2].

Due to the combustion treatment the upper molecule layers are oxidised and carbonyl, carboxyl and hydroxyl groups are formed. These groups will then react with succeeding coatings. These reactions are based on van der Waals forces between polar atomic groups. A weak point of these reactive groups is their poor resistance to hydrolysis. Furthermore the increase of the surface activity is reversible and will fall back to the original situation within a short period of time (30–120 minutes depending on the polymer).

Due to the combustion treatment the surface energy of a polyolefin for example is increased from 30 mN/m to 40 mN/m. To achieve a permanent

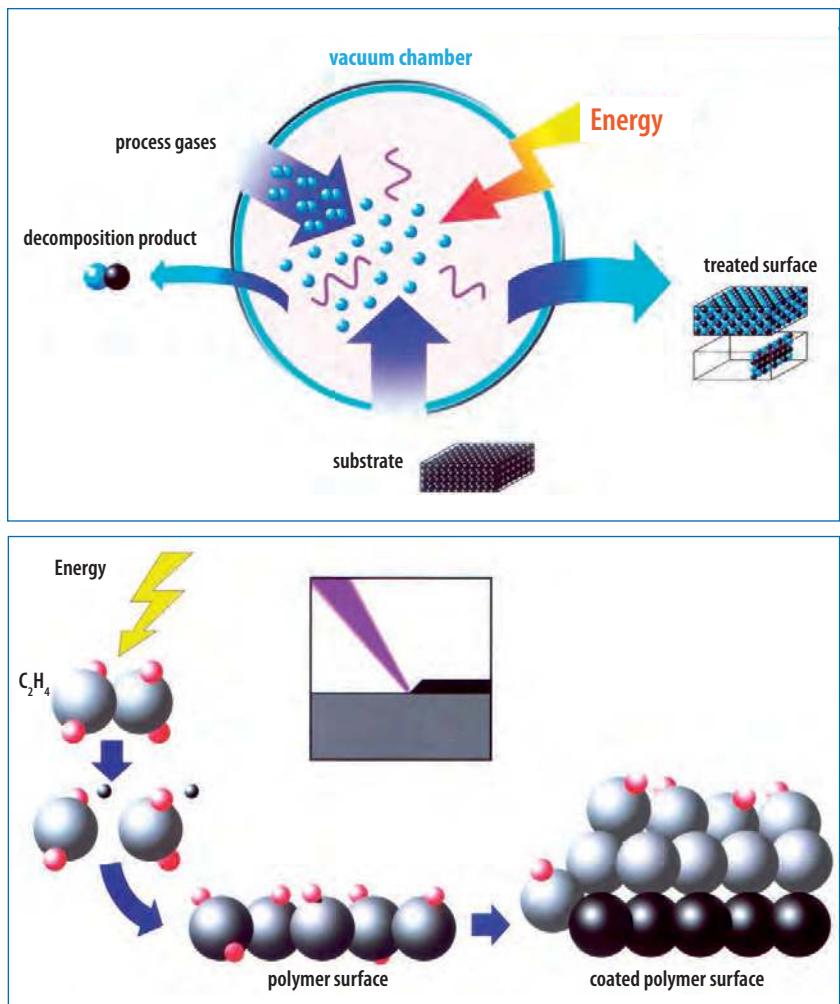


FIGURE 1: Schematic presentation of the chemical vapor deposition with TMS as precursor.

and hydrolysis-resistant modification one needs to modify the surface profoundly.

The combustion-CVD treatment by using a precursor is such a way to modify the surface significantly. In addition

SUMMARY

In this paper, flame-pyrolytic treatment methods of metal surfaces are compared to vacuum-based CVD processes. There is a practical consideration of the aforementioned methods. The layers formed were analyzed

by scanning electron microscopy, changes in properties such as surface energy and adhesion of subsequent layers of paint were detected by measurement.



FIGURE 2: Combustion treatment of a stainless steel substrate.

the combustion-CVD of amorphous silicates is very cheap and flexible to be used. The disadvantage is that only very thin layers or more precisely numerous silicate particles are deposited, which will (depending on the magnification) appear as a thin layer.

Because of the combustion pyrolysis the silane precursor (TMS or HMDSO) will react and SiOH rich layers of SiO_x ($x = 1.5 - 2.5$) will be deposited on the surface. In this manner activated surfaces contain more Si-OH groups than untreated surfaces. We therefore assume that the increased number of Si-OH groups improves the adhesion of the hydrophobic coating to be followed and increases the long-term durability of the coating system significantly in respect of:

- ▶ chemical resistance,
- ▶ mechanical resistance,
- ▶ durability against ambient influences,
- ▶ increase of the water contact angle.

ZUSAMMENFASSUNG

Flammpyrolytische Abscheidung – Eine Technologie zur Erzeugung haftverbessernder Oberflächen

In dieser Arbeit werden flammpyrolytische Vorbehandlungsmethoden von Metallocberflächen vakuumbasierten CVD-Prozessen gegenübergestellt. Es erfolgt eine praktische Betrachtung der vorgenannten Verfahren. Die erzeugten Schichten wurden mittels Rasterelektronenmikroskopie analysiert. Veränderungen der Eigenschaften wie Oberflächenenergie und Haftung nachfolgender Lackschichten wurden messtechnisch nachgewiesen.

Fig. 3 shows the binding mechanism of a silane based hydrophobic coating in comparison of an untreated and a combustion-CVD treated surface.

Experiments and Results

To prove and demonstrate the advantages of the combustion-CVD process of amorphous silicates SiO_x ($x = 1.5 - 2.5$) metal samples with electro polished surface were used in order to prevent any unforeseen interferences.

The untreated surface was observed in a SEM (scanning electron microscope) with increasing magnification up to 186,000 times. The corresponding combustion CVD treated samples were documented with similar magnification.

Fig. 4 shows an electro polished stainless steel surface at a magnification

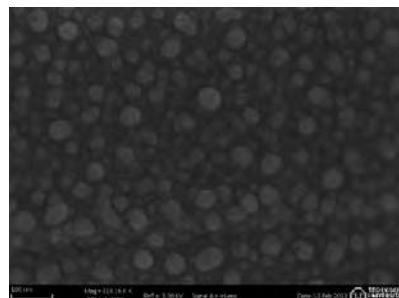


FIGURE 4: Electropolished stainless steel sample, magnification 118,000 x [4].

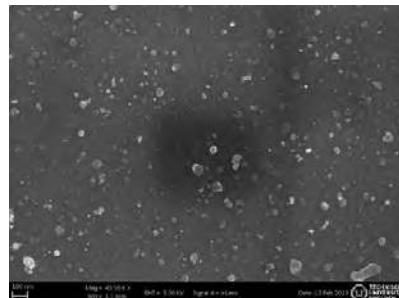


FIGURE 6: SiO_x particles on an electropolished stainless steel sample deposited by combustion-CVD process, magnification 43,000 x [4].

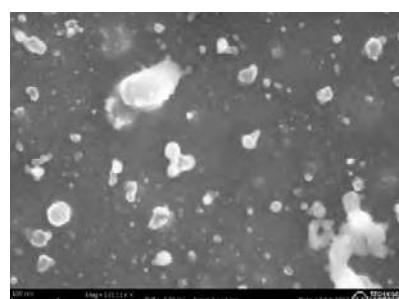


FIGURE 8: SiO_x particles on an electropolished stainless steel sample deposited by combustion-CVD process, magnification 131,000 x [4].

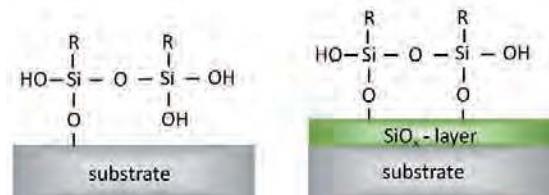


FIGURE 3: Comparison of the bonding process of a silane based hydrophobic coating on an uncoated surface with a SiO_x coated surface [3].

of 118,000 x. In Fig. 5 the same sample at 186,000 times magnification is displayed. On both SEM-micrographs a stochastic distributed structure can be observed, which is typical for any electropolished steel surface. These structures consist of spherical protrusions with a diameter of estimated 20 nm. The height is difficult to assess, but one can assume that it is smaller than 20 nm, because the protrusions cannot be no-

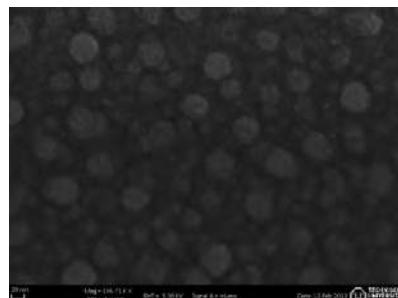


FIGURE 5: Electropolished stainless steel sample, magnification 186,000 x [4].

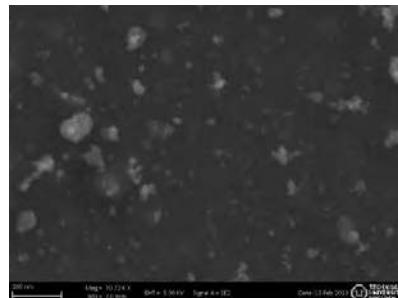


FIGURE 7: SiO_x particles on an electropolished stainless steel sample deposited by combustion-CVD process, magnification 70,000 x [4].



FIGURE 9: SiO_x particles on an electropolished stainless steel sample deposited by combustion-CVD process, magnification 271,000 x [4].

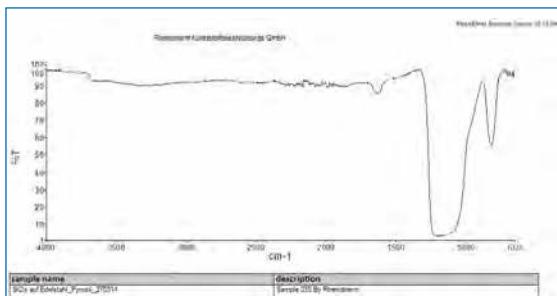


FIGURE 10: IR-Spectrum of a SiO_x deposit on an electropolished stainless steel sample.

ticed when looking at the coated (or deposited) surface.

Fig. 6 shows an electro polished sample which has amorphous silicate particles deposited by the combustion-CVD process. At a magnification of 43,000 x one can observe the stochastical distribution of the deposited SiO_x particles which cover a significant area of the surface.

Fig. 7 shows the 70,000 x magnification of the latter described surface and Fig. 8 the same sample at a 131,000 x magnification. On both SEM-micrographs the deposited SiO_x particles can be observed very accurately.

At a magnification of 271,000 times in Fig. 9 the dimensions of the SiO_x particles can be determined easily. The size of these particles ranges from 5 – 50 nm. The structure on the uncoated electropolished samples can be observed well under the deposited SiO_x particles at a magnification of 40,000 times. At a magnification of about 100,000 times we merely can guess the electropolished structure. We therefore assume that the height of these spherical protrusions must be significantly smaller than the height of the SiO_x particles. The explanation to this assumption is that the depth of the focus is getting shallower with an increasing magnification. So it is fair to assume that the height of the protrusions due to the electro polishing process is less than 20 nm.

A further proof of the SiO_x deposition can be determined by infrared spectral analysis.

In Fig. 10 showing the IR-spectrum of a combustion-CVD treated surface the fingerprints of the silicon oxide bindings belonging to the SiO_x depositions can be detected very clearly.

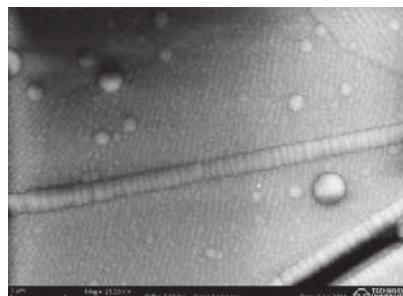


FIGURE 11: SiO_x layer deposited with low pressure plasma, magnification 15,000 x [4].

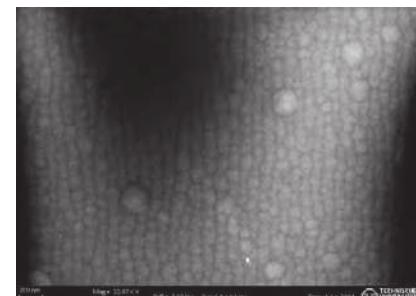


FIGURE 12: SiO_x layer deposited with low pressure plasma, magnification 32,000 x [4].

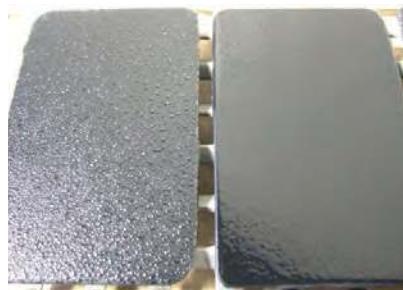


FIGURE 13: stainless steel samples in the wetted stage of coating; left sample without special treatment, right sample after combustion-CVD.



FIGURE 14: samples after flash of at 50 °C; left sample without special treatment, right sample after combustion-CVD.

Deposition of SiO_x through low pressure plasma

The deposition of SiO_x particles by means of a low pressure plasma using also TMS or HMDSO as precursor gives significant higher deposition rates. With this technique layers of up to 1 μm can be achieved.

Fig. 11 and Fig. 12 are showing SiO_x layers which were deposited via low pressure plasma technique.

The layers thickness of 1 μm was determined by using an ellipsometric test

method. As seen in Fig. 11 and Fig. 12 a layer which completely covers the metal-surface is generated. This layer consists of numerous particles of SiO_x with a size of about 50 nm. They are equivalent to the particles deposited by the combustion-CVD method, but the packing density is significantly higher, so to this effect we can talk about a complete layer.

Both deposition techniques have a significant influence on the three important bonding elements which are essential for the adhesion of organic

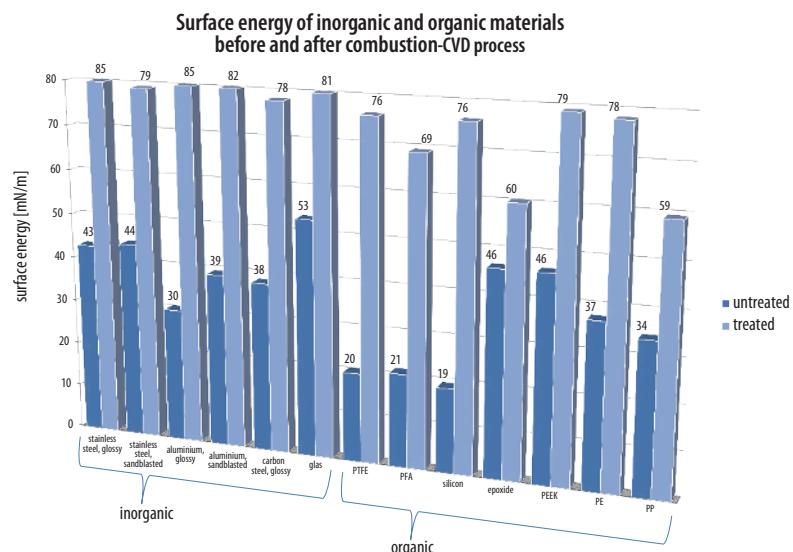


FIGURE 15: Surface energy before and after combustion-CVD treatment on different materials.

coating materials on substrates like metals, ceramics or glasses [1]:

- ▶ adhesion of the silicates to the substrate surface,
- ▶ microporous surface structure for the mechanical bond of the organic component,
- ▶ chemical-covalent bonding of the organic component to the OH groups of the silicates.

In summary it can be said that the deposition of a combustion-CVD technique by using precursors like TMS or HMDSO can be observed very well with a scanning electron microscope. The coverage of the SiO_x particles with this technique differs significantly from the vacuum technique. Nevertheless the planned effects like increased wettability with water based dispersions and improved adhesion or bonding of coatings can be demonstrated. Most important for the use of this technique are the low costs and its flexibility.

Wettability

The increased wettability can be demonstrated when coating stainless steel samples with a 32 wt% aqueous dispersion of PFA (perfluoroalkoxy copolymer; supplier Dyneon). One sample was treated with the combustion-CVD technique, the second sample remained untreated. Fig. 12 shows both samples directly after the coating process. It can be observed that the treated sample on the right side is wetted significantly better; a consistently closed coating film provides an optically smooth surface. Whereas the untreated sample on the left side shows wetting defects and the coating is irregular.

Fig. 14 shows both samples in a dry stage flashed of at 50 °C. The evenness of the coating is significant and proofs the effect of the increased wettability.

Surface energy

The surface energy was measured with a Krüss drop shape analyzer DSA100 according to the method of Wu. All samples were degreased with perchloroethylene and / or isopropyl alcohol. Half of them were left untreated the other half was treated with combustion-CVD.

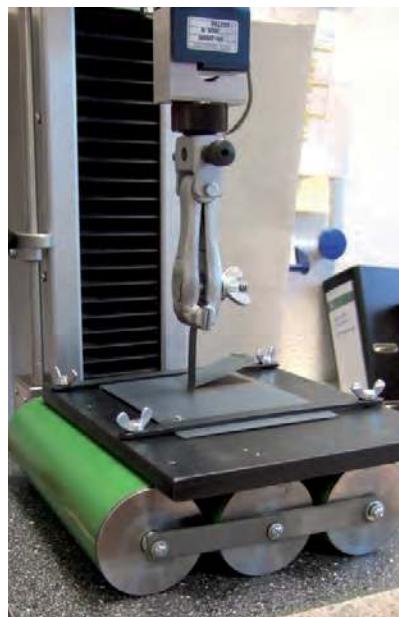


FIGURE 16: General set-up for the 90° peel test of tesa® tape.

In Fig. 15 the surface energies of different materials untreated and treated with combustion-CVD is shown. The tested samples were differentiated into inorganic materials (especially glossy and sandblasted metals) and organic materials.

With inorganic materials a doubling of the surface energy due to combustion-CVD treatment could be achieved. The sandblasting does not affect the results significantly. The organic materials give different results. With fluoropolymer materials (PTFE and PFA) the results nearly quadrupled.

The biggest increase of surface energy could be detected with silicon,

the value increased from 19 mN/m to 76 mN/m. This explains the experience one envisages when coating a silicon surface. One starts from a practical non-wetting surface to a surface which is easily coatable with aqueous paints.

Improved bonding

To demonstrate that an increase of the wettability as a result of the increased surface energy is directly related to the bonding of a tape (tesa® 07475) a 90° peel test was conducted (see test set-up in Fig.16).

The bonding force was measured on stainless steel, carbon steel and on aluminium samples with and without combustion-CVD treatment.

In Fig. 17 the different peel-forces were plotted. In order to get information about the long-term effect of SiO_x deposition the test was conducted five times on the very same panel. As substrate materials stainless steel, carbon steel and aluminum were used. As an overall result we found the peel-forces on a treated surface being considerable higher than on the untreated. However the initial peel-force is being reduced after the first peel, but on subsequent peels it levels off and is still significant higher in comparison to the corresponding untreated sample. This can be explained such that at the initial peel off some of the SiO_x particles are breaking loose from the substrate. On stainless steel the increase is about 25 %, on carbon steel it is 40 % and on aluminium even 66 %.

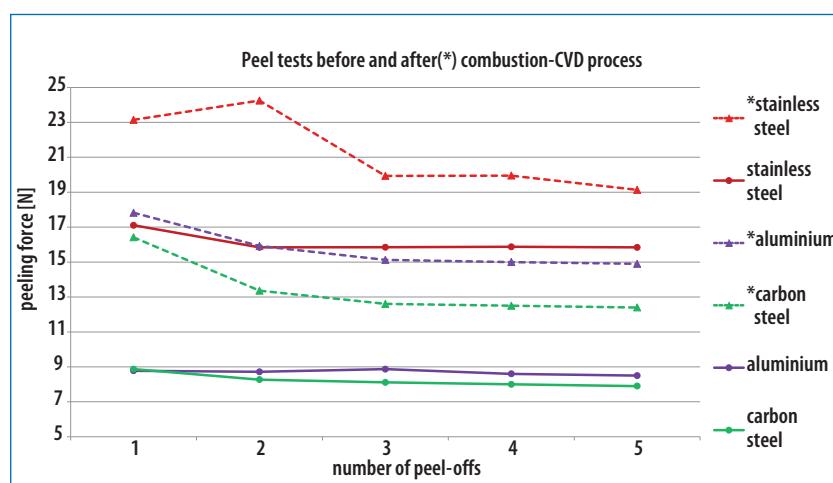


FIGURE 17: Peel tests on different substrates before and after combustion-CVD process.

Conclusion

The deposition of SiO_x ($x=1.5-2.5$) particles or layers on inorganic substrates (metals, glass or ceramic) or on organic substrates (PP, PE, PFA, PTFE, epoxide, silicon) is significantly improving the wettability of surfaces with finishes, paints and glue which will subsequently be applied. Furthermore a remarkable increase of the surface energy could be detected. This increase differs depending on the material. Inorganic materials react different than organic materials.

The adhesion of the deposited SiO_x particles or layers is demonstrated via a 90° peel test with tesa® tape. This test shows that even after the fifth peel the

necessary force to peel off the tape is significantly higher than on untreated surfaces.

These results lead to the conclusion that the combustion-CVD process improves the long-term stability of subsequently applied coatings. This is related to the chemical resistance, the mechanical strength and the resistance to ambient influences. The chemical explanation to this is the increase of Si-OH groups on the treated surface.

Considering the low procedural requirements and the flexibility of this technique it is highly recommended to use the combustion-CVD process as a pretreatment for a lot of coating tasks. The highest barrier for the practical ap-

plication is to overcome the resistance to believe in an effect which cannot be recognized by human senses.

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