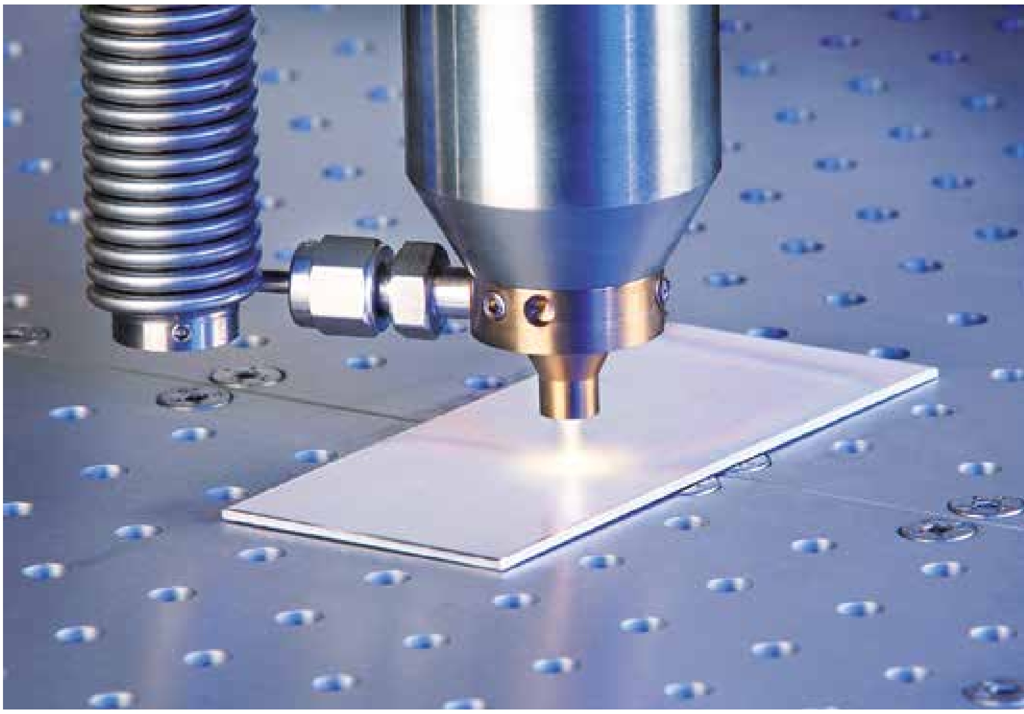
Resistant and Non-Toxic Surfaces Created Inline

A Pioneering Method that Improves Surfaces in Medical Technology

Especially in the medical and plastics technology, the change of the surface is often essential to meet the desired requirements. A novelty in the inline coating of surfaces offer Openair plasma systems that can be integrated into virtually any process and are versatile.



Plasma coating with atmospheric pressure: The openair plasmatechnic is operating without a vacuum chamber and due to that suitable for inline production (© Plasmatreat)

Surfaces are often wet-chemically coated. However, these complicated processes slow down production and aggravate inline production. Plasma processes offer here an alternative that can replace wet chemical processes completely in some cases. Also processes for pretreatment, for example, etching or sandblasting, can be reduced. Plasma processes can modify surfaces by coating or activation, which can increase the biocompatibility of the components.

In order to obtain plasma, gas is ionized by energy supply. In this "fourth state of matter", reactive species are created, which can attach to the surface and thus change the properties of the treated components. A formerly commonly used technique is the vacuum plasma technique. It is also used in medical technology, however, it has disadvantages: The production is only possible in batch process and requires expensive and complex vacuum chambers and pumps. Moreover, the components are always fully treated by plasma or have to be time-consuming masqueraded.

Openair Plasma Technology

An alternative for the inline production offers the Openair plasma technology by Plasmatreat GmbH in Steinhagen, Germany. The special feature is that this is a plasma nozzle which operates at atmospheric pressure. For this purpose, an intense plasma is generated in a long-shaped electrode, which is blown out [1].

Many medical moldings are made of plastic in an inline process. Most plastics, because of their hydrophobic surface are hardly chemically reactive. This can be changed by means of plasma treatment. The reactive species from the plasma bring functional groups into the surface of plastics, especially –OH and –NH groups. By this, many plastics can be glued, coated or painted, after plasma treatment [2]. Furthermore, the plasma can be used for cleaning the surface. By using the Openair plasma, a treatment during the manufacturing process is possible [3].

The advantages of Openair plasma jets are also significant improvements over the prior state-of-the-art technologies [3]:

- Process-compatible, can be easily integrated into various processes,
- flexible, because selectively insertable,
- universal, because all geometries can be coated,
- fewer components, since no expensive vacuum equipment is needed,
- shorter cycle times due to the rapid process.

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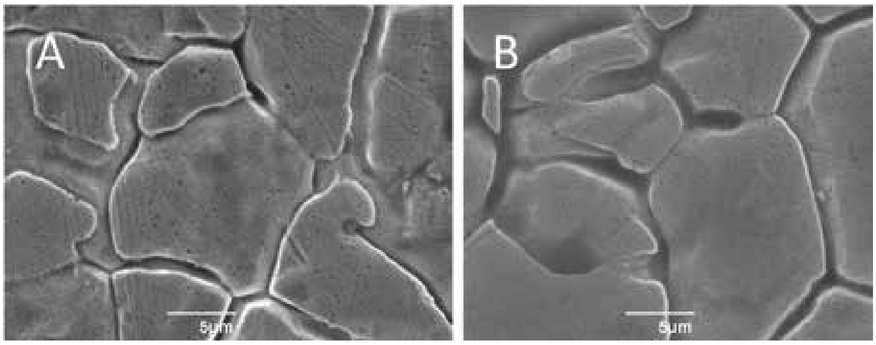

Fig. 1. Different carbon content: The SEM pictures of a hotter (A, about 160 °C) and a colder (B, about 140 °C) plasma coated surface (© Christin Rapp, Institute of Medical and Polymer Engineering, TUM)

Coatings in Medical Technology

In medical technology, it is necessary to modify surfaces since their nature plays an important role in the integration of the implant into the surrounding tissue (surface biocompatibility). Frequently, coatings are being used, as they are long-term stable compared to plasma activations, where only the surface is treated with plasma. In addition, coatings can change the properties of the surface fundamentally, so that the characteristics of the desired substrate can be combined with other surface properties. This opens up a big variety of material combinations.

An attractive basic material for coatings is hexamethyldisiloxane (HMDSO) [4]. It forms on the surface silane-like coatings and is industrially widely used to bond plastics and as a barrier [5, 6].

The Institute of Medical and Polymer Engineering at the Technische Universität München (TUM), Germany, is testing Openair plasma coatings out of HMDSO for biocompatibility, which can for example serve as a bonding agent between two components in implants. Here especially hard-soft connections or linking a coating of particles on the surface are of interest. Furthermore, the coating may be applied as a barrier layer on an implant to prevent contact with body media. It is also thinkable to shield a metal stent from the bloodstream. The coating prevents that on the stainless steel surface thrombosis are happening. Furthermore, barrier coatings can protect sensitive sensors in the body against corrosion and improve the resistance of active implants towards body fluids.

The aim is therefore to deposit a versatile coating that is non-cytotoxic and shows optimal surface properties in the body.

Characterization of the Coating

In order to influence the coating properties, the plasma parameters were varied. The coating was deposited with a hotter (approximately 160 °C) and a colder plasma (approximately 140 °C) (each 10 cm below the nozzle outlet). The structure of the coating was investigated by X-ray photoelectron spectroscopy (XPS), and the surface energy was estimated by contact angle measurement. For both coatings the contact angle with water was about 95°, so the surface is classified as slightly hydrophobic. The XPS data showed that the layer consists mainly of

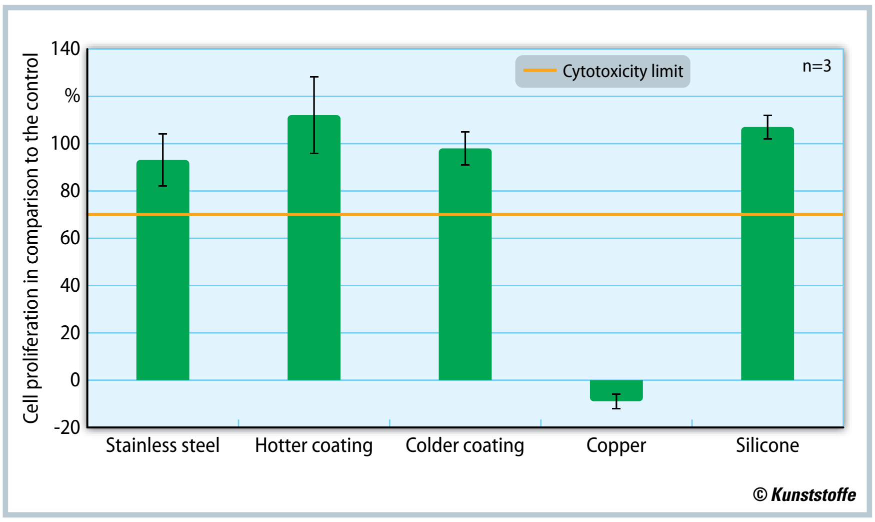

Fig. 2. Not cytotoxic: The cell renewal on plasma coated surfaces tested with WST-8 tests with eluates was above the limit (source: Christin Rapp, Institute of Medical and Polymer Engineering, TUM)

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References & Digital Version

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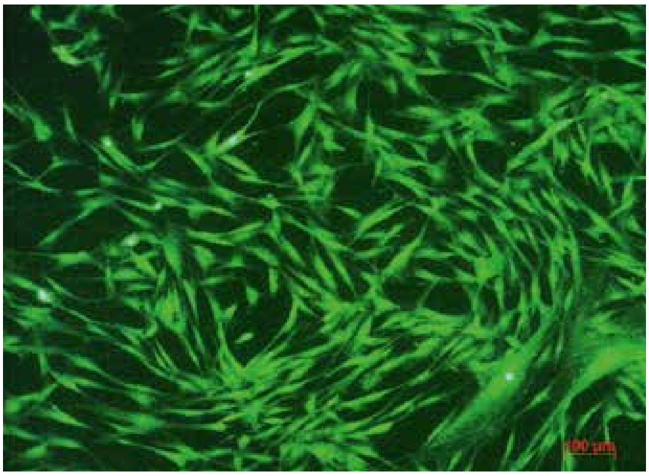

Fig. 3. Well attached: Fixed and dried fibroblasts on a plasma coated surface via fluorescence staining (© Marie Klose, Institute of Medical and Polymer Engineering, TUM)

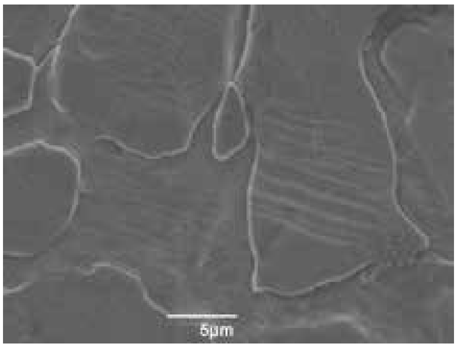

Fig. 4. Tensile test sustained: The coating is obviously stable on the surface, no cracks are visible (© Christin Rapp, Institute of Medical and Polymer Engineering, TUM)

Si-H_x, Si-CH_X and Si-C bonds, which corresponds to a silane-type structure.

The colder and the hotter coating differ in their carbon content. It could be demonstrated that the plasma with 140 °C had more carbon on the surface than the hotter plasma. The cold plasma layer is more organic like. This was expected, as the precursor is higher fragmented by high energy plasma and increased heat of the precursor. This leads to smaller molecules and less carbon on the surface, because carbon usually reacts to CO or CO_2 and by that evaporating. Investigations with the scanning electron microscope (SEM) showed that in both cases, a very thin, homogeneous coating was created (**Fig. 1**).

Evaluation of Cytotoxicity

Due to the fact that the plasma produced coatings should also be used for implants, it is important to investigate their cytotoxicity. For this, tests in accordance with DIN EN ISO 10993-5 with the cell line Hs27 were performed. This cell line is a human fibroblast that occurs in the connective tissue. For testing, the WST-8 test with eluates, extracts from the materials, was chosen. In addition, the cells on the surface were examined by means of SEM and fluorescence staining.

The WST-8-tests revealed that the produced silane-like layers are not cytotoxic; this applies as soon as the formation of new cells (proliferation) is over 70 % compared to the DIN control sample (**Fig. 2**). The hotter coated sample has a cell proliferation of 112 % and the colder coated of 98 %. The growth of fibroblasts on the coated samples has also been studied and shown by SEM and fluorescence staining (**Fig. 3**).

In summary, it can be said that the material is non-cytotoxic and the cells grow on the surface. The hotter coated sample had even an improvement in the profileration compared to the control. This is probably due to releasable silica, which can stimulate cell growth. Missing cytotoxicity and a good growth behavior are two of the most important properties for the application of the coating in medical technology.

Resistance of the Silane Coating

An indication of the resistance can be proofed by intercalating the coating in liquid media. Therefore, stainless steel plates have been coated, placed in the medium and stored for one month in an incubator at 37 °C.

Another method for determining the resistance of coatings is the tensile test. Assumption was that the coating was carried out on a stent. Therefore, the tension rods were made according to DIN EN ISO 6892 out of surgical stainless steel 316L with a thickness of 1 mm. When loading the sample the loading was orientated on the load of the stent upon expansion in an artery. The maximum load in this process is unclear; some studies, however, expect a maximum tension of 700 MPa [7, 8]. Since the samples used here were, when charged with these forces, already above the elongation at break, a maximum tension of 500 MPa was applied, which is above the yield strength of the sample, but is indeed below the elongation at break of the stainless steel.

The samples showed after loading a rejuvenation of the layer at the load by stretching points, but the film remained stable on the surface and there were no cracks visible (**Fig. 4**). The storage in simulated body fluid (SBF) and the standard medium for cell culture (Dulbecco's Modified Eagle Medium, DMEM) showed that a tempered layer in these medias is largely stable over a month.

The DMEM from the storage test, was also tested for cytotoxicity. In this case, no reduction in cell proliferation was determined. These results show that the coatings are very stable and therefore suitable for mechanically stressed components.

Conclusion and Outlook

HMDSO coatings are very promising for use in medical technology. As the chemical characterization showed, by plasma treatment hydrophobic silane-like coatings are formed. The tensile tests showed that the layers may be used on loaded implants (such as stents), since no cracking or tearing of the coating was recognized. The examination of the cytotoxicity showed that the investigated layers do not affect the cell proliferation. All results of the study indicate that the silane-like with Openair plasma created coatings show a good resistance and no signs of cytotoxicity.

So far, the layers were mainly deposited on metals for the use on stents, but the first experiments on plastics also provided promising results. These coated plastics could be used as artificial arteries or heart valves. All properties of the coating suggest that they are suitable for use in the body and that with Openair plasma promising and novel inline produced implants can be created. ■