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**B. Dzur / J. Eckert**

## **Plasma sprayed ceramic wear resistant coatings for biomedical implants**

### **Functionalization of Material Surfaces / Nano Processing**

#### **1. Introduction**

Although thermal spraying of ceramics, especially of alumina coatings has been state of the art for more than 50 years, one general problem has not been solved satisfactorily up to now: The thermally induced transformations of the crystalline lattice to meta-stable modifications at its pass through material depending temperatures. Such transformations also will occur during the heating of the particles in the plasma or flame and can be frozen during the solidification and cooling down of the particles after their impact on the substrate surface. Besides the properties of the particles and the substrate surface, the velocity of the solidification and cooling down can be assumed as the main parameter. The main intent of this transformations is the contemporaneously change of important properties. Especially the change of the density may become a problem because it leads to an increasing amount of porosity. Also the formation of internal stress and micro cracks will be a consequence.

Alumina is a spraying material where besides the thermodynamically stable Alpha-lattice of corundum at least 9 metastable modifications are described in the literature. It is also widely used for medical implants but only as massive sintered bodies. A main problem for using plasma sprayed alumina containing coatings for such applications is the Gamma-phase. This modification in contrast to the Alpha-phase is solvable in the human body.

1947 BABAT for the first time described a high energy discharge under atmospheric conditions, generated by inductive coupling of energy, now known as the inductively coupled thermal RF plasma (ICP). Even though a lot of excellent work has been done during the years to investigate the ICP and possible applications also for the fabrication of various coating systems and even though IC-plasma equipment is commercially available it is exciting, that up to now only the treatment of powders is a commercially established application of the ICP.

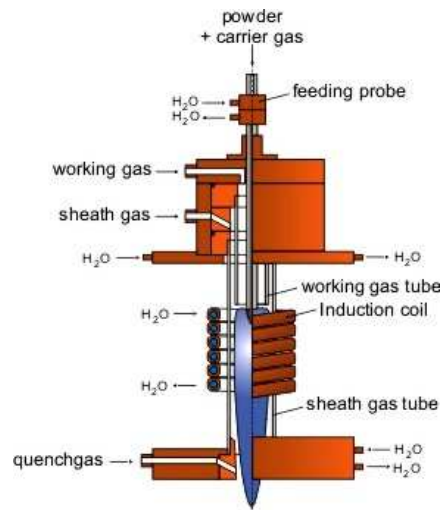
The ICP is characterized by the absence of electrodes, its large volume, relatively low plasma and particle velocities (compared with DCP at the same pressure) and the possibility of an axial injection of the powder into the plasma core. Moreover, due to the low plasma velocity (especially at atmospheric conditions) the axially injected powder passes the plasma with no significant acceleration as it is gained with DC or HVOF spraying. This leads to larger dwell times of the particles in the plasma and so larger grain sizes even of materials with high melting points can be used. The molten particles hit the surface with a low kinetic energy and form large “pancakes”. The velocity of deformation and cooling down was found to be up to one magnitude lower, compared with other technologies. Because of this special features of an IC-plasma it can be expected, that phase transformations can be reduced or avoided [1, 2].

This effect has been intensively investigated for many years in various projects of the Department for Plasma Engineering and Surface Technologies of the TU Ilmenau [1,3,4, 5]. Pure alumina and mixtures with Titania were used and it was possible, to spray thick ceramic coatings of a high quality level with a significant lower ratio of Gamma compared with DCP- or flame sprayed coatings, even with no Gamma. A first application could be a new design of knee implants. This is a subject of our actual research.

## **2. Generation principle and special features of the ICP**

An ICP is formed by electromagnetic induction of a high frequency voltage to a gas flow. Today ICP-torches consist of three concentric tubes, placed centered in an induction coil (Fig. 1). Commonly used frequencies are in the range of some MHz. The special features of an ICP are leading to larger dwell times of the particles in the plasma and so larger grain sizes even of materials with high melting points can be used.

Especially under atmospheric spraying conditions the molten particles will hit the surface of the substrate with a low kinetic energy. A so called pancake structure is typical for its deformation. Especially the effects connected to the deformation and cooling down of the particles may lead to other, interesting coating properties as it will be shown in the following chapters.



**Fig. 1: ICP-Torch-Assembly (TU Ilmenau)**

### **3. The formation of metastable phases during the spraying process**

Although thermal spraying of ceramics has been state of the art for many years, one general problem has not been solved satisfactorily up to now: The thermally induced transformations of the crystalline lattice to meta-stable modifications at the pass through material depending temperatures. Such transformations will occur during the heating of the particles in the plasma or flame and can be frozen during the solidification and cooling down of the particles after their impact on the substrate surface. Besides the properties of the particles and the substrate surface, the velocity of the solidification and cooling down can be assumed as the main parameter.

The main intent of this transformations is the contemporaneously change of important properties. An example is given in Table 1 for Alumina, a material were besides the thermodynamically stable, Alpha-lattice of corundum at least 9 metastable modifications are described in the literature.

Especially the change of the density may become a problem because it leads to an increasing amount of porosity. Also the formation of internal stress and micro cracks will be a consequence. The amount on metastable phases can reach up to 100 %.

**Table 1: Properties of important Alumina modifications [6]**

	Alpha (trigonal)	Delta (tetragonal)	Gamma (cubic)
Density (kg/m <sup>3</sup> )	4.000	3.800	3.600
Specific heat (J/kg K)	1.363	1.402	1.425
Melting point (K)	2.327	2.308	2.289
Latent heat of fusion (kJ/kg)	1.090	915	770
Linear kinetic coefficient (mm/s K)	2,47	2,11	1,80

The use of ceramic materials like Alumina and Zirconia for implant parts is state of the art. But because of the mentioned problem with the formation of the Gamma modification only sintered bodies are used for instance in hip-, shoulder- or dental implants. Beside VPS-sprayed structured Ti-coatings, only the following plasma sprayed ceramic coatings have been established:

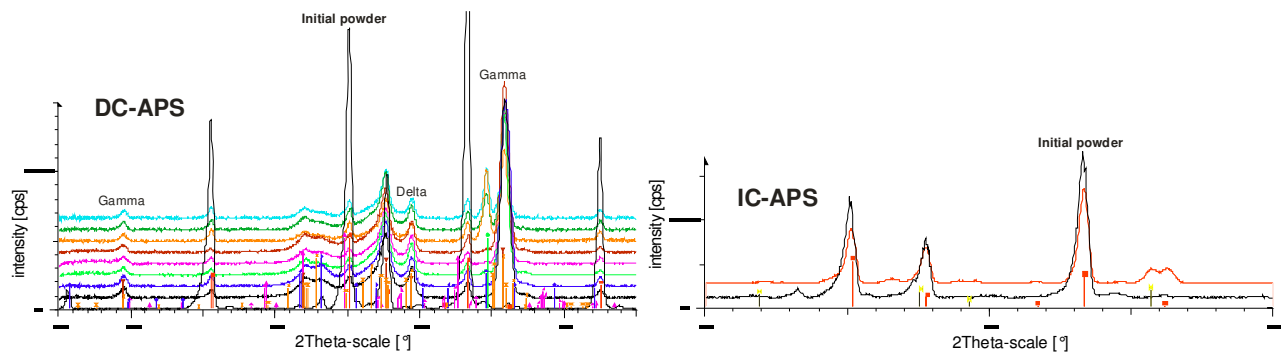
- porous bioactive Hydroxyle Apatite (HA)-coatings, formula:  $\text{Ca}_5(\text{PO}_4)_3[\text{X}]$
- structured Ca-Triphosphate (Apatite) [9], formula:  $\text{Ca}_3(\text{PO}_4)_2$

#### **4. IC-Plasma sprayed wear resistant coatings for implants**

In [1] ICP-spraying of various ceramic materials under atmospheric conditions was investigated. It was found, that for materials like alumina, YSZ, pure zirconia and  $\text{SiO}_2$  the effect of phase transformations can be drastically reduced and using optimized parameters (first of all an adapted grain size of the initial powder) even eliminated completely. A following comparative study has confirmed these results also for various ICP-sprayed alumina-titania mixtures. In contrast thereto, it was not possible to spray coatings without Gamma using the DC-APS-process although the parameters were intensively changed to reduce the particles temperature and velocity [3]. The parameters are summarized in table 2 and in Fig. 2 examples of XRD-patterns are shown.

**Table 2: Parameter of a comparative study [3]**

DCP		ICP	
Plasma gas Ar	44 slpm	Working gas Ar	30 slpm
Plasma gas H <sub>2</sub>	6,0 slpm	Sheath gas Ar	40 slpm
Carrier gas Ar	4,5 slpm	Sheath gas N <sub>2</sub>	4,0 slpm
I [A]	700, 500, 300	Carrier gas Ar	2,0 slpm
$\dot{m}$ (powder) [g/min]	12, 9, 6	Plate Power	20 kW
distance [mm]	100	Frequency	5,0 MHz
		$\dot{m}$ (powder) [g/min]	10 g/min



**Fig. 2: XRD-pattern of alumina coatings [3]**

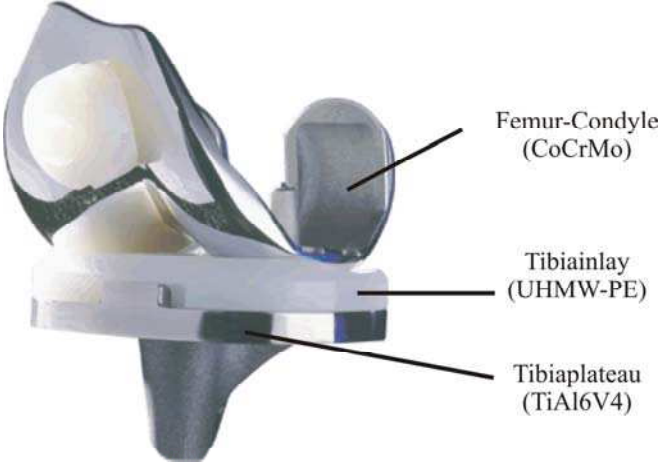
Besides the absence of the Gamma modification, a wear resistant coating for medical implants some other important properties are required:

- a minimum porosity
- a defined size and distribution of the pores (important for a post surface treatment)
- a bond strength of more than 50 MPa

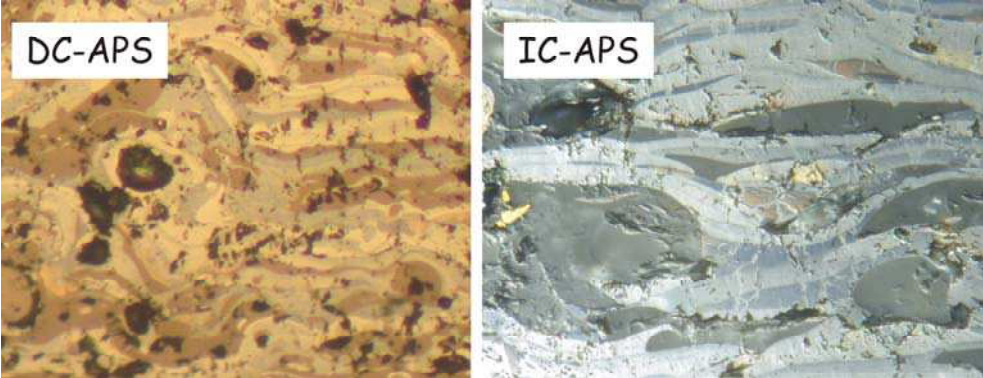
In [4] the IC-plasma spraying of an Titania-Alumina mixture was investigated. A possible application is the first use of such a coating in knee implants. The main problem of such a part is the meniscus replacement, actually made of an special polymer material (Fig. 3). It is the aim to use a ceramic part for it, but to decrease the coefficient of friction the metallic femur condyle has to be coated with a ceramic, too.

First coatings made of Titania/Alumina – 80/20 (grain size: -60+80  $\mu\text{m}$ ) with a thickness of up to 500  $\mu\text{m}$  have a porosity of less than 5 %. Although also Titania tends to phase transformations and thus the interpretation of the XRD-pattern becomes challenging (overlapping of Alumina and Titania peaks), it can be assumed, that the coatings are free of gamma.

To use such a coating for real implant a lot of work has to be done in the future, but the first results are very promising. It has to be mentioned, that according to the different deformation and coating structure also the roughness of the as-sprayed surface is increased compared with commonly sprayed coatings and an extended finishing may become necessary (Fig. 4).



**Fig. 3: Knee implant (Matthys GmbH)**



**Fig. 4: Cross sections of Titania/Alumina – 80/20-coatings (same magnification)**



## 5. Summary

It can be summarized, that coatings of a comparable high quality can be sprayed with all technologies but only the ICP offers the possibility to produce coatings with advanced properties. In contrast to common thermal spray technologies such coatings also for instance could be used for medical implants because of the absence of metastable modifications of the crystalline lattice. Further investigations are necessary to optimize the coatings properties for applications as wear resistant coatings for medical implants. This also could become a first industrial coating process using the ICP-technology.

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