Open Access

Nicola Vogt, Katarzyna Wozniak, Armando Salito and Michael de Wild*

Biocompatible wear-resistant thick ceramic coating

Characterization of the hardness and porosity

DOI 10.1515/cdbme-2016-0010

Abstract: Sensitisation to immunologically active elements like chromium, cobalt or nickel and debris particle due to wear are serious problems for patients with metallic implants. We tested the approach of using a hard and thick ceramic coating as a wear-resistant protection of titanium implants, avoiding those sensitisation and foreign body problems. We showed that the process parameters strongly influence the coating porosity and, as a consequence, also its hardness.

Keywords: anti-allergy implants; hardness testing; implant coating; wear resistant.

1 Introduction

Sensitisation to chromium (1%), cobalt (2.4–3%), nickel (13.1%) of patients who received endoprosthetic surgery is a growing problem [1]. The ionic release of these immunologically active elements from the implant material can lead to allergic responses of the host like eczema, swelling, sterile osteomyelitis, aseptic loosening and in worst cases also to the loss of the implant [2, 3]. Furthermore, particular debris of articulating joints can lead to wear problem in metal-on-metal [4] but also in metal-on-polymer systems [5]. CoCr alloys are used for endoprosthetic devices since the sixties [6] and today 80% of the artificial joints are made of CoCr. It cannot simply be replaced by titanium because its wear-resistivity is not sufficient [7], even though titanium is biocompatible and its mechanical strength is high enough [8]. One approach is to compensate the wear resistance by applying a hard ceramic coating onto the titanium parts, in particular onto the sliding surface.

Advanced plasma spray (PS) method allows coating of complex geometries and is not limited to small implants sizes. Coatings with thicknesses of several hundreds of microns are feasible while other coating technologies like PVD or thermal oxidation [9] are limited to few microns. Whereas commercial implant surfaces in direct contact with bone have been coated by titanium-spraying (TPS) since decades and show good long-term survival rates [10], plasma sprayed coatings of the Al-oxide- and Ti-oxide-based system are so far not used as slide bearing of implants but for research purpose [11] or photocatalytic application [12]. In this study, the morphology, hardness and the porosity of biocompatible advanced plasma spray coating consisting of a mix of oxides were investigated.

2 Material and methods

2.1 Sample production

Discs (ø25 mm, height 6 mm) made of CoCr were sandblasted with corundum and coated by advanced plasma spraying. Different process parameters were use in order to optimize the coating towards porosity and hardness.

2.2 Sample preparation

The coated samples were prepared for subsequent microscopic and materialographic characterization. The specimens were fixed in a polymeric 2-component cold embedding material. Cross sections were then produced on the TegraPol 21 grinding and polishing system with

***Corresponding author: Michael de Wild,** University of Applied Sciences Northwestern Switzerland, FHNW, School of Life Sciences, Institute for Medical and Analytical Technologies, Gründenstrasse 40, CH-4132 Muttenz, Switzerland, E-mail: michael.dewild@fhnw.ch
Nicola Vogt: University of Applied Sciences Northwestern Switzerland, FHNW, School of Life Sciences, Institute for Medical and Analytical Technologies, Gründenstrasse 40, CH-4132 Muttenz, Switzerland
Katarzyna Wozniak and Armando Salito: Orchid Orthopaedics Switzerland, Täfernstrasse 39, CH-5405 Dättwil AG, Switzerland

a Tegra Force 5 head from Struers. SiC grinding paper from BUEHLER followed by polishing paper from the same manufacturer has been used.

2.3 SEM/EDX analysis

The scanning electron microscope (SEM) TM3030 Plus (acceleration voltage $U_0 = 15$ kV, backscattered electron and secondary electron detectors, Hitachi) with the integrated energy dispersive X-ray spectroscopy (EDX) system (Quantax 70, Bruker) enables the materialographic analysis.

2.4 Roughness analysis

The FORM Talysurf PGI 800 device from Taylor Hobson, equipped with a standard 2 µm, 90° diamond tip, a cut-off $\lambda_C = 2.5$ mm/0.08 mm and a measuring length $l = 15$ mm has been used for roughness determination.

2.5 Analysis of the porosity

The porosity of the coating was optically determined in polished cross sections according to ASTM F1854 [13] with light microscope Axiovert 40 MAT ZEISS, AxioCam MRc CCD camera, Epiplan x10/0.20HD ocular, AxioVision 40 V.4.8.2.0 Software used for image analysis. Five microscopic images of every sample were analysed ($n_p = 5$).

2.6 XRD analysis

The crystallographic phases were characterized with the diffractometer D2 PHASER (Bruker) and the Diffrac EVA software V.4.0, applying Co-Kα radiation ($\lambda_{Co} = 1.79$ Å), angular θ-range 20–120°, power 300 W, sample φ-rotation of 15°/min. The ICDD database served for the identification of the phases.

2.7 Hardness testing

The hardness of the coating was determined by the Zwick Roell ZHV 10 system at a load of 2.94 N and a holding time of 15 s. Four spots were measured for each specimen ($n_h = 4$).

3 Results

3.1 SEM/EDX analysis

While the native PS surface shows a rough morphology, see Figure 1A, the polished surface is smooth and only a few pores can be seen, see Figure 1B. The coating homogeneously consists of titanium, aluminium and oxygen, see EDX mapping in Figure 1C. No foreign elements were detected. The elementary composition is given in Table 1.

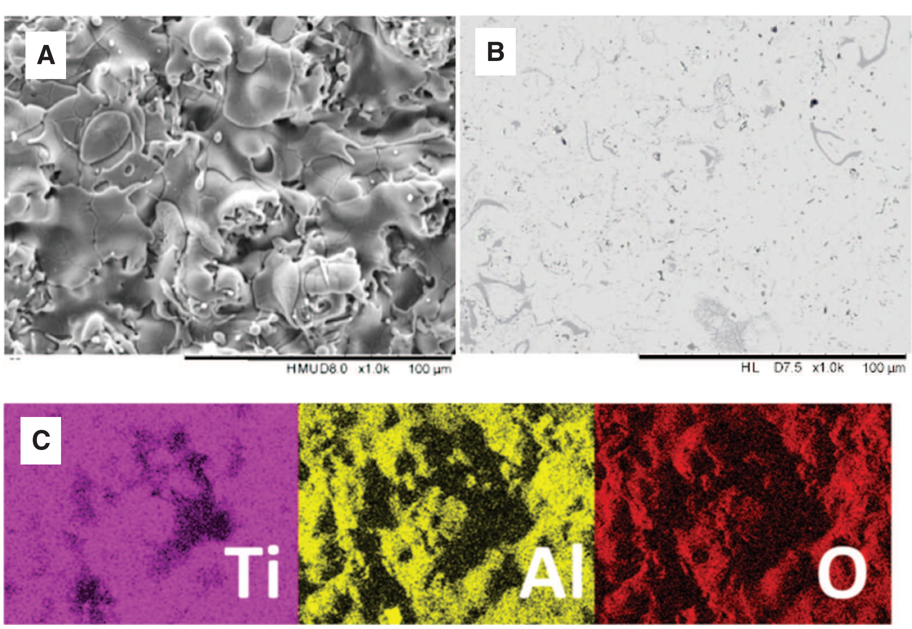

Figure 1: SEM image of PS coating (A) before and (B) after polishing. (C) EDX mapping of the native surface with elements: Ti (pink), Al (yellow) and O (red).

Table 1: Elementary composition of the PS coating determined by EDX.

Element	[at.%]
Ti	49.9 ± 0.2
Al	7.9 ± 0.1
O	42.2 ± 0.2

The cross section through the coating is shown in Figure 2. The coating in tight contact with the rough substrate shows a layered microstructure originating from the deposition process and a low porosity. A thickness of about 100 μm was estimated.

3.2 Roughness analysis

The roughness values of the native PS coating and the polished specimen are shown in Table 2.

3.3 XRD analysis

The crystallographic phases of the coating were identified as different modifications of TiO_2 (Brookite, Anatase, Rutile) and Al_2O_3. No signals from the metallic substrate were observed.

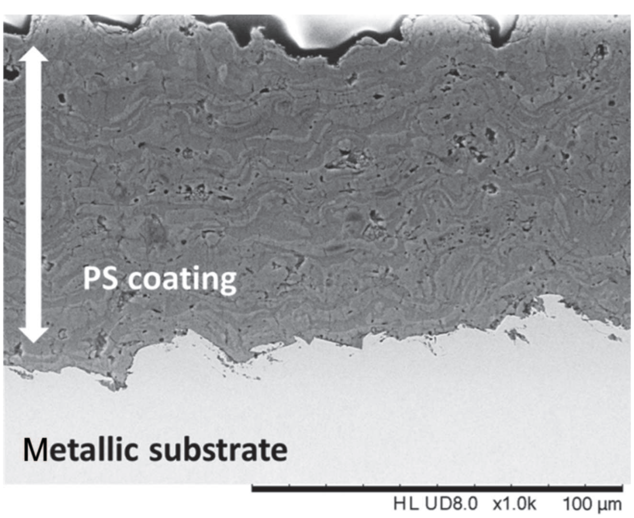

Figure 2: Cross section of the PS coating on a metallic substrate.

Table 2: Roughness of the native and polished PS coating.

Roughness	Native [μm] (n = 9)	Polished [μm] (n = 9)
R_a	8.15 ± 2.07	0.016 ± 0.005
R_t	65.54 ± 13.98	0.67 ± 0.33
R_z	53.72 ± 10.75	0.13 ± 0.04

3.4 Hardness testing

The impressions of the pyramidal diamond tip had a diagonal of 26.9 ± 3.3 μm, see Figure 3. The values of the Vickers hardness are quantified in Figure 4.

3.5 Analysis of the porosity

The optical quantification of the porosity and its relation to the observed hardness is illustrated in Figure 4. Porosity values between 0.43% and 12.95% were found, depending on the applied process parameters.

4 Conclusion

The investigation of the hard plasma spray process coatings indicate a trend between the hardness and the

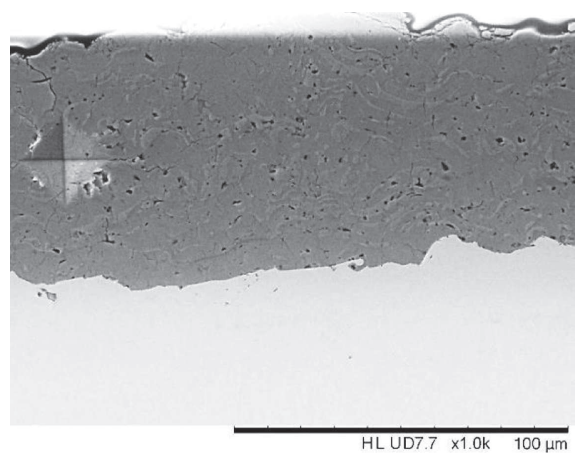

Figure 3: SEM image of hardness impression in PS cross section.

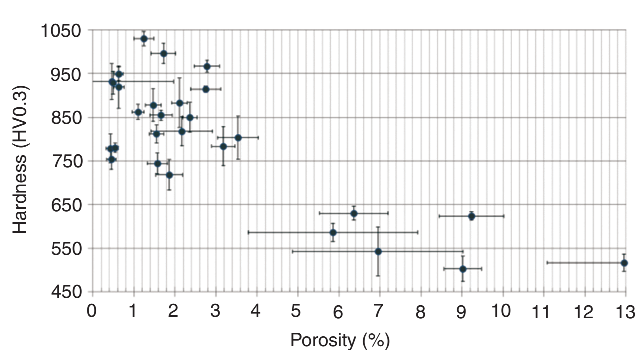

Figure 4: Comparison between hardness and porosity of the ceramic coating ($n_p = 5$, $n_h = 4$).

porosity as expected. According to [14] the hardness is related to the abrasive wear resistance. The quality of the coating can be optimized using specific process parameters to reduce surface roughness and porosity while simultaneously increasing the hardness, both important prerequisites to prevent friction. The proven feasibility of polishing the hard coating to surface roughness in the sub-micrometer range and expose a low-porous sliding surface opens perspectives for new biomedical applications. This novel biocompatible hard-coating could enhance the wear resistivity of titanium implants that are free from Co, Cr and Ni.

Author's Statement

Research funding: This study was supported by the Hightech Zentrum Aargau AG. Conflict of interest: Authors state no conflict of interest. Material and Methods: Informed consent: Informed consent has been obtained from all individuals included in this study. Ethical approval: The conducted research is not related to either human or animal use.

References

[1] Schafer T, Bohler E, Ruhdorfer S, Weigl L, Wessner D, Filipiak B, et al. Epidemiology of contact allergy in adults. Allergy. 2001;56:1192–6.

[2] Pacheco KA. Allergy to surgical implants. J Allergy Clin Immunol Pract. 2015;3:683–95.

[3] Guenther D, Thomas P, Kendoff D, Omar M, Gehrke T, Haasper C. Allergic reactions in arthroplasty: myth or serious problem? Int Orthop. 2016;40:239–44.

[4] Vendittoli PA, Roy A, Mottard S, Girard J, Lusignan D, Lavigne M. Metal ion release from bearing wear and corrosion with 28 mm and large-diameter metal-on-metal bearing articulations: a follow-up study. J Bone Joint Surg Br. 2010;92:12–9.

[5] Stahnke JT, Sharpe KP. Pseudotumor formation in a metal-on-polyethylene total hip arthroplasty due to trunnionosis at the head-neck taper. Surg Technol Int. 2015;27:245–50.

[6] Morscher EW. Endoprosthetics, Springer Verlag 1995.

[7] Budinski KG. Tribological properties of titanium alloys. Wear. 1991;151:203–17.

[8] ASTM F67 – 13, Standard Specification for Unalloyed Titanium, for Surgical Implant Applications, 2013.

[9] Wen M, Wen C, Hodgson P, Li Y. Improvement of the biomedical properties of titanium using SMAT and thermal oxidation. Colloids Surf B Biointerfaces. 2014;116:658–65.

[10] Becker ST, Beck-Broichsitter BE, Rossmann CM, Behrens E, Jochens A, Wiltfang J. Long-term survival of Straumann dental implants with TPS surfaces: a retrospective study with a follow-up of 12 to 23 years. Clin Implant Dent Relat Res. 2015; doi: 10.1111/cid.12334.

[11] Wang Y, Tian W, Yang Y. Preparation and characterization of rare earth modified nanocrystalline Al_2O_3/13 wt%TiO_2 feedstock for plasma spraying. J Nanosci Nanotechnol. 2009;9:1445–8.

[12] Stengl V, Ageorges H, Ctibor P, Murafa N. Atmospheric plasma sprayed (APS) coatings of Al_2O_3-TiO_2 system for photocatalytic application. Photochem Photobiol Sci. 2009;8: 733–8.

[13] ASTM F1854-15, Standard Test Method for Stereological Evaluation of Porous Coatings on Medical Implants, 2015.

[14] Härteprüfverfahren nach Vickers DIN EN 843-4:2005.