A New Procedure of a Calcium-Containing Coating on Implants of Titanium Alloy

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Introduction

Implants of titanium or titanium alloys are proved as bioinert. For improving the biological properties the implants were coated to cause a contact between implant and bone without connective tissue. Several coating techniques are well known, e.g. the procedure of plasma spraying [1], CVD [2], electrolytic depositing [3], ion implantation [4] or biomimetic methods [5]. This paper describes a new method for covering titanium alloys with calcium containing surface layers by treating the samples with a salt melt.

Materials and Methods

The treatment of the scoured and cleaned TiAl6V4 samples with the $CaNO_3$ salt melt was carried out in a gas-tight furnace in a nitrogen atmosphere at a temperature of 520-560 °C (treatment time varied between 0.5 and 16 hrs). After treatment, the sample were set free of adhering $CaNO_3$ in hot water in an ultrasound bath and cleaned. For the determination of the layer thickness discs were cut from TiAl6V4 rods, drilled and polished before being scoured. The structure of the surface layers was identified by TF-XRD. Depth profiles were obtained by Auger electron spectrometry (AES) and the layer thickness was determined. Several methods like cross cut, sphere cut, ellipsometry and eddy current were used for checking their suitability as process controlling. The micro hardness was determined and the tribological behaviour of the covered samples compared with that of untreated samples.

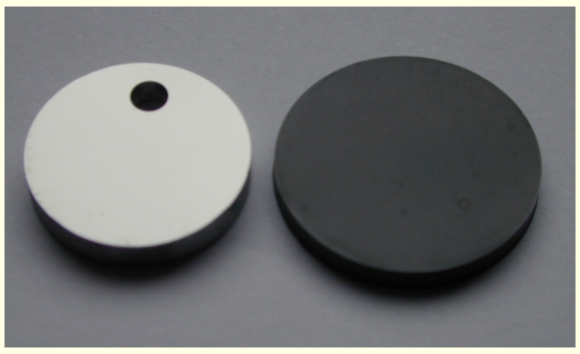

Fig. 1 Untreated (left) and treated (right) TiAl6V4 discs

Results

The procedure is suitable to generate a surface layer on TiAl6V4 implants by the treatment of the samples with a $CaNO_3$ melt. The layer had a deeper grey colour than the untreated samples (*Fig. 1*). By means of TF-XRD, the crystalline phase of the surface layer was shown to be the CaO-rich calcium titanate ($Ca_4Ti_3O_{10}$). The layer was generated after 30 min but their depth varied heavily. Treatment times of 2 hrs until 8 hrs lead to layers with increased depth and decreased differences in thickness. Using higher treatment times like e.g. 16 hrs the thickness of calcium titanate layer was markedly increased. The thickness of the intermediate TiO_2 layer is broadened compared to that of untreated TiAl6V4. *Fig. 2* shows a cross cut of a treated screw as used in surgery for fixing of bone and *Fig. 3* shows the microscopic picture of the cross cut. By means of the AES measurement, the thickness of a calcium titanate layer was estimated to be 1.2 µm (*Fig. 4*). The surface layers were elastic (average hardness 4.3 GPa, average e-modulus 128 GPa). The determination of the layer thickness by means of eddy current is suitable for process controlling. Determination of the layer thickness with treatment time yielded that there is no significant difference in the layer thickness if compared the treatment times of 2 until 8 hrs.

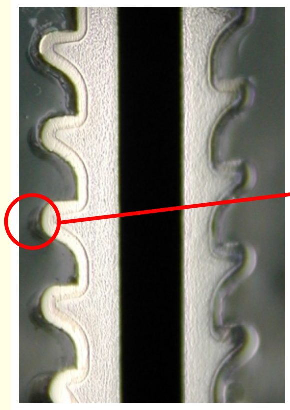

Fig. 2 Cross cut of a treated and embedded screw

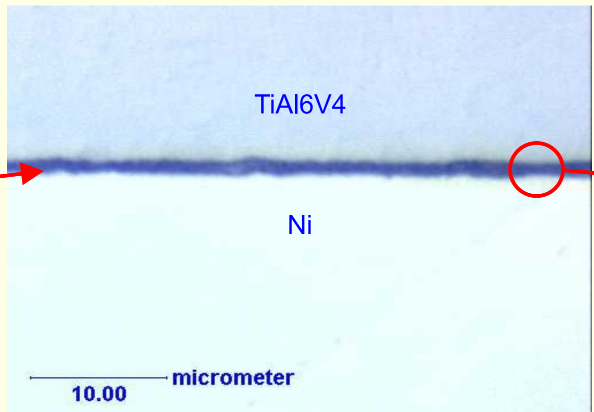

Fig. 3 Light micoscopic picture of the cross cut

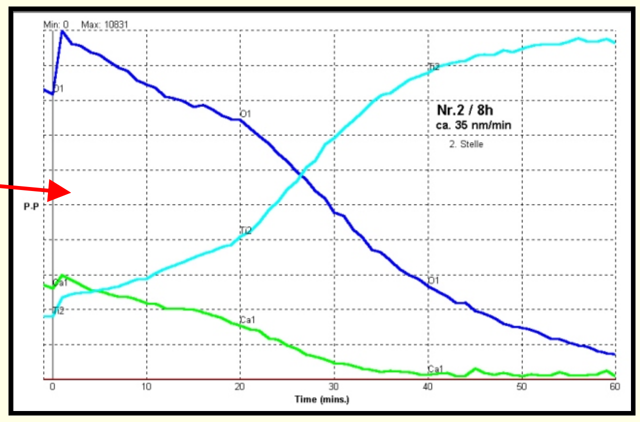

Fig. 4 Depth profile of the covered TiAl6V4 disc (AES)

Discussion and Conclusion

The surface layers have an elastic behaviour. No cracks are obvious at the area of the intender's smash even not at the borderline of the smash. A reaction time of 2 hrs is sufficient to generate the calcium titanate surface layer. Longer reaction times (>8 hrs) led to a slightly larger thickness of the calcium titanate layer but also to higher thickness of the TiO_2 intermediate layer resulting in a loss of adhesive strength. For process controlling, methods based on cross cutting or eddy current seemed to be suitable. Irregular forms can be coated well for the whole area of the samples is in contact with the melt. The presented procedure can be used for generating calcium containing surface layers on implants of titanium alloys even with complicated forms.

Acknowledgements

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