A Study of Glass-Ceramic Coatings in Contact with the Biological Environment

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Abstract

Glass-ceramic enamel coating is a final product of physical and chemical reactions in the process of heat processing of vitreous, chemical and inorganic compounds at temperatures between 800 and 900°C. These compounds combining properties of glass and ceramics form a strong possibility of adhesion to a surface of a substrate on with a metal base. In the mechanical engineering industry, enamel coatings are used mainly for their corrosion behaviour and resistance to surface abrasion. A wide scope of usage can also be found in the field of health service, food industry, architecture, civil engineering, energy and ecological industries. As the properties of glass-ceramic enamel coatings include high resistance to aggressive atmospheres, long service life, chemical stability and, above all, minimal contents of harmful substances, usage of glass-ceramic coatings is much wider. This contribution deals with the study of glass-ceramic coatings on the basis of enamels which are suitable to be in contact with the biological environment, so that growth of cell cultures occur or does not occur. With respect to the composition of glass-ceramic coatings on the basis of vitreous enamels, they can be included into a group of bioactive ceramics which can be used, for example, for implantation purposes. First of all, the size of input compounds during creation of glass-ceramic coatings plays an important role for the roots and growth of cells. The contribution deals with the possibility of using these coatings and it presents the first experimental test results concerning the possibility of cell cultures growing on these coatings. Further, the influence of individual input compounds of enamelling suspension on resultant properties of glass-ceramic enamel coatings is examined.

Key words: glass-enamel coating, bioactive ceramics, cell growth, clay, kaolin

1. INTRODUCTION

Glass-ceramic coatings are characteristic of high-quality anticorrosive protection and resistance to aggressive environments. Their great properties also include chemical resistance to acids, abrasion resistance and wholesomeness. The glass-ceramic coatings are included into the group of the bioactive materials which form the conditions for total symbiosis between an implant and live tissue. Input compounds added to these coatings have an influence on adaptation and proliferation of cell cultures. In the field of medicine, glass-ceramics are used on the experimental level mainly for the coating of titanium implants. The advantage of glass-ceramics consists in its porosity which makes it easier for the cells creating the bone tissue to attach to the implant. The dominant element in glass-ceramic coatings is silicon.
2. EXPERIMENTAL MATERIALS

Pure titanium Ti-ISO 5832-2 was used as a substrate. The sample surface was mechanically pre-treated by grinding and brushing. Another substrate material was a sample of titanium alloy Ti6Al4V-ISO 5832-2. Surfaces of the samples were made by turning work with no other mechanical surface treatments. All samples were cut from rod material 8 mm in diameter and 3 mm in length. The samples were degreased at a temperature of 25°C and pH 9.44 for 5 minutes. Rinsing was done by submersion into a water bath at a temperature of 22.3°C and pH 8.27 for 1 minute. Then enamelling slurry was applied, followed by burning at temperatures between 820 and 840°C for 8 to 12 minutes, during which vitreous enamel coating emerged.

Photographic documentation of the samples was made with a scanning electron microscope (SEM). The following snapshots of individual surfaces were taken with Phillips XL30 Series device in the Laboratory of Electron Microscopy of the Nanotechnology Centre of VGB-TU Ostrava.

The surface of the pure-Ti samples was further mechanically treated by grinding and brushing (see fig. 1 and 2).

![Fig. 1 SEM Ti-sample snapshot, (SE) [1]](image1)

![Fig. 2 SEM Ti-sample snapshot, (BSE) [1]](image2)

Ti6Al4V alloy samples parting-turned with no other mechanical surface treatments (see fig. 3 and 4).

![Fig. 3 SEM Ti6Al4V sample snapshot, (SE) [1]](image3)

![Fig. 4 SEM Ti6Al4V sample snapshot, (BSE) [1]](image4)

An enamelling suspension was made in a typical way with the respective volume of typical-sized clay in microns and fine-milled clay in nano-size. The clay was replaced by kaolins in four suspensions. Application of the enamelling suspension was carried out manually by means of a brush. The samples prepared in this way were dried out in a drier at a temperature of 100°C for 5 minutes. Burning was carried out in a furnace at temperatures between 820 and 840°C for 8 to 12 minutes with follow-up cooling in the air.
3. EXPERIMENTAL WORK

Measuring of glass-ceramic coating sample roughness parameters was carried out by means of a touch profilometer MITUTOYO SURFTEST SJ i 301, according to ČSN EN ISO 4287.

The highest Rz-profile unevenness value is defined as a mean value from the absolute values of the heights of the five highest profile projections and the depths of the five lowest hollows. The value of the roughness parameter may have a positive effect on adhesion of cell structures and their further cultivation. The preliminary glass-ceramic coating with contents of finely milled clay MIC showed the highest average value of Rz. Clay compounds showed higher average values of Rz for the preliminary + surface coating, in comparison with the kaolin compounds used. The highest average value, Rz 14.414 µm, was shown by the glass-ceramic coating when a clay compound of classic MIC had been used. The fine-milled clay showed the average value of Rz 11.192 µm on the preliminary + surface glass-ceramic coating. The glass-ceramic coatings showed lower values of Rz when kaolin compounds had been used. These values resulted in a smoother surface as contrasted to the clay compounds used. The kaolin compound marked T3 showed the lowest average measured value of RZ 2.38 µm. A higher average value of Rz, 4.579 µm was measured for the kaolin compound marked T4.

Graph 1 - Rz of the preliminary glass-ceramic coating on pure Ti

Graph 2 - Rz of the preliminary+surface glass-ceramic coating on pure Ti

Graph 3 - Rz of the preliminary glass-ceramic coating on Ti6Al4V alloy

Graph 4 - Rz of the preliminary+surface glass-ceramic coating on Ti6Al4V alloy
It follows from the graph nr. 3 that the preliminary glass-ceramic coating applied on Ti6Al4V alloy showed the highest average values of the Rz roughness parameter. The value of the Rz parameter was 18.61 µm on the preliminary glass-ceramic coating containing the fine-milled clay MIC. The glass-ceramic coating with contents of the kaolin compounds T3 and T4 showed the average values of the Rz roughness parameter much lower, see graph 3. The highest average values of the Rz roughness parameter, 16.154 µm, were measured for the preliminary + surface glass-ceramic coating with the compound of classic MIC clay. The average value of Rz roughness parameter, 12.412 µm, showed the glass-ceramic coating with the contents of fine-milled MIC clay. Using of the kaolin compounds marked T3 and T4 in glass-ceramic coatings showed average measured values of the Rz roughness parameter 3.21 µm and 6.314 µm, see graph 4.

3.1 Application of Cell Cultures on Selected Glass-Ceramic Coatings

Application of cell cultures with the type designation MG-63 (20 000 b/ml) were carried out onto the prepared samples with glass-ceramic coating in the Biological Centre of the Academy of Sciences of the Czech Republic in Nové Hrady, where the SEM microscopic analysis was also executed. The cell cultures applied onto enamel titanium samples were left in sterile environment for cultivation for 72 hours. Subsequently, the target microscopic analysis SEM was carried out in order to determine the suitability of the glass-ceramic coating for the life of cell cultures.

3.2 Evaluation of the SEM Microscopic Analysis

Preliminary glass-enamel coating with finely milled clay of Ti6Al4V alloy

![Fig. 5 SEM snapshot of cell culture, magnification 3000x [1]](image)

![Fig. 6 SEM snapshot of cell culture, magnification 5000x [1]](image)

The cell culture is spread enough in the examined sample and adhered to the surface of the examined sample. In fig. 5 and 6, one can observe close contacts among cells serving for metabolic changes (signal and signalization transfer) as well as long, thick contacts serving for exploring of the surface by the cell.
Preliminary glass-ceramic coating with the T4 kaolin compound on pure Ti

Figures 7 and 8 show a well-spread confluent layer. Cytoplasmatic projections, which are spread enough and with well-defined cell spaces, are recorded here. The cell culture is spread enough on the sample and adhered to the surface of the examined sample.

Preliminary and surface glass-ceramic coating with the T4 kaolin compound of Ti6Al4V alloy

Figures 9 and 10 show remnants of pathological dead cells. The snapshots show the very bad condition of the cell culture applied onto the respective material. The examined surface does not show any marks of cell cultivation. Cell adherence is negligible here.

4. CONCLUSION

It follows from the examined samples that the best results causing high-quality cell cultivation were obtained on two samples. The first one is formed by Ti6Al4V titanium alloy, on the surface of which the preliminary glass-ceramic coating with fine-milled clay was applied; the other is formed by pure Ti, on the surface of which the preliminary glass-ceramic coating with the T4 kaolin compound was applied. The samples with these glass-ceramic coatings showed live and already-cultivated cell culture, which was adhered enough and with spread cytoplasmatic projections. This result indicates the suitability of using the glass-ceramic coating in the biological environment. The worst result was obtained for Ti6Al4V alloy, on the surface of
which the preliminary and surface glass-ceramic coating with the T4 kaolin compound had been applied. This sample did not sow any marks of viable cells or other possible cultivation, only some cells of pathological character.

LITERATURE
