Properties of Zirconia after Plasma Treatment

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Abstract. The influence of high-frequency plasma treatment on the properties of zirconia powder is shown in the work. The powder was produced by a plasma-chemical method. The powders had a foamy form with the size of agglomerates of 5–10 μm and crystallites of 20–50 nm. The powders were treated by the pulse plasma unit with dielectric barrier discharge generator. It was shown that the plasma processing changes the acidity of water-powder suspensions from 8.1 to 4.3 pH, which signifies the powders' wettability improvement. It was revealed that more intensive mixing using ultrasound influences the acidity level, reducing it in comparison with mixing by paddle-type agitator. It was shown that these changes of surface properties have relaxation by 4% per day and extrapolation of this dependence shows that the powder will have initial properties after 400 hours storage at room conditions.

INTRODUCTION

One of the major problems for reconstructive surgery is restoration of bone defects which result in injuries after removal of tumor mass or inflammation. For these reconstructive surgery processes one can apply implants made using inorganic materials which should have such properties as biological inertness; mechanical strength, resistance to wear; hemocompatibility; resistance to internal organism liquids [1]. However, reactions with body tissues, biological liquids will stipulate corrosion or failure effects on implants. Therefore, the investigations of such materials behavior in these conditions are of interest.

Well known, advanced materials like ceramics (alumina and zirconia) which are permitted to use in medicine are biocompatible, have high strength, corrosion and chemical stability and biological inertness [1–3]. Also, it was shown [1] that the implants made of high-porous alumina ceramics have osteoinductive properties.

The surface properties of implants play an important role in adhesion and proliferation of cells. Since interactions of implants with blood, liquids, soft and solid body tissues happen on an implant surface, the implant survival or failure depends on various properties of the surface—pore and surface morphology, roughness, wettability, chemical composition.

For example, in [4–6] it was shown that implants after laser modification of surface have three times increasing of wettability of a surface, resulting in proliferation of osteoblast cells. According to [5] this increase in the growth rate and subsequent improvements of adhesive properties of the surface of implants are the result of the increase of free surface energy characterized by wettability increasing.

Besides laser processing for the purpose of surface modification, plasma processing is widely used for such treatments. These studies of plasma treatments influence on ceramics surfaces will be more efficient for the powders as they have a highly specific surface and effects of plasma processing will be more considerable.

The result of plasma processing is a change of chemical reactivity of active centers which are formed on the surface. It can be easily detected during a reaction of powders with water molecules when products of this reaction (H^+ or OH^-) change the level of acidity of a water-powder suspension. In [7] it was shown that an increase of acidity level demonstrates the improvement of wettability of powders, i.e. increase of their hydrophilic properties. Thus, the pH-level of water-powder suspensions after and before the plasma processing of powders will be an effective method of studying the changes of powders wettability.

The aim of this work was to study the changes in hydrophilic properties of zirconium dioxide powders after processing by low-temperature non-equilibrium plasma in the air environment with an atmospheric pressure.

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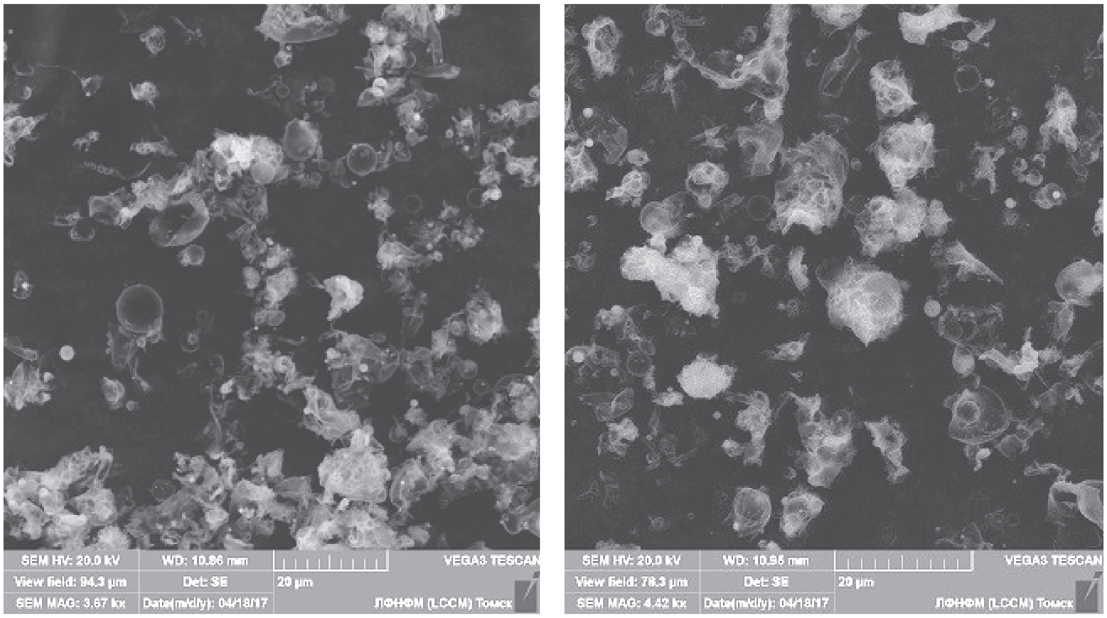

(a) (b)

FIGURE 1. SEM images of zirconia powders in initial (a) and after ten-minute plasma processing (b) states

MATERIALS AND METHODS

Zirconia powders stabilized by 3 mol % of MgO produced by a plasma-chemical method are investigated. The powders had a foamy form (Fig. 1) with the size of agglomerates of 5–10 μm and crystallites of 20–50 nm.

The powders were treated by the pulse plasma unit with dielectric barrier discharge generator. The powders were put in the working space (quartz glass tube) in which plasma was generated. The plasma frequency and pulses duration was 855 Hz and 10 ns, energy of each pulse was 0.22 kJ. During plasma treatment the powders were mixed by rotation of the tube, the rotation rate was 80 rpm.

The scanning electron microscope Tescan VEGA 3SBH was used to examine ceramics powder. Acidity level of the water-powder suspensions was measured by pH-150 device. The suspensions consisted of 1.1 g of powder and 50 ml of distilled water.

Suspensions were mixed by two different methods—by the mixing by paddle-type agitator (with a rotation rate equal 100 rpm, during 30 s) and ultrasound mixing (with a frequency of 18 kHz, during 1 min).

RESULTS AND DISCUSSION

In Fig. 1 SEM images of zirconia powders in initial and after ten-minute plasma processing states are shown. As one can see, grain sizes and particles morphology structure have no changes, i.e. plasma treatment does not affect powder macrostructure.

The results of the measurements of the acidity level of water-powder suspension depending on processing time are presented in Fig. 2, which shows that the more processing time the less the value of pH is, i.e. the suspension passes from alkaline area into acid when the processing time is more than 6 minutes. Moreover, this dependence of pH-value has a linear character. According to [7] this decrease of pH-level indicates an improvement of a hydrophilic property of materials. A similar effect is already known for the polymeric and other organic materials processed by atmospheric plasma in the air or oxygen environment. According to [8] this effect indicates the appearance of polar oxygen-containing groups on the surface of processed materials. For the zirconium dioxide, as well as for the aluminum oxide which is described in [8], the decrease of pH-value indicates a change of a bond character of hydroxyl groups with Zr atoms. It is possible that there was plasma cleaning of the surface of powder which was not specially prepared for experiments, however, it demands additional research.

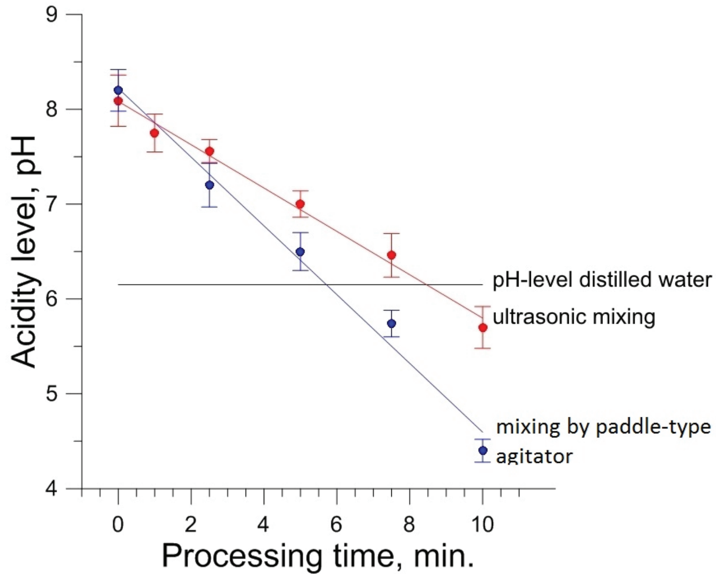

FIGURE 2. Acidity level of water-powder suspensions as a function of processing time

PH-level after ultrasonic mixing of suspension is shown in Fig. 2. As one can see, the pH of the suspension is higher when the ultrasonic mixing is used with respect to the mixing by paddle-type agitator, especially in the area of a long processing time. However, at this moment it is not possible to explain this influence of ultrasonic mixing on the acidity level and additional research is necessary. But it is likely to be the result of mixing intensity because the power of an ultrasonic agitator is three times larger than the power of a paddle-type agitator.

According to [9] the effect of plasma processing can be changed and the powders come back to the initial state. Therefore, we carried out the measurement of suspension pH-level after storage of the treated powder at normal condition (the powders were stored in the air at room temperature) for a long time; these results are presented in Fig. 3 for powder after ten-minute plasma treatment and mixing by paddle-type agitator.

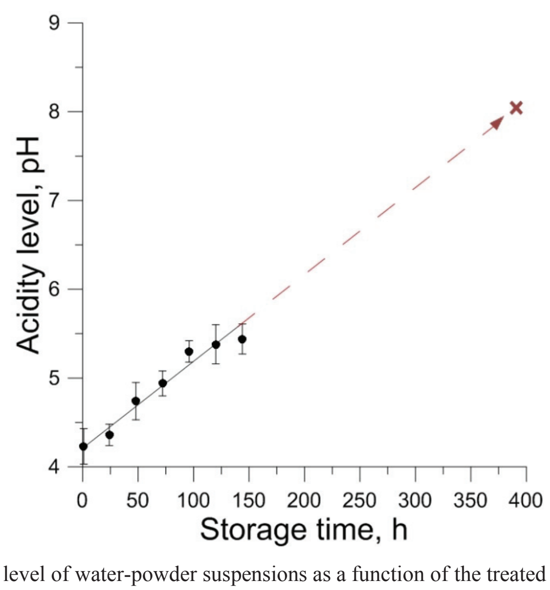

FIGURE 3. Acidity level of water-powder suspensions as a function of the treated powder storage time. Powder plasma processing time is 10 min, mixing by paddle-type agitator

As one can see in Fig. 3, the storage up to 150 h leads to decreasing of pH-level and extrapolation of this dependence to the initial state of powder shows that in 400 hours pH-level will have initial level, i.e. the effect of treatment decreases approximately by 4% a day. This well-known phenomenon is also called the "effect of aging". Several factors of this effect are described in [9], but in the case of oxides surfaces we can talk about two factors. First of all, the elements of the environment are sediment on the powder surface, and this reduces the wettability. Depending on the extent of influence of the environment, this process of sedimentation can have various intensity values. The second factor of aging effect of plasma activation of the surface is reactions of free radicals and other active particles of surface among themselves.

CONCLUSION

It was shown that treatment of zirconia powders by high-frequency plasma changes pH-level of water-powder suspension from 8.1 to 4.3, this dependence has a linear character.

It was revealed that the higher intensity of mixing of water-powder suspension leads to decreasing in the pH-level, especially for the long plasma treatment. After ten-minute plasma processing the acidity levels were 4.3 pH and 5.7 pH for the mixing by paddle-type agitator and ultrasonic mixing, respectively.

It was revealed that there is an aging effect for treated powder—the pH-level of water-powder suspension decreased approximately by 4% per day for powders stored at normal laboratory conditions in the air at room temperature. According to extrapolation of the obtained data, pH-level will have an initial level in 400 hours.

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