POST-PROCESSING OF TITANIUM 3D PRINTOUTS WITH RADIO FREQUENCY PLASMA

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Abstract

Additive manufacturing is a technology of great interest for biomedical engineering and medicine since it enables to mimic natural structures. The 3D printouts require post-processing to ensure desired surface properties and interaction with living matter. The presented research focuses on novel approaches involving plasma treatment of Ti6Al4V scaffolds obtained by Direct Metal Printing. Solid samples and scaffolds of two various geometries were treated in atmospheres of pure argon, argon and oxygen or pure oxygen. The effect of post-processing was evaluated with scanning electron microscopy, measurements of mass, and surface roughness.

In all the examined cases the proposed post-processing method reduces the amount of loosely bonded powder particles remaining after printing. The changes of mass before and after the treatment are much lower than in the case of popular wet chemical methods. The character of undergoing post-processing depends on the process atmosphere resulting in physical etching or the combination of physical etching and chemical oxidation. The action of argon or argon/oxygen plasma reduces mass to the level of only 1% while by use of pure oxygen atmosphere even the slight increase of the overall sample mass is observed.

The plasma etching was successfully introduced for the treatment of titanium 3D printouts to minimize the detachment of powder particles. That method not only is much softer than chemical etching but it can also lead to specific surface structurization that may be beneficial regarding medical applications of such printouts.

Keywords: *post-processing, plasma treatment, 3D printing, titanium printouts, RF plasma*

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Introduction

Additive manufacturing is of great interest to scientific teams from around the world and from various industries [1]. That collective name applies to a group of methods resulting in three-dimensional elements by application of successive layers of material – i.e. 3D printing. This approach enables manufacturing of low-quantity series of products, or even individual personalized details, almost regardless of the complexity of their shape. 3D printing techniques are of great interest, especially regarding applications in biomedical engineering or medicine [2-4].

Currently, it is possible to control the size and distribution of implant pores [5,6], which has a significant impact on the processes of the implant/body integration by inducing angiogenesis and the mammalian cells growth [7]. Nevertheless, the structure of human and animal tissues is characterized by a complex architecture, often a hierarchical structure with complex porosity [8,9], the reconstruction of which goes beyond the scope of conventional design and manufacturing approaches. However, 3D printing techniques give more freedom to develop new structures for such specific applications requiring mimicry of nature.

An important aspect of 3D printing for potential biomedical applications is the use of additional surface treatments that can modify its porosity, change the surface energy, and influence the biological response [10]. Technologies based on powder sintering may leave residues on the both the elements surface and in the pores which are not integrated with any constituent. Therefore, in the case of medicine and biomedicine living tissues, it is necessary to remove such residues to prevent their uncontrolled release to the surrounding environment. Currently, the post-processing of metal prints involves mechanical methods [11], such as shaking, blowing, shot blasting, and those related with chemical treatment, such as baths in acid solutions [12,13] or electrochemical treatment [14,15]. The new approach to post-processing of 3D prints may involve their plasma etching. So far, such an approach is rather used for polymers [16] or modification of the metal powders [17] and not the metal prints themselves.

It should be remembered that the element subjected to post-processing to remove unbound powder residues undergo significant changes that highly affect its main properties. The main effect is smoothening of the scaffold. Wu et al. [14] reached over the 5-time improvement in the level of Ra between the untreated and the chemically polished 3D titanium prints. These changes can improve biological response [18], but also reduce mechanical properties [19] or even cause the loss of material integrity, especially due to single struts thinning [20]. Wysocki et al. [13] showed that only 3 minutes of chemical polishing with the mixture of HF and HNO_3 can lead to an over 50% mass reduction of the treated scaffold.

The following article is focused on the description of the novel approach to post-processing of metal 3D prints. The investigations were conducted on the Ti6Al4V scaffolds prepared by means of DMP (Direct Metal Printing) method so as to determine the effectiveness of plasma-ion treatment of such elements in order to eliminate defects and impurities remaining after the printing process.

Materials and Methods

Samples preparation

The tested samples were cylinders – 16 mm in diameter and 5 mm of height, prepared by means of ProX DMP 320 printer. The laser power was 500 W, the layer thickness ranged from 30 to 60 microns and the accuracy of the printout was ± 0.2%. The printing material was the Ti6Al4V ELI alloy available under the trade name LaserForm® Ti Gr23 (A).

Samples of variable filling resulting in different geometry of obtained scaffolds were analyzed within this study. FIG. 1 presents images of the examined 3D printouts: 100% infill (no intentional voids were left during printing either on the surface or inside the sample), scaffolds with beams oriented at right or variable angles (denoted respectively solid, geo1, and geo2).

Post-processing

The plasma-ion post-processing was carried with radio frequency etching. Modified samples were placed in the vacuum chamber directly on the electrode. Three types of the working atmosphere were analyzed: argon (99.999% purity), oxygen (99.999% purity) and the mixture of argon and oxygen. The working pressure was 15 Pa for the usage of single gas and 20 Pa double gases. In all the cases the flow rate of each used gas was set for 8 sccm. The etching was conducted under the negative potential bias of 2200 V. The temperature of the modified elements was 500°C. The duration of the post-processing was constant in all the analyzed cases and equalled 4 h. The list of used parameters and the designation of the type of modification is presented in TABLE 1.

Scanning electron microscopy (SEM)

The SEM investigation was used to visualize and evaluate the topography of all the examined samples. SM-6610LV (JEOL, USA) equipped with X-Max 80 energy dispersive X-ray spectroscopy (EDS) analyzer (Oxford Instruments, UK) was used for observations with secondary imaging mode (SEI – secondary electron image) – acquiring topographic images. The SEM observations at randomly selected spots were carried out under high vacuum with an electron beam acceleration voltage of 10-20 kV.

Mass control

Five samples of each type of the examined printouts (solid, geo1, and geo2) were used to determine the impact of the proposed post-processing method on the mass change. For each sample, the measurements were conducted prior to plasma etching and after that process. The evaluation of mass variation was conducted with an Asix AGS60 moisture analyzer with a weight accuracy of 0.001 g. The samples were heated to 100°C and kept at that temperature until a constant mass of the sample was obtained for at least 60 s.

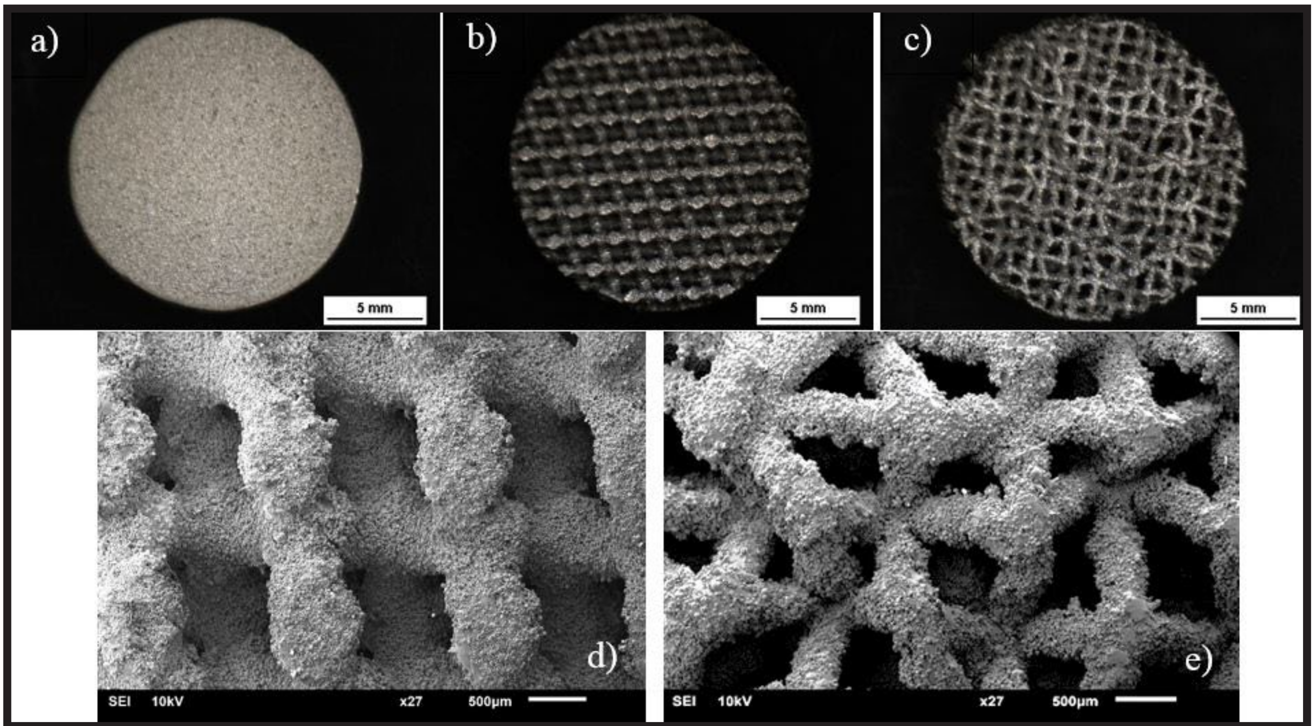

FIG. 1. Macroscopic images of analyzed samples: a) solid sample – 100% infill, b) geo1 – right angles beams, c) geo2 - individual beams crossing at variable angles; and SEM images of scaffolds d) geo1, e) geo2.

TABLE 1. Parameters of used plasma etching.

No.	Working gas	Potential [V]	Pressure [Pa]	Gas flow [sccm]	Temperature [°C]	Time [h]	Code of modification
1	Oxygen	-2200	15	8	500	4	O_2
2	Argon		15	8			Ar
3	Oxygen & Argon		20	8 (Ar) 8 (O_2)			Ar/O_2

Surface characterization

The evaluation of surface roughness was conducted via contact profilometry by means of Hommel Tester T1000. For each sample, 6 profiles were collected before and after post-processing. The values of the following parameters: Ra, Rz, Rmax were analyzed.

Results and Discussions

The roughness measurement carried out after plasma etching of solid samples (FIG. 2) revealed differences, in relation to the unmodified sample, only for the argon plasma. In this case, the Rz and Rmax parameters increased by about 20%. However, no significant differences were found for the O_2 and Ar/O_2 modification. Usually, post-processing reduces surface roughness. The results of chemical or electrochemical polishing presented by Pyka et al. [19] or Wu et al. [14] show a decrease of printouts roughness, respectively by up to 25% and even about 5 times (for Ra parameter). Also, other methods like jet-blasting show a similar tendency but with minor effects, e.g. the results of Kim et al. [16]. In that study, the areal surface roughness of scaffolds single struts changed from 11.0 ± 4.1 µm to 10.6 ± 3.8 µm after post-processing.

The argon plasma resulting from the high negative potential of electrode autopolarization is related with a basically physical effect of surface etching - the predominant result is a spontaneous change in topography.

The incorporation of oxygen into the plasma atmosphere mitigates this effect. Oxidation takes place in addition to the physical etching of the surface. In the case of etching in pure oxygen, this effect is dominating, which results in a slight increase in the mass of samples after the modification. Such an effect is in opposition to the mass loss observed in other types of etching. The results of the EDS surface examination (FIG. 3) show that the highest oxygen content in the surface of the sample etched in oxygen plasma which reaches the level of about 40%, while for the sample modified in the mixture of argon and oxygen, this value is only about 25%. The least amount of oxygen is present in the case of samples etched in pure argon, only about 10%. When discussing the change in the sample mass values after the plasma etching process, it should be noted that the measured differences are small. They are in the range of 0.3-0.5% for the solid samples and 0.5-0.7% for the scaffolds (FIG. 4). This is a much better effect than in the case of chemical cleaning of 3D prints, where the weight loss can be up to several dozen percent [13].

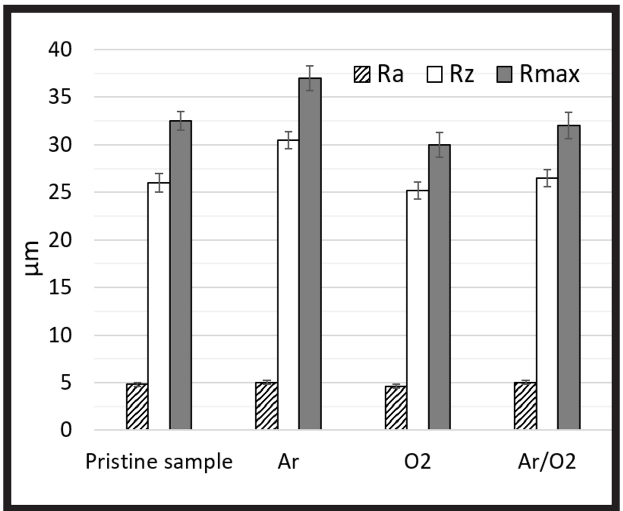

FIG. 2. Comparison of the roughness changes of pristine solid 3D printouts and those modified by plasma etching in various working atmospheres.

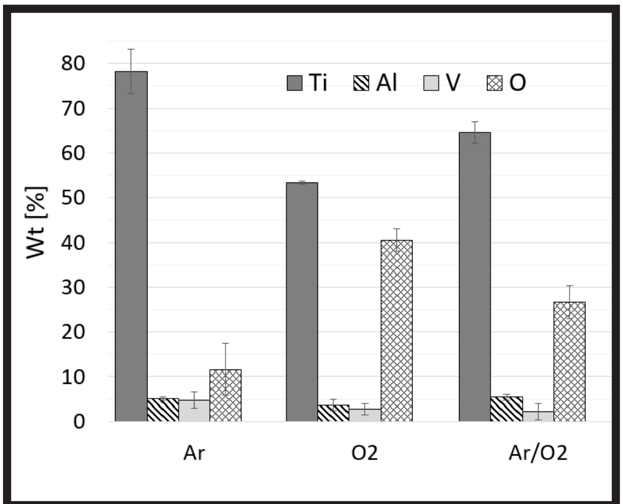

FIG. 3. Chemical composition of solid samples modified by plasma etching in various working atmospheres.

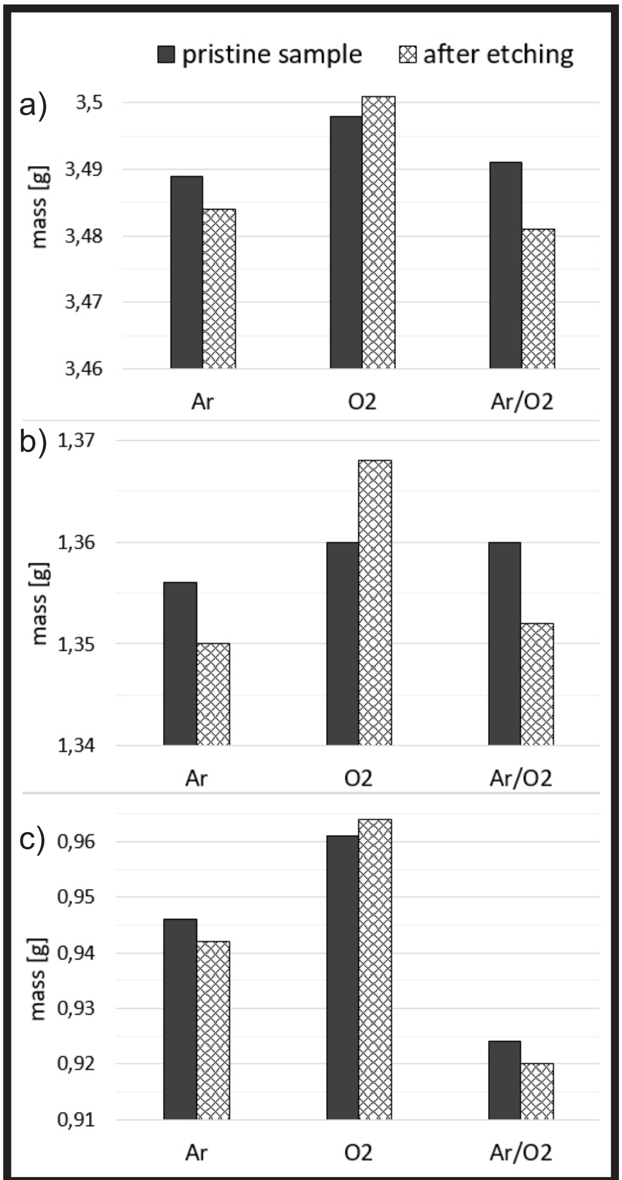

FIG. 4. Changes of mass of printouts modified by plasma etching in various working atmospheres. a) solid, b) geo1, c) geo2.

The SEM analysis of the plasma-treated solid samples showed high efficiency of that post-processing method in removing residual powders from the surface (FIG. 5). Regardless of the chemical composition of the reaction atmosphere, the etching effect is similar. Only a few residues of powders with a larger diameter, that are more tightly bound to the substrate, remained on the examined surfaces. Similar effects were achieved by other research groups working with standard methods of post-processing [12-14]. More loosen powder particles – contacting the substrate with only a small part of the surface, are completely removed. Higher magnifications (FIG. 6) reveal the differences in the effect of Ar and O_2/Ar modification. The argon plasma etching creates a specific microstructure on the sample surface. As a result, the increase of surface roughness appears, which was confirmed not only by the SEM images but also by profilometry (FIG. 2). Additionally, the structure defects remaining after the printing process, such as microcracks, are more visible, which may additionally contribute to increasing the roughness, especially the Rmax parameter. The oxygen plasma etching, especially in pure oxygen, results in significantly smoother surfaces of the printouts. This difference results from the previously discussed coexisting chemical oxidation and physical etching. This may also be favoured by the surface temperature during the plasma process, stabilizing at about 500°C. The oxidation effect also masks possible structure defects.

The etching effect is slightly different for treated scaffolds but looks similar in the case of both examined geometries of the printouts (FIGs 7 and 8). The cleaning, in this case, is not as effective as in the case of solid samples. Powder residues are visible on all surfaces. The weakest cleaning effect was obtained for the Ar/O_2 modification – minor, insignificant changes in the amount or geometry of residual powders. Usage of argon or pure oxygen plasma leads to the similar final state of the examined samples. In both cases, there are visible the remaining particles of used powders on the surface of scaffolds. What is more, the change in their geometry is clear – swap from round to more angular shape of individual particles. There are no observed powders whose contact surface with the substrate would be small enough to cause a risk of their easy detachment. Therefore, it can be concluded that the obtained effect of etching is satisfactory in these cases. A different etching effect for scaffolds and solid samples may be due to two reasons. The first is possibly scattering of the plasm in the subsurface area leading to decrease of the efficiency of the process, resulting from larger and more complicated geometries. Secondly, the structure of the scaffold printouts is uneven. It seems that there exist areas of beams that can be treated as solid and those where the powder has not been melted well enough, resulting in the formation of something like a porous sinter produced by the chaotic thermal fusion of a large group of powder particles. Due to the small size of the individual beams forming the overall structures, the attempt to completely remove such mentioned above porous structures would involve a significant reduction in their size, which in turn may lead to a weakening of the strength properties of the printout.

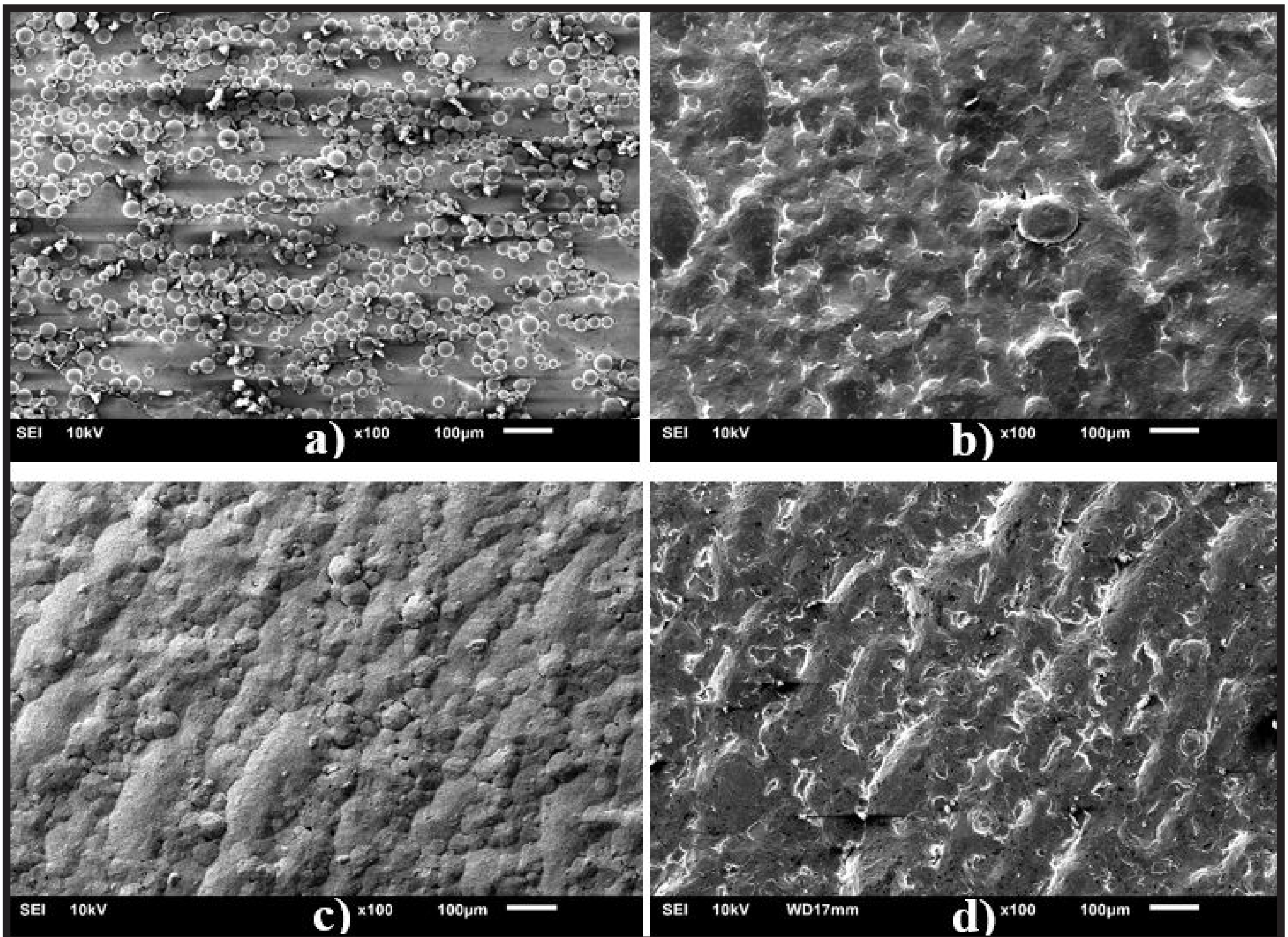

FIG. 5. SEM images of the surface of solid samples modified in various manners – 100x magnification. a) Pristine state, b) O_2 modification, c) Ar modification, d) Ar/O_2 modification.

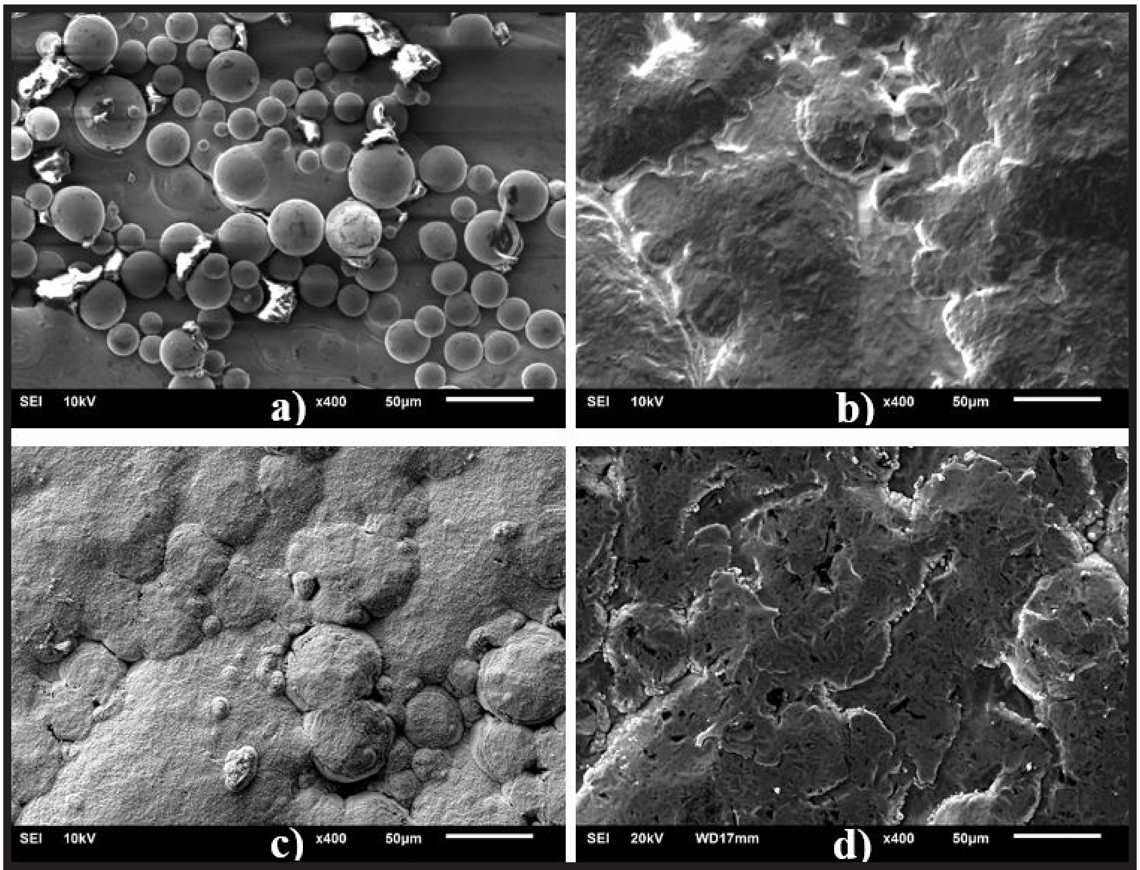

FIG. 6. SEM images of the surface of solid samples modified in various manners – 400x. a) Pristine state, b) O_2 modification, c) Ar modification, d) Ar/O_2 modification.

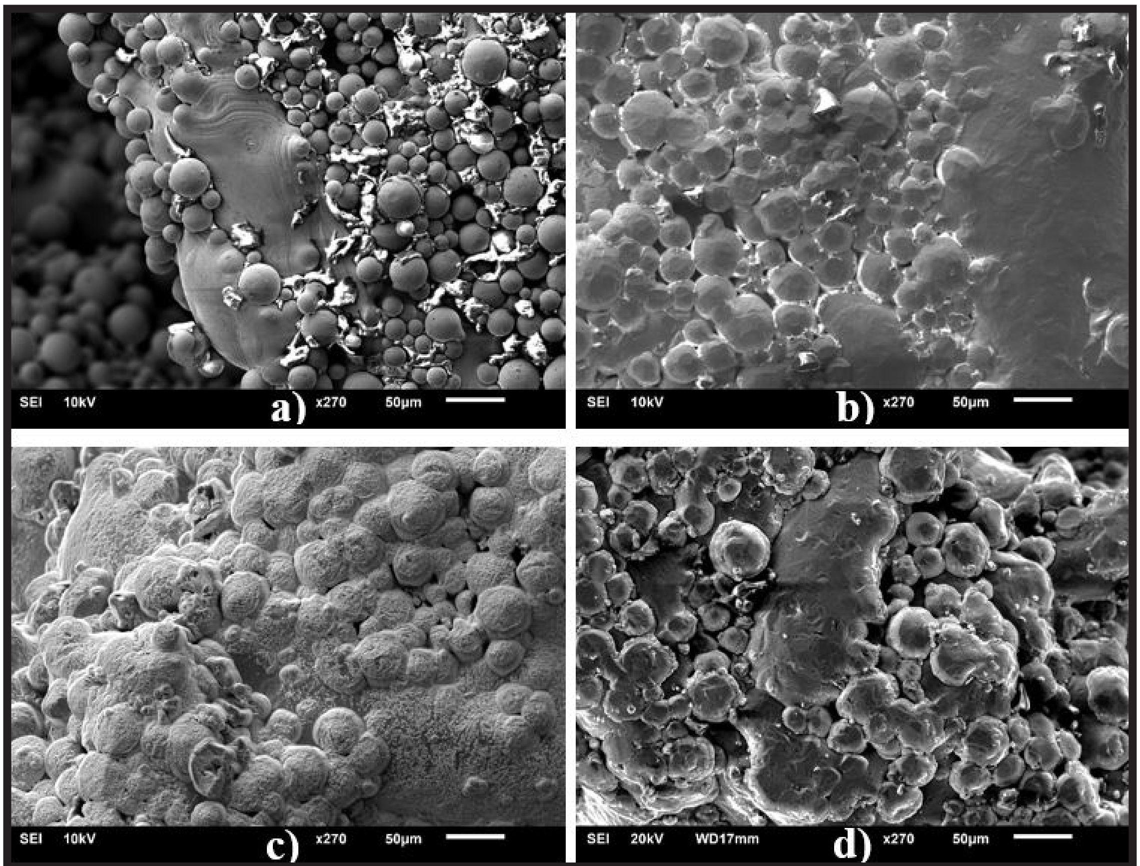

FIG. 7. SEM images of the surface of geo1 samples modified in various manners. a) Pristine state, b) O_2 modification, c) Ar modification, d) Ar/O_2 modification.

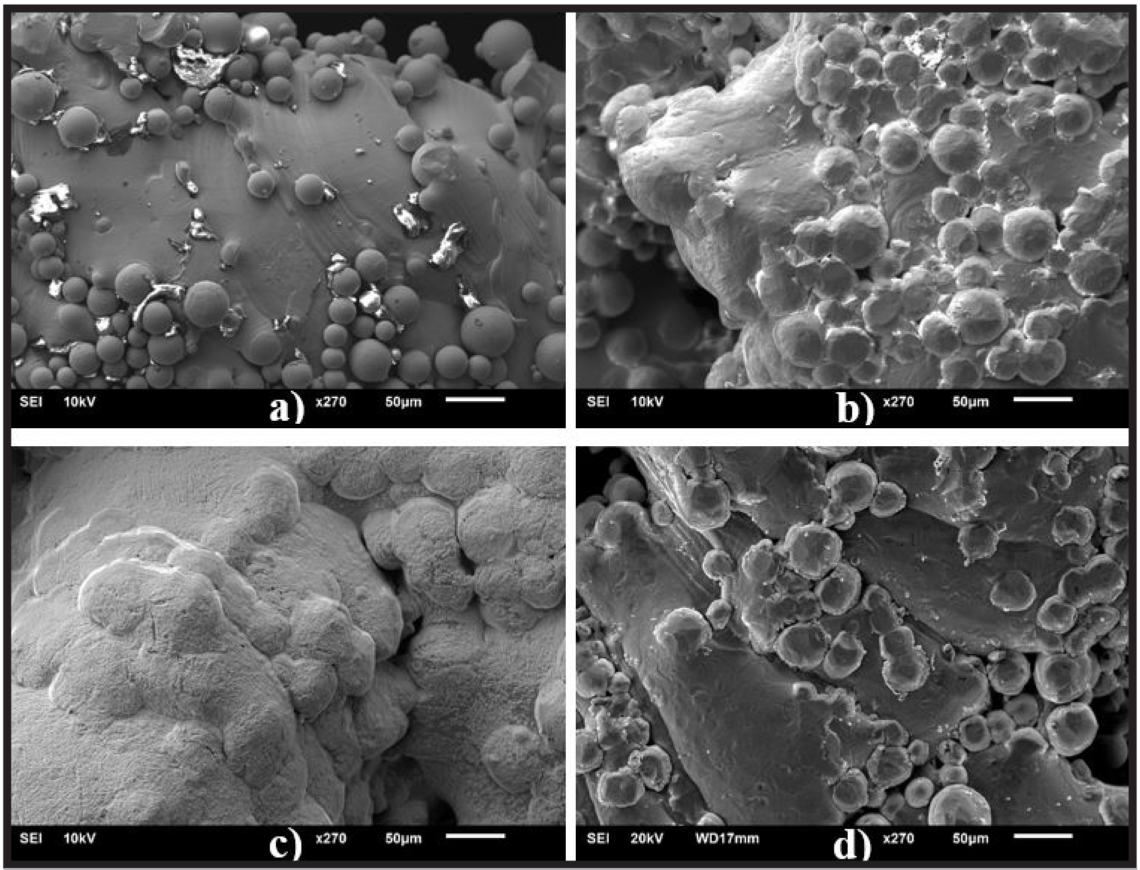

FIG. 8. SEM images of the surface of geo2 samples modified in various manners. a) Pristine state, b) O_2 modification, c) Ar modification, d) Ar/O_2 modification.

Conclusions

The presented results show that the plasma treatment of titanium elements obtained via the DMP method is a possible novel approach to the post-processing of 3D printouts which reduces loosely bonded remaining particles of the powders used during manufacturing. Depending on the applied kind of the working atmosphere, it is possible to conduct predominantly physical etching (action of Ar plasma) or a combination of physical etching and chemical oxidation (use of O_2, or Ar/O_2 plasma).

The proposed method is much less invasive than common chemical etching and results in the mass reduction of the examined printouts of less than 1% (for the usage of pure argon or its mixture with oxygen) or even a slight increase of that parameter due to the formation of the oxide layer. The proposed approach was more effective in cleaning loosely attached powder particles from elements with simpler geometry, but in all the examined cases the possible detachment of powders particles was effectively minimized.

The disadvantage of the plasma method may be its time-consuming nature. In the presented research, etching was carried out for up to 4 h, while in the currently most popular method of wet chemical etching, this process does not exceed several minutes. However, the increase in processing time can be compensated by the advantages. The first benefit is a small, even negligible loss of weight, important especially in scaffolds printouts as it does not change their strength properties. The second advantage is the obtained microstructure which can be related with more favourable conditions of the surface for cell adhesion.

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