Porous Titanium by Additive Manufacturing: A Focus on Surfaces for Bone Integration

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Review

Porous Titanium by Additive Manufacturing: A Focus on Surfaces for Bone Integration

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Abstract: Additive manufacturing (AM) is gaining increasing interest for realization of customized porous titanium constructs for biomedical applications and, in particular, for bone substitution. As first, the present review gives a short introduction on the techniques used for additive manufacturing of Ti/Ti-Alloys (Direct Energy Deposition—DED, Selective Laser Melting—SLM and Electron Beam Melting—EBM) and on the main bulk properties of additively manufactured titanium porous structures. Then, it discusses the main advancements in surface modifications of additively manufactured titanium constructs for bone contact applications. Even if specific surface modifications of constructs from AM are currently not widely explored, it is a critical open issue for application in biomedical implants. Some thermal, chemical, electrochemical, and hydrothermal treatments as well as different coatings are here described. The main aim of these treatments is the development of surface micro/nano textures, specific ion release, and addition of bioactivity to induce bone bonding and antibacterial activity. Physicochemical characterizations, in vitro bioactivity tests, protein absorption, in vitro (cellular/bacterial) and in vivo tests reported in the literature for bare and surface modified AM Ti-based constructs are here reviewed. Future perspectives for development of innovative additively manufactured titanium implants are also discussed.

Keywords: additive manufacturing; titanium; surface; bone

1. Introduction

The main advantage associated with the use of Additive Manufacturing (AM) technologies in the medical field is the possibility to produce highly complex shapes and customized implants and products. Implants, medical models, and saw guides can be cited as the most common examples [1]. Moreover, AM allows us to design objects with different materials in specific areas requiring peculiar features (e.g., by means of multiple materials feeding in laser directed deposition techniques) [2] or by the production of customized scaffolds with gradient porosity mimicking the natural bone [3]. These kind of structures are of particular interest for the realization of bone substitutes with customized shape and porosity able to match the characteristic of bone defects and natural bone structure.

Titanium and its alloys have a high cost, related both to raw material and conventional manufacturing [4]: innovative manufacturing routes with limited waste and obtainment of near net-shape products, with reduced post processing, represent a challenge [4,5].

The present review gives a short overview on additive manufacturing technologies used for Ti-based materials and their main properties (microstructures, mechanical properties, and peculiar defects); then it is focused on surface treatments of Ti-based AM constructs intended for bone contact applications.

In fact, surface properties have a key role in tissue integration, but, despite the wide literature on AM, limited research has been performed up to now on surface modifications of AM Ti-based materials for biomedical applications. The surface modification of AM constructs is a promising strategy for the modulation of the biological response of AM implants, and in particular for the enhancement of their bone bonding ability as well as to counteract bacterial infections.

The strategies reported in literature for the surface treatment of AM Ti-based materials (e.g., mechanical finishing, chemical, and electrochemical treatments, thermal treatments and coatings) are presented and discussed.

The main features required for post processing suitable for AM Ti-based materials are finally evidenced together with future perspectives for the research in this field.

2. Additive Manufacturing of Titanium Alloys

2.1. AM Processes for Ti-Based Materials

Additive manufacturing (AM), in contrast with conventional subtractive manufacturing techniques (e.g., machining, cutting . . .), produces 3D shaped parts by means of layer-by-layer apposition of material [1,6]. The object building is driven by a computer aided designed (CAD) 3D model, divided in slices of defined thickness, which becomes the toolpath of the AM machine [4,6]. Each slice corresponds to a single AM building passage. In the medical field, the CAD file can be obtained from patient anatomical investigations (e.g., Computed Tomography—CT) [1].

AM includes different techniques, such as powder bed fusion (PBF), material extrusion (ME), VAT photopolymerization (VP), material jetting (MJ), binder jetting (BJ), sheet lamination (SL), and directed energy deposition (DED) [1]. However, PBF and DED are the most widespread AM techniques for titanium-based products for medical applications.

The main PBF techniques are Selective Laser Melting (SLM) and Electron Beam Melting (EBM), which use laser or electron beams, respectively, as heating sources for powder fusion.

PBF techniques are based on the deposition of a metal powder layer on the building platform. The section drawing (slice of the 3D object model) drives the laser/e-beam scanning of the powder layer, which produces the partial or complete melting of the powders. The procedure is repeated for each model slice until the object is complete. The melting and re-solidification (or sintering) of the powders determine the bonding between the different layers [4].

In the case of Directed Energy Deposition (DED), the material is introduced in the nozzle of the laser or electron beam where it is melted and then deposited on the substrate following the slice drawing. The material is fed in the form of metallic powders from a coaxial nozzle for a laser or in the form of a metallic wire for an e-beam [4].

Both PBF and DED laser-based technologies are performed under inert atmosphere, while the electron beam ones work under vacuum.

DED techniques allow more freedom in composition and design because different materials can be introduced in the process by different feeding nozzles used in the same building process. Moreover, both building of new components and reparation of damaged parts can be performed by this route [5,6].

PBF technologies are characterized by a smaller beam size (50–500 µm for SLM and 140–250 µm for EBM) and smaller layer thickness (15–150 µm for SLM and 50–200 µm for EBM) compared to the DED ones (2000–4000 µm of beam size and 300–1000 µm for Laser Metal Deposition) [5]. As a consequence, PBF techniques allow a better surface finishing, but require longer process times. Therefore, PBF is preferred for small objects with high shape complexity and accuracy requirements, while DED is more indicated for large parts with coarser finishing [4].

2.2. Microstructures of AM Titanium-Based Components

The microstructure of AM built Ti-based materials depends on the repeated heating/cooling cycles as well as on the heating transfer characteristic of the specific process [5].

Ti6Al4V alloys, produced by EBM, SLM and DED, are characterized by columnar β-grains, elongated along the building direction [5,6]. These grains have dimensions up to tens of millimeters, which implies that they grow through different deposited layers [6]. The multiple thermal cycles caused by the layer-by-layer method induce grain coarsening in the overlapping regions [6]. This microstructure, coupled with fine acicular α' martensite, usually involves high strength and low ductility, as well as mechanical anisotropy. Heat

treatments (at around 650 °C of SLM CP-Ti) can be used to create an equiaxed structure, resulting in a weakened texture [7].

The rapid cooling from a temperature above the β-transus to room temperature, characteristic of the laser-based AM technologies, induces the formation of acicular α-martensite in AM Ti6Al4V [4,6]; Ti6Al4V by DED can have a similar microstructure. As an example, after annealing (940 °C/1 h/air cooling), DED Ti6Al4V shows an α + β dual phase. On the other hand, the high build temperature characteristic of EBM technology acts as an in-process thermal treatment which transforms α-martensite into equilibrium fine α + β dual phase microstructure [6].

With AM, bulk metallic glasses or surface glassy layers can be produced as the melt pool is very small and solidification can be achieved so rapidly to bypass crystallization. Crystals may form by devitrification, upon heating of the amorphous phase, because of the thermal cycling involved in the following layers formation. However, a peculiar glassy structure, topography, and microstructure can occur on the outermost layer, where no further heating occurs after a first fast solidification. Bulk metallic glasses have attracted increased attention as biomaterials because of their combination of properties: high corrosion resistance, high yield strength, low wear rates, low Young's modulus, and good fatigue resistance [8]. In the orthopedic field, high load-bearing capability and reduced stress-shielding or generation of wear debris are of great interest. However, Ti-based alloys with high glass forming ability contain Be and are potentially toxic and bulk metallic glasses have poor workability. The investigation of biocompatible compositions of metallic glasses (such as $Ti_{47}Cu_{38}Zr_{7.5}Fe_{2.5}Sn_2Si_1Ag_2$ at %) and the use of AM to overcome machinability limits are of great interest for the future.

2.3. Mechanical Properties of AM Ti-Based Components

2.3.1. Tensile/Compressive Properties

It must be underlined that the as-built AM parts show a dramatic reduction in mechanical performances associated with their poor surface finish; the values of mechanical properties reported in the literature are referred to machined samples of AM materials [6].

AM materials obtained from laser-based technologies (SLM and DED) present increased tensile and yield strength, but lower elongation compared to EBM and wrought counterparts. This behavior can be associated with the previously discussed formation of martensite in laser processed AM components [5,6]. Due to the negligible residual stresses, EBM processed parts show improved ductility compared to SLM and DED [4].

Tensile properties of AM Ti-based components can be adjusted by high temperature thermal treatments (annealing at 500–1000 °C) or HIP (Hot Isostatic Pressing) [6]. HIP and heat treatments can reduce porosity and modify the microstructure (formation of grain boundary α and intergranular α-plates) with consequent elongation improvements with moderate reduction in tensile and yield strength [4]. As an example, mechanical properties comparable to the ones of hot forged components and standard commercial hip stem implants were found for Ti-15Zr-4Nb-4Ta and Ti-6Al-4V alloy stems annealed after selective laser melting [9].

Tensile properties of AM built samples are anisotropic due to characteristic elongated columnar β-grains and to the presence of grain boundary α [6].

The type and shape of the cells in porous AM structures significantly affect their compressive properties [10,11]. It has been reported, for example, that the compressive properties (e.g., yield strength, ultimate compressive strength) of structures with cubic unit cells are higher than those of dodecahedron lattices. This behavior can be explained considering that the deformation mechanism is dominated by buckling in the cubic unit cells and by bending in the dodecahedron ones [11]. A proper design of the lattice structure can allow the obtainment of structures with an elastic modulus close to the one of human bone, avoiding stress shielding.

2.3.2. Fatigue Properties

Fatigue properties are of particular interest for biomedical applications of AM Ti-based components because medical implants are always subjected to cyclic loads (e.g., chewing or walking loads on dental and orthopedic implants, respectively).

Since fatigue properties are significantly influenced by surface finishing, surface polishing (by machining, chemical etching or vibratory finishing) of AM components is mandatory to avoid a critical decrease in fatigue resistance [6]. In fact, the presence of unmelted particles and lack of fusion defects significantly decreases the fatigue strength of AM Ti6Al4V samples [12].

Higher fatigue strength and lower fatigue toughness have been observed on laser-based AM processed Ti-based samples than on the EBM ones. The higher fatigue strength of SLM and DED samples, compared to EBM ones, can be correlated with the presence of fine martensite (high density of dislocations and fine structure) [6]. A significant improvement of fatigue properties can be obtained for example with HIP by means of porosity reduction [6] or by chemically accelerated vibratory finishing (CAVF) [13].

2.3.3. Hardness and Wear Properties

Higher hardness values have been reported for AM samples (SLM and EBM) compared to their forged, casted, and powder metallurgy produced counterparts [11,14]. Moreover, hardness values are higher for SLM components due to the presence of fine martensitic microstructure [11,14].

An improved wear resistance has also been evidenced for SLM and EBM samples, compared to traditional manufactured ones [11,14]. In this case a lower wear rate has been reported for EBM components respect to SLM ones [11].

2.4. Defects in AM Ti-Based Components

Several thermal phenomena occur during the additive manufacturing processes, such as powder melting, melt pool formation, mixing of materials, rapid solidification, remelting, high thermal gradient, reheating, and cooling. These phenomena result in several types of pores, defects, irregular surfaces, bending, and residual stress [15]; most of these defects can be controlled through the process parameters.

One of the possible defects of AM titanium-based components is uncontrolled porosity. It can derive from gas entrapment or to lack of fusion (keyholing pores). Gas pores are generally spherical with dimensions comprised between 1 and 100 μm and random distribution. Lack of fusion pores have bigger dimensions, irregular shape, and are generally concentrated at the boundary between two building layers; this type of porosity can usually be linked to incorrect processing parameters. Differently from designed porosity, which is strictly controlled and is necessary for bone ingrowth, uncontrolled porosity can uncontrollably reduce the mechanical properties of the component and should be reduced. Actually, HIP has been reported as the only effective solution to this kind of defect [6].

Surface roughness and irregularity is another questioning point of the AM component. The AM technique is always accompanied by the presence of partially melted/unmelted metallic particles on the final object surfaces. This feature, together with the layer-by-layer metal apposition and the eventual presence of open pores, is the cause of quite high surface roughness of AM parts: $R_a \approx 0.2$–13 μm (DED), $R_a \approx 5$–40 μm (SLM), $R_a \approx 25$–130 μm (EBM) [6]. Even if surface roughness can improve bone bonding for some kinds of implants, this parameter should be accurately controlled and designed in order to optimize the biological response. The opportunity to modify the surface roughness of AM components to modulate the biological response is actually poorly investigated and will be discussed in Section 3 of the present review.

Due to the high thermal gradients involved in laser-based AM technologies, residual stresses can be enumerated among the possible defects of these structures. Residual stresses are generally proportional to the number of layers and higher at the outermost surface.

Their presence can be deleterious for the mechanical properties of the component because they can induce cracks and should be relieved by means of proper thermal treatments [6].

A final issue concerns oxidation of the material during the AM processing because of the high affinity of titanium with oxygen. The temperature of the Ti melt during the SLM process can rise up to 2150 °C and the oxygen partial pressure inside the SLM chamber is expected to be around 1×10^3 atm, which is much higher than the equilibrium oxygen partial pressure. Therefore, oxidation is expected to occur during the SLM process, and the oxygen concentration of the SLM sample increased compared to the initial powder [16].

3. Surface Modifications of AM Ti-Based Materials

The surface of biomaterials represents the first layer which will come in contact with the biological environment. Surface features, such as roughness and topography (at the micro and nano scale), chemical composition, wettability, and charge can significantly affect the interaction between the biomaterial and biological environment (adsorption of water molecules, ions, proteins, and subsequently interactions with cells and bacteria) [17]. This is why there is a wide literature concerning surface treatments and coatings of Ti-based bulk materials [18] aimed at multifunctional properties: bioactive behavior (in vivo precipitation of hydroxyapatite), osteoconductive or osteogenic ability (bone on-growth or in-growth), contact guidance effect on soft tissues, antibacterial, or antimicrofouling properties. Some of these treatments or coatings can be adapted for additively manufactured materials, but a specific development work must be implemented for highly porous constructs. Moreover, specific post-processing surface treatments have been developed for materials from AM to remove the defects coming from these manufacturing processes.

As discussed in Section 2 of the present review, AM technologies allow the production of customized titanium-based structures which can be optimized in order to match mechanical requirements and 3D porosity (distribution and interconnection) suitable for bone integration and are gaining increasing interest for the production of orthopedic implants [19]. On the other hand, surface finishing of AM constructs is often poor and not optimized neither from the mechanical standpoint neither from the biological one.

Another relevant issue is related to oxygen surface contamination, as already mentioned. Ti and its alloys have a very high affinity to oxygen, nitrogen, and hydrogen at high temperature. The building chamber for EBM is usually pumped out to about 10^{-4}–10^{-5} mbar and that for the DED and SLM has a larger air content [6]: this means that some gas contamination can occur during AM besides contaminations coming from the feed powders. The presence of some interstitial elements, oxides, or other compounds derived from gas contaminations can affect both bulk (lower ductility, highly hardness) and surface properties. On the surface, a high contamination of oxygen can be noticed by observing the surface color: the surface changes from silver to straw and further to blue with an increased oxide film thickness. This contaminated layer can be removed by surface treatments.

In conclusion, surface modifications can improve surface properties of the AM components without altering their bulk features.

Figure 1 represents the rationale of surface modifications of AM Ti-based constructs. AM allows the production of customized implants with tailored macro-porosity suitable for bone substitution and reconstruction. However, the surface of the implant is the first interface with the biological environment (water molecules, ions, proteins, cells, and eventually bacteria) and should be properly designed to optimize the biological response of an implant. The combination of additive manufacturing and surface treatments is extremely promising for the obtainment of customized multifunctional implants with tailorable properties for bone integration.
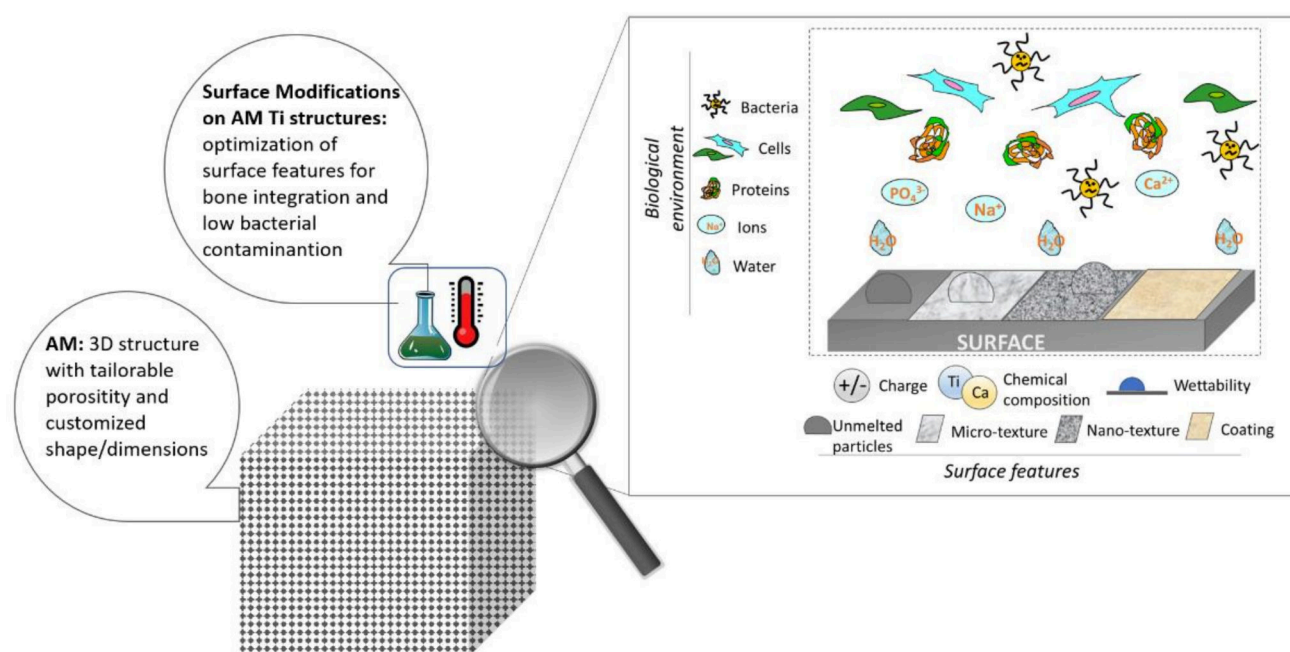
Figure 1. Scheme of the idea beyond the combination of additive manufacturing and surface modifications.

Even if research related to this specific topic is still limited, compared to the wide literature singly on AM or surface modification of Ti-based materials, some recent papers can be found [19].

Table 1 summarizes the recent scientific works on the surface modification of AM Ti-based materials for bone contact applications. For each example, the material and AM technology, the specific surface treatment applied, the resultant surface feature and the eventual biological (cell and bacterial adhesion) response are reported. The cited references are compared and critically discussed in the second part of this paragraph.

Table 1. Surface modifications of AM Ti-based materials for bone contact applications.

Material and AM Strategy	Surface Treatment	Surface Features	Biologica Response	Ref.
Ti6Al4V-EBM and SLM	Variation of the building angle (0°, 15°, 30°, 45°) and evaluation of surface features. No post treatments.	Spherical unmelted particles on all the surfaces. More particles aggregates on EBM samples. Slight decrease in particles with increasing building angle. SLM samples slightly more hydrophibic (CA = 113–133°) than EBM (CA = 91–111°), no significant effect of building angle. SLM samples showed lower roughness and negligible effect of the building angle, while EBM presented higher roughness which decreases, increasing the building angle.	Both materials support osteoblasts adhesion proliferation and differentiation. Cell adhesion is quite high on SLM surfaces, however the hydrphobicity induce cell clustering on the samples center. SLM samples accelerate cellular mineralization, especially with low building angles.	[20]
Ti6Al4V-SLM	Sandblasting (SiC) or Vibratory finishing (Al$_2$O$_3$) of the top and bottom surfaces.	Sandblasting completely removes the unmelted particles, slightly reduces roughness and wettability, but it contaminates the surface with SiC. Vibratory finishing does not completely remove the surface unmelted particles and slightly reduces wettability.	A certain reduction in bacterial (*S. epidermidis* and *P. aeruginosa*) adhesion can be observed on sandblasted and vibratory finished surfaces.	[21]

Table 1. *Cont.*

Material and AM Strategy	Surface Treatment	Surface Features	Biologica Response	Ref.
Ti6Al4V-SLM	Chemical polishing (HF-HNO$_3$ solution)	Removal of unmelted particles from the surface. Reduction in most of the surface defects. Process parameters should be optimized for specific lattice structures in order to maintain the main geometrical features.	-	[22]
Pure Ti (grade 2)-SLM	• Heat treatment 1300 °C. • Chemical treatment (5 M NaOH 60 °C 24 h, 0.5 M HCl 40 °C 3 h) in continuous flow, followed by thermal treatment (600 °C 3 h)	The heat treatment at 1300 °C melts the particles on the surface and smoothens it. A submicrometric surface texture appears after the chemical and heat treatment and uniformly also covers the inner surface of the pores. Chemically treated samples are completely covered by apatite after 3 days in Simulated Body Fluid (SBF).	In vivo implantation in rabbits evidences the ability of the chemically treated implants to promote direct bonding of bone and new bone formation on all the surfaces (even into pores).	[23]
Pure Ti-SLM	Chemical treatment in mixed solution of H$_2$SO$_4$ and HCl at 70 °C		High bone bonding ability during in vivo test (rat implantation)	[24]
Pure Ti mesh-SLM	• Mixed acids (H$_2$SO$_4$-HCl) treatment followed by thermal treatment (600 °C) • Alkali treatment (NaOH) followed by thermal treatment (600 °C) • Alkali treatment (NaOH) followed by HCl treatment and then by thermal treatment (600 °C) • Alkali treatment (NaOH) followed by CaCl$_2$ soaking, thermal treatment (600 °C) and final hot water soaking.	Trated surfaces are able to promote hydroxyapatite precipitation after 24 h in SBF. The surface treated with mixed acids shows microscale apatite while nanoscale apatite was observed on the other surfaces.	After 2 weeks implantation in rats significantly higher bone formation was observed on the surfaces treated with mixed acids and thermal treatment.	[25]
Ti6Al4V-SLM	Plasma Electrolytic Oxidation (PEO) in electrolyte containing calcium acetate, calcium glycerophosphate, strontium acetate, and silver nanoparticles.	After PEO treatment the surface presents a microporos surface layer constituted of titanium oxide, hydroxyapatite and Sr-substituted hydroxyapatite and silver nanoparticles. Release of silver and strontium ions up to 28 days.	Strong antibacterial activity against *S. aureus* MRSA. Biocompatibility and osteogenic activity for osteoblasts.	[26]
Ti6Al4V-SLM	Chemical treatment (hydrogen peroxide and hydrochloric acid)	Surface nanotexture superimposed to the typical SLM microtopography (unmelted particles). Significant improvement of surface wettability.	Osteoblast increased mineralization in vitro and increased bone contact in vivo at short times (2 weeks).	[27]
Ti6Al4V-EBM	Coating with polycaprolactone (PCL) or polycaprolactone/hydroxyapatite by dip coating	Uniform coating of the porous structure with reduction in the surface roughness. Top surface porous for solvent evaporation. Possibility to use recycled Ti6Al4V particles.	Increased adhesion and proliferation of mesenchymal stem cells on the coated scaffolds. Higher penetration of cells in the porous structure for the coated samples.	[28]

Table 1. *Cont.*

Material and AM Strategy	Surface Treatment	Surface Features	Biologica Response	Ref.
Ti6Al4V-SLM	Variation of SLM parameters and hydrothermal treatment in NaOH.	Variation of SLM parameters to tailor surface microtexture (stripy, bulbous or combined textures). Hydrothermal treatment in NaOH produces surface nanotexturing superimposed on microtexture but induce also Al_2O_3 particles precipitation. Surface treatments increase protein absorption.	Increased cell adhesion was observed on bulbous and stripy-bulbous combined microtextures. Cell proliferation and differentiation were enhanced by bulbosus structures and nanotextures.	[29]
Ti6Al4V-xCu-SLM	-	Cu presence induces antibacterial activity, however the proposed technology is not effective to obtain nanotextures	-	[30]
Ti6Al4V-SLM	Acid etching (HCl-H_2SO_4), chemical oxidation (HCl-H_2O_2) and thermochemical treatment (400 °C).	The complete process produced micro and sub-micrometric surface texture and growth of a surface anatase layer.	-	[31]
Ti-Ta porous coating on Ti6Al4V by DED	Anodic oxidation	DED allows the production of a porous coating of Ti-Ta alloy on Ti6Al4V substrate. The elastic modulus is reduced compared to Ti6Al4V. Anodic oxidation produces surface nanotubes containing both Ti and Ta oxides. The modified surface induces apatite deposition in vitro.	The modified surface promotes osteoblasts adhesion in vitro and bone formation in vivo.	[32]
Ti6Al4V SLM	High temperature thermal treatment (1050 °C), HCl etching in inert atmosphere and NaOH treatment.	High temperature thermal treatment homogenizes the microstructure and removes unmelted particles from the surface. HCl etching and NaOH chemical treatment produce surface nanotexture and allows hydroxyapatite coating after 14 days immersion in simulated body fluid.	-	[33]
Ti6Al4V, SLM	Laser polishing	Optimized laser polishing reduces surface roughness eliminating unmelted particles and surface defects. Tensile properties are not affected while fatigue life is improved.	Improved osteoblast adhesion and proliferation	[34]

As already discussed in Section 2, AM Ti-based surfaces are characterized by numerous unmelted particles on their surfaces. An example of unmelted particles on the surface of SLM Ti is reported in Figure 2a [23] and Figure 2d [29]. More particles aggregates have been evidenced on EBM structures, with consequent higher roughness and a less homogeneous surface finishing, compared to the SLM ones [20]. Surface finishing is minimally affected by the building angle [20]. Even if both EBM and SLM structures are able to support osteoblasts growth, the SLM ones seem to be better for cellular mineralization [20].

Post treatments, such as sandblasting and vibratory finishing [21] applied to the top and bottom surfaces of the test samples, chemical/electro or plasma polishing [22,33], high temperature (1300 °C or 1050 °C) heat treatments [23,35], or coatings [28] can remove or attenuate the presence of surface unmelted particles and improve the biological performance.
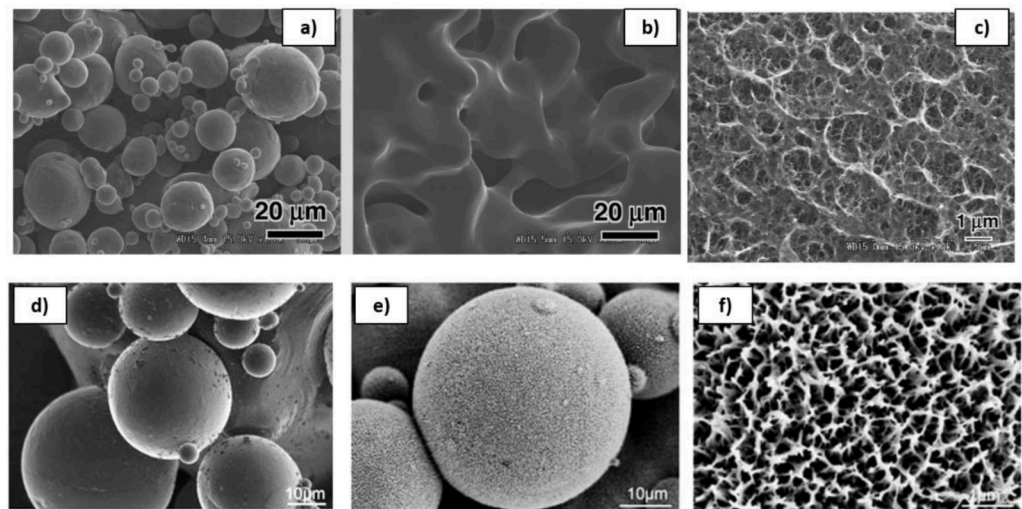
Figure 2. Surface morphology of bare and surface treated AM Ti-based materials. (**a**) Unmelted particles on SLM Ti; (**b**) thermally treated (1300 °C) SLM Ti with disappearance of unmelted particles, and (**c**) nanotexture on SLM Ti after high temperature thermal treatment, chemical, and heat treatment, reprinted from [23] with Elsevier's permission; (**d**) unmelted particles on the surface of SLM Ti with bulbous-stripy structure, (**e**) detail of the microtopography, and (**f**) nanotexture obtained by hydrothermal treatment, reprinted from [29].

The effective disappearance of unmelted particles after 1300 °C thermal treatment is shown in Figure 2b compared to Figure 2a [23].

Laser surface treatment can also be used as a post-processing step in order to reduce surface roughness of additively manufactured materials (laser polishing) [34]. The laser beam can neatly ablate the aggregates of metallic globules and repair cracks and pores on the surface, resulting in a smooth surface. By this way, surface morphology is optimized to favor fatigue behavior and, in case of orthopedic implants, osteoblastic differentiation.

Moreover, chemical treatments such as alkali treatments (NaOH) [23,33], mixed acids (H_2SO_4-HCl) treatments [24,25], combination of acid (HCl) and hydrogen peroxide (H_2O_2), with eventual pre-etching of the surface [27,28], hydrothermal treatments in NaOH [29], and electrochemical oxidation [26,32] can produce peculiar micro/nanotextured layers on the surface of AM Ti-based structures. The appearance of nanotexture, after chemical or hydrothermal treatments, is shown, as examples, in Figure 2c,f. It can be observed that the nanotexture can be obtained both on the surface after the removal of unmelted particles, or superimposed to the surface particles. Most of these surfaces are characterized by inorganic bioactivity (ability to induce hydroxyapatite precipitation in simulated body fluid) [23,25,33], by the ability to stimulate osteoblast activity [26,27,29,32], and direct bone bonding [23–25,32].

Bone implants, in addition to the ability to support bone growth and integration, should reduce bacterial contamination in order to avoid the development of infections, which represent a critical open problem.

Even in absence of an antibacterial agent, a certain reduction in bacterial adhesion (*S. epidermidis* and *P. aeruginosa*) has been observed after sandblasting and vibratory finishing post treatments, probably due to removal of high roughness and niches for bacteria [21]; it is of interest to investigate if a specific topography with antimicrofouling properties is developed on these surfaces. The use of a Cu containing Ti alloy for the SLM manufacturing of porous structures can induce an active antibacterial activity, because of copper ion release, however SLM technique alone is not able to induce a surface nanotexture with antimicrofouling properties [30]. Finally, the electrochemical oxidation in electrolytes containing calcium, phosphorous, and strontium together with silver nanoparticles allows the development of a bioactive and antibacterial microtextured surface layer able to promote both antibacterial and osteogenic activities, as reported in [26].

Finally, the use of additive manufacturing (SLM) to produce specific surface patterning and heat treatment in a nitrogen atmosphere to produce a TiN coating has been considered for the improvement of bio-tribological performances of Ti-based implants [36].

4. Conclusions and Future Perspectives

Additive Manufacturing of titanium alloys for biomedical applications is gaining increasing interest due to its ability to produce customized implants in terms of shape, dimensions, porosity, and even composition and mechanical properties, of particular interest for bone substitution. All these features make it an attractive technology for medicine/implantology that are becoming highly personalized.

In addition, AM technologies can guarantee fast and easy scalable production with limited post processing and with material and cost saving.

On the other hand, one of the main criticisms of AM products is their poor surface finishing which can lead to poor static and fatigue resistance and eventually to poor/uncontrolled biological response.

The possibility to modify the surface of AM components can improve both their mechanical (mainly fatigue) and biological performances (e.g., bone integration and bacterial contamination).

Some considerations can be made on surface treatments suitable for AM components and are briefly discussed below.

Treatments should be able to treat the whole component surface (even the inner surface of pores) in a homogeneous way, so wet processes (chemical and electrochemical processes as well as dip coatings and functionalization) can be the most suitable ones to guarantee this feature.

The post processing step should not alter the 3D microporous structures produced by AM, so a strict design and control of the parameters should be performed.

Moreover, the selected strategies should not be detrimental to the fatigue resistance of the component in order to avoid a worsening of the final device performances.

Finally, time and costs of the treatments should be compatible with the whole process duration and cost in order not to vanish the economic advantages of AM.

Future perspective of surface treatments of titanium-based materials from AM can be foreseen in the direction not only to remove defects, but also to add specific functionalities such as osteogenic, antibacterial, and/or anti-inflammatory compounds or biomolecules through functionalization or coatings. The combination of additive manufacturing production routes with surface modification ones can lead to the development of fully customized bone implants (shape, porosity, mechanical properties, bioactivity, antibacterial/anti-inflammatory activity, to cite some examples) able to match specific clinical needs.

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