Chapter 10
Laser Cladding of Ti Alloys for Biomedical Applications

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10.1 Introduction

Many people lose or experience a damaged organ or tissue due to age, illnesses, or accidents. So, the design and development of biocompatible materials with generally suitable properties called "biomaterials" for repairing or replacing diseased or damaged tissues is needed. Biomaterials are synthetic or natural substances used to improve, treat, heal, or substitute living tissues or organs, and in the design of medical implants and medical devices and diagnostic treatments in pharmaceuticals, surgeries, dentistry, nuclear medicine, and basic medical sciences (Bhat and Kumar 2013; Chaudhuri et al. 2017). Biomaterials must be blood compatible, noninflammatory, nonpyrogenic, nonallergenic, nontoxic, noncarcinogenic, chemically inert, stable, and mechanically strong enough to withstand repeated forces during a lifetime.

There are a wide range of materials such as metals, ceramics, polymers, and composites which have been investigated as biomaterials. Metals have been exclusively used almost for load-bearing implants, such as artificial joints, bone plates, screws, intramedullary nails, spinal fixations and spacers, external fixators, pacemaker cases, and dental implants. Stainless steel (Patel and Gohil 2012, Navarro et al. 2008), cobalt chromium alloys (Qizhi and George 2015), and titanium and

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titanium-based alloys (Eisenbarth et al. 2004; Nag et al. 2009) are the most common metallic biomaterials.

Titanium and its alloys such as Ti-6Al-4 V, as one of the most promising engineering materials, have been of interest in biomedical applications due to their excellent mechanical and tribological properties. However, inertness and low biocompatibility are the most serious obstacles that hindered their usages in biomedical fields. In particular, aluminum has a neurotoxicity effect and vanadium is a strong cytotoxin element causing long-term health problems like Alzheimer's and neuropathy, and therefore, it is dangerous for Ti–6Al–4 V to remain in the human body for a long time (Geetha et al. 2008; Navarro et al. 2008). So, surface modification of titanium and its alloys seems to be necessary for enhancing their application in various fields of science and industry.

Laser technology is widely used in the surface modification of different metals, owing to their high coherence, directionality, and high energy density. Laser surface remelting (Singh et al. 2006) and laser cladding (Mukherjeea et al. 2017; Wang et al. 2008) have been studied to improve the surface properties of different types of metals. Laser cladding technique has been widely used to prepare many kinds of coatings because it can provide high production efficiency, excellent control of the deposition process, and a mechanical interlock at the interface between the coating and the substrate. In light of this, the present work aims to carry out an exploratory study on laser surface modification of Ti alloys by laser cladding.

10.2 Biomaterials

Biomaterials consist of substances without toxicity/immunological reactions in contact with the body or biological systems, which are intended to for therapeutic purposes (treat, repair, or replace a tissue function of the body). Biocompatibility is the most important and essential condition for various kinds of biomaterials to be used as a medical product (Tathe et al. 2010). Indeed, biocompatibility signifies the feature of any natural or artificial material being compatible with the living tissue. So, biocompatibility can be defined as the acceptance of an implant by the surrounding tissues and the entire tissues of the body (Park and Bronzino 2002).

In general, biomaterials should have the following properties:

- Chemical neutrality and no adverse effects on adjacent tissues
- Lifetime and fatigue strength
- No harmful effect on the metabolism of the body

All biomaterials are classified into three categories: bioinert, biodegradable, and bioactive. Bioinert is a material that does not directly bond with any of the surrounding tissues. Bioactive materials are chemically bonded with the adjacent tissues, and biodegradable materials are destroyed over time and replaced by natural substitutes. Various biomaterials include a wide range of natural or synthetic biocompatible materials that are used daily in pharmaceutical, surgery, and dental medicine. In

Table 10.1 Biomaterials, properties, and applications

Biomaterial applications	Uses of biomaterials	Types of biomaterials
Orthopedic implants	Total joint replacement	Metals and alloys such as, titanium, titanium alloys, cobalt chromium alloys, and stainless steel
	Total knee replacement	Ceramics such as, aluminum and zirconia
	Bone repair	Polymers such as, polyethylene, silicone rubber, polyurethane, polypropylene, and polymethylmethacrylate
Dental applications	Dental bridges	Ceramics such as, aluminum and zirconia
Prosthesis in cardiovascular medical devices	Cardiac pacemakers	Metals and alloys such as, stainless steel, cobalt chromium alloys, and titanium alloys
	Heart valves	Polymers such as, polyamide, polyolefin, polyesters, polytetrafluoroethylene, and polyurethanes
Ophthalmological	Intraocular lenses	Polymethylmethacrylate (PMMA), silicone, and hydrophilic and hydrophobic acrylic
Reconstructive surgery	Vascular grafts	Polymers such as, polytetrafluoroethylene, Dacron, and polyurethene
Wound healing	Synthetic sutures	Polymers such as UHMWPE
	Fracture devices	Metals such as stainless steel
Drug delivery systems	Drug eluting leads	Titanium alloys as fixation leads
		Ceramic collars surrounding the electrode tip
Bio-electrodes and sensors	Glucose monitoring biosensors	Polyurethane
		Vinyl pyridine–styrene copolymer

Data were adapted with permission from the following citation: Hassanein and Amleh (2018)

Table 10.1, a selection of different biomaterials, their properties, and applications is indicated.

10.2.1 Metallic Biomaterials

Metallic biomaterials are often used to replace the structural components of the human body because they are better than polymeric or ceramic materials in terms of tensile strength, fatigue strength, and toughness. As a result, they are widely used in various medical devices such as artificial joints, dental implants, artificial hearts, bone plates, wires, and stents. Also, metallic biomaterials due to better electrical conductivity are applied to prepare electronic parts such as heart pacemakers and artificial ears. Nowadays, the most common metallic biomaterials used are stainless steel, cobalt, titanium, and nickel, and their alloys. Some of their properties are listed in Table 10.2.

Table 10.2 Characteristics of some metals and alloys used in biomedical fields

Material	Normal analysis (w/o)	Modulus of elasticity GN/m^2 (psi $\times 10^6$)	Ultimate tensile strength MN/m^2 (ksi)	Elongation to fracture (%)	Surface
Titanium	99 + Ti	97 (14)	240–550 (25–70)	>15	Ti oxide
Titanium-aluminum-vanadium (Ti-Al-V)	90Ti-6Al-4V	117 (17)	869–896 (125–130)	>12	Ti oxide
Cobalt-chromium-molybdenum (casting)	66Co-27Cr-7Mo	235 (34)	655 (95)	>8	Cr oxide
(Co-Cr-Mo)					
Stainless steel (316 L)	70Fe-18Cr-12Ni	193 (28)	480–1000 (70–145)	>30	Cr oxide
Zirconium (Zr)	99 + Zr	97 (14)	552 (80)	20	Zr oxide
Tantalum (Ta)	99 + Ta	–	690 (100)	11	Ta oxide
Gold (Au)	99 + Au	97 (14)	207–310 (30–45)	>30	Au
Platinum (Pt)	99 + Pt	166 (24)	131 (19)		Pt

Data were adapted with permission from the following citation: Imam and Froes (2010)

10.2.1.1 Titanium and Its Alloys

Titanium and its alloys such as Ti–6Al–4V are widely used for making implants under load in dental and bone applications because of their superior mechanical properties, biocompatibility, and resistance to corrosion in a physiological environment. Titanium alloys can be classified into three main groups: α phase, β + α mixture, and β solid solution. As can be seen in Fig. 10.1, the addition of aluminum to titanium results in the stabilization of the α phase (HCP) and the production of a high-strength alloy. Also, the addition of vanadium causes the formation of β (BCC) in α background and increases the flexibility and resistance of the alloy to impact. Thus, the Ti-6Al-4V alloy is an α-bivalent alloy, which is one of the most crucial titanium alloys (Gammon et al. 2004). In β + α alloys, morphology or α phase shape plays a vital role in hammering and fatigue strength.

Currently, Ti-6Al-4V alloys are used as hip and knee joint prostheses and dental implants in the medical industry (Li et al. 2014). The hip and knee replacement traditional implants are shown in Fig. 10.2.

However, despite its remarkable advantages, the toxicity of Ti-6Al-4V components, such as aluminum and vanadium, has become an issue of concern (Okazaki and Gotoh 2005). The release of aluminum and particularly vanadium ions from this alloy can generate long-term health problems such as peripheral neuropathy, osteomalacia, and Alzheimer's disease (Lin et al. 2005).

Ti alloys have very similar mechanical properties to those of the bone. However, the low hardness and poor resistance to wear and oxidation of Ti alloys can restrict their applications, especially where tribological behavior is experienced, such as in

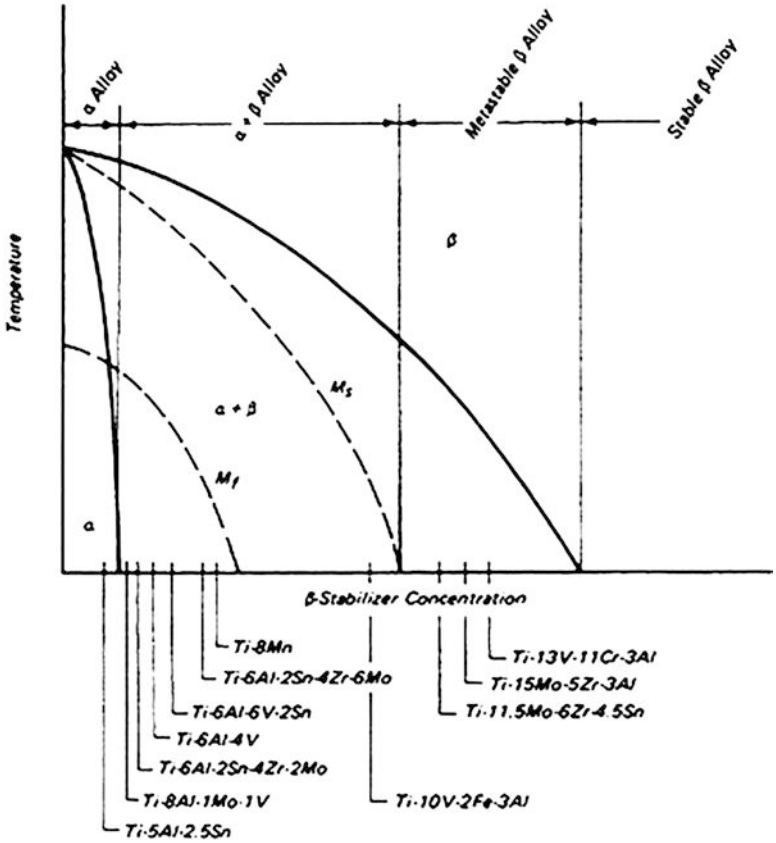

Fig. 10.1 The effects of stable elements of beta phase on the equilibrium phases of Ti alloys (Data were adapted with permission from the following citation: Lütjering et al. 2000)

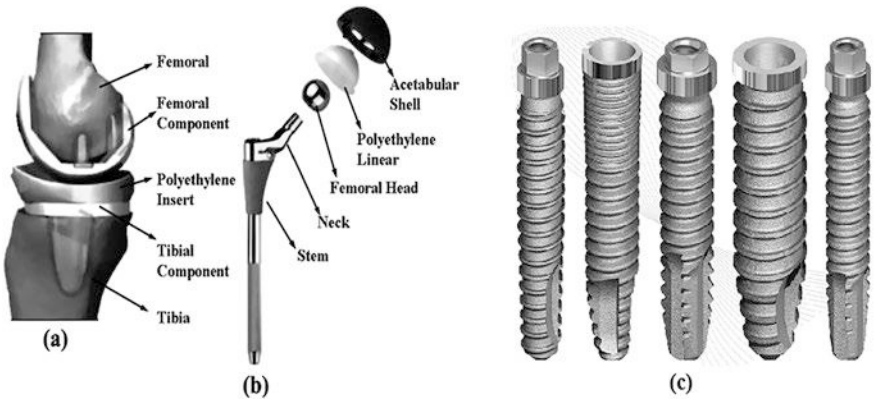

Fig. 10.2 Typical scheme of the (**a**) knee, (**b**) hip, and (**c**) dental implants (Data were adapted with permission from the following citation: Li et al. 2014, Elias et al. 2013)

valves and pin connections. Particularly, the most encountered problem by Ti alloys is in joint replacements such as total knee and hip replacements, where sliding of the ball in the socket occurs due to the movement of the hip joints; therefore, aluminum and vanadium ions are released in the body. The poor tribological properties of these alloys have limited their use in articulating the components of hip and knee prostheses. So, it is required to change the nature of the surface of Ti alloy using different surface engineering techniques.

Surface Modifications of Ti Alloys

To improve the biocompatibility and the mechanical and corrosion properties of Ti and also to enhance its surface integrity, as discussed in the previous section, Ti alloys are subjected to surface modifications by using different materials and coating techniques. The selection of materials is the key parameter in having a successful coating that effects impacts on mechanical properties of the material such as fatigue strength, hardness corrosion, and wears resistance. Metals, ceramics, polymers, and composites are used to coat metallic surfaces as a protective layer. However, a variety of coating processes and material properties can cause difficulties in choosing the best composition of the applied layer. Bioceramic materials are usually considered for this application (Salinas 2014; Peddi et al. 2008; Rodriguez et al. 2016; Kasuga et al. 2004; Braem et al. 2012). These materials and techniques will be explained in detail, in the following sections.

10.2.2 Bioceramic Materials

Bioceramics are a class of advanced ceramics that are commonly employed for repair or replacement of damaged parts in medical and dental applications (Thamaraiselvi and Rajeswari 2004; Salinas and Vallet-Regí 2013). Bioceramics are nonmetallic inorganic compounds formed from metallic and nonmetallic elements combined with ionic or covalent bonds, having high compressive strength, but low tensile strength (brittle) characteristics. The high biocompatibility of bioceramics makes these materials an ideal alternative for the reconstruction and replacement of hard tissues in the body. The biocompatibility of bioceramics can be attributed to their chemical composition. The chemical composition of bioceramics includes ions like K^+, Na^+, Mg^{2+}, and Ca^{2+} which can be found in physiological environments. The main bioceramics used in the biomedical field are shown in the Fig. 10.3.

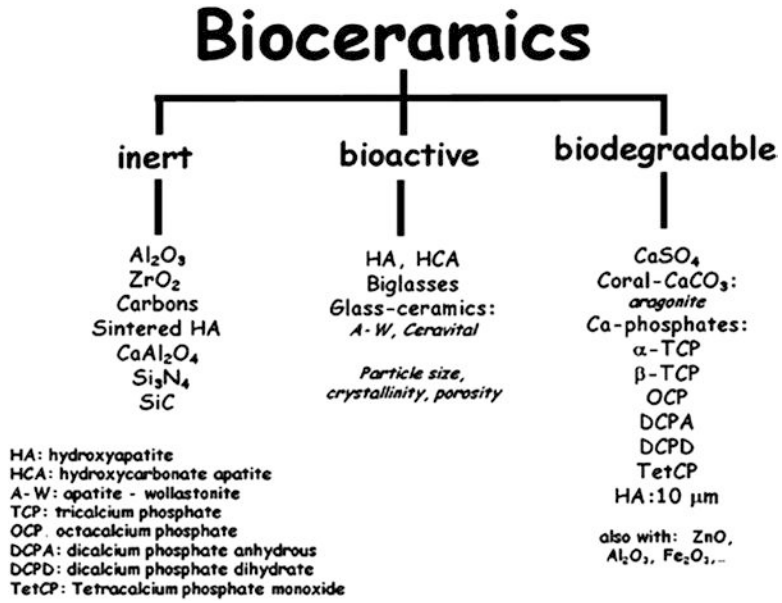

Fig. 10.3 Main bioceramics used in the biomedical field (Data were adapted with permission from the following citation: Salinas et al. 2013)

10.2.2.1 Alumina

Alumina (Al_2O_3) or aluminum oxide is the first bioceramics that is widely used in orthopedic implants in orthopedics, specifically for total hip/*knee arthroplasty*, and in dentistry due to a combination of desirable properties such as suitable biocompatibility, excellent corrosion resistance, and reasonable wear rates (Thamaraiselvi and Rajeswari 2004).

10.2.2.2 Zirconia

Zirconium dioxide *(zirconia)* ceramics have improved properties, in comparison to alumina, such as high toughness, high strength, and high-*performance abrasiveness*, and have been introduced as an *alternative* material to *alumina* (Turon-Vinas and Anglada 2018; Kumar et al. 1991). The fatigue strength of zirconia has led to producing femoral head prosthesis. Table 10.3 shows some of the applications of Al_2O_3 and ZrO_2 as implant materials.

Table 10.3 Biomedical applications of Al_2O_3 and Zro_2

Materials	Advantages	Disadvantages	Applications
Metals: stainless steel, cobalt chromium, titanium alloys, Pt, Pt–Ir alloys	High impact strength, high resistance to wear, ductile, absorption of high strain energy, high conductivity	Low biocompatibility, corrosion in physiological environment, mismatch for mechanical properties with soft connective tissue, low mechanical strength	Orthopedic load bearing and fixation devices, dental implants, neuromuscular stimulation
Ceramics: aluminum, zironia, calcium phosphate ceramics	Good biocompatibility, inert, corrosion resistance, high tensile strength, biodegradable	Undesirable surface properties, special techniques are needed for material fabrication, degradation not controllable	Hip and knee prostheses, dental implants, improving biocompatibility, temporary support, assists regeneration of natural tissues
Polymers: polyacrylates, polyesters, polyamides, polyurethanes, polyether, polyolefines, silicone rubber	Low density, easy to fabricate	Low mechanical strength; additive oligomers may cause tissue reaction	Cardiovascular, maxillofacial, soft skeletal tissue such as tendon, ligament, space filling devices, dental implants, bone cement, lens, intraocular and middle ear prostheses

Data were adapted with permission from the following citation: Balamurugan et al. (2008)

10.2.2.3 Bioactive Glass

Bioactive glasses are a group of biomaterials based on glass and can form a strong chemical bond with the tissues. However, due to their poor mechanical properties (especially weak tensile strength and fracture toughness), bioactive glasses alone cannot be used under load but can be used as coatings on metals and devices (Heimo 2017; Mozafari et al. 2013). Due to the biocompatibility of these glasses, they have been used as bone cement, bioactive coatings, and scaffolds in bone tissue engineering. The first successful use of bioactive glass was for middle ear prosthesis. Today, various clinical applications of bioactive glasses such as craniofacial procedures, grafting of benign bone tumor defects, instrumental spondylodesis, and the treatment of osteomyelitis have been reported (McAndrew et al. 2013; Lindfors et al. 2009; Frantzén et al. 2011).

10.2.2.4 Calcium Phosphates

Calcium phosphate (CaP) is the common name of a family of minerals containing calcium cations (Ca^{2+}) together with orthophosphate ($PO3^{-4}$), metaphosphate (PO^{-3}), or pyrophosphate ($P_2O_4^{-7}$) anions, and sometimes hydrogen (H^+) or

Table 10.4 Calcium phosphates and their properties

Ca:P	Mineral name	Formula	Chemical name
1.0	Monenite	$CaHPO_4$	Dicalcium phosphate (DCP)
1.0	Brushite	$CaHPO_4 + 2H_2O$	Dicalcium phosphate dehydrate (DCPD)
1.3	–	$Ca_8(HPO_4)_2(PO_4) + 5H_2O$	Octocalcium phosphate (OCP)
1.43	Whitockite	$Ca_{10}(HPO_4)_6$	–
1.5	–	$Ca_3(PO_4)_2$	Tricalcium phosphate
1.67	Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	–
2.0	–	$Ca_4P_2O_9$	Tetracalcium phosphate (TTCP)

Data were adapted with permission from the following citation: Adzila et al. (2012)

hydroxide (OH^-) ions. Biocompatibility, bioavailability, and high bone resemblance make them a very suitable option for bone regeneration (Vallet-Regí and González-Calbet 2004). The most critical issue in calcium phosphates is the *calcium* and *phosphorus concentrations* and the *calcium/phosphorus ratio* in these materials, which has a significant influence on the calcium phosphate qualities. A lower Ca/P ratio increases acidity and solubility, but at a ratio of 1.67 (hydroxyapatite stoichiometry) they are decreased (Dorozhkin 2007, 2009). Table 10.4 shows several calcium phosphates and their properties.

Among the studied calcium phosphates, hydroxyapatite (HA) is the most biocompatible one because bone and teeth mineral composition is mainly composed of HA (Habraken et al. 2016). Nanosized HA may present some priorities rather than macro-scale HA (Li et al. 2008). It has been reported that ceramic biomaterials based on nanosized HA exhibit enhanced restorability and higher bioactivity (Pepla et al. 2014). Also, the release of calcium ions from nanosized HA is similar to that from biological apatite and significantly faster than that from coarser crystals (Gentile et al. 2015).

10.3 Coating Techniques

Coating methods can affect parameters such as coating-to-surface adhesion, uniformity and nonuniformity of the coating, coating thickness, etc. (Xuanyong et al. 2004; Zhecheva et al. 2005). The advantages of bonded implantation attachment include the mechanical properties of the metal section and the chemical and biological properties of the implant coating work together.

Many coating methods are used on Ti alloy substrates including plasma spray (Cooper et al. 1999), sol–gel (Pourhashem and Afshar 2014), electrophoretic deposition (Heise et al. 2018), pulsed laser deposition (PLD) (Rajesh et al. 2011; Mróz et al. 2015), and ion beam (Kim et al. 2013). Each of these methods is suitable for different applications as they offer different deposition methods, different materials, second phases, and different thicknesses and densities. As a result, mechanical stability, corrosion properties, biocompatibility (for biomedical applications), and

enhancement of material behavior for a specific type of coating have to be considered carefully (Thakare et al. 2007; Fotovvati et al. 2019; Prasad et al. 2017).

Although plasma spray is widely used in this field and has advantages such as rapid deposition rate, the high processing temperature induces dihydroxylation and decomposition of calcium phosphates like hydroxyapatite (HAp) (Heimann 2016; Demnati et al. 2014) and nonuniform coating with cracks (Choudhury and Agrawal 2012), and demands high-cost equipment and an elaborate setup. Therefore, the sol–gel deposition method due to the simplified and low-temperature processing is used in this area. However, the disadvantages of this method, such as poor adhesion between the coatings and metallic substrates and difficult porosity control, have limited its application in bioengineering (Kumar et al. 2015). So, what is the potential alternative technique to fabricate bioactive coating?

10.4 Laser Surface Treatment (LST)

On the basis of consecutive uses, the surfaces of tools and components are often investigated wear and corrosion resistance. Therefore, many techniques are used to modified surfaces. Therefore, various surface modification techniques were developed to improve their tribological properties. Among all conventional chemical and physical methods, Laser Surface Treatment (LST) is one of the most efficient techniques due to economic, fast, simple, repeatable techniques to control surface properties (Filho et al. 2011; Ghayad et al. 2015).

This approach can even be applied to repair damaged components and surfaces of tools significantly. In each of the specific applications, LST can be utilized to

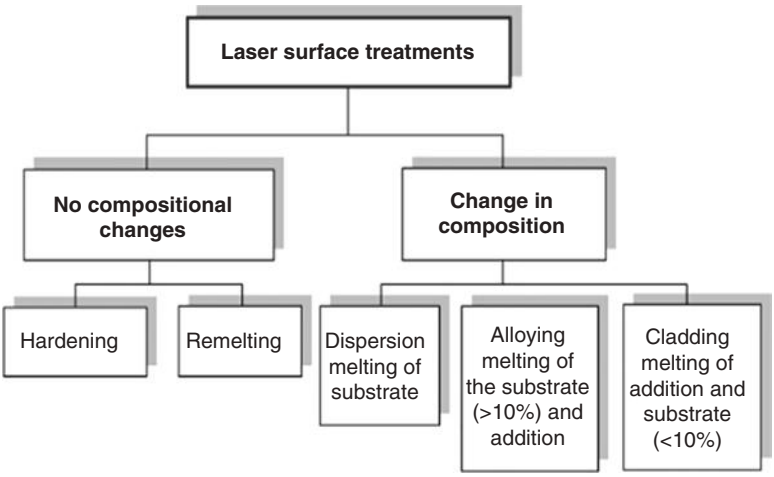

Fig. 10.4 Laser surface treatment techniques (Data were adapted with permission from the following citation: Steen 2003)

treat local repairs in flexibly and customized cover parts of components and tools. Therefore, the advantages of component surface functionalization are as follows:

- Flexible improvement and modification of tools and component surfaces to assort the collective loads
- Considerably longer components and tool life
- Broad spectrum of applications

Laser surface treatment techniques are shown in Fig. 10.4.

10.4.1 Different Laser Coating Methods for Surface Modification of Ti Alloys

On the basis of Laser Surface Treatments (LSTs), Melting (LSM), Alloying (LSA) and Cladding (LSC) are the three aspects of principal laser techniques utilized for the fabrication of wear and corrosion-resistant metallic surfaces because of the overall advantages and disadvantages of these processes to enhance wear and corrosion features.

10.4.1.1 Laser Surface Melting and Alloying

Since LSM and LSA severely relate to each other because of LSTs initial exposure to a physical phenomenon called "melting" to achieve alloying and cladding of materials, the processing has to be continued until the next stages. It is that both LSM and LSA are involved simultaneously. The alloying process is achieved during the melting process, so, by studying the alloying process, it is simultaneously possible to first express the melting processing of materials in this task.

Fulfilling laser melting on the metallic beds achieves a broad range of applications in sciences and industries due to the precise operational treatment and products with high depth/width ratios in the fusion zone, which minimizes the final amount of the affected material using laser beam scanning. The absorbed high-intensity (energy density) beam causes a fast increase of the substrate temperature. If the intensity is enough, the increasing surface temperature can reach the melting point of the substrate material. Therefore, the melting occurs on the surface of the substrate. The interface between the liquid and solid phases distributes inside the material, while the opto-thermal phenomenon causes an increase in the surface temperature. After the conducted heat spreads from the surface into the bulk material, the surface temperature rises until heat conduction and the heats of melting and evaporation modify the surface energy deposition.

In selected laser melting (SLM), the laser beam defined is focused on the metallic powder to successively melt layers, while the laser and setup parameters such as laser wavelength, power density, frequency rate, scanning rate, environmental temperature and pressure, granule size, and inner gas can be precisely controlled to

customize the products. The main goal of using the SLM technique in material surface processing is to modify their features such as wear and corrosion resistance due to the formation of a robust and homogenous structure of surface layers, avoiding any change in their chemical compositions. SLM on the surface layers causes the formation of grain refinement, ultra-high saturated solid dilutions, and good diffusion of particles, known as metallurgical changes. All these reasons should be considered to obtain a harder, stronger, and more resistant surface layer of the materials selected.

By laser beam scanning, particles on the surface of the substrate absorbed the laser wavelength and the powders in the certain paths on the metallic matrix have been locally heated until entirely be melted. However, a CAD 3D file commands where the melting will be fulfilled. Considering the ability to sufficiently manufacture of a rapid prototyping, 3D printing, or additive manufacturing, a powerful laser have been used to melting and fusing the metallic powders (Wood field et al. 2017). Although the most of SLM processings have been considered in the subcategory of selective laser sintering (SLS), SLMs can even used to producing melted powders in a solid 3D sector on the matrix accordingly (See Fig. 10.5).

Considering the above advantages, LMP can then harden alloys that cannot be hardened so adequately by other traditional material methods. Regarding, previous decades, in particular literature, the process of alloying along the melting process, a suitable application in the preparation of new and worthy products for today human needs, which, can be manufactured by proper thermal sources of high-power lasers. Figure 10.6 shows a summary of the applications of the laser in LST (Dowden 2009). In each of these types of LS processings, the laser intensity and the interaction/

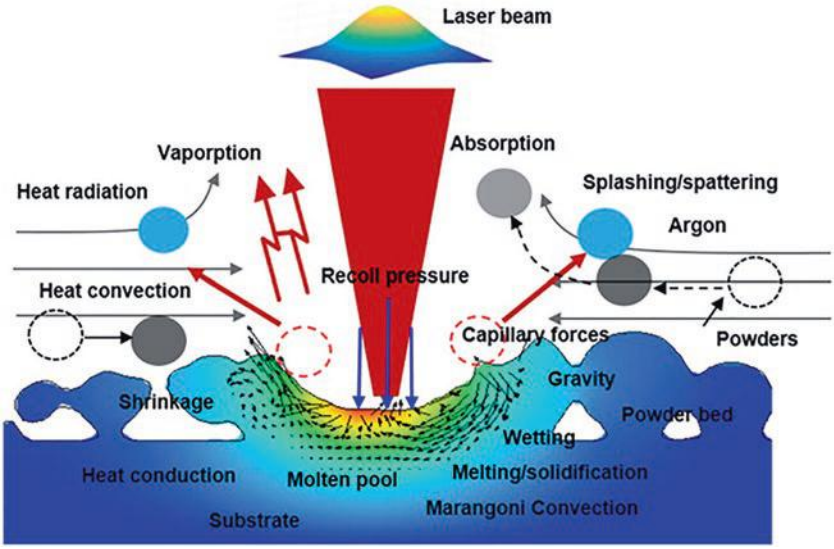

Fig. 10.5 Schematic of selective laser melting and the heat transfer in the molten pool (Data were adapted with permission from the following citation: Chen et al. 2018)

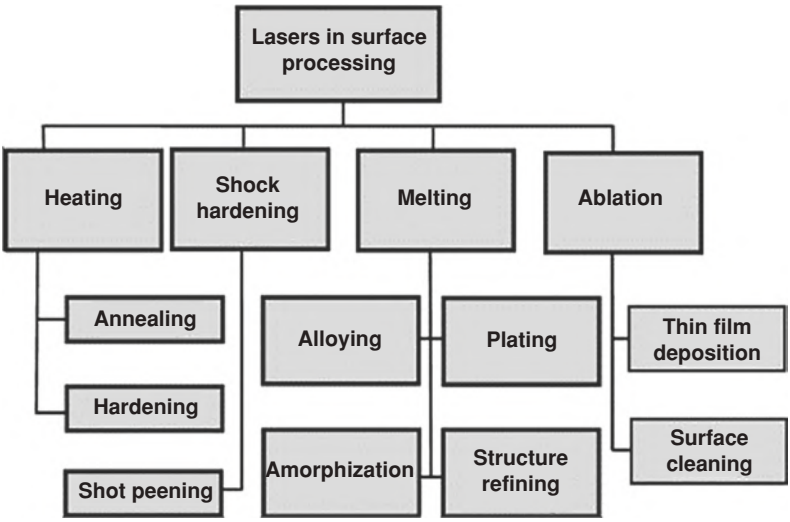

Fig. 10.6 Laser applications in surface processing (Data were adapted with permission from the following citation: Kusinski et al. 2012)

pulse duration time are specially selected in terms of acquiring the desirable temperature and phase transition.

10.4.1.2 Laser Cladding

Laser cladding (LC) for manufacturing the composite coatings is a coating technique that involves melting and adding another material as in the alloying process. A new crack- and porosity-free layer is created on the surface, in this regard (Toyserkani et al. 2005). Moreover, dilution in this process is kept to a minimum and less than the dilution required in the laser alloying process. LC can be used to manufacture a board range of surface alloys and composites with customized properties under demand. This secure processing even leads to coating multilayers with complex geometry on the material surfaces rapidly (using the laser pulse width). Besides, the modification and repairing of material surface properties are done, whereas this approach can be applied to produce 3D components (Brandt 2017; Munsch 2017).

Different Methods of Laser Cladding

There are several feeding ways of cladding a material, such as paste feeding, powder injection, and wire feeding. LC with powder injection is more general due to its almost infinite potential to change the alloy composition (Ganjali et al. 2018).

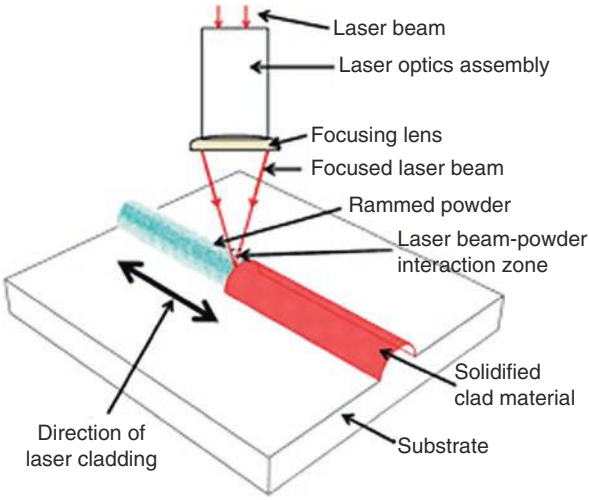

Fig. 10.7 Laser cladding by paste feeding (Data were adapted with permission from the following citation: Paul et al. 2015)

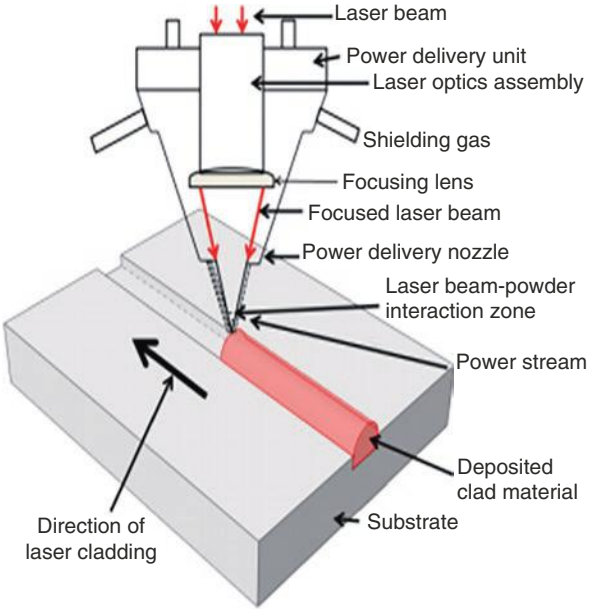

Fig. 10.8 Laser cladding by injected powder (Data were adapted with permission from the following citation: Santanu et al. 2016)

Paste Feeding

This process is a two-step approach for coating substrates. In the *first stage,* the powder is mixed with a chemical binder to ensure that it will stick to the substrate during the process and the *substrate* surface is *covered* with the paste, and in the second stage, heat provided by scanning of the laser beam is strictly transferred over the powder that melts along the substrate (Fig. 10.7). Although a homogeneous and crack-free coating with a strong metallurgical bond is formed between the liner and

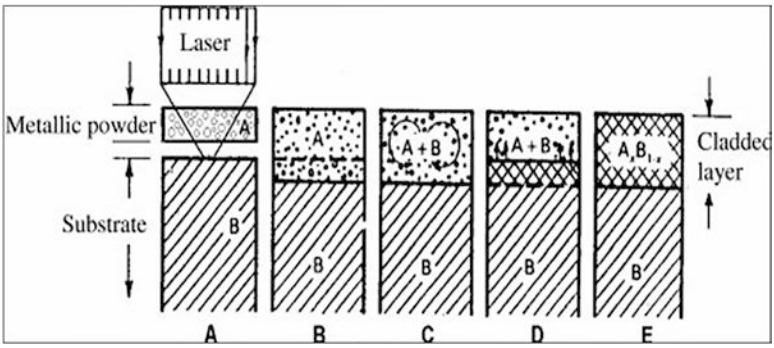

Fig. 10.9 Schematic steps involved during the laser surface cladding (Data were adapted with permission from the following citation: Picasso et al. 1994)

the substrate by this method, the method is not suitable for components with complex geometric shapes (Jayakumar et al. 2015).

Injection Powder

In this method, the powder particles are injected into the laser beam through an inert gas nozzle. Feeding powders are melted by the laser beam and a thin layer with minimum dilution is formed after solidification of the melting pool (Fig. 10.8).

To process the sample, the laser beam is placed to scan above the material surface which should be stripped by the hard material. Inert gas and the composite powder simultaneously are injected by the laser head, while the laser beam with the defined laser intensity and scanning rate is targeted, melting those powders on the surface at the same time. To accomplish this, both powder particles (metal and ceramic) and a thin layer of the substrate should absorb the laser power/energy per area, simultaneously (Fig. 10.9a). Due to the photon energy absorption, the powder and thin layer of the substrate rapidly reach their melting points. In a fraction of a milli/microsecond the liquid/solid interface is brought to the substrate (Fig. 10.9b). As is given in the formula, the height of the substrate-melted zone directly depends on the laser intensity and the interaction time. This stage involves mixing of the molten metallic powder with the substrate and the partially dissolved ceramic material using a convective fluid flow mechanism (Fig. 10.9c). Due to the half-width of laser pulse relaxed (during the decay time), the composite materials melted very fast (less than 10 m/s) and were crystallized in the molten pool as shown in Fig. 10.9. In Fig. 10.9, the solid/liquid interface, therefore, enters part A, where the composite powders existed before. Consequently, as shown in Fig. 10.9e, the cladded composite layer is uniformly formed on the substrate surface (Picasso et al. 1994; Smurov 2008).

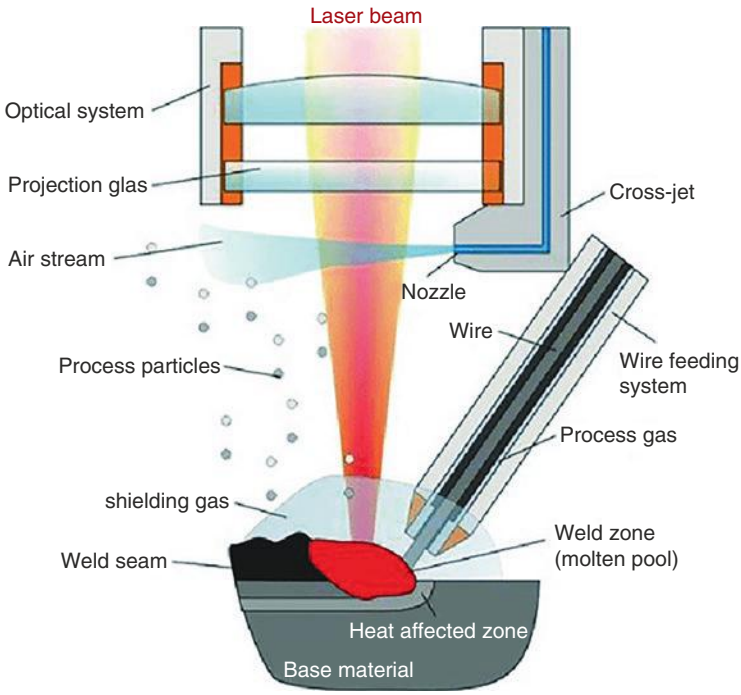

Fig. 10.10 Laser cladding with the wire feeding method (Data were adapted with permission from the following citation: Klocke et al. 2012)

Wire Feeding

The clad material is used in the wire form in this method (see Fig. 10.10). Laser cladding with wire has more advantages compared to usingboth powders and the paste feeding methods : cleaner process environment, higher material deposition efficiency, improved surface quality, and reduced material wastage, which serve to enhance the process economy (Quintino 2014).

Advantages and Disadvantages of Laser Cladding

Advantages of the laser cladding technique are as follows:

1. Low dilution (minimum %1–5) between the material cladded and the substrate
2. Laser beam as a controllable heat source with high power/energy density with the ability to focus on a tiny area
3. Controlling the coating thickness
4. Possessing a very narrow heat-affected zone (HAZ) due to the high heat created within the laser power/energy and spot size
5. Economical in terms of cost compared with conventional methods and logical guidance

However, the high cost of investment, low productivity of laser resources, and lack of control over the coating process are the disadvantages of using this cladding technology. Nowadays, with the continuing developments in the manufacturing of high-power diode lasers (HPDLs), fiber laser, and sophisticated knowledge-based control, the laser cladding process seriously has a great industrial potential for use in the coating of metals, and prototyping.

Factors Affecting the Laser Cladding Process

The selective additive materials, substrate, beam, and operating parameters substantially affect the microstructure, bonding, and quality of the cladded layer. Beam and feeding parameters are generally fixed and are dictated by the choice of equipment, lasers, and optics. The effective energy measures the amount of energy delivered to the process by the laser. This energy is principally responsible for melting the substrate surface and powder and is defined by Eq. (10.1) (Toyserkani et al. 2005):

$$E = P / VD \tag{10.1}$$

In which P – is laser power, V – is the scanning speed of the substrate, and D – is the laser beam diameter. The effective energy E is measured in units of j/cm^2.

The powder deposition density is also a good indicator of the amount of powder fed to a unit area of the substrate during deposition. The powder deposition density is calculated by Eq. (10.2) (Toyserkani et al. 2005):

$$PDD = R / VD \tag{10.2}$$

where R is the powder feed rate. The powder deposition density PDD is measured in units of g/mm^2.

As a result of increasing the scanning speed, the absorb of the laser beam by both the feeding powder and the substrate is decreased and the width, depth, and thickness of the coated layer are reduced, consequently (Vilar and Almeida 2016; Ocelík and De Hosson 2010). On the other hand, increasing the laser intensity at a lower scanning speed increase input energy density and increase clad depth after rapid solidification (Xiong et al. 2009; Tellez 2010; Hu et al. 2009; Ju et al. 2018).

The quality of the laser cladded layer is defined by the dilution ratio, so a better quality of cladded layer is required in lower dilution (Steen and Watkins 1993; Steen 2003; Hofman et al. 2011). An increase of laser power and a decrease of the laser beam spot size led to an increase in the input laser intensity, and then an increase in the dilution ratio (Pekkarinen et al. 2012; Abioye et al. 2013; Zhao et al. 2003).

The dilution rate γ is calculated by the formula (10.3) (Wu et al. 2015).

$$\gamma = b / b + h \tag{10.3}$$

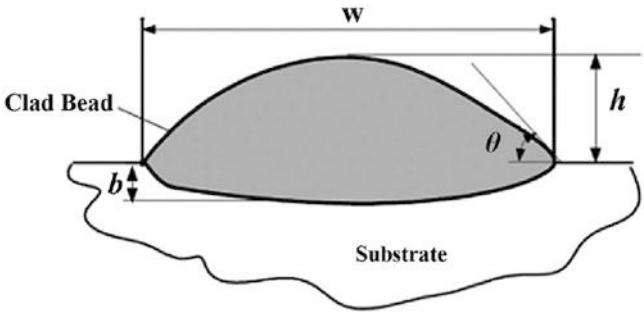

Fig. 10.11 Typical cladded cross-section with most common geometrical characteristics (Data were adapted with permission from the following citation: Toyserkani et al. 2005)

where, h – clad height, b – clad depth, w – clad width, and α – contact angle (see Fig. 10.11). The main effect of laser power and scanning speed on the cladded layer properties is shown in Fig. 10.12.

Indeed, bonding between cladding layer and substrate and fine microstructure of clad layer depends on the feeding powder shape and rate. Irregularly shaped feeding powder causes decrease flowability and as a result, the powders melt incompletely, and pores appear on the interface and surface clad layer. Moreover, the metallurgical bonding between the clad layer and substrate cannot be achieved in case of high rate feeding powder due to the partial melting of feeding powder (Frazier 2014; Sun et al. 2016).

Laser Cladding of Bioceramics – Calcium Phosphates

Many studies have been reported about laser cladding in biomedical applications (Mohammadzadeh Asl et al. 2019; Paital et al. 2010), and the effect of the pulse laser frequency (10–40 Hz) on the wettability and biocompatibility of calcium phosphate coated on the surface of samples was successfully investigated.

According to X-ray diffraction (XRD) analysis, different phases such as $CaTiO_3$, $Ca_3(PO_4)_2$, TiO_2 (anatase), and TiO_2 (rutile) in the coated layer were obtained. They showed that the hydrophilicity (wettability) of the coated samples was increased by decreasing the pulse lase frequency.

CO_2 laser was used to clad gradient coating pure $CaHPO_4{\cdot}2H_2O$, $CaCO_3$, and Ti (45–50 μm) powders on Ti-6Al-4V (Zhu et al. 2016). The bioactive results showed that there was no toxicity in the osteoclast precursors and this functional design was suitable for the growth of osteoclast precursors.

Zheng et al. (2008, 2010) investigated the microstructure and osteoblast response of gradient bioceramic coating hydroxyapatite (HAp) on a titanium alloy fabricated using LC. In another study (Lusquiños et al. 2005; Huang et al. 2013), a homogeneous HAp layer on the Ti alloy substrate and a gradient composite design by LC were fabricated. In the whole process, suitable metallurgical and chemical bonding

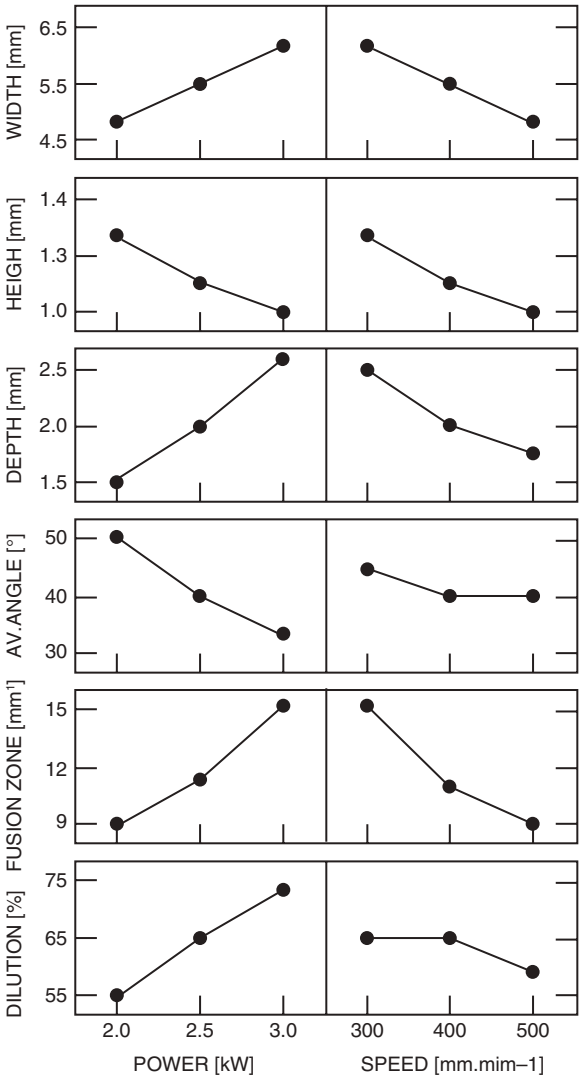

Fig. 10.12 The effect of laser power and scanning speed on the cladded layer properties (Data were adapted with permission from the following citation: Caiazzo et al. 2017)

with the substrate was achieved without any crack and pores. However, there is a limitation to using HAp in clinical research because of the defects in HAp particles, such as brittleness, weak intensity, fatigue failure, and inability to induce vascularization (Rahmandoust and Ayatollahi 2019). So, they can be used in bioresorbable composites made from HAp and biodegradable polymers. Chien et al. (2009) studied the effect of two different HAp binders on the morphology, Ca/P ratio, and hardness of Nd-YAG laser clad coatings. In this work, HAp was mixed with various binders such as water glass (WG) and polyvinyl alcohol (PVA), and then samples were cladded by a laser at two different output powers (740 and 1150 W) and at three different scanning speeds (200, 300, and 400 mm/min). They concluded that

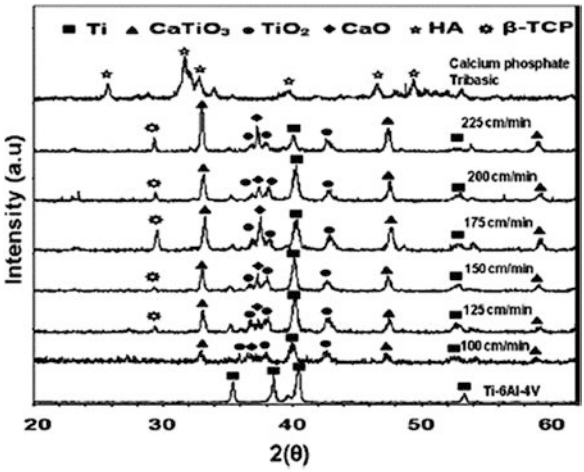

Fig. 10.13 XRD pattern of the coating at different laser scanning speeds (Data were adapted with permission from the following citation: Kurella et al. 2008)

the number and severity of the cracks formed and the porosity in the transition layer weld bead in the cladded samples, PVA and WG binder, were increased, respectively. Moreover, the hardness of the WG binder was higher than the prepared sample using the PVA binder. Recently, it has been reported that the chemical phase of the surface plays a role in Osseo-integration (Moritz et al. 2004; Tian et al. 2005; Khor et al. 2004). In this regard, LC was used for coating hydroxyapatite (HAp) on Ti alloy surfaces at multiple processing speeds (Kurella et al. 2008). They showed that the processing speeds affect the surface morphology, phase composition, and microstructure, which leads to improving the wettability in water (liquid). According to the XRD results (Fig. 10.13), at a lower laser scanning speed and a higher temperature, the wettability and, hence, biocompatibility were decreased due to the dissociation of calcium phosphate through interactions with the substrate titanium and the surrounding air.

The high dissolution rate of hydroxyapatite around the coating surface during the biological fixation effect on bone formation rate and long-term implant success. Therefore, in some cases secondary surgery is unavoidable (Qu and Wei 2006). Therefore, substitute ion such as Mg, Sr, Ag, and F acts as an inhibitor of HA nucleation and crystallization and destabilizes its structure and is decreased the c-axis of the lattice. Other weaknesses of hydroxyapatite include weak mechanical properties such as low impact resistance. These considerations have severely restricted the use of hydroxyapatite in many applications. The apatite structure is a good host for a variety of chemical ionic substituents in its construction. This substitution causes changes in some properties of apatite such as the lattice parameter, morphology, and solubility. The following section will introduce some of these materials.

Ionic Substitution in Hydroxyapatite

As mentioned above, good metallurgical and chemical bonding between the substrate and HA coating after laser cladding was achieved. But due to the presence of TCP in the cladded layer after laser treatment, the solubility of HAp is increased, and as a result, the stability of the HAp coating and also the long-term implant function are decreased (Huang et al. 2013). *Hence,* there is a *need* for the enhancement of *the solubility* of HAp. Since fluorapatite (fHAp) has lower biocompatibility degradation compared with HAp when exposed under higher laser power, it has attracted much more attention for coating on Ti alloys. Chien et al. (2014) utilized an Nd-YAG laser for HAp and fHAp coatings on Ti-6Al-4V substrates. The SEM images revealed slight differences between the surface roughness of HAp and fHAp. Also, the fHAp coated samples had a finer and denser microstructure than HAp coated samples, which led to improving the interfacial and structural strength. Meanwhile, FA has not only better chemical stability and biocompatibility than HA, but also higher interatomic bonding strength (Clarkson et al. 2000). Consequently, during the laser radiation process, FA was reported to have a more stable structure than HA.

Laser Cladding of Bioceramics – Ceramics and Bioglass Ceramics

Balovi et al. (2014) used zirconium and zirconia. Zirconium powder was mixed with the binder poly vinyl alcohol (PVA) and cold glue (CG) for coating of Ti6Al4V to improve the base material's resistance to corrosion and wear. They suggested two applications of these coatings: (1) zirconium and Zr/PVA coatings can be used to prevent the release of toxic Al and V ions in corrosive environments and (2) Zr/CG coating can be used in applications where improved hardness is required. Wang et al. (2019) investigated laser cladding of $CeO_{2/}$ Ti-based ceramic nanoparticle coatings on the Ti-6Al-4V alloy. The experimental results showed the positive effect of the addition of CeO_2 nanoparticles on the enhancement of microhardness and wear resistance of the substrate. Liu et al. (2019) studied the surface modification of the biomedical titanium alloy: micromorphology, microstructure evolution, and biomedical applications. Simulated body fluids (SBFs) results showed that the appearance of the flake-like and cotton-like morphology of apatite provides favorable conditions for osseoconnection. In a recent study by Po-Hsuen Kuo et al. (2019), SiO_2-Na_2O-CaO-P_2O_5 bioactive glass coated on the Ti-6Al-4V alloy by LC is used for bioimplant application. The SEM images of the cross-section showed good metallurgical bonding between the bio-glass coating and the substrate alloy. Meanwhile, according to the EDS results, the bioactivity decreased because of the loss of crucial species such as Na and P and addition of some elements like Ti and Al to the coating (See Fig. 10.14).

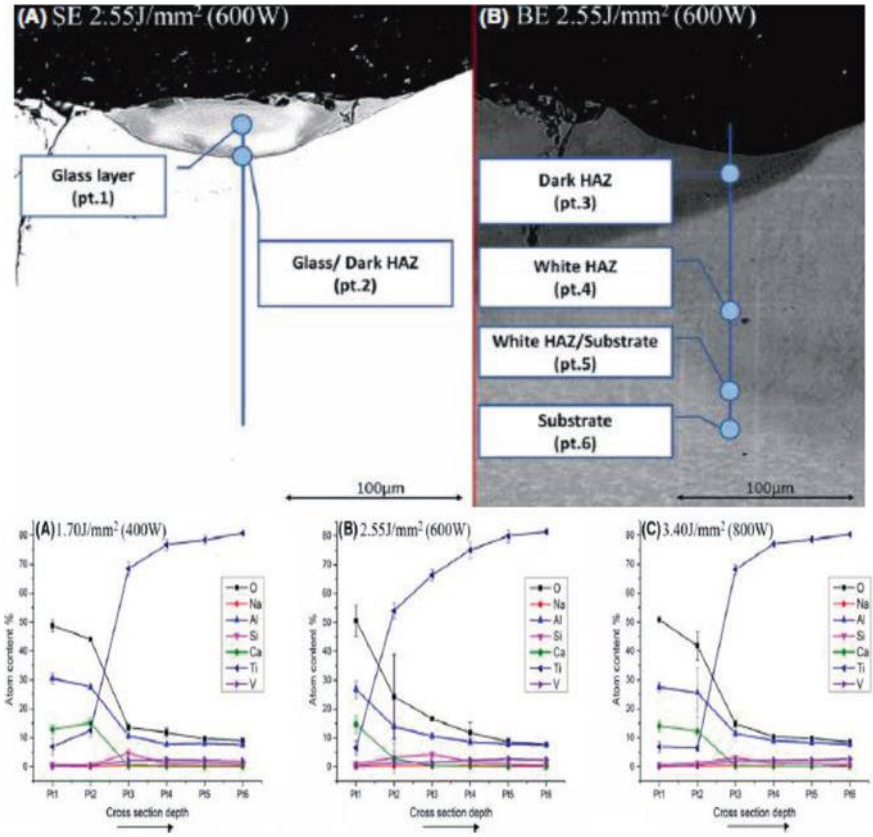

Fig. 10.14 SEM images of cross-section and EDS results of coating at different laser power; (**a**) 400 W, (**b**) 600 W, and (**c**) 800 W (Data were adapted with permission from the following citation: Kuo et al. 2019)

10.5 Conclusion

The conclusions of this work are summarized as follows:

- The application of laser cladding to generate uniform, homogeneous, compact, and well-bonded coatings on the Ti alloy substrates without the necessity of any previous treatment of the surface.
- The technique can be used to produce crack-free coating with higher microhardness and corrosion and wear resistance during the welding process and in presence of intermetallic compounds.
- Based on the literature, surface modification of Ti alloy-based biomedical devices by laser cladding could be a promising method toward more biocompatible and resistant biomedical devices.

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