Oxidation of Biocompatible Graphite–Ti Composite after Laser Ablation in Different Atmospheres

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Abstract. The field of biocompatible material surfaces is a widely researched topic. Surface energy, surface topography and surface chemistry are important properties of biocompatible surfaces. These properties contribute to better osseointegration and adhesion of cells to implant surfaces. This article investigates the chemical and phase composition of the surface of a new titanium composite produced by powder metallurgy. Surface oxidation of the graphite–titanium metal matrix composite (TiMMC) after laser beam micromachining (LBMM) is discussed in this paper. Laser micromachining was performed in an argon shielding atmosphere and air. The aim was to determine the influence of the shielding atmosphere and the input parameters of LBMM on the presence of oxygen on the surface. Laser-treated surfaces were examined with scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The phase composition was analysed with X-ray diffraction (XRD). Experiments confirmed that an argon shielding atmosphere reduces surface oxidation. The oxidation was also affected by the energy of the laser beam acting on the material. The maximum amount of oxygen detected on the surface after LBMM in air and argon was 38.6 wt. % and 24.2 wt. %, respectively. The presence of TiO, TiO2 and Ti2O3 oxides were detected on the surface after laser ablation in air. In contrast, Ti2O3 and TiO oxides were detected after laser ablation in the argon shielding atmosphere.
1. Introduction

Metallic materials are commonly used in orthopaedics and dentistry as hard tissue replacements [1]. Titanium and its alloys, stainless steels and co-based alloys are routinely applied and have an irreplaceable position in the field of implant production [2, 3]. Titanium-based materials in particular possess good biocompatibility, high wear and corrosion resistance and suitable mechanical properties [4].

The success of implantation depends on the interaction of biological tissue with the implant body. After the implant is inserted into living tissue, the interface between the implant and the bone is formed. Interaction between the organic environment and implanted bone replacement is affected by the surface properties of the implant [5]. The osseointegration process can be improved and a reaction of the living tissue can be modified by the surface properties, including surface energy, wettability, electrical charge, topography, the roughness of the implant surface and the surface’s chemical composition [6, 7].

Morphological characteristics, such as distance, distribution, shape and height of the protrusions are taken into account when evaluating the topography of the implant surface and the tissue response to it [8]. In terms of topography, important characteristics include the arithmetic average of the roughness profile Ra, area surface roughness Sa, surface flatness and surface area [9]. An extensive review of research in [10] shows that a moderate Sa between 1 and 2 µm elicits the most suitable bone response to the implant surface.

Implant surface modification technologies include chemical modification, grit blasting, laser beam micromachining, bioactive and antibacterial coatings, or a combination of these methods [11–13]. The advantages of applying laser technology are the efficient control of depth and energy density, repeatability, short work cycles and accuracy [14]. Compared to chemical machining, an advantage is non-pollution of the surface of the modified material [9]. LBMM is considered a non-isothermal process that is exhibited by non-uniform energy distribution causing a large thermal gradient. This effect can result in the presence of structural defects and residual stresses [15].

Titanium reacts with light elements, such as O₂, N₂, C from the surrounding atmosphere at high temperatures. Titanium-based oxides and TiN phases presented on the surface of titanium and its alloys are products of diffusion-driven processes that emerge during laser treatment of the surface. Oxygen and nitrogen from the atmosphere or shielding gas create oxides and nitrides of titanium within the process of so-called laser gas alloying. These oxides and nitrides can improve some surface properties, such as hardness, corrosion and wear resistance and biocompatibility [15, 16]. Many authors investigated the reactions and surface characteristics of biocompatible Ti materials during laser irradiation in different atmospheres with different input laser beam machining parameters.

Different surface modifications were evaluated by Wang et al. [9]. Biocompatible Ti6Al4V alloy was processed using three different techniques, namely, grinding, sandblasting and then etching and laser treating by a nanosecond UV laser. In that case, easy cell migration and good proliferation along the grooves produced by laser beam treatment was documented. Additionally, the surface was characterised by the anisotropic wettability and periodic oxygen distribution on the machined surface.

Moura et al. [14] textured Ti6Al4V with an Nd:YAG laser in atmospheric air. The textured surface was grooved and consisted of α-Ti and oxides Ti₃O and Ti₂O.

Rajab et al. [17] developed a hydrophobic surface of Ti6Al4V alloy using picosecond laser etching. This process can reduce the adhesion of bacteria on the surface of the treated alloy. The surface topography consisted of self-organised structures and rounded peaks with an
average Sa between 0.29 \mu m and 1.38 \mu m. The different types of TiO\textsubscript{2} combined with nitrogen – (TiO\textsubscript{2})\textsubscript{x}N\textsubscript{y} and TiO\textsubscript{x}N\textsubscript{y} – were formed on the laser-textured surface due to titanium reactivity at high temperatures.

Zeng et al. [15] treated a commercially pure (cp) Ti surface with a continual-wave mode laser at different scanning speeds. The scanning speed rate was reflected in the overall change in the density of energy introduced into the material. The lower scanning speed caused a longer heating time of the material. The O and N reacted with Ti and diffused deeper into the substrate. The resulting surface consisted of TiO\textsubscript{2} and TiN, which appeared in the form of dendrites under the treated surface.

Lavisse et al. [18] investigated the chemical composition of a cp Ti-grade-4 surface after industrial Nd:YAG laser irradiation. The energy density was in a range from 100 to 1,200 J.cm\textsuperscript{-2}. A titanium oxynitride Ti\textsubscript{x}N\textsubscript{y} layer with hexagonal symmetry and a thickness of around 2 \mu m was formed on the machined surface. They expected the formation of titanium oxynitrocarbides Ti (C, N, O).

Adams et al. [19] treated the surface of cp titanium grade-2 using a nanosecond pulsed-laser with different laser fluencies to grow titanium oxide/oxynitride coatings with various colour appearances according to their thickness. They found that the coatings consisted of three layers, namely, a thin TiO\textsubscript{2} upper coating, TiO middle coating with trace amounts of N and the bottom TiO\textsubscript{x}N\textsubscript{1-x} layer. The dependence of colour on the coating thickness was documented. The thinnest oxide (TiO) coating produced with low fluence was characterised by a gold colour.

Based on previous research, it can be concluded that the topic of laser ablation of pure titanium and its alloys has been studied intensively. However, there is still a lack of information about the laser ablation of graphite–Ti composites produced by powder metallurgy. This article studies the influence of input process parameters in two different atmospheres (air and argon) on chemical and phase composition of the composite ablated surfaces with an emphasis on oxide formation.

2. Experimental Setup
The recently developed powder metallurgy (PM)-processed TiMMC was micro-machined by a laser beam. The nanosecond pulse Yb-doped fibre laser (Lasertec 80Shape from DMG Mori GmbH, Germany) was employed for laser beam machining the graphite–Ti composite. This industrial-grade laser system has a 1,064 nm wavelength, a maximum pulse repetition rate of 100 kHz and 100 W maximal power.

Six square-shaped surfaces with a side length of 6 mm were irradiated by a laser beam. The experimental setup is shown in Figure 1. Within the experiment, cavities were ablated at three different energy densities E\textsubscript{D} (0.10, 0.30 and 0.50 J.mm\textsuperscript{-2}) and three different lateral pulse distances D\textsubscript{L} (0.5, 10 and 20 \mu m). The material was ablated in two layers with a crosshatching machining strategy, which is depicted in Figure 2.
Figure 1 Experimental setup and parts of the experiment equipment

Figure 2 LBM crosshatching strategy scheme: 1 – first layer, 2 – second layer, 3 – laser beam tracks

Constant parameters of the laser beam machining were pulse duration at 120 ns, pulse diameter of 50 µm and transverse pulse distance $D_T$ of 10 µm, which means transverse pulses overlapped $O_T$ by 80%. A schematic representation of the pulse distances and pulse overlap is shown in Figure 3. When machining in a shielding atmosphere, the argon shielding gas flow rate was set at 10 l.min$^{-1}$. The laser beam machining parameters are listed in Table 1, where $f$ is the pulse frequency and $v_s$ is the laser beam scanning speed.

Figure 3 Schematic representation of pulse overlap: $D$ – laser spot diameter, $D_L$ – lateral pulse distance, $O_L$ – lateral pulse overlap, $D_T$ – transverse pulse distance, $O_T$ – transverse pulse overlap
Table 1 Input parameters of laser beam machining the graphite–Ti composite samples

| Sample | f [kHz] | v_s [mm.s⁻¹] | D_L [µm] | O_L [%] | E_D [J.mm⁻²] |
|--------|---------|--------------|----------|---------|--------------|
| A10, A11 | 20      | 1000         | 50       | 0       | 0.10         |
| A20, A21 | 20      | 1000         | 50       | 0       | 0.30         |
| A30, A31 | 20      | 1000         | 50       | 0       | 0.50         |
| B10, B11 | 100     | 50           | 0.5      | 99      | 0.50         |
| B20, B21 | 100     | 1000         | 10       | 80      | 0.50         |
| B30, B31 | 100     | 2000         | 20       | 60      | 0.50         |

2.1 Materials
The titanium matrix composite produced by powder metallurgy was used as experimental material. Commercially pure Ti powder with 15 vol. % graphite flakes were mixed in a Turbula mixer for 30 min and then compacted [20, 21]. The theoretical density of this mixture was 4.16 g.cm⁻³ when a graphite density of 2.2 g.cm⁻³ and titanium density of 4.506 g.cm⁻³ was considered. Then, the weight percentage was 92.07 wt. % for Ti and 7.93 wt. % for graphite. Cp Ti powder was fabricated using a hydride–dehydride (HDH) process (Kimet Special Metal Precision Casting Co. Ltd., China). A typical feature of this process is the presence of angular-shaped Ti particles below 32 µm in size. Graphite flakes with a purity of 99.9% and an average particle size of 16 µm were used as the reinforcement. The powder size distribution was determined using Fritch Analysette 22 laboratory equipment using wet dispersion. The obtained results were \( d_{50} = 24.9 \mu m \) and \( d_{90} = 46.3 \mu m \) for titanium powder and \( d_{50} = 5.6 \mu m \) and \( d_{90} = 13.9 \mu m \) for graphite flakes. Cold isostatic pressing (at 200 MPa) followed by a hot vacuum press at working temperatures in the range of 450–470 °C and a pressure of 500 MPa were used for compacting. The final sample density was in the range of 4.1–4.15 g.cm⁻³ and the porosity of the finished compact was 2.44 % ± 0.15 % [22].

2.2 Methods
Before laser ablation, the samples were prepared in a standard metallographic procedure that consisted of cutting with the precision saw, hot mounting in conductive resin and grinding up to P1200 (15.3 µm) emery paper. To study the topography of laser-treated surfaces, a JEOL JSM 7600F high-resolution scanning electron microscope (SEM) was utilised. The ablated surfaces were observed in a secondary electron imaging regime (SEI) with the following parameters: \( U = 15 \) keV, \( I = 1.0 \) nA and \( WD = 15 \) mm. The chemical composition was determined with an Oxford Instruments Inca X-Max 50 mm² energy-dispersive X-ray spectrocope (EDS) operated at the same parameters. Three measurements of chemical composition were also performed for each sample. The phase composition of the surfaces after laser ablation was studied using a Brucker D8 diffractometer (XRD) with the Cu anode (\( \lambda = 1.5406 \) Å). The following parameters were used during the measurements: \( U = 40 \) kV and \( I = 30 \) mA. Diffraction patterns were taken in a range from 15° to 105° with a step size of 0.05°. Finally, the influence of input parameters (laser pulse distance and energy density) and shielding gas (Ar) on the oxygen content presented on the laser-ablated surfaces was evaluated with statistical one-way analysis of variance (one-way ANOVA) followed by Welch’s tests using Minitab v.17 software. In this case, the level of significance at 95% (\( \alpha = 0.05 \)) was chosen.
3. Results

Table 2 illustrates the chemical composition of graphite–Ti surfaces after laser ablation at different input parameters, namely, energy densities (0.10, 0.30 and 0.50 J.mm\(^{-2}\)) and lateral pulse distances (0.5, 10 and 20 µm). Additionally, the influence of air and the protective argon atmosphere was also evaluated. The individual samples were designated in the following way: A1–A3 samples were processed with a different pulse density and B1–B3 samples were treated with different values of lateral pulse distances. The latter digit distinguishes whether the sample was ablated in the air (digit 0) or the shielding Ar (digit 1). Not surprisingly, in most cases, higher oxygen content up to 38.6 ± 0.02 wt. % was documented after the laser ablation without shielding Ar (in the air), which is caused by weak protection of the processed surfaces. Furthermore, the change in energy densities and lateral pulse distances had a strong influence on the oxygen content. As energy density increased from 0.10 to 0.50 J.mm\(^{-2}\), the oxygen content increased from 18.3 ± 0.07 wt. % to 28.1 ± 0.03 wt. % for the samples ablated in the air. Meanwhile, the Ti content decreased from 73.3 ± 0.23 wt. % to 62.4 ± 0.38 wt. % and the C content slightly increased from 8.3 ± 0.23 wt. % to 9.5 ± 0.38 wt. %. When the samples were the same but ablated using shielding Ar, the increase in oxygen content with energy density was less significant (~7 wt. %). As the energy density increased, the oxygen content first increased from 17.2 ± 0.02 wt. % to 24.2 ± 0.47 wt. % and then decreased to 22.5 ± 0.59 wt. %. The Ti and C contents slightly decreased from 72.5 ± 0.21 and 10.3 ± 0.22 wt. % to 68.8 ± 0.72 and 8.8 ± 0.14 wt. %, respectively. Different behaviour was observed in the samples treated with different lateral pulse distances. In general, oxygen content decreased with an increasing lateral pulse distance after processing in the air and Ar atmosphere from 38.6 ± 0.02 wt. % and 23.2 ± 0.41 wt. % to 23.7 ± 0.04 wt. % and 15.4 ± 0.92 wt. %, respectively. Vice versa, the drop in C content was observed for B samples processed in the air (from 15.8 ± 0.29 wt. % to 11.7 ± 0.45 wt. %) and the Ar atmosphere (from 9.5 ± 2.76 wt. % to 7.9 ± 0.24 wt. %). It was possible to adjust the oxygen content by varying the energy density and lateral pulse distances during laser ablation.

Table 2 Chemical composition of graphite–Ti composite as a function of laser input parameters and type of atmosphere

| Sample | Ti ± St. Dev. | C ± St. Dev. | O\(_2\) ± St. Dev. | Sample | Ti ± St. Dev. | C ± St. Dev. | O\(_2\) ± St. Dev. |
|--------|--------------|--------------|--------------------|--------|--------------|--------------|--------------------|
| A10    | 73.3±0.23    | 8.3±0.23     | 18.3±0.07          | A11    | 72.5±0.21    | 10.3±0.22    | 17.2±0.02         |
| A20    | 70.8±0.11    | 7.5±0.13     | 21.8±0.03          | A21    | 65.9±0.64    | 9.8±0.23     | 24.2±0.47          |
| A30    | 62.4±0.38    | 9.5±0.38     | 28.1±0.06          | A31    | 68.8±0.72    | 8.8±0.14     | 22.5±0.59          |
| B10    | 45.6±0.29    | 15.8±0.29    | 38.6±0.02          | B11    | 67.3±3.13    | 9.5±2.76     | 23.2±0.41          |
| B20    | 64.4±0.13    | 9.7±0.14     | 25.9±0.02          | B21    | 68.5±1.99    | 10.3±0.41    | 21.2±1.64          |
| B30    | 64.6±0.41    | 11.7±0.45    | 23.7±0.04          | B31    | 76.7±1.03    | 7.9±0.24     | 15.4±0.92          |

Graphically, the amount of oxygen is shown in Figure 4 for A samples and in Figure 5 for B samples.
Figure 4 Oxygen content on the surface of the graphite–Ti composite after laser ablation as a function of energy density (0.10, 0.30 and 0.50 J.mm\(^{-2}\)) at a constant lateral pulse distance (50 µm)

Figure 5 Oxygen content on the surface of the graphite–Ti composite after laser ablation as a function of lateral pulse distance (0.5, 10 and 20 µm) at a constant energy density (0.50 J.mm\(^{-2}\))

Figure 6 shows the EDS spectra of laser-ablated surfaces in air and Ar of the A2 and B3 samples accompanied by their surface morphologies. It is clear that the shielding of the samples with Ar gas had no significant impact on their surface morphology.
Figure 6 Results of EDS analysis for A-group samples machined at a lateral pulse distance of 50 µm and energy density of 0.30 J.mm\(^{-2}\): A20 (machined in air), A21 (machined in Ar) and B-group samples machined at a lateral pulse distance of 20 µm and energy density of 0.50 J.mm\(^{-2}\): B30 (machined in air), B31 (machined in Ar)

Figure 7 shows the XRD patterns of the B1 sample before and after laser ablation in air and Ar. The diffraction pattern of the unprocessed sample evicted multiple orientations of (010), (002), (012), (110), (013), (020), (112) and (021) of α-Ti crystal planes (ICSD 98-005-2522). The phase belongs to the hexagonal system (P63/mmc) with the most intense (011) plane at 40.2° 2θ and unit cell parameters of a = b = 2.951 Å, c = 4.686 Å and α = β = 90°, γ = 120°. After laser ablation in shielding Ar, Ti\(_2\)O\(_3\) and TiO oxides were detected on the surface of the sample. The TiO oxide (ICDD 00-002-1196) is characterised by a cubic crystal structure with the space group Fm-3m and following unit cell parameters a = b = c = 4.235 Å and α = β = γ = 90°. Compared to TiO oxide, Ti2O3 (ICDD 01-071-1047) belongs to the rhombohedral crystal system (R-3c, a = b = 5.125 Å and c = 13.957 Å, α = β = 90° and γ = 120°). The shielding Ar did not protect the surface of the sample against oxidation. The same types of oxides were also observed after laser ablation in air, without Ar protection. Furthermore, the presence of tetragonal rutile (P42/mmm) TiO\(_2\) oxide (ICDD 01-072-1148) was documented (a = b = 4.594, c = 2.959 Å and α = β = γ = 90°). However, the diffraction patterns of the above-mentioned phases overlap and their precise identification is, therefore, difficult.
The amount of oxygen on the surface of the samples was statistically evaluated by one-way ANOVA – Welch’s test. Statistical analysis confirmed that the amount of oxygen was statistically significantly different between samples machined in air and argon.

Table 3 One-way ANOVA for groups of samples machined in air and Ar

| Samples     | DF | F-value | p-value | R²     |
|-------------|----|---------|---------|--------|
| A10 – A11   | 1  | 381.73  | 0.001*  | 98.96% |
| A20 – A21   | 1  | 53.90   | 0.018*  | 93.09% |
| A30 – A31   | 1  | 182.81  | 0.005*  | 97.86% |
| B10 – B11   | 1  | 2820.01 | 0.000*  | 99.86% |
| B20 – B21   | 1  | 58.14   | 0.017*  | 93.56% |
| B30 – B31   | 1  | 163.64  | 0.006*  | 97.61% |

*p < 0.05 means are different for significance level α = 0.05

4. Discussion
After the laser ablation of samples in the air environment (A10–A30 and B10–B30), a large amount of oxygen (up to 38.6 ± 0.02 wt. %) was detected on their surfaces. The oxygen content increased along with energy density. This could be explained by the phenomenon of the recoil pressure of laser-induced plasma, which improves the diffusion of atoms in reactive gas (oxygen) to interstitial positions. The influence of laser radiation during ablation causes the...
dissociation of molecular oxygen (O\textsubscript{2}) to atomic oxygen (O). The titanium surface has a better adsorption capacity of atomic oxygen compared to molecular oxygen. It resulted in enhanced diffusion and, therefore, higher oxygen content on the surface of the samples processed in air [23]. In contrast, the oxygen content on the surface of samples B10–B30 decreased with the increase in lateral pulse distance. The heat generated by overlapping laser pulses improves oxygen diffusion into the sample surface efficiently. Oxygen diffusion across the grain boundaries makes them distinct and wider. This effect also supports the formation of oxides on the laser-ablated surfaces. From that point of view, it could be stated that the shorter the laser pulse distance the more heat is generated on the sample surface and the conditions are better for the formation of oxides. So, increasing the lateral pulse distance causes a decrease in oxygen content [24]. Surprisingly, the presence of oxygen up to 24.2 ± 0.47 wt. % was also documented on the surfaces of the samples after laser ablation in the shielding Ar (A11–A31 and B11–B13). This unexpected effect could be easily explained by the insufficient flow of the shielding gas into the molten pool during laser ablation. Additionally, blowing the shielding Ar onto the sample surface had a negative impact on oxygen diffusion and, thus, the growth of oxide layers because of its cooling effect.

Following previous results, the character of the surface morphology was strongly affected by laser ablation parameters, including laser power, pulse frequency and scanning speed [20]. However, the influence of Ar shielding gas on the surface morphology of laser-processed samples was not observed. The absence of diffraction peaks corresponding to carbon that could confirm the presence of graphite after laser ablation of the graphite–Ti composite (sample B1) was confirmed by XRD. This phenomenon is related to the evaporation of graphite during ablation. However, Hu et al. observed a XRD pattern of graphite-Ti composite after laser sintering. They found a narrow peak at 43.3° 2θ that corresponds to (101) diffracting plane of multilayer graphene. This means that graphene existed in the composites even after laser sintering [25]. In contrast, the presence of carbon up to ~15 wt. % was observed by EDS analysis after laser ablation in the Ar atmosphere. Regardless of the input parameters and use of shielding gas, carbon was detected in all cases. The amount of carbon ranged from its minimal value of 7.5 ± 0.13 wt. % for the A20 sample treated in the air to the maximal content of 15.8 ± 0.29 wt. % for the B11 sample processed in the shielding gas. This suggests that carbon could be present on the surface of laser-treated samples in the form of amorphous graphite undetectable by XRD.

Two types of oxides were detected on the surface of samples after laser ablation in the Ar shielding gas, namely, cubic TiO\textsubscript{2} (ICDD 00-002-1196) and rhombohedral Ti\textsubscript{2}O\textsubscript{3} (ICDD 01-071-1047). TiO\textsubscript{2} and Ti\textsubscript{2}O\textsubscript{3} oxides have a lower oxygen content, 50 at. % and 60 at. %, respectively. The formation of these oxides took place even after laser ablation in insufficient Ar shielding gas. The level of oxygen present in the environment during laser ablation in the air (without the Ar atmosphere) enabled the formation of oxygen-rich (~67 at. %) tetragonal rutile-type TiO\textsubscript{2} oxide (ICDD 01-072-1148). The diffracting planes of TiO\textsubscript{2} oxide (111), (210), (211) and (301) were clearly distinguished at Bragg angles of 41.2°, 44.0°, 54.3° and 68.9° 2θ, respectively, in the XRD pattern of the sample after laser treatment in the air. In vivo, Hanawa et al. grew a passive film that was mostly based on TiO\textsubscript{2} oxide with a small amount of Ti\textsubscript{3}O\textsubscript{3} and TiO oxides. They found that the presence of Ti\textsubscript{3}O\textsubscript{3} and TiO oxides depends on the local microenvironment [26]. It was found that the biocompatibility of titanium can be improved by
applying a coating covered with bioactive TiO$_2$ oxide and by using micro- and nanoscale structures [27].

5. Conclusion
In this research, graphite–Ti metal matrix composite produced via low-temperature powder metallurgy was ablated by laser beam in two different atmospheres: air and argon shielding gas. Based on the results of the experiments, the following conclusions can be drawn:

1. In all cases, the amount of oxygen on the surface decreased when machining in an argon shielding atmosphere.
2. TiO, TiO$_2$ and Ti$_2$O$_3$ oxides with α-Ti were detected on the machined surface in air.
3. TiO and Ti$_2$O$_3$ with α-Ti were detected on the surface after laser treatment in the argon shielding gas.
4. Statistical analysis showed significant differences in the amount of oxygen on the surface after machining in air and argon.
5. Based on the experiment results, it is possible to adjust the oxygen content by both input process parameters and shielding atmosphere. Obviously, it is possible to adjust the oxygen content by varying the energy density and lateral pulse distances.

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