

Article

pH-Dependent Long-Term Degradation and Mechanical Integrity of LPBF-Fabricated Porous Ti-6Al-4V in Hank's Solutions with Different pH Values

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Abstract

Titanium alloys are widely used as bone graft materials due to their excellent corrosion resistance and biocompatibility. Implant failure can result from long-term exposure to body fluids and inflammation-induced pH decreases, both of which compromise the material's corrosion resistance and mechanical stability. To address this issue, porous Ti-6Al-4V alloy was selected in this work. Immersion tests were conducted in Hank's solution with different pH values (3, 5, and 7) for 90 days to simulate the in vivo microenvironment under various physiological conditions. The degradation behavior of porous Ti-6Al-4V alloy during the 90-day immersion period was systematically investigated using a combination of characterization techniques. The results indicated that TiO₂, Ca₃(PO₄)₂, and Ca(H₂PO₄)₂ phases were formed on the surface of the after 90 days of immersion. Massive dissolution of TiO₂ was observed in solutions with high H⁺ concentration (low pH). Ion release tests revealed that the concentration of titanium ions released was significantly higher in acidic solutions, suggesting that the passive film formed on porous Ti-6Al-4V alloy was unstable and prone to dissolution under acidic conditions. Consequently, a large amount of corrosion products accumulated on the specimen surfaces immersed in acidic solutions for a long duration. Moreover, the compression properties of the samples deteriorated after immersion. Specifically, the compressive strength decreased by 12.68 MPa, 11.67 MPa, and 5.84 MPa for sample immersed in solutions with pH = 3, 5, and 7, respectively. The significant reduction in compressive performance of the alloy in high H⁺ concentration solutions was attributed to the decreased compactness caused by ion release. The fracture mode of the porous Ti-6Al-4V alloy after immersion was identified as a mixed mode of ductile and brittle fracture.

Keywords: degradation behavior; porous Ti-6Al-4V; Hank's solutions; different pH values



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1. Introduction

With the global increase in traffic accidents, rising rates of sports injuries, and the intensifying aging process, the incidence of orthopedic conditions such as bone defects, fractures, and joint diseases continues to climb, creating an urgent demand for clinical bone repair and replacement materials [1]. Clinical practice has demonstrated that most cases involving complex fractures, joint replacements, and spinal injuries cannot achieve stable healing and functional reconstruction through topical medications or non-surgical therapies alone.

Instead, they rely on artificial repair materials to establish a mechanical support framework that creates a suitable microenvironment for bone tissue regeneration. Against this backdrop, biomedical metallic materials have become indispensable core materials in the field of orthopedic implants due to their superior mechanical load-bearing capabilities [2–4]. Among these, titanium alloys are widely utilized in the research, development, and clinical translation of bone repair devices due to their comprehensive advantages, including light weight, high strength, excellent biocompatibility, and corrosion resistance [5–8].

Among various titanium alloy systems, the Ti-6Al-4V alloy has become the mainstream material for orthopedic implants such as hip replacement prostheses, spinal fixation devices, and dental implants due to its balanced strength, fracture toughness, and exceptional corrosion resistance in physiological environments [9,10]. Its clinical safety and reliability have been recognized by medical systems worldwide [11]. However, the elastic modulus of traditional bulk Ti-6Al-4V alloy (approximately 110 GPa) is significantly higher than that of natural bone (0.02–30 GPa). Implantation into the body can easily trigger the “stress shielding effect”. This ultimately causes implant loosening and detachment, seriously affecting the long-term service stability of the device [12,13]. This issue has driven the development of porous biomedical materials. Porous titanium materials can not only regulate the elastic modulus to match natural bone through pore structure design, thereby eliminating the stress shielding effect, but also provide channels for osteocyte adhesion, proliferation, and bone tissue ingrowth via interconnected pores. This achieves biological integration between the implant and the host bone, making it one of the optimal candidates for implants in load-bearing areas such as the knee and hip joints [14,15].

Additive manufacturing (AM) technology provides technical support for the precise fabrication of porous titanium alloys. Compared with traditional manufacturing processes, AM enables the design and regulation of complex topological structures and fine micropores through the principle of layer-by-layer superposition, thereby significantly enhancing the structural flexibility and performance adaptability of porous materials [16,17]. Among these techniques, Laser powder bed fusion (LPBF) utilizes ultra-high forming precision and structural control capabilities to accurately construct Ti-6Al-4V porous structures with controllable porosity, pore size distribution, and topology [18,19]. Devices such as acetabular cups fabricated via this method can simulate the mechanical properties and structural characteristics of natural bone, effectively promoting bone-implant interface integration and offering a novel technical pathway to address the challenges of stress shielding and osseointegration [20,21]. Currently, LPBF-fabricated Ti-6Al-4V porous implants (including surgical assistance components, knee prostheses, and spinal elements) have entered clinical application phases in developed countries such as Germany, confirming the feasibility of this technical route [22,23]. To further optimize the mechanical adaptability of porous structures, Falkowska [24], Ataee [25], and Bartolomeu et al. [26] conducted systematic studies on LPBF-fabricated Ti-6Al-4V lattice structures. Their findings confirmed that porous modification enables the material’s mechanical properties to better match those of natural bone while significantly enhancing cell adhesion capabilities and osteoinductivity, demonstrating distinct advantages over traditional bulk materials.

In recent years, the academic community has conducted extensive research on the structural design and performance optimization of porous titanium alloys. Liu et al. [27] investigated cubic, optimized, and rhombic dodecahedral β -type Ti-24Nb-4Zr-8Sn porous alloys fabricated via LPBF. They found that the unit topology directly influences the energy absorption characteristics and stress distribution during the early deformation stage, and the optimized structure can effectively alleviate the stress concentration effect. Zhao et al. [28] compared Ti-based octahedral and tetrahedral porous structures with pore sizes of 500 μm and 1000 μm , confirming that small-pore structures possess superior compressive

properties and fatigue life. However, reducing the pore size leads to lower cell density, revealing an inherent trade-off between mechanical and biological properties. Through process parameter optimization experiments, Liu et al. [29] discovered that the scanning speed only exerts a directional influence on the strut thickness of the porous structure. Furthermore, under the same relative density conditions, parts fabricated at a scanning speed of 750 mm/s exhibited the optimal mechanical properties, clarifying the critical regulatory role of scanning speed in the LPBF process for porous titanium alloys. While the previous research provides significant theoretical support for the structural design and process optimization of porous titanium alloys, the issue of stability during long-term *in vivo* service remains inadequately resolved.

Orthopedic implants are required to serve for extended periods within the complex physiological environment of the human body; some devices must even accompany the patient for a lifetime. The interaction between the implant surface and body fluids, as well as its degradation behavior, directly determines the service life and biosafety of the device [30]. Under long-term immersion in physiological environments, corrosion reactions occur on the surface of titanium alloy implants, generating corrosion products and releasing metal ions. This process may trigger inflammatory responses and tissue toxicity, while also causing the deterioration of material mechanical properties, ultimately leading to implant failure [31]. Regarding the corrosion behavior of titanium alloys, existing research has achieved certain progress. Chen et al. [32] immersed LPBF-fabricated Ti-6Al-4V in dynamic and static Hank's solutions for 30 days. They found that a passive film forms rapidly on the sample surface; however, this film exists in a dynamic equilibrium of dissolution and regeneration, and its long-term stability remains to be verified. Caha et al. [33] compared the corrosion behavior of Ti-15Nb, Ti-40Nb, and Ti-6Al-4V in NaCl solutions, confirming that Ti-Nb alloys exhibit superior corrosion resistance due to their more stable open-circuit potential. Vasilescu et al. [34] investigated the long-term immersion behavior of a novel Ti-15Ta-5Zr alloy in Ringer's solution at different pH values. They discovered that its passive film is synergistically composed of TiO₂, Ta₂O₅, and ZrO₂, and the phosphides generated on the surface significantly enhance substrate protection and bioactivity.

After implantation, local tissue inflammatory responses can lead to a decrease in the pH value of body fluids (acidic microenvironment). This pathological condition disrupts the stability of the passive film on the titanium alloy surface, accelerates the corrosion process and ion release, and consequently affects the degradation behavior and mechanical properties of the material. Existing research has primarily focused on neutral or single corrosion environments. Systematic studies on the long-term degradation behavior of LPBF-fabricated Ti-6Al-4V porous alloys under acidic pathological microenvironments remain scarce, and the coupled effects of pH values on phase evolution, corrosion product formation, and mechanical degradation mechanisms are not yet fully understood. Therefore, addressing the current research status where most studies focus on traditionally forged or cast Ti-6Al-4V alloys (bulk materials), while systematic investigations into the degradation behavior of porous Ti-6Al-4V alloys under complex pathological environments (especially long-term acidic inflammatory environments) are insufficient, this work selects rhombic dodecahedral porous Ti-6Al-4V alloys fabricated via LPBF (with a pore structure suitable for bone ingrowth requirements) as the research object. Lactic acid, a human metabolite, is used to adjust the pH value of Hank's solution to 3, 5, and 7, respectively, to simulate pathological environments with varying degrees of inflammation (where lactic acid produced by the metabolism of inflamed tissues leads to acidification of body fluids). A long-term immersion experiment lasting 90 days is conducted, breaking the limitation of existing short-term immersion experiments (mostly within 30 days), thereby better aligning with the actual preparation process and service scenarios of clinical implants. The Hank's

solution environment with pH = 5 corresponds to mild to moderate inflammation (e.g., early postoperative inflammation, chronic non-infectious inflammation), while pH = 3 corresponds to severe inflammation or infectious inflammation (e.g., suppurative inflammation, severe peri-implantitis). The two form a gradient coverage, enabling systematic investigation of the corrosion and degradation behaviors of materials under different inflammatory intensities [35]. Numerous studies have confirmed that lactic acid is an effective method for adjusting the pH value of Hank's solution [28]. As the main metabolic acidic product in inflamed tissues of the human body, the acidic system regulated by lactic acid can accurately replicate the erosion mechanism of H^+ on Ti-6Al-4V alloys in the in vivo inflammatory microenvironment. Furthermore, lactate ions are endogenous ions that do not introduce exogenous harmful anions [32,34] or alter the chemical composition of the alloy surface. On this basis, characterization techniques such as scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), combined with ion release testing, were employed to systematically analyze the micromorphology, phase composition, elemental distribution, and ion release patterns of the material at different immersion stages, thereby revealing the regulatory mechanisms of pH value and immersion time on the degradation behavior of porous Ti-6Al-4V alloy. Furthermore, compression tests were conducted to simulate the stress characteristics of load-bearing sites such as the knee and hip joints, investigating the influence of corrosive environments on mechanical properties and fracture modes. This work provides theoretical basis and experimental support for the long-term service safety assessment and clinical application optimization of LPBF-fabricated Ti-6Al-4V porous implants [36].

2. Experimental

2.1. Materials and Solutions

Porous Ti-6Al-4V alloy was fabricated in-house via LPBF technology using a Realizer SLM 100 system (Realizer GmbH, Borcheln, Germany). The chemical composition of the material is summarized in Table 1. It features a rhombic dodecahedral structure with dimensions of 10 mm × 10 mm × 10 mm (as illustrated in Figure 1). The LPBF process parameters were set as follows: laser power of 200 W, scanning speed of 1000 mm/s, laser beam diameter of 40 µm, and layer thickness of 50 µm. The unit cell was produced by Magics software 27.0 (Materialize, Leuven, Belgium) and had a dimension of 3.33 mm × 3.33 mm × 3.33 mm with a nominal porosity of 80%. Since the unit cell is a rhombic dodecahedral structure, the pores are all interconnected.

Table 1. Compositions of porous Ti-6Al-4V (wt%).

Element	C	O	N	Fe	Al	V	Ti	B
content	0.01	0.14	0.02	0.22	6.25	4.04	Bal	—

To eliminate the surface oxide layer and impurities, the underwent an acid pickling pretreatment prior to immersion. The volume ratio of the pickling solution was $H_2O:HNO_3:HF = 10:9:1$. Following acid pickling, the samples were repeatedly rinsed with deionized water, blotted with filter paper, and dried in a vacuum oven for 24 h. The immersion tests were conducted in Hank's solutions (Zhonghuihecai Co., Ltd., Xi'an, China) with varying acidity (pH = 3, 5 and 7), where the pH values were adjusted using lactic acid. During the experiments, the samples were suspended in the center of the solution using chemically inert nylon lines to prevent contact with the beaker walls, ensuring uniform exposure and corrosion within the simulated body fluid environment.

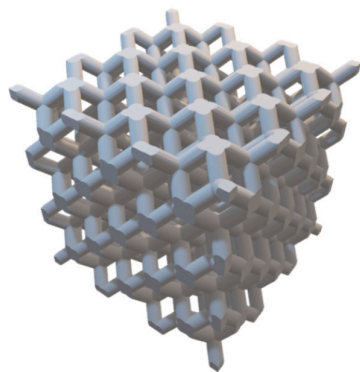


Figure 1. Structure diagram of rhombic dodecahedron of porous Ti-6Al-4V.

2.2. Testing and Characterization

2.2.1. Weight Change Test

The pretreated porous Ti-6Al-4V samples were first weighed using an analytical balance, with the initial mass recorded as m_1 . Subsequently, the samples were immersed in Hank's solutions with different pH values (3, 5 and 7) for 90 days, and the containers were placed in a constant temperature water bath at 37 °C. The ratio of the exposed area of the samples (cm^2) to the volume of Hank's solution (mL) was 1:10, and fresh Hank's solution was replaced every 24 h. Samples were retrieved at intervals of 30 days, 60 days, and 90 days. After rinsing with deionized water to remove residual salts, air-drying with a cold blower, and further drying in a vacuum oven for 24 h, the final mass was recorded as m_2 . Three samples were tested in parallel for each environment, and the average value was calculated to ensure data accuracy and repeatability. To quantitatively characterize the weight change in the alloy, the weight change rate was adopted for analysis, as expressed in Equation (1).

$$\Delta = \frac{m_2 - m_1}{m_1} \times 100\% \quad (1)$$

Δ is the weight change rate (%), m_1 is the initial weight of the porous Ti-6Al-4V alloy sample before immersion (g), and m_2 is the dry weight of the sample after immersion for a specific duration (g).

2.2.2. Phase Analysis

The phase composition of the immersed porous Ti-6Al-4V samples was analyzed using X-ray diffraction (D8 Advance, Bruker, Bremen, Germany). A Cu-K α radiation source was employed, with the scanning range set from 30° to 80° and a scanning rate of 0.03°/s. After the test, the raw diffraction data were subjected to qualitative phase analysis and identification using Jade 6.5 software (Livermore, CA, USA). By comparing the obtained patterns with standard PDF cards, the phase changes on the sample surfaces in Hank's solutions with different pH values were identified and characterized.

The surface elemental distribution after immersion was characterized using X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, Waltham, MA, USA). A monochromatic Al-K α X-ray source was utilized, with a spot diameter of 500 μm and a photoelectric emission angle of 90°. Following a general survey scan, high-resolution narrow scans were performed for core elements, including Ti, Al, V, O, Ca, P, with a pass energy of 30 eV. Data analysis and peak fitting were conducted using Thermo Advantage 6.7 (Waltham, MA, USA) software.

2.2.3. Microstructure and Composition Analysis

Microscopic morphology observation and elemental analysis of the immersed porous Ti-6Al-4V samples were conducted using a ZEISS Merlin Compact field emission scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany) equipped with an energy dispersive spectroscopy (EDS) detector (JEOL Ltd., Tokyo, Japan).

2.2.4. Ion Release Test

For each group, 20 mL of the post-immersion solution was collected for quantitative analysis via inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies, Santa Clara, CA, USA). Prior to testing, each sample was diluted 10-fold. The concentrations of ions released from the alloy, Ti, Al, V and the residual components of Hank's solution, Ca, P were measured. The chemical stability of the porous Ti-6Al-4V and the extent of calcium-phosphorus salt deposition were evaluated by monitoring the concentration changes over time. Each group was tested in triplicate to ensure data accuracy, and the average values were reported.

2.2.5. Compressive Test

Room-temperature static compression tests were performed on the porous Ti-6Al-4V samples using a universal testing machine (Instron Corporation, Norwood, MA, USA). Prior to testing, a preload of 20 N was applied to ensure tight contact between the indenter and the sample, and the displacement loading rate was maintained at a constant 0.1 mm/min throughout the testing phase. Stress-strain curves were plotted from the load-displacement data, and the yield strength and compressive strength of the samples were calculated. Each test group was repeated three times, and the average value was taken. After the compression tests, the fractured cross-sections of the samples were sectioned, and the fracture micro-morphologies were observed using a ZEISS Merlin Compact field-emission scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany). The fracture mechanism of the material was evaluated by analyzing the characteristics of dimples and quasi-cleavage fractures.

3. Results and Discussion

3.1. Weight Changes in Ti-6Al-4V Alloy Immersed in Hank's Solution with Different pH Values for Various Durations

Weight change is one of the most critical indicators for characterizing the degradation behavior of biomedical metallic materials in simulated body fluids. Its variation directly reflects the dynamic competitive equilibrium between “ion release” and “corrosion product deposition” on the material surface. For porous Ti-6Al-4V alloys fabricated via LPBF, the porous architecture provides abundant interfacial areas for ion transport and chemical reactions, thereby rendering the regulatory effects of pH value and immersion time on weight change more pronounced. Figure 2 illustrates the trend of weight change rate for the alloy during a 90-day immersion period in Hank's simulated body fluid at different pH values (3, 5 and 7). The weight change in the porous Ti-6Al-4V alloy in Hank's solution is primarily governed by two competing processes, first, the ion release process induced by the dissolution of the alloy and surface passive film, which leads to a decrease in material weight, and second, the deposition process where ions such as Ca^{2+} and PO_4^{3-} in the solution adsorb and precipitate onto the material surface to form Ca-P corrosion products, which promotes an increase in material weight [37]. Upon contact between the porous Ti-6Al-4V alloy and Hank's solution, a passive film forms rapidly on the surface, establishing a dynamic formation-dissolution equilibrium. When the dissolution rate of the passive film exceeds the formation rate, the exposed area of the matrix increases, leading to a significant

rise in ion release, which in turn dominates the weight change trend. Conversely, the deposition process becomes the controlling factor.

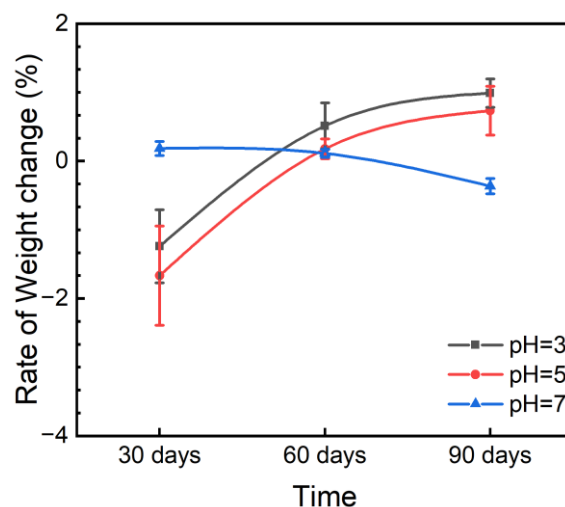


Figure 2. Weight change rate of porous Ti-6Al-4V in Hank's solution with different pH values for 90 days.

As illustrated in Figure 2, the weight change patterns of the porous Ti-6Al-4V alloy differ significantly across environments with varying pH values, and all exhibit a phased evolution with immersion time. In the initial stage of immersion (30 days), the alloy in the neutral environment (pH = 7) exhibited a distinct weight gain behavior, with a weight change rate of 1.80%, representing the highest increase among the three groups. This phenomenon indicates that during the 30-day immersion in the neutral environment, the deposition rate of corrosion products on the alloy surface was significantly higher than the dissolution rate of the matrix and passive film, rendering the process deposition-dominant. Combined with the subsequent phase analysis results, this stage is primarily characterized by the adsorption and mineralization reactions of Ca^{2+} and PO_4^{3-} from Hank's solution on the alloy surface, forming a Ca-P compound deposition layer, which consequently leads to a significant increase in sample weight. In contrast to the neutral environment, the alloys in acidic environments (pH = 3, 5) exhibited weight loss after 30 days of immersion, with minimal difference between the two groups, the weight loss rate was 2.23% at pH = 3 and 3.00% at pH = 5. The high concentration of H^+ preferentially erodes the TiO_2 passive film, triggering film damage and dissolution, while simultaneously accelerating the dissolution and ion release of matrix elements such as Ti, Al, and V. At this stage, the degradation of the alloy itself and the decomposition of the passive film dominate, resulting in an ion release volume that exceeds the deposition product volume, ultimately leading to a decrease in sample weight.

As the immersion time extended to 60 days, a distinct turning point emerged in the weight change trends of the alloys under different environments. In the neutral environment, the weight gain trend ceased, and slight weight loss began to occur, indicating that the dissolution rate of the matrix and passive film gradually exceeded the deposition rate during this stage, making the degradation process dominant. Conversely, in the acidic environments, the weight change transitioned from a state of loss to gain, with weight gain rates of 0.92% at pH = 3 and 0.32% at pH = 5. This suggests that long term immersion in acidic environments promotes the gradual dominance of the deposition process. Firstly, the sustained ion release provides additional active sites for the deposition of Ca-P compounds, secondly, the accumulation of corrosion products forms a physical covering layer on the surface, slowing down the matrix dissolution rate and thereby shifting the “dissolution-

deposition” equilibrium towards deposition. When the immersion time was extended to 90 days, the weight gain rate of the alloy in the acidic environment continued to increase compared to 60 days, indicating that the deposition of corrosion products remained the dominant mechanism. In contrast, the weight loss rate of the alloy in the neutral environment rose to 0.37%, becoming the group with the highest weight loss among the three environments. This implies that the deposition of corrosion products on the alloy surface was relatively low at this point, signifying better corrosion resistance of the alloy.

3.2. Phase Changes in Porous Ti-6Al-4V with Different Immersion Duration

Phase characterization of the alloy after different immersion durations was performed using XRD and the results are presented in Figure 3. As observed in Figure 3, compared to the non-immersed pristine porous Ti-6Al-4V alloy, diffraction peaks corresponding to TiO_2 and Ca-P compounds $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ appeared on the surface of the alloys immersed in Hank’s solutions of varying pH values, although their contents were relatively low. This indicates that a dynamic equilibrium process of “ion release-deposition of corrosion products” occurred during the immersion of the alloys in Hank’s solution. Although XRD phase analysis identified the primary phase composition (TiO_2 , $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}(\text{H}_2\text{PO}_4)_2$) of the porous Ti-6Al-4V alloys after immersion, trace phases such as Ti_2O_3 and TiO , which are commonly reported in the literature, could not be effectively detected due to the limited sensitivity of XRD [38]. To accurately elucidate the complete composition, elemental valence distribution, and evolution mechanism of the passive film on the alloy surface, and to compensate for the limitations of XRD analysis, XPS measurements were conducted on porous Ti-6Al-4V immersed in Hank’s solutions of different pH values for 30, 60, and 90 days. Through peak fitting of narrow-scan spectra, quantitative analysis of trace oxidation products and elemental valences was achieved. The test results are illustrated in Figures 4–7 and Tables 2 and 3.

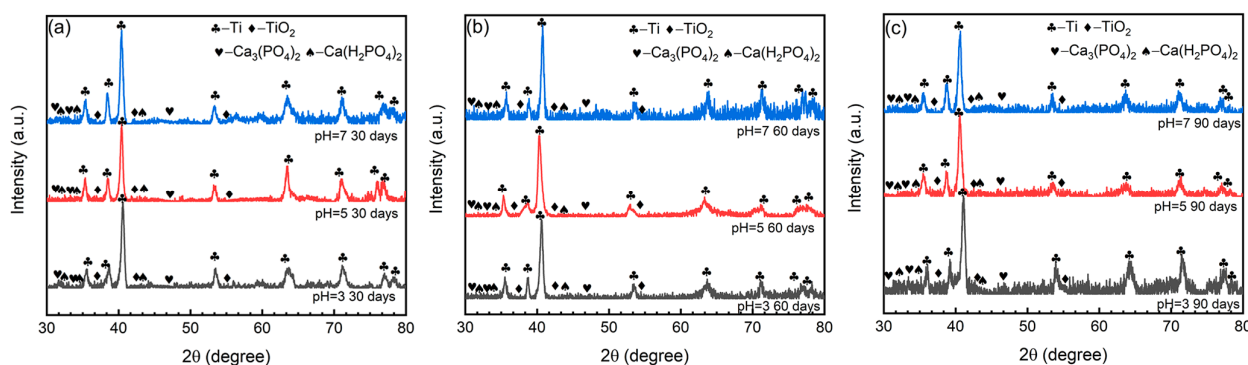


Figure 3. XRD of porous Ti-6Al-4V in Hank’s solution with different pH values for 90 days: (a) 30 days; (b) 60 days; (c) 90 days.

Table 2. The proportion of titanium ions of porous Ti-6Al-4V in Hank’s solution at different pH values (pH = 3, pH = 5, pH = 7) within 90 days.

Immersion Time (Days)	Solution pH	Ti ⁴⁺ (at %)	Ti ³⁺ (at %)	Ti ²⁺ (at %)
30	pH = 3	74	17	11
30	pH = 5	78	17	5
30	pH = 7	80	17	3
60	pH = 3	75	15	10
60	pH = 5	79	17	4
60	pH = 7	81	16	3
90	pH = 3	81	13	6
90	pH = 5	85	11	4
90	pH = 7	87	13	0

Table 3. The proportion of oxygen in different states of porous Ti-6Al-4V in Hank's solution at different 3. pH = 5, pH = 7) for 90 days.

Immersion Time (Days)	Solution pH	O ⁻ (at %)	OH ⁻ (at %)	H ₂ O (at %)
30	pH = 3	55	42	3
30	pH = 5	66	32	2
30	pH = 7	68	26	6
60	pH = 3	63	36	1
60	pH = 5	72	26	2
60	pH = 7	78	21	1
90	pH = 3	72	26	2
90	pH = 5	79	20	1
90	pH = 7	83	16	1

Figure 4 displays the Ti 2p narrow-scan spectra of the alloy immersed in Hank's solutions with different pH values for various durations. As observed, the Ti 2p spectra exhibit two characteristic main peaks corresponding to Ti 2p_{1/2} (464 eV) and Ti 2p_{3/2} (458 eV). Through peak fitting, these two main peaks can be further deconvoluted into three characteristic peaks corresponding to the binding energies of Ti⁴⁺ (TiO₂), Ti³⁺ (Ti₂O₃), and Ti²⁺ (TiO). This confirms that a multi-step oxidation reaction occurred during the immersion of the porous Ti-6Al-4V alloy in Hank's solution, resulting in the formation of a mixed-valence oxide film. Table 2 presents the relative content distribution of titanium ions in various valences after peak fitting of the Ti 2p spectra. After 30 days of immersion, significant differences in the content of various titanium valences were observed under different pH environments: in the acidic environment of pH = 3, Ti⁴⁺ accounted for 72%, Ti³⁺ for 17%, and Ti²⁺ for 11%; in the acidic environment of pH = 5, the proportion of Ti⁴⁺ increased to 78%, Ti³⁺ remained at 17%, and Ti²⁺ decreased to 5%; in the neutral environment of pH = 7, the proportion of Ti⁴⁺ further rose to 80%, Ti³⁺ remained at 17%, and Ti²⁺ was only 3%. These results indicate that the content of TiO₂ (Ti⁴⁺) increases with increasing pH value, while the content of TiO (Ti²⁺) decreases. In contrast, the content of Ti₂O₃ (Ti³⁺) remains largely unaffected by pH and maintains a stable level.

When the immersion time was extended to 60 and 90 days, the trend of increasing Ti⁴⁺ content with rising pH remained consistent. Furthermore, the overall content of Ti⁴⁺ exhibited a cumulative growth trend with prolonged immersion, whereas the content of TiO (Ti²⁺) continued to decrease, showing an evolution trend completely opposite to that of TiO₂. Notably, the specimen immersed in the neutral environment for 90 days exhibited the optimal integrity of the passive film, where Ti⁴⁺ accounted for as high as 87% and Ti²⁺ completely disappeared. This indicates that the passive film was dominated by highly stable TiO₂ without the presence of lower-valence titanium oxides. This is attributed to the high chemical inertness of TiO₂, which can maintain a dynamic dissolution-repassivation equilibrium in neutral Hank's solution and is resistant to significant decomposition. Moreover, with prolonged immersion, the continuous oxidation of the substrate generates TiO₂, promoting the transformation of the passive film into a highly stable Ti⁴⁺ dominant type.

Conversely, in acidic Hank's solutions, the presence of H⁺ disrupts the dynamic equilibrium of the passive film and becomes the primary factor influencing the valence composition. The high concentration of H⁺ in acidic environments exerts a significant erosive effect on TiO₂, accelerating its dissolution via the following reaction (Equation (2)) to generate soluble Ti⁴⁺ ions that enter the solution, thereby reducing the relative content of Ti⁴⁺. Simultaneously, the breakdown of the TiO₂ passive film exposes the underlying substrate, triggering the lower-valence oxidation of titanium to form TiO (Ti²⁺) and Ti₂O₃ (Ti³⁺). This is the core reason why the content of Ti²⁺ in acidic environments is significantly higher than that in neutral environments. As the pH value decreases, the H⁺ concentration rises, accelerating the dissolution rate of TiO₂ and exacerbating the degree of passive film

breakdown. Consequently, the proportion of lower-valence titanium oxides increases, further weakening the protective performance of the passive film and accelerating substrate corrosion and ion release [39].

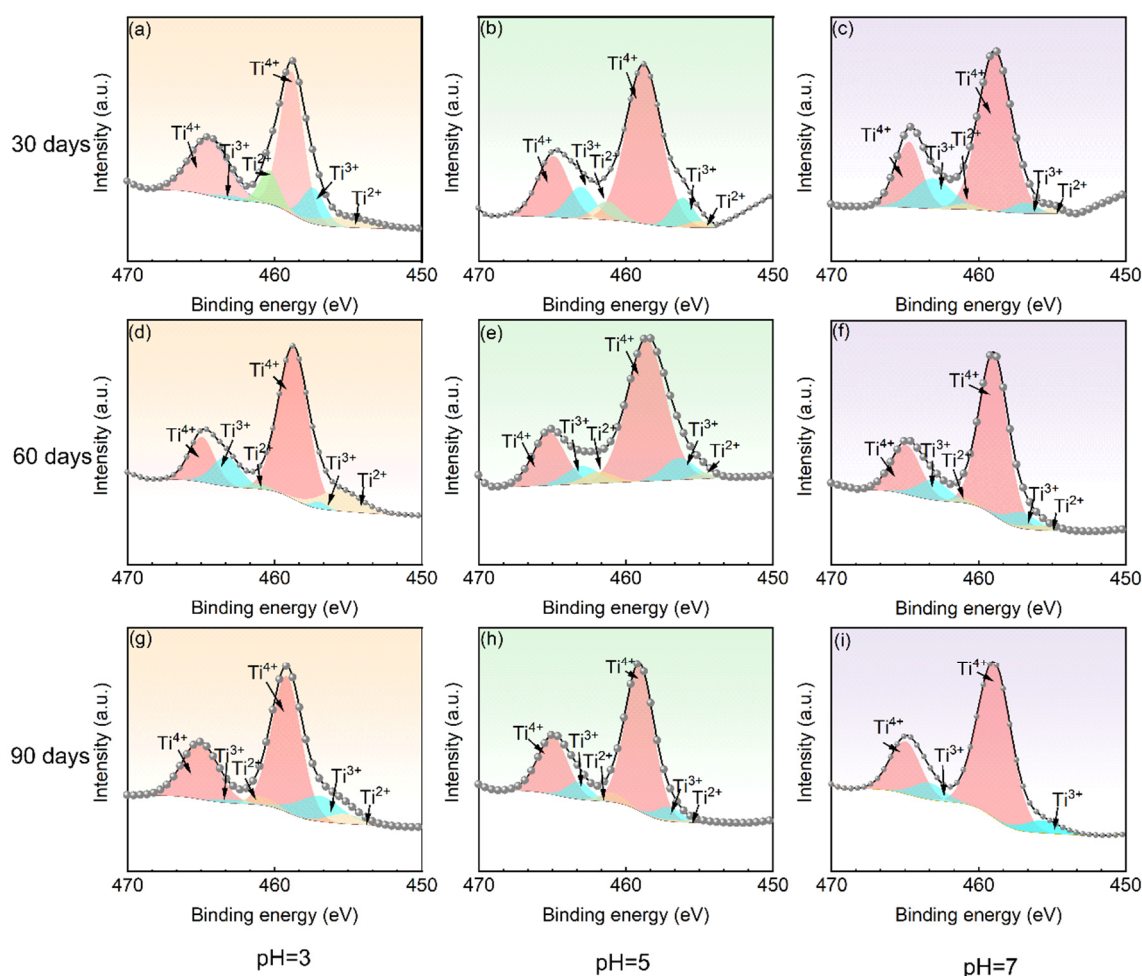


Figure 4. Ti 2p spectra of porous Ti-6Al-4V in Hank's solution at different pH values for 90 days: (a) pH = 3, 30 days; (b) pH = 5, 30 days; (c) pH = 7, 30 days; (d) pH = 3, 60 days; (e) pH = 5, 60 days; (f) pH = 7, 60 days; (g) pH = 3, 90 days; (h) pH = 5, 90 days; (i) pH = 7, 90 days.



Figure 5 presents the O 1s narrow-scan spectra of the alloy immersed in Hank's solutions of different pH values for 90 days. Through peak fitting, the O 1s peak can be deconvoluted into three characteristic peaks corresponding to oxide oxygen (O^{2-}), hydroxyl oxygen ($-\text{OH}$), and adsorbed water oxygen (H_2O), with their specific relative contents listed in Table 3. The chemical states of oxygen directly reflect the composition of the oxide film and the adsorption behavior on the alloy surface. Specifically, oxide oxygen is primarily derived from titanium oxidation products (especially TiO_2), hydroxyl oxygen is associated with the deposition of calcium-phosphorus compounds and the hydroxylation reaction of the passive film, and adsorbed water oxygen originates from water molecules adsorbed on the specimen surface. As indicated by the data in Table 3, after 30 days of immersion, the distribution of oxygen species exhibited a regular variation with pH. In the acidic environment of pH = 3, oxide oxygen accounted for 55%, hydroxyl oxygen for 42%, and adsorbed water oxygen for 3%. In the acidic environment of pH = 5, the proportion of oxide oxygen increased to 66%, while in the neutral environment of pH = 7,

it further rose to 68%, and the proportion of hydroxyl oxygen decreased to approximately 30%. immersed for 60 and 90 days followed the same trend, the proportion of oxide oxygen increased with rising pH and exhibited a continuous growth trend with prolonged immersion time. It can be observed from the table that the proportion of hydroxyl oxygen in acidic environments is significantly higher than that in the neutral environment. This phenomenon is closely related to the conclusion from the previous phase analysis that the content of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ is higher in acidic environments. The formation process of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ is accompanied by hydroxylation reactions. Furthermore, the numerous defect sites generated by the breakdown of the passive film in acidic environments promote the adsorption and dissociation of water molecules in the solution, generating more hydroxyl groups ($-\text{OH}$) and leading to a higher proportion of hydroxyl oxygen. Conversely, in the neutral environment, the highly stable TiO_2 passive film possesses fewer surface defects and weaker capabilities for water molecule adsorption and dissociation, resulting in a relatively lower proportion of hydroxyl oxygen [40].

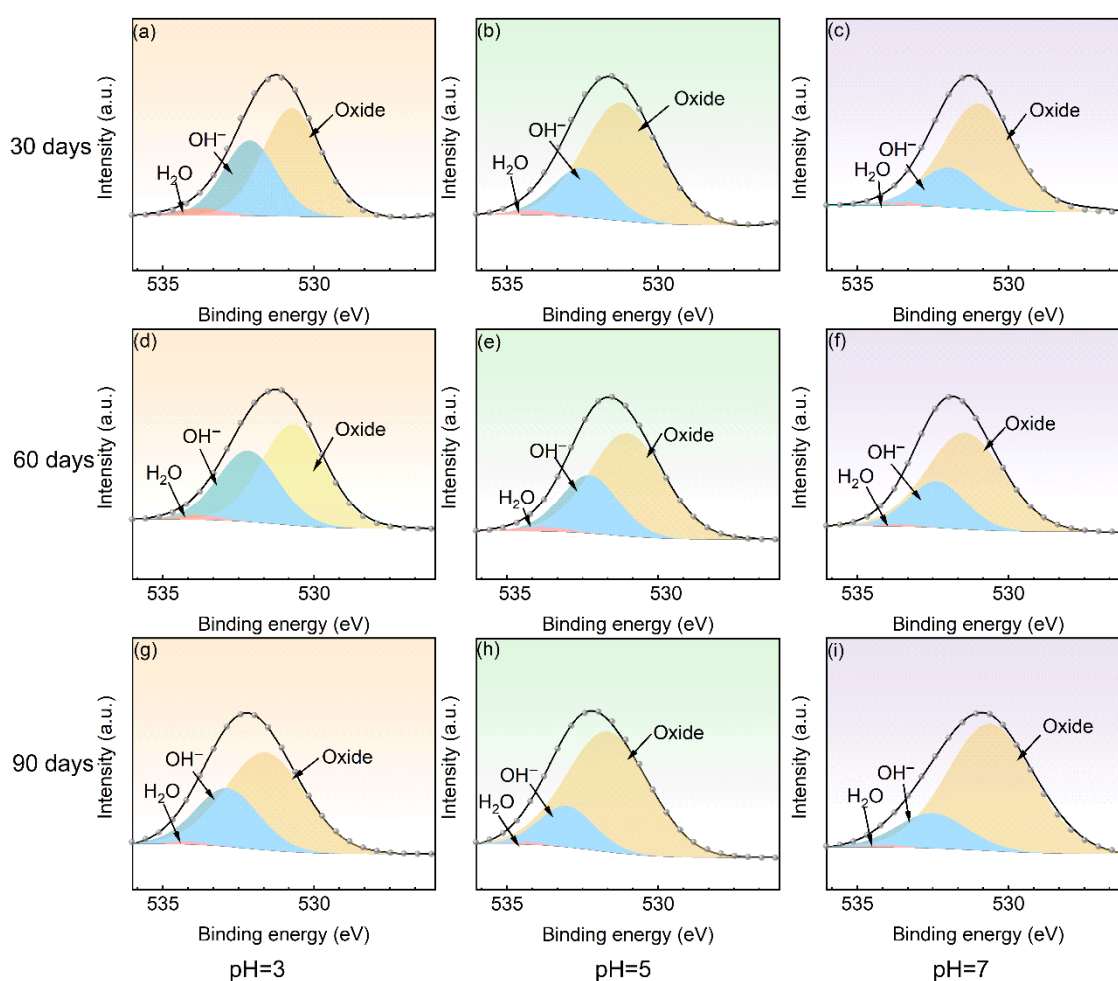


Figure 5. O 1s spectra of porous Ti-6Al-4V in Hank's solution at different pH values for 90 day: (a) pH = 3, 30 days; (b) pH = 5, 30 days; (c) pH = 7, 30 days; (d) pH = 3, 60 days; (e) pH = 5, 60 days; (f) pH = 7, 60 days; (g) pH = 3, 90 days; (h) pH = 5, 90 days; (i) pH = 7, 90 days.

Figures 6 and 7 display the narrow-scan spectra of Ca 2p and P 2p for the alloy respectively. As observed in Figure 6, the Ca 2p spectrum exhibits two characteristic main peaks corresponding to $\text{Ca } 2p^{1/2}$ and $\text{Ca } 2p^{3/2}$, with binding energies of approximately 351 eV and 347.5 eV respectively, which are characteristic of Ca^{2+} . The characteristic peak in the P 2p spectrum (Figure 7) corresponds to P^{5+} at a binding energy of approximately 133.5 eV.

These results confirm the presence of Ca^{2+} and PO_4^{3-} on the alloy surface. Combining the presence of hydroxyl oxygen observed in Figure 5 with existing literature [41], it can be inferred that the calcium-phosphorus compounds deposited on the alloy surface include not only $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ detected by XRD but may also include bioactive calcium-phosphorus compounds such as hydroxyapatite (HA) or octacalcium phosphate (OCP)-like phases. The formation of such compounds is closely related to the induction effect of surface hydroxyl groups [42].

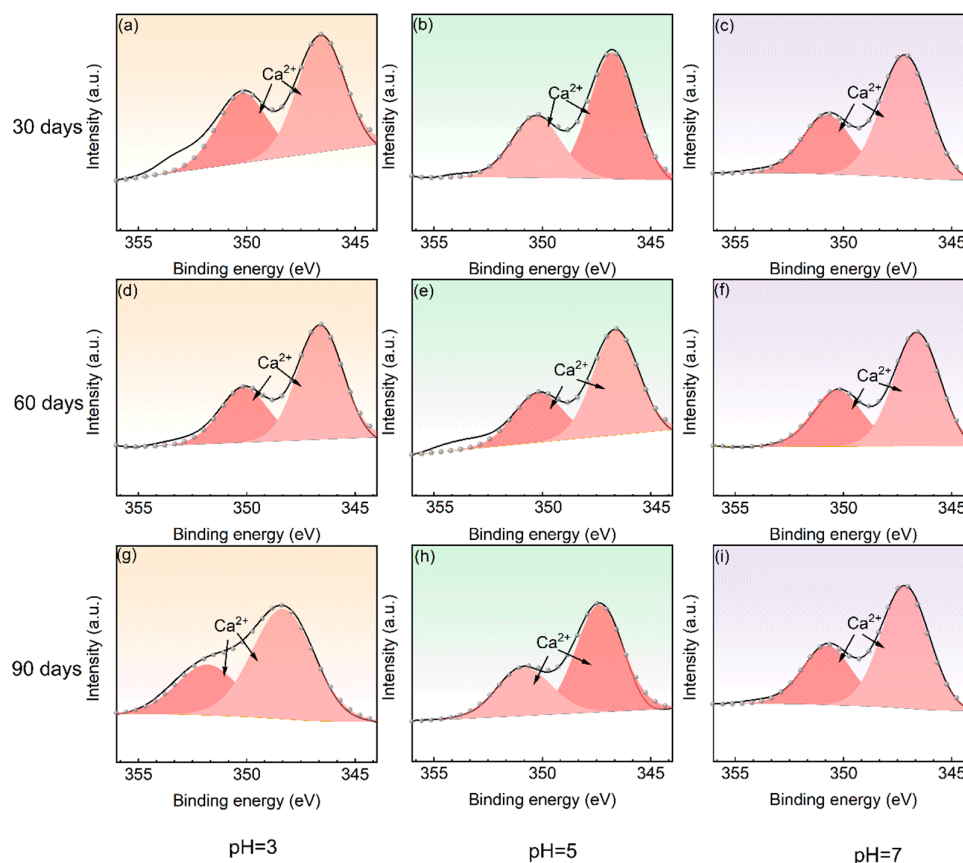


Figure 6. Ca 2p spectra of porous Ti-6Al-4V in Hank's solution at different pH values within 90 days: (a) pH = 3, 30 days; (b) pH = 5, 30 days; (c) pH = 7, 30 days; (d) pH = 3, 60 days; (e) pH = 5, 60 days; (f) pH = 7, 60 days; (g) pH = 3, 90 days; (h) pH = 5, 90 days; (i) pH = 7, 90 days.

Based on existing literature and the aforementioned analysis, during long-term immersion in Hank's solution, the surface of the porous Ti-6Al-4V alloy forms a mixed oxide film dominated by amorphous TiO_2 , supplemented by trace amounts of Ti_2O_3 and TiO . Simultaneously, Ca^{2+} and PO_4^{3-} from the Hank's solution are adsorbed onto the alloy surface, leading to the formation of a calcium-phosphorus compound deposition layer [37]. Conversely, the passive film on the titanium alloy surface reconstructs to facilitate the formation of calcium phosphate. Calcium and phosphate ions interact directly on the surface of the Ti-6Al-4V passive film, and the formation of phosphate is influenced by the defect kinetics of the passive film. Specifically, phosphate ions are preferentially adsorbed because calcium ions can only be stably adsorbed by titanium in the presence of phosphates; calcium ions alone cannot bind stably to the titanium surface without phosphate ions [43]. Once both are adsorbed, calcium and phosphate ions rapidly combine to form Ca-P deposition products, establishing the initial foundation of the deposition layer [44]. In Hank's solution, phosphate ions exist in the forms of H_2PO_4^- and HPO_4^{2-} . With the extension of immersion time, H_2PO_4^- and HPO_4^{2-} are first adsorbed onto the titanium surface. As protons are gradually replaced by calcium ions, H_2PO_4^- and HPO_4^{2-} are

gradually converted into PO_4^{3-} . Meanwhile, as immersion time increases, the TiO_2 content in the alloy gradually rises. On the one hand, TiO_2 can accelerate the precipitation of calcium phosphate [24], on the other hand, the presence of TiO_2 increases surface roughness, accelerating the absorption of calcium ions. Therefore, with the extension of immersion time, the contents of TiO_2 and $\text{Ca}_3(\text{PO}_4)_2$ gradually increase.

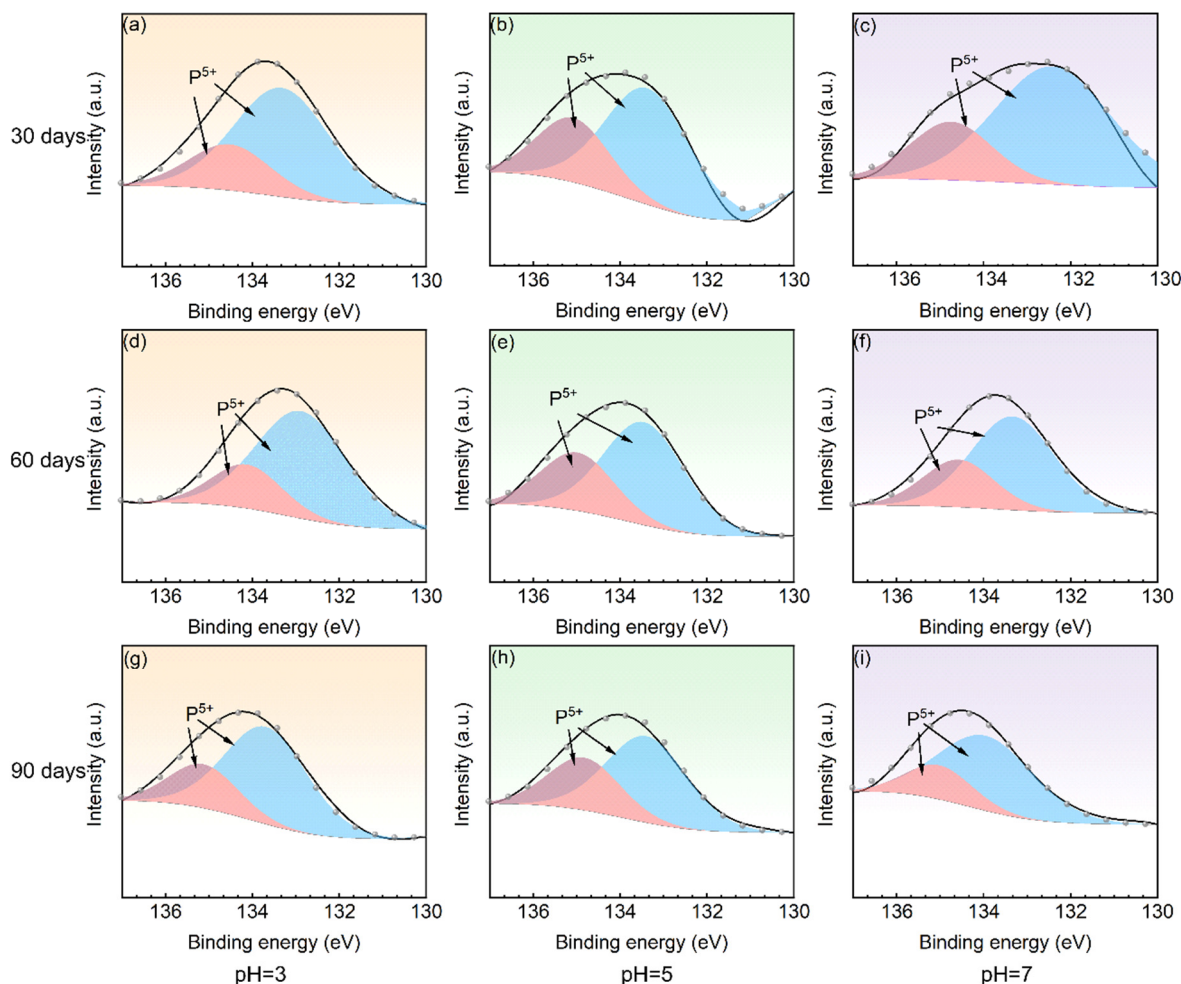


Figure 7. P 2p spectra of porous Ti-6Al-4V in Hank's solution at different pH values within 90 days: (a) pH = 3, 30 days; (b) pH = 5, 30 days; (c) pH = 7, 30 days; (d) pH = 3, 60 days; (e) pH = 5, 60 days; (f) pH = 7, 60 days; (g) pH = 3, 90 days; (h) pH = 5, 90 days; (i) pH = 7, 90 days.

Based on the analysis results such as XRD and XPS of the alloy after long-term immersion in different Hank's solutions, the formation, dissolution, and phase evolution of TiO_2 (including low-valent titanium oxides) and calcium phosphate phases ($\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}(\text{H}_2\text{PO}_4)_2$) on the surface of porous Ti-6Al-4V alloys fabricated by LPBF are dominated by the H^+ concentration regulated by pH value. In the neutral environment, the TiO_2 passive film can maintain a stable dissolution-repassivation balance, mainly forming dense TiO_2 with extremely low content of low-valent titanium oxides; for the calcium phosphate phases, thermodynamically stable $\text{Ca}_3(\text{PO}_4)_2$ is preferentially formed, with deposition dominating and dissolution being negligible. In acidic environments (pH = 3, and 5), H^+ accelerates the dissolution of the TiO_2 film, leading to the exposure of the alloy matrix and incomplete oxidation, thereby generating low-valent titanium oxides such as Ti_2O_3 and TiO , and this effect becomes more significant with increasing acidity. Meanwhile, H^+ causes PO_4^{3-} in the solution to mainly exist in the form of H_2PO_4^- , so the calcium phosphate phases preferentially form unstable $\text{Ca}(\text{H}_2\text{PO}_4)_2$, which can gradually transform

into $\text{Ca}_3(\text{PO}_4)_2$ after long-term immersion, but the transformation is significantly delayed in the strongly acidic environment ($\text{pH} = 3$).

3.3. Morphological Analysis of Porous Ti-6Al-4V Alloy After Different Immersion Durations

3.3.1. Macroscopic Morphology

Combined with previous analyses of weight change, phase composition, and other aspects, the evolution law of the macroscopic morphology of porous Ti-6Al-4V alloy immersed in Hank's solutions with different pH values for 90 days was investigated. Figure 8 compares the macroscopic morphological characteristics of the as-received alloy and the sample under different immersion conditions. The as-received non-immersed sample (Figure 8a) exhibits a uniform silvery-gray metallic luster, with a clear outline of the porous structure and good pore connectivity. The strut surfaces are smooth without impurity adhesion, reflecting the excellent forming quality of the LPBF process. Its regular porous structure can meet the bone ingrowth requirements of biomedical implant materials. After 30 days of immersion (Figure 8b–d), significant differences in the morphology of the samples are observed under different pH environments. In acidic environments, milky-white corrosion products appear on the specimen surfaces, mainly filling the pore channels of the porous structure to form a continuous and loose covering layer. In contrast, the samples in the neutral environment basically retain their original metallic luster and structural integrity, with only trace amounts of light-colored deposits at the pore edges, indicating that the initial corrosion-deposition reaction is weak in the neutral environment and the alloy surface has better stability.



Figure 8. Macroscopic morphology of porous Ti-6Al-4V in Hank's solution with different pH values for 90 days: (a) original sample (b) pH = 3, 30 days; (c) pH = 5, 30 days; (d) pH = 7, 30 days; (e) pH = 3, 60 days; (f) pH = 5, 60 days; (g) pH = 7, 60 days; (h) pH = 3, 90 days; (i) pH = 5, 90 days; (j) pH = 7, 90 days.

When the immersion time is extended to 60 and 90 days, the macroscopic morphology of the sample in acidic environments undergoes a transformation. The milky-white corrosion products gradually turn black, and their distribution shifts from the pore channels to the strut surfaces, forming a dense covering layer. Among them, the specimen immersed in the pH = 3 environment for 90 days is completely covered by black corrosion products, and the original outline of the porous structure is almost indistinguishable, indicating that the corrosion-deposition reaction is the most intense under long-term immersion in a strongly acidic environment. In the neutral environment, the macroscopic morphology of the sample immersed for 60 and 90 days (Figure 8g,j) shows no significant changes, with only trace amounts of light-colored deposits at the pore edges of the 90-day specimen. This confirms that the neutral environment can effectively maintain the surface stability of the alloy, and the intensity of the corrosion-deposition reaction is much lower than that in acidic environments. All samples immersed for 90 days in the three environments basically maintain the integrity of the original porous structure without obvious structural collapse or fracture. This indicates that the porous Ti-6Al-4V alloy fabricated by LPBF has excellent structural stability, which can ensure that the material can maintain basic mechanical load-bearing capacity even if surface corrosion reactions occur during long-term service in simulated body fluids, avoiding defects such as implant loosening caused by structural failure.

3.3.2. Microscopic Morphology

The microscopic morphologies of the porous Ti-6Al-4V alloy during the 90-day immersion in different Hank's solutions are illustrated in Figure 9. As observed in the figures, after 30 days of immersion, the alloy surfaces in acidic solutions exhibited web-like flocculent substances, as indicated by the arrows in Figure 9a,b. Additionally, molten droplets of varying sizes were distributed on the alloy surface [45]. Elemental analysis revealed that the flocculent substances were primarily corrosion products such as TiO_2 , accompanied by a small amount of P. This indicates that during this stage in the acidic environment, the corrosion products were dominated by titanium oxides (mainly TiO_2), with minimal deposition of Ca-P compounds. This is attributed to the high concentration of H^+ in the acidic environment, which not only accelerated the dissolution of the TiO_2 passive film but also inhibited the transformation of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ to $\text{Ca}_3(\text{PO}_4)_2$, while simultaneously hindering the adsorption and mineralization of Ca^{2+} and PO_4^{3-} , resulting in limited formation of Ca-P products. Conversely, TiO_2 formed a loose, web-like flocculent structure due to its rapid dissolution-regeneration rate. This structure possesses high porosity and weak bonding with the matrix, failing to form an effective protective barrier and thereby further exacerbating matrix corrosion. The sample immersed in the neutral environment for 30 days (Figure 9c) exhibited fewer web-like flocculent substances but contained white granular substances. EDS analysis demonstrated that the white substances contained high contents of Ca and P elements, confirming them as Ca-P compounds (primarily $\text{Ca}_3(\text{PO}_4)_2$). This suggests that the initial deposition reaction dominated in the neutral environment, where Ca^{2+} and PO_4^{3-} rapidly adsorbed and mineralized on the surface of the highly stable TiO_2 passive film, forming granular Ca-P deposition products with high crystallinity. Furthermore, these products bonded relatively tightly with the matrix, forming a thin and dense protective barrier that mitigated subsequent corrosion reactions, which explains why no significant changes were observed in the macroscopic morphology of the sample at this stage.

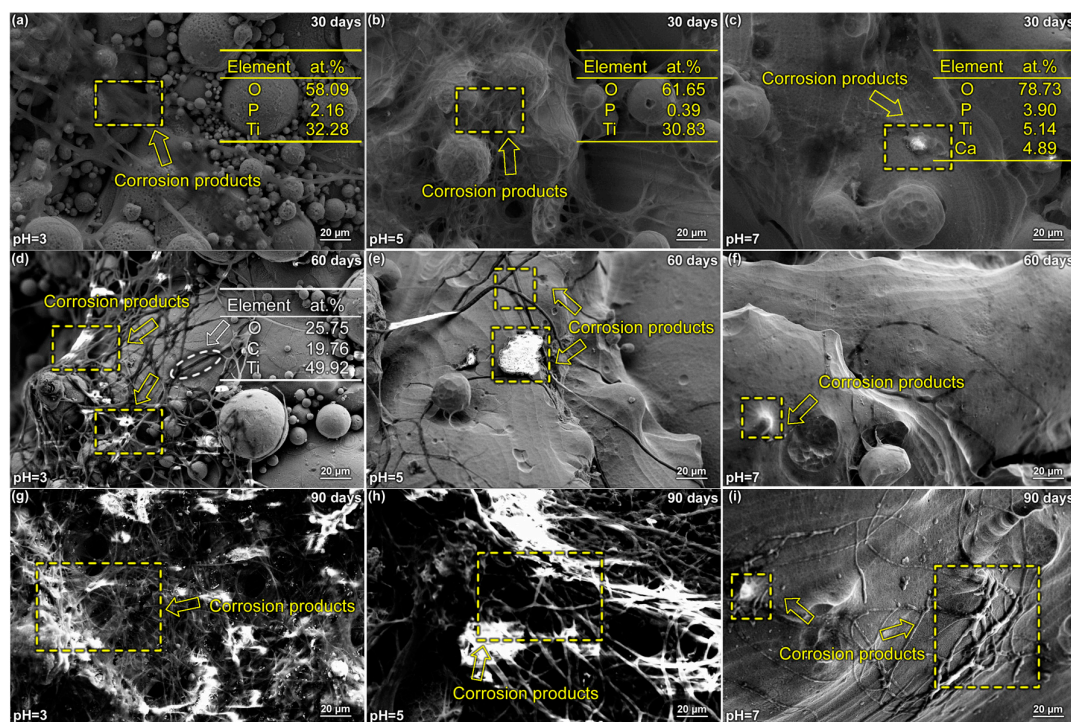


Figure 9. Microscopic morphology of porous Ti-6Al-4V in Hank's solution with different pH values for 90 days: (a) pH = 3, 30 days; (b) pH = 5, 30 days; (c) pH = 7, 30 days; (d) pH = 3, 60 days; (e) pH = 5, 60 days; (f) pH = 7, 60 days; (g) pH = 3, 90 days; (h) pH = 5, 90 days; (i) pH = 7, 90 days.

As the immersion time extended to 60 days, the web-like flocculent substances on acidic environment-immersed samples disappeared, replaced by black filamentous corrosion products (multivalent titanium oxides dominated by TiO_2) and bright white granular Ca-P deposits (marked in Figure 9d,e). EDS confirmed the high Ti and O contents in the black filaments. In contrast, the neutral environment sample (Figure 9f) only showed trace black filaments and sparse white Ca-P particles, indicating weak oxidation, slow Ca-P accumulation with high crystallinity, and good surface stability-consistent with the earlier finding that neutral environment-induced weight loss and degradation became dominant at 60 days. After 90 days of immersion, acidic environment samples (Figure 9g,h) were fully covered by a composite corrosion layer of black oxides and white Ca-P particles, obscuring the matrix. Despite high product coverage, interfacial micropores caused by weak bonding failed to inhibit solution penetration, sustaining matrix corrosion. For the neutral environment sample (Figure 9i), the matrix morphology remained clear with only localized trace Ca-P deposits and no obvious oxidation products, demonstrating excellent surface stability under long-term neutral immersion, which is more favorable for implant long-term service.

3.4. Ion Release Behavior of Porous Ti-6Al-4V in Hank's Solutions with Different pH Values

Ion release behavior serves as a core evaluation index for the long-term service safety and biocompatibility of biomedical titanium alloys, directly determining the adaptability and service life of implants within the human microenvironment. As orthopedic implant materials, titanium and its alloys must remain in long-term contact with human body fluids. During service, the dissolution of the surface passive film, matrix corrosion, and decomposition of corrosion products all lead to the release of metal ions such as Ti, Al, and V into the surrounding body fluids [5,45]. This work quantitatively analyzed the dynamic release of these three metal ions from the alloy during 90 days of immersion in Hank's

solutions with different pH values, while simultaneously monitoring the residual content changes in the inherent Ca and P ions in the Hank's solution.

Figures 10 and 11 present the release amounts and dynamic evolution curves of Ti, Al, and V ions for porous Ti-6Al-4V alloys immersed in Hank's solutions of different pH values respectively. The results indicate that after 30 days of immersion, the metal ion release patterns vary significantly across different pH environments. In acidic environments, the release of Ti ions is significantly higher than that of Al and V ions, making Ti the dominant released element; furthermore, the lower the pH value, the higher the Ti ion release. Conversely, in the neutral environment, the ion release order shifts to $\text{Al} > \text{Ti} > \text{V}$, with Al ions accounting for the highest proportion, while Ti and V ion releases remain at low levels. This is attributed to the high concentration of H^+ in acidic environments, which disrupts the dissolution-regeneration equilibrium of the surface TiO_2 passive film, accelerating TiO_2 dissolution and causing a large amount of Ti^{4+} ions to be released from both the passive film and the exposed matrix into the solution, resulting in significantly higher Ti release compared to other elements [42]. Simultaneously, the damage to the passive film in acidic environments further exposes the matrix, triggering continuous corrosion and exacerbating Ti ion release. The relatively high release of Al ions in the neutral environment can be explained by the Ellingham-Richardson theory [46]. Within the range of human physiological temperature and room temperature, the Gibbs free energy required for the oxidation of different elements follows the order $\text{V} > \text{Ti} > \text{Al}$. A lower Gibbs free energy indicates a greater tendency for oxidation; therefore, Al is more easily oxidized to Al^{3+} and released during corrosion compared to Ti and V. The results of this work are the same with existing literature, verifying the scientific validity and universality of these ion release patterns. Sway et al. [47] reported that after immersing Ti-6Al-4V alloy in artificial saliva (a near-neutral environment) for 7 days, the detected Al ion release (163 ppb) was 4.18 times that of Ti ions (39 ppb). In this work, the porous Ti-6Al-4V alloy maintained the ion release order of $\text{Al} > \text{Ti} > \text{V}$ even after 60 and 90 days of immersion in $\text{pH} = 7$ Hank's solution (Figure 10c,e), indicating the long-term stability of this release pattern.

As immersion time extends, the release amounts of Ti, Al, and V ions exhibit a continuous increasing trend under all three pH conditions (Figure 11a–c). In the strongly acidic environment of $\text{pH} = 3$, the increase in ion release is the most significant, exhibiting a characteristic of explosive growth. At 90 days of immersion, the Ti ion release reached $157.58 \mu\text{g/L}$, approximately 2.41 times the release at 30 days ($65.56 \mu\text{g/L}$); the Al ion release increased from $7.35 \mu\text{g/L}$ at 30 days to $45.09 \mu\text{g/L}$ at 90 days, a 6.13-fold increase; and the V ion release increased from $2.97 \mu\text{g/L}$ to $22.69 \mu\text{g/L}$, a substantial 7.64-fold increase. This is again due to the continuous erosion of the TiO_2 passive film by H^+ during long-term immersion in the strongly acidic environment, causing the exposed area of the matrix to expand continuously. Furthermore, the micropores present within the corrosion product layer cannot effectively block solution penetration, further accelerating matrix dissolution and ion release. In the neutral environment, the release amounts of Ti, Al, and V ions remain at the lowest levels, and the rate of increase over time is minimal, the ion release curves are almost flat. This confirms that the porous Ti-6Al-4V alloy possesses optimal chemical stability in a neutral environment, where the passive film can maintain a complete physical barrier effect over the long term, effectively inhibiting ion release. Relevant studies have indicated that the cytotoxicity thresholds of Ti, Al, and V ions are as follows: $\text{Ti}^{4+} > 1000 \mu\text{g/L}$, $\text{Al}^{3+} \approx 500 \mu\text{g/L}$, and $\text{V}^{5+} \approx 200 \mu\text{g/L}$ [5]. Even when the porous alloy prepared in this study was immersed in the most corrosive environment ($\text{pH} = 3$) for 90 days, the release concentrations of Ti, Al, and V ions were all far below the aforementioned cytotoxicity thresholds. Moreover, the ion release concentrations were even lower after 90 days of immersion in a neutral environment ($\text{pH} = 7$). In addition, according to the safety

standards for clinical implant materials [8], the clinical safety limits of Ti, Al, and V ions in human body fluids are $< 500 \mu\text{g/L}$, $< 100 \mu\text{g/L}$, and $< 50 \mu\text{g/L}$, respectively. The ion release concentrations under all immersion conditions in this work did not exceed the above safety limits, which fully proves that the material possesses good clinical application safety. Therefore, the porous Ti-6Al-4V alloy fabricated by LPBF can maintain ion release within a safe range in both normal physiological and inflammatory pathological environments, and can effectively avoid clinical risks such as inflammatory reactions and tissue damage caused by ion toxicity.

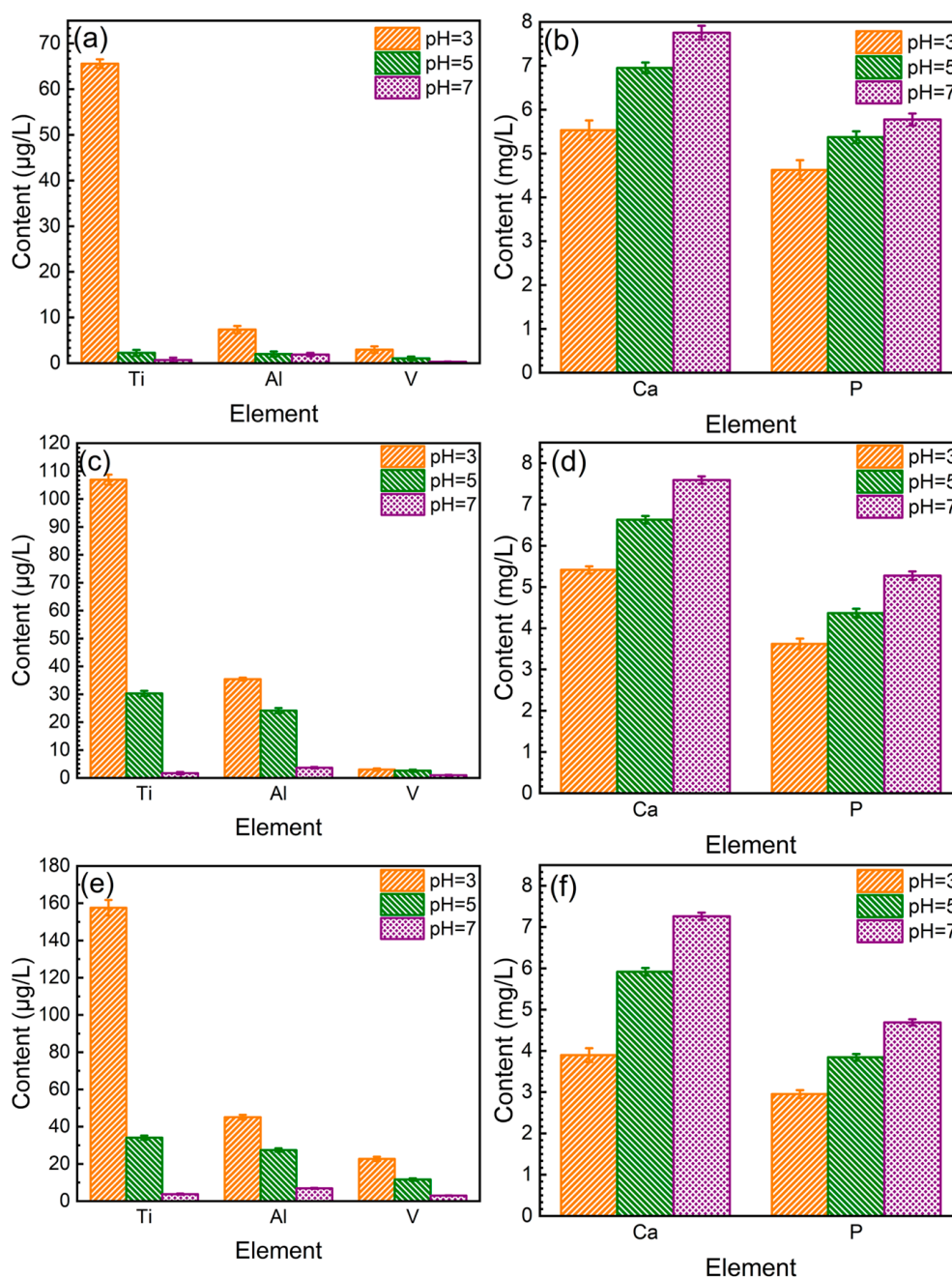


Figure 10. Ion release of porous Ti-6Al-4V in Hank's solution with different pH values for 90 days: (a,c,e) are the release amounts of Ti, Al and V at 30, 60 and 90 days; (b,d,f) are the amount of Ca and P remaining in solution at 30, 60, and 90 days.

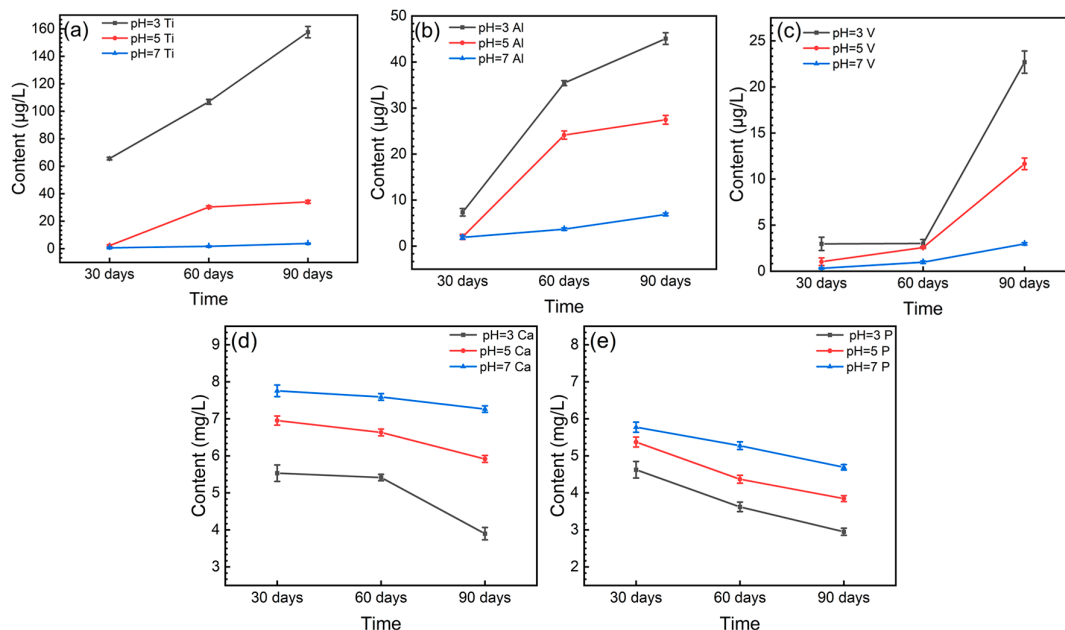


Figure 11. Ion release curve of porous Ti-6Al-4V in Hank's solution with different pH values within 90 days: (a) change in Ti; (b) change in Al; (c) change in V; (d) change in Ca; (e) change in P.

As inherent components of the Hank's solution, changes in Ca^{2+} and PO_4^{3-} ion contents directly reflect the formation of Ca-P deposition products on the alloy surface through adsorption and mineralization reactions of Ca^{2+} and PO_4^{3-} . The test results show that the contents of Ca and P ions in the solution decrease as pH decreases (Figure 10b,d,f), indicating that acidic environments more readily induce the deposition of Ca-P compounds and generate more corrosion products. Although H^+ inhibits the transformation of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ to $\text{Ca}_3(\text{PO}_4)_2$ in acidic environments, the large number of active sites (such as passive film defects and exposed matrix areas) generated by oxidation-corrosion reactions during long-term immersion can accelerate the adsorption and mineralization of Ca^{2+} and PO_4^{3-} . Consequently, the overall amount of deposition products generated is higher than in the neutral environment, leading to greater consumption of Ca and P ions in the solution. As immersion time extends, the contents of Ca and P ions in the solution show a continuous downward trend, and the lower the pH, the greater the magnitude of the decrease. When immersed for 90 days, the residual amounts of Ca and P ions in the pH = 3 environment are the lowest, at 3.90 mg/L and 2.95 mg/L, respectively, indicating that the largest amount of Ca-P deposition products is generated under long-term immersion in a strongly acidic environment. The decrease in Ca and P ion contents in the neutral environment is the smallest, indicating a slow deposition rate of calcium-phosphorus compounds and a low yield of deposition products.

3.5. Compressive Properties of Porous Ti-6Al-4V in Hank's Solutions with Different pH Values

Figure 12a displays the stress-strain curves of the porous Ti-6Al-4V alloys under different immersion conditions, and Table 4 presents the fitted mechanical parameters corresponding to these curves. As observed in Figure 12a, the stress-strain curves of all samples exhibit typical compression characteristics of porous materials, showing distinct yielding behavior and a certain degree of plastic deformation before failure. In the initial stage of compression, the strain of the porous structure is dominated by elastic deformation. As the load increases, the strain gradually transitions from elastic to plastic deformation, and the stress rises significantly with plastic deformation. When compressed to the end of the curve, densification of the porous structure occurs, and the stress continues to increase

with strain. Relevant literature confirms that compression tests of porous materials can maintain load transfer capabilities even after significant deformation of most unit cells [48], and their deformation mode is primarily tension-dominated. For a single unit structure, the region with the most significant stress concentration typically appears at the thin struts with uneven dimensions and heterogeneous composition, which are also the weak links for compression failure of the porous structure [49].

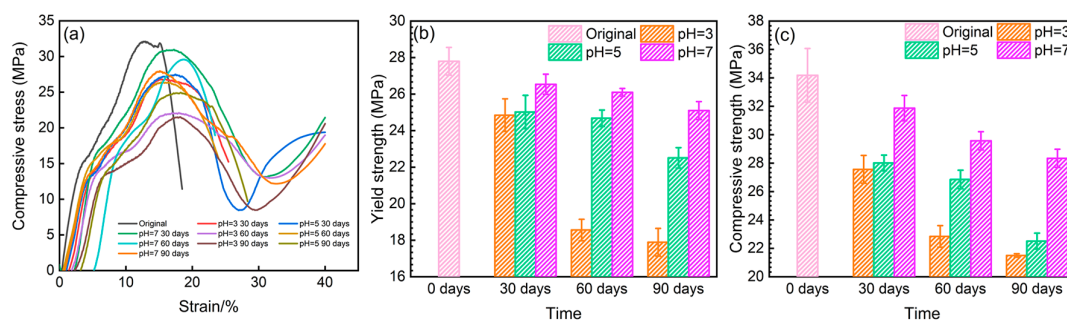


Figure 12. Compressive properties of porous Ti-6Al-4V in Hank's solution with different pH values for 90 days: (a) stress–strain curve; (b) yield strength; (c) compressive strength.

Table 4. Fitting data in Figure 12a.

Solution pH	Number of Samples	Time (Days)	Yield Strength (MPa)	Compressive Strength (MPa)
—	3	0	27.80 ± 0.76	34.18 ± 1.89
pH = 3	3	30	24.85 ± 0.89	27.56 ± 0.98
pH = 5	3	30	25.02 ± 0.91	28.01 ± 0.55
pH = 7	3	30	26.54 ± 0.55	31.87 ± 0.89
pH = 3	3	60	18.56 ± 0.59	22.84 ± 0.76
pH = 5	3	60	24.68 ± 0.45	26.85 ± 0.65
pH = 7	3	60	26.10 ± 0.21	29.57 ± 0.64
pH = 3	3	90	17.89 ± 0.76	21.50 ± 0.12
pH = 5	3	90	22.51 ± 0.56	22.51 ± 0.56
pH = 7	3	90	25.10 ± 0.49	28.34 ± 0.64

As shown in Table 4, the yield strength and compressive strength of the non-immersed sample are 27.80 ± 0.76 MPa and 34.18 ± 1.89 MPa, respectively, which are higher than those of all immersed samples. In acidic solutions, under the same Hank's solution environment, the yield strength and compressive strength of the samples show a continuous downward trend with the extension of immersion time. Furthermore, at the same immersion time, the lower the pH value of the solution, the more obvious the degradation of mechanical properties. For the neutral solution, the decreasing trend of the alloy's yield strength and compressive strength is relatively slow (Figure 12b,c). Combined with the previous ion release test results, the core of mechanical property attenuation is the ion release effect during long-term immersion. Corrosion of the alloy matrix and passive film leads to the continuous release of Ti, Al, and V ions, reducing the relative density of the samples, thinning the pore wall thickness, and decreasing the structural load-bearing capacity [49]. Although Ca-P compounds and titanium oxide corrosion products are generated on the alloy surface during immersion, the strength of these products and their bonding force with the matrix are much lower than those of the alloy matrix. Moreover, they cannot achieve effective load transfer or form effective mechanical support [50], failing to compensate for the structural damage caused by ion release, ultimately leading to a decrease in overall strength. The acidic environment exacerbates mechanical property degradation due to accelerated ion release and passive film damage. Although only static compression tests were conducted in this study without direct fatigue assessment, the degradation in strength

during immersion can be qualitatively interpreted as a decline in fatigue resistance over time. This phenomenon is expected to be more pronounced in acidic environments. While dedicated fatigue testing and investigations mimicking more realistic service environments will be addressed in future work, the present study focuses on the impact of pH variation on the mechanical evolution of these lattice structures.

Figure 13 shows the compressive fracture morphologies of porous Ti-6Al-4V alloys after 90 days of immersion in Hank's solutions with different pH values. Immersion conditions have a significant impact on the fracture mechanism of the alloy, pH value dominates the degree of corrosion damage and surface phase evolution, while long-term immersion amplifies this effect, collectively influencing the composition of the fracture mode and the manifestation of fracture characteristics. The crater-like morphologies within the yellow dashed rectangles in the figure are dimples, and the locations indicated by the blue arrows exhibit typical quasi-cleavage fracture characteristics with step and river-like patterns. Dimples are typical morphological markers of ductile fracture, usually formed during plastic deformation, reflecting the material's high deformation capacity [51]. In contrast, quasi-cleavage fracture belongs to the category of brittle fracture, representing sudden fracture caused by local stress concentration in the structure. Based on the fracture morphology characteristics in Figure 13, the compressive fracture mode of the porous Ti-6Al-4V alloy is a mixed fracture mode where ductile fracture and brittle fracture coexist, and the proportion of this mixed mode is affected by the pH value of the solution. In the neutral environment, the dense TiO_2 passive film and stable $\text{Ca}_3(\text{PO}_4)_2$ deposition layer formed after long-term immersion can alleviate corrosion damage, resulting in a relatively low proportion of brittle fracture. In acidic environments ($\text{pH} = 3, 5$), H^+ accelerates the dissolution of the TiO_2 film and the release of ions (Ti, Al, V) during long-term immersion, leading to an increase in surface defects of the alloy and a decrease in structural integrity. Meanwhile, the transformation of calcium phosphate phases is delayed with weak bonding force, which further exacerbates local stress concentration and promotes an increase in the proportion of brittle fracture. The highly elongated dimples distributed on the fracture surface indicate that shear force is the main driving force for fracture. However, in acidic environments, the plastic deformation space under shear force is compressed by corrosion damage, resulting in poor dimple development. In addition, the fracture surfaces of samples immersed in acidic environments have a higher proportion of quasi-cleavage fracture regions, with smaller and more unevenly distributed dimples. This is closely related to the more severe oxide film damage, matrix corrosion pit formation, and stress concentration effects caused by long-term immersion under strongly acidic conditions. Based on the above analysis, after long-term immersion in acidic environments, the mechanical properties of porous Ti-6Al-4V alloys deteriorate significantly due to the mixed fracture mode dominated by immersion conditions (increased proportion of brittleness), structural damage caused by ion release, and surface protection failure resulting from phase evolution. This indicates that the inflammatory acidic microenvironment weakens the mechanical reliability of porous titanium alloy implants, and the stronger the acidity and the longer the immersion time, the more obvious this weakening effect becomes.

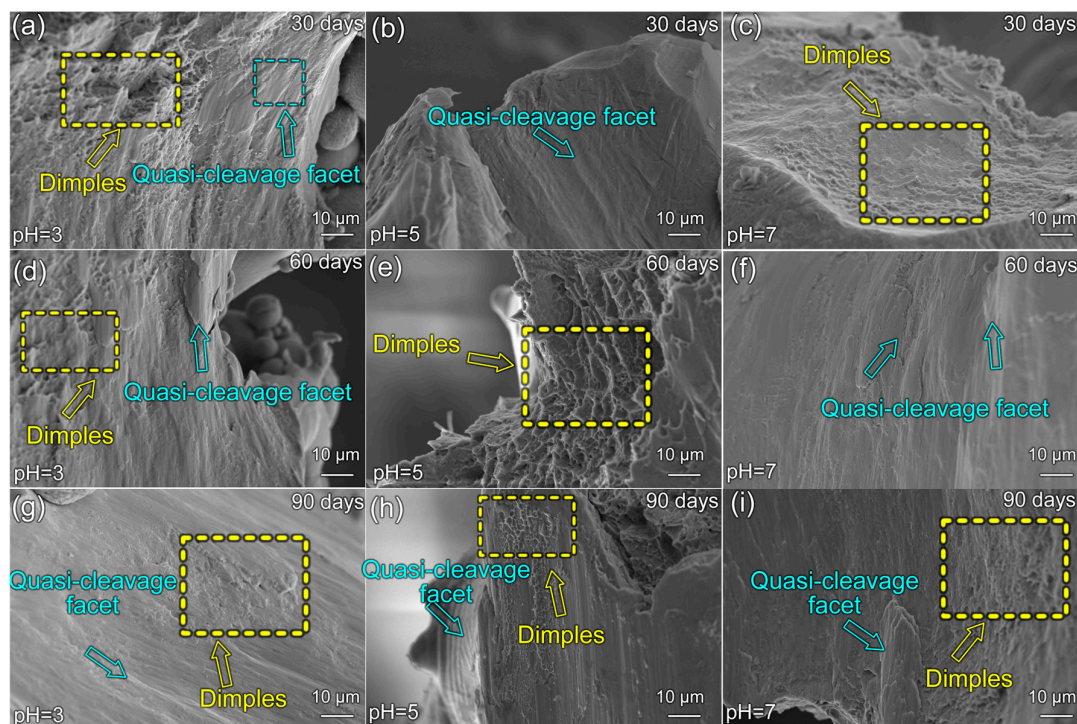


Figure 13. Fracture morphology of porous Ti-6Al-4V after compression in Hank's solution with different pH values for 90 days: (a) pH = 3, 30 days; (b) pH = 5, 30 days; (c) pH = 7, 30 days; (d) pH = 3, 60 days; (e) pH = 5, 60 days; (f) pH = 7, 60 days; (g) pH = 3, 90 days; (h) pH = 5, 90 days; (i) pH = 7, 90 days.

4. Conclusions

Porous Ti-6Al-4V alloys prepared by LPBF were immersed in Hank's solution at pH 3, 5, and 7 for 90 days to simulate degradation in normal and inflammatory pathological environments. The degradation behavior, encompassing weight change, phase composition, microstructure, ion release, and mechanical evolution, was analyzed, leading to the following conclusions:

- (1) Oxidation-deposition reactions occur during the long-term immersion of the alloy, forming a mixed oxide film dominated by TiO_2 with trace amounts of Ti_2O_3 and TiO . The content of TiO_2 increases with prolonged immersion time and elevated pH value. Acidic environments accelerate the dissolution of TiO_2 , induce the formation of low-valence titanium oxides, and reduce the film stability. Meanwhile, Ca^{2+} and PO_4^{3-} in the solution deposit on the alloy surface to form Ca-P compounds mainly composed of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and $\text{Ca}_3(\text{PO}_4)_2$. Acidic conditions favor the formation of $\text{Ca}(\text{H}_2\text{PO}_4)_2$, which can be transformed into the more thermodynamically stable $\text{Ca}_3(\text{PO}_4)_2$ after long-term immersion.
- (2) In the neutral environment, only slight Ca-P salt deposition occurs without obvious corrosion damage. In acidic environments, corrosion products accumulate continuously, and the distribution shifting from pore channels to strut surfaces. H^+ erodes and damages the oxide film in acidic conditions, intensifying matrix dissolution and ion deposition, thereby impairing the surface stability of the alloy.
- (3) In the neutral environment, ion release follows the order of $\text{Al} > \text{Ti} > \text{V}$, with low overall levels increasing slowly over time. Acidic environments activate ion release, altering the order to $\text{Ti} > \text{Al} > \text{V}$. A large amount of Ti ions is released due to oxide film damage and become the dominant species, with significantly higher release levels than those in the neutral environment. After long-term immersion, the compressive mechanical

properties of the alloy all decrease to varying degrees. Acidic environments accelerate oxide film damage and matrix corrosion, triggering the generation and propagation of microcracks on pore walls, and ultimately transforming the fracture mode of the alloy into a ductile-brittle mixed fracture.

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