

Article

Anisotropy in Microstructure and Corrosion Behavior of NiTi Alloys Produced by Laser Powder Bed Fusion

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Abstract

Laser powder bed fusion (LPBF) induces pronounced microstructural anisotropy in NiTi alloys, which strongly governs their corrosion behavior in physiological environments. Here, the orientation-dependent microstructure and corrosion performance of LPBF NiTi alloys were systematically investigated on the XY (perpendicular to build direction) and XZ (parallel to build direction) planes. The XY plane is dominated by polygonal B2 grains, whereas semi-quantitative XRD analysis and TEM observations indicate a relatively larger contribution of lamellar B19' martensite on the XZ plane. Electrochemical tests in Hank's solution (pH 3–7) reveal pronounced corrosion anisotropy. At pH 7, the XZ plane exhibits a higher charge transfer resistance (143.9 vs. 109.1 kΩ cm²) and a lower corrosion current density (0.231 vs. 0.599 μA cm⁻²) than the XY plane. After 72 h immersion, the R_{ct} of the XZ plane remains approximately 31% higher than that of the XY plane at pH 7, while its apparent donor density is lower than that of the XY plane at pH 3 (7.38×10^{29} vs. 12.33×10^{29} cm⁻³). The superior electrochemical response of the XZ plane correlates with its denser lamellar B19' morphology and lower passive-film donor density. Competition between interface-assisted passivation and interface-related electrochemical heterogeneity is proposed as a possible contributor to the anisotropic corrosion response.

Keywords: laser powder bed fusion; corrosion behavior; passive film; NiTi alloy; anisotropic behavior

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1. Introduction

Near-equiatom NiTi was selected for the present study because it combines transformation-enabled mechanical functionality with direct relevance to biomedical, aerospace, and smart-device applications. Its reversible thermoelastic transformation between B2 austenite and B19' martensite gives rise to the shape-memory effect and superelasticity, which are characterized by a stress-induced transformation plateau and recoverable strains of several percent. Under appropriate thermomechanical and processing conditions, NiTi can exhibit recoverable strains approaching 6–8%, while LPBF-fabricated NiTi has also demonstrated recoverable strains exceeding 5% [1–4]. The mechanical response of NiTi is strongly phase- and temperature-dependent. Representative literature values indicate an elastic modulus of approximately 70 GPa for B2 austenite and approximately

25–50 GPa for stress-induced B19' martensite, although the measured values vary with composition, texture, heat treatment, loading mode, and test temperature [1,3]. NiTi also combines relatively high strength, substantial damping capacity, and resistance to permanent deformation. These characteristics enable large reversible deformation and mechanical compliance in cardiovascular stents, guidewires, orthodontic devices, actuators, and orthopedic fixation systems. However, the fabrication of geometrically complex NiTi components remains challenging for conventional manufacturing routes, including casting and forging, due to stringent requirements on dimensional precision, compositional control, and functional stability [5]. In this context, additive manufacturing (AM), particularly laser powder bed fusion (LPBF), has emerged as a promising alternative, enabling the near-net-shape fabrication of intricate NiTi architectures with enhanced design freedom and process controllability [5–8].

LPBF is a layer-wise manufacturing process in which repeated localized melting and rapid solidification generate highly non-equilibrium thermal histories [9–11]. The resulting melt-pool behavior, porosity, elemental evaporation, residual stress, distortion, and microstructural evolution are jointly governed by laser power, scanning speed, hatch spacing, layer thickness, scanning strategy, atmosphere, and component geometry [12–14]. Kaščák et al. [8] have further emphasized the role of simulation-assisted parameter selection in predicting temperature fields, residual stresses, distortion, and process-induced defects before physical fabrication. For NiTi alloys, these coupled variables are particularly important because small changes in composition and thermal history can substantially alter the stability of B2 austenite, B19' martensite, and intermediate precipitates. Thermally coupled finite-element simulations, combined with cellular-automaton or phase-field approaches, may predict melt-pool-scale thermal histories and qualitative trends in epitaxial grain growth, columnar grain morphology, and crystallographic texture.

Several studies have demonstrated that LPBF parameters affect not only densification but also the phase-transformation response of NiTi. Bormann et al. [15] varied the applied process energy and used DSC, XRD, and metallographic analysis to show that the transformation temperatures could be deliberately adjusted within LPBF-fabricated NiTi components. Dadbakhsh et al. [16] compared high-power/high-speed and low-power/low-speed parameter combinations within a similar energy-density range. The former condition produced predominantly austenitic and pseudoelastic material at room temperature, whereas the latter produced a greater martensitic contribution and a more pronounced thermal shape-memory response. Speirs et al. [17] further varied the scanning conditions and processing atmosphere, comparing oxygen levels of approximately 1800 and 220 ppm, and demonstrated that the transformation response was sensitive to both the fabrication environment and subsequent solution treatment. These findings establish that the phase constitution and functional response of LPBF NiTi cannot be interpreted from nominal alloy composition alone.

The directional heat flow inherent to LPBF also produces orientation-dependent grain morphology, crystallographic texture, phase distribution, and residual stress. Dadbakhsh et al. [18] reported pronounced texture and anisotropic behavior in selectively laser-melted NiTi, linking the preferred solidification direction to orientation-dependent deformation characteristics. Nematollahi et al. [19] fabricated tensile and compression specimens at build orientations of 0°, 45°, and 90° using identical process parameters and showed that build orientation modified the crystallographic texture and produced distinct tensile, compressive, and shape-memory responses. Safaei et al. [20] similarly demonstrated that manipulation of build orientation could be used to alter the crystallographic texture and thermomechanical response of LPBF NiTi. Carlucci et al. [21] subsequently examined the combined effects of build orientation and post-processing heat treatment,

confirming that both factors influence the pseudoelastic behavior of the fabricated alloy. More recently, Wang et al. [22] compared NiTi samples fabricated in three building directions and found orientation-dependent differences in preferred orientation, geometrically necessary dislocation density, impurity-element content, phase-transformation behavior, and hardness. Collectively, these studies demonstrate that build orientation is a major structural variable in LPBF NiTi. However, most of them focused primarily on phase transformation and mechanical or functional performance rather than on passive-film evolution and corrosion kinetics.

Corrosion studies on LPBF-fabricated NiTi have shown that processing route, microstructure, phase constitution, and surface condition all affect the electrochemical response. Studies of passive-film formation have shown that LPBF processing and the resulting surface condition can influence film protectiveness and electrochemical stability in Hank's solution [23,24]. Chmielewska et al. [25] compared NiTi fabricated from pre-alloyed powder with material produced by in situ alloying of elemental Ni and Ti powders. Electrochemical tests conducted in phosphate-buffered saline at 37 °C showed that the in situ alloyed material exhibited slightly lower corrosion resistance and a less protective passive layer, although the two materials showed broadly comparable biological responses. Liu et al. [24] examined LPBF NiTi produced under different process settings in 0.9 wt.% NaCl solution at 37 °C and showed that the processing conditions altered both passive-film characteristics and corrosion resistance. Phase-resolved measurements by Chen et al. [26] further showed that B2 austenite and B19' martensite possess different local electrochemical potentials, indicating that phase constitution and spatial phase distribution may generate local electrochemical heterogeneity. Perumal et al. recently investigated the combined effects of volume energy density and observation plane on the microstructure and corrosion behavior of LPBF NiTi in 3.5 wt.% NaCl solution [27]. Their comparison of the XY and XZ planes showed that higher energy input promoted grain refinement and improved corrosion resistance; XPS analysis associated this response with a more homogeneous TiO₂-enriched passive layer. Other studies have demonstrated that crystallographic texture and residual microstrain affect passive-film formation and corrosion resistance, with strong (001) or (100) textures and reduced internal strain generally producing a more favorable electrochemical response [28,29]. Collectively, these studies establish that the corrosion behavior of LPBF NiTi is sensitive to crystallographic texture, strain state, phase constitution, and passive-film characteristics. However, these factors have generally been examined separately or on a single selected surface, most commonly the plane perpendicular to the building direction. Consequently, the manner in which build-direction-dependent phase morphology and spatial phase distribution influence passive-film defect chemistry and long-term corrosion kinetics on different planes remains insufficiently understood.

Accordingly, the present work compares the XY plane, perpendicular to the building direction, and the XZ plane, parallel to the building direction, of LPBF-fabricated NiTi produced using an identical optimized processing condition. Phase constitution, multiscale microstructure, and hardness response were characterized using DSC, XRD, optical microscopy, TEM, and Vickers indentation. Orientation-dependent electrochemical behavior was evaluated in Hank's solutions over a pH range of 3–7 using EIS and potentiodynamic polarization. The evolution of the surface-film response during 24–72 h immersion was further examined using EIS and Mott–Schottky analysis. Rather than attributing corrosion anisotropy solely to the relative contributions of B2 and B19', this study evaluates its correlation with phase morphology, spatial phase distribution, corrosion kinetics, and apparent passive-film donor density. The results provide an orientation-resolved microstructure–electrochemical framework for understanding the degradation of LPBF-fabricated NiTi under neutral and acidified physiological conditions.

2. Experimental Procedure

2.1. Materials

Cubic NiTi blocks of $10 \times 10 \times 10 \text{ mm}^3$ were fabricated using commercial LPBF equipment (EOS M 290, EOS GmbH, Krailling, Germany). The equiatomic NiTi alloy powder, with a particle size from $15 \mu\text{m}$ to $53 \mu\text{m}$ (d_{10} : $16.5 \mu\text{m}$, d_{50} : $31.23 \mu\text{m}$, d_{90} : $48.01 \mu\text{m}$), was supplied from Avimetal Powder Metallurgy Technology Co., Ltd. (Beijing, China). The powder was produced via electrode induction melting gas atomization.

The LPBF processing parameters were set as follows: laser power of 180 W, scanning speed of 720 mm s^{-1} , hatch spacing of $100 \mu\text{m}$, and layer thickness of $30 \mu\text{m}$. These parameters were determined through extensive preliminary optimization to minimize porosity. The porosity of the fabricated blocks, measured by the Archimedes method, was below 1%. Given the passive nature of NiTi alloys, the influence of such a low porosity level on corrosion behavior is expected to be minimal.

A bidirectional (back-and-forth) scanning strategy was employed for all samples. All samples were examined in the as-fabricated condition without any post-processing heat treatment. The building direction was defined as the Z-direction, while the transverse directions were denoted as the X- and Y-directions. Accordingly, surfaces perpendicular to the building direction (XY plane) and parallel to the building direction (XZ plane) are hereafter referred to as the XY and XZ planes, respectively.

2.2. Differential Scanning Calorimetry (DSC)

Phase transformation temperatures of the samples were determined using differential scanning calorimetry (DSC 3500 Sirius, NETZSCH-Gerätebau GmbH, Selb, Germany) under an argon atmosphere. The measurements were carried out over a temperature range from $-80 \text{ }^{\circ}\text{C}$ to $117 \text{ }^{\circ}\text{C}$ at a heating and cooling rate of $5 \text{ }^{\circ}\text{C min}^{-1}$. Each DSC run consisted of a heating cycle followed by a subsequent cooling cycle.

2.3. Microstructural Characterizations

Phase constituents of the samples were identified by X-ray diffraction (XRD, Empyrean, Malvern Panalytical B.V., Almelo, the Netherlands) using $\text{Cu K}\alpha$ radiation. The diffraction patterns were collected over a 2θ range of $30\text{--}80^{\circ}$ with a scan speed of $0.026^{\circ} \text{ s}^{-1}$, and the obtained data were analyzed using Jade 9 software. The relative contributions of the B2 and B19' phases were estimated from their integrated diffraction-peak areas using Jade 9 software. Because LPBF-fabricated NiTi may exhibit orientation-dependent texture, preferred orientation, and overlapping reflections, this peak-area method was used only for semi-quantitative comparison between the XY and XZ planes and should not be interpreted as an absolute determination of phase volume fractions. Microstructural features at different length scales were characterized using optical microscopy (OM, Axioskop 2 MAT, Carl Zeiss Microscopy GmbH, Jena, Germany) and transmission electron microscopy (TEM, JEM-2100F, JEOL Ltd., Akishima, Tokyo, Japan).

Samples for OM observations were ground and mechanically polished following standard metallographic procedures. Prior to OM observation, the polished samples were etched in a mixed solution of HF, HNO_3 , and H_2O (1:9:9, in volume) for 10 s. TEM specimens were prepared by cutting the samples into 3 mm diameter discs, followed by twin-jet electropolishing using a solution of HClO_4 , $\text{C}_4\text{H}_9\text{OH}$, and CH_3OH (6:39:55, v/v) at an applied voltage of 15 V and a temperature of $-30 \text{ }^{\circ}\text{C}$.

2.4. Hardness Test

Vickers hardness measurements were performed using a digital hardness tester (KB 30 S, KB Prüftechnik GmbH, Hochdorf-Assenheim, Germany) under an applied load of 5

N with a dwell time of 20 s. Ten indentations were randomly placed on each sample, and the reported hardness values represent the average of these measurements. Prior to testing, all samples were ground using silicon carbide paper up to 2000 grit to ensure a uniform surface condition.

2.5. Electrochemical Measurement and Solution

Prior to electrochemical measurements, the samples were electrically connected using copper wires and embedded in epoxy resin, leaving only the designated surface exposed to the electrolyte. The interface between the sample and the resin was further sealed with silicone to prevent crevice corrosion. All samples were ground and polished to a mirror finish before testing.

Hank's solution was used as the electrolyte to simulate physiological conditions. The solution contained $0.140 \text{ g}\cdot\text{L}^{-1}$ CaCl_2 , $0.098 \text{ g}\cdot\text{L}^{-1}$ MgSO_4 , $0.4 \text{ g}\cdot\text{L}^{-1}$ KCl , $0.06 \text{ g}\cdot\text{L}^{-1}$ KH_2PO_4 , $8 \text{ g}\cdot\text{L}^{-1}$ NaCl , $0.048 \text{ g}\cdot\text{L}^{-1}$ Na_2HPO_4 , $1 \text{ g}\cdot\text{L}^{-1}$ $\text{C}_6\text{H}_{12}\text{O}_6$, $0.35 \text{ g}\cdot\text{L}^{-1}$ NaHCO_3 , and $0.011 \text{ g}\cdot\text{L}^{-1}$ $\text{C}_{19}\text{H}_{14}\text{O}_5\text{SNa}$. The pH values of Hank's solutions were adjusted to 3, 5, and 7 using lactic acid. All electrochemical measurements and immersion tests were conducted at 37°C . Analytical-grade reagents and distilled water were used throughout.

Electrochemical measurements were performed using a CHI660E electrochemical workstation (Chenhua Ltd., Shanghai, China) with a conventional three-electrode configuration, in which the LPBF-fabricated NiTi sample served as the working electrode, a platinum sheet as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The open circuit potential (OCP) was monitored for 3600 s to achieve a steady state prior to subsequent measurements. Electrochemical impedance spectroscopy (EIS) was then carried out under potentiostatic control by applying a sinusoidal perturbation of 10 mV over a frequency range from 0.01 Hz to 10^5 Hz. The EIS data were fitted using ZsimpWin 3.5 software. Potentiodynamic polarization (Tafel) measurements were conducted by scanning the potential from -200 mV (vs. OCP) to 0.1 V at a scan rate of 0.001 V s^{-1} , and the resulting curves were analyzed using Cview 2.6 software.

To further investigate the evolution of passive films, the samples were immersed in Hank's solution for 24, 48, and 72 h prior to EIS measurements. Subsequently, Mott–Schottky analyses were performed at a fixed frequency of 1000 Hz by sweeping the potential from 0.1 V to -1 V at a rate of 10 mV s^{-1} . All reported potentials in this work are referenced to the SCE.

3. Results

3.1. General Microstructural Information

DSC analysis and XRD patterns of the LPBF-fabricated NiTi alloy are presented in Figure 1 to characterize the phase transformation behavior and phase constitution. The DSC measurement was performed on a bulk three-dimensional sample; therefore, no distinction between the XY and XZ planes was made. As shown in Figure 1a, the martensitic transformation of the as-fabricated sample is characterized by a martensite start temperature (M_s) of 21.88°C and a martensite finish temperature (M_f) of -23.89°C upon cooling, while the reverse transformation occurs with an austenite start temperature (A_s) of 8.98°C and an austenite finish temperature (A_f) of 56.66°C upon heating. The presence of a single transformation peak without noticeable splitting suggests a chemically homogeneous microstructure in the as-fabricated alloy [30].

Figure 1b shows the XRD patterns obtained from the XY and XZ planes. Both patterns reveal the coexistence of the B2 austenite and B19' martensite phases, which are the dominant phases in NiTi alloys and can reversibly transform into each other depending on temperature [31]. Semi-quantitative analysis of the integrated diffraction-peak areas sug-

gests apparent B2/B19' proportions of 84.05/15.95 for the XY plane and 79.04/20.96 for the XZ plane. These values indicate a relative tendency toward a larger B19' contribution on the XZ plane, rather than rigorous absolute phase fractions. The estimates may be influenced by preferred orientation, crystallographic texture, peak overlap, and orientation-dependent diffraction intensity in the LPBF-fabricated material. Therefore, the XRD results are interpreted together with the TEM observations, which independently reveal denser and more spatially continuous lamellar B19' variants on the XZ plane. Although intermediate precipitate phases such as Ni_4Ti_3 and Ni_3Ti have been reported in LPBF-fabricated NiTi alloys [9,23], no discernible diffraction peaks associated with these phases were detected in the present XRD patterns, likely due to their low volume fractions being below the detection limit of the instrument.

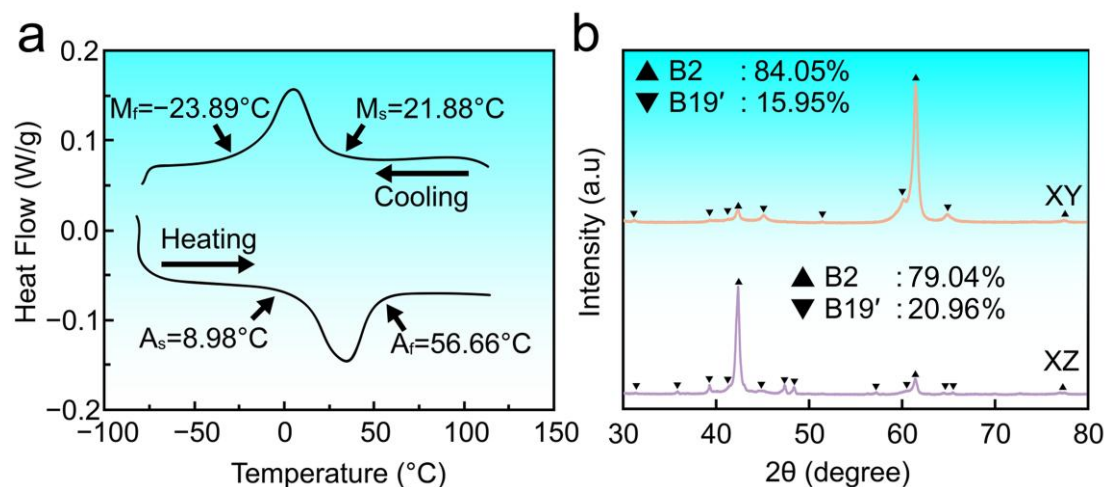


Figure 1. Phase transformation behavior and phase constitution of the LPBF-fabricated NiTi alloy: (a) DSC curves and (b) XRD patterns obtained from the XY and XZ planes.

The optical microstructures of the samples observed on the two characteristic planes are presented in Figure 2. On the XY plane, the microstructure is dominated by polygonal B2 grains (Figure 2a), whereas elongated epitaxial B2 grains are observed on the XZ plane (Figure 2b). This microstructural difference originates from the intrinsic thermal conditions during the LPBF process. Owing to the much lower thermal conductivity of the powder bed compared with the solidified material, a steep temperature gradient is established at the solid–liquid interface, particularly along the building direction [5]. As a result, B2 grains preferentially grow epitaxially along the direction of the maximum thermal gradient, giving rise to columnar grain morphologies on the XZ plane. In both planes, dark band-like features are observed, which are attributed to melt pool boundaries revealed by chemical etching [29]. These regions are generally associated with stress concentration in LPBF-fabricated NiTi alloys [32], making them more susceptible to preferential corrosion during etching. Similar microstructural features have been reported in previous studies [2,5]. It should be noted that, due to the limited spatial resolution of optical microscopy, the B19' martensite phase cannot be distinguished at this scale. Therefore, a more detailed crystallographic characterization is required and will be discussed in the following sections.

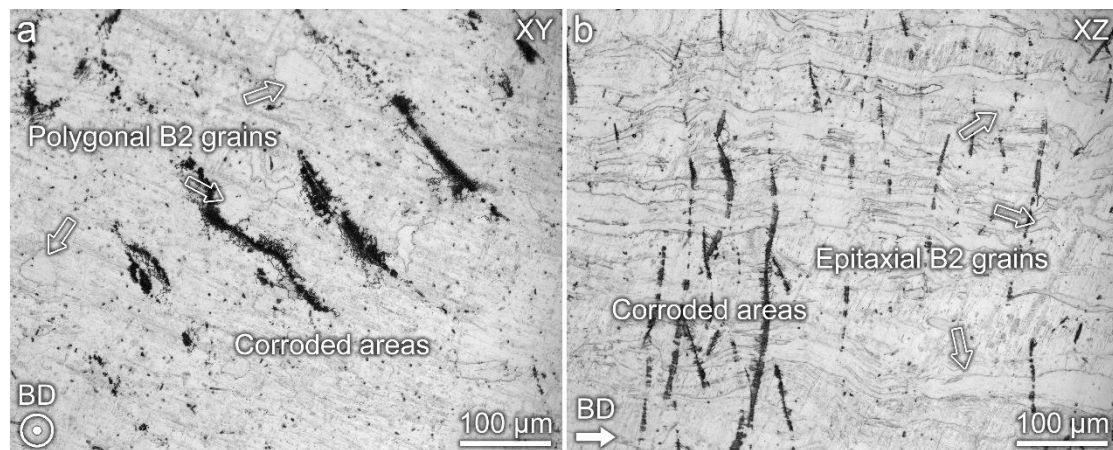


Figure 2. Optical microstructures of LPBF-fabricated NiTi alloy observed on different planes: (a) XY plane and (b) XZ plane. BD is building direction of the sample.

3.2. TEM Results

The detailed substructures of the XY and XZ planes were further characterized by TEM, as shown in Figures 3 and 4. Figure 3a presents a low-magnification TEM image of the XY plane, revealing the coexistence of the B2 austenite matrix and B19' martensite. The B19' phase appears as plate- or lath-like variants embedded within the B2 matrix, indicating that the martensitic transformation is only partially completed under the as-fabricated condition. This heterogeneous microstructure reflects a transformation process strongly influenced by local compositional fluctuations and residual stress fields inherent to the LPBF process. A bright-field TEM image of the B2 matrix is shown in Figure 3b, where a high density of nanoscale precipitates is observed to be homogeneously distributed. The corresponding selected-area electron diffraction (SAED) pattern (inset of Figure 3b) can be indexed to the B2 phase along the [010] zone axis, confirming the retention of the ordered B2 structure. To enhance the visibility of the precipitates, a dark-field image is presented in Figure 3c, in which the precipitates exhibit bright contrast, indicating that they are crystallographically distinct from the surrounding B2 matrix. The crystallographic identity of these precipitates was therefore further examined using selected-area electron diffraction, as discussed below.

A higher-magnification TEM image of a precipitate-containing region is shown in Figure 3d. The precipitate highlighted by the dashed circle is embedded within the B2 matrix. The corresponding SAED pattern (inset of Figure 3d) shows strong diffraction spots from the B2 matrix along the [010] zone axis, together with additional weak reflections that can be indexed to the Ni_4Ti_3 phase along the [001] zone axis. This result unambiguously identifies the precipitates as Ni_4Ti_3 with a rhombohedral structure and indicates a semi-coherent orientation relationship with the B2 matrix. The corresponding dark-field image in Figure 3e further reveals its isolated, disk-like morphology and a characteristic size of approximately 100 nm. It should be emphasized that these local TEM observations confirm the presence and morphology of Ni_4Ti_3 precipitates but do not provide a statistically representative phase fraction or number density.

The crystallographic relationship between the B2 matrix and the B19' martensite is illustrated in Figure 3f. The bright-field image shows the close coexistence of the two phases, and the corresponding SAED pattern (inset of Figure 3f) contains diffraction spots from both phases, which can be indexed to B2 along the [111] zone axis and B19' along the [010] zone axis. This confirms that the martensitic transformation follows a specific orientation relationship, namely, $[111]_{\text{B2}} \parallel [010]_{\text{B19'}}$. The morphology of the B19' martensite is further highlighted in the dark-field image shown in Figure 3g, where the martensite appears as parallel lath-like variants extending over several hundred nanometers.

A higher-magnification TEM image (Figure 3h) reveals multiple intersecting martensitic variants. The boxed region marked “I” was selected for high-resolution analysis. The high-resolution TEM (HRTEM) image of the selected region is shown in Figure 3i. Well-defined lattice fringes are observed, and the measured interplanar spacing of approximately 0.459 nm corresponds to the (001) plane of the B19' phase. Fast Fourier transform (FFT) patterns obtained from regions A, B, and C can all be indexed to the B19' structure, confirming the crystallographic identity of the martensite and the internal consistency of lattice orientation within the observed variants. Notably, no deformation twins were observed in the analyzed region, suggesting that the B19' martensite is primarily accommodated by variant formation rather than twinning under the present conditions [33].

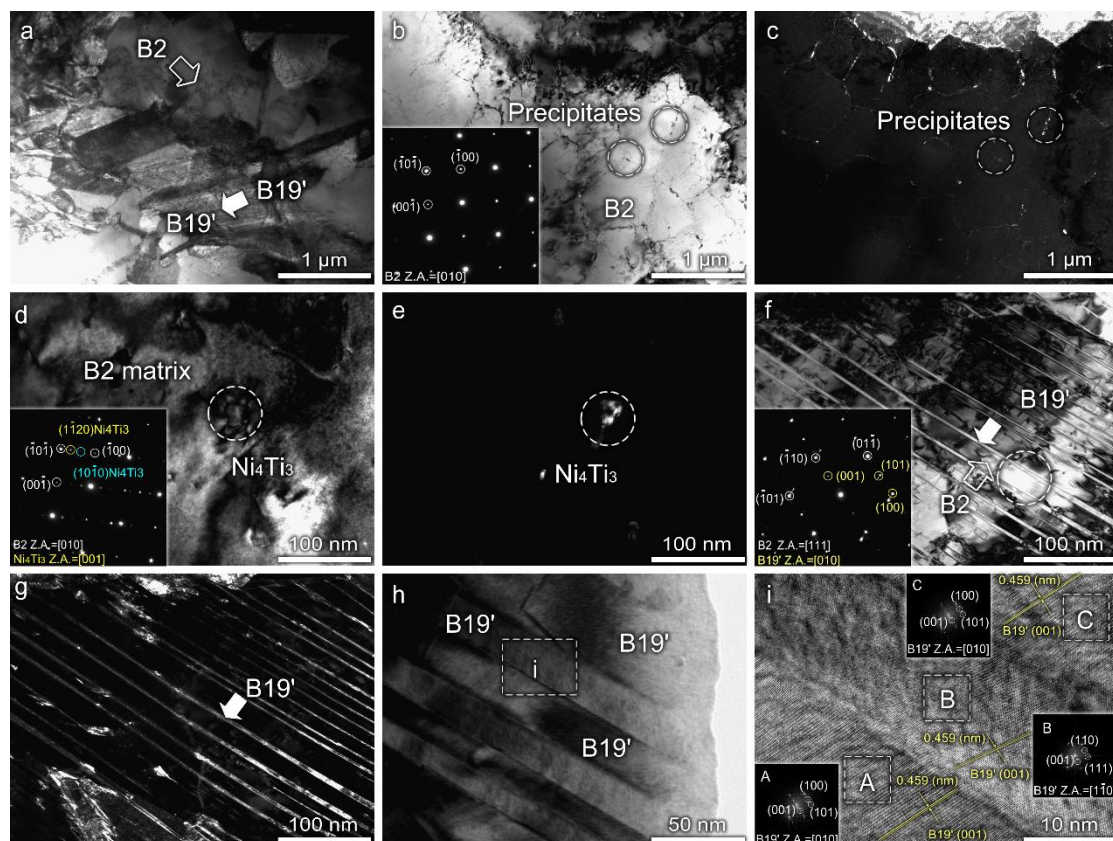


Figure 3. TEM characterization of the XY-plane microstructure in the LPBF-fabricated NiTi alloy: (a) bright-field (BF) image showing the overall microstructure; (b) enlarged BF image highlighting the morphology and spatial distribution of nanoscale precipitates; (c) corresponding dark-field (DF) image; (d) BF image showing a Ni_4Ti_3 precipitate embedded in the B2 matrix; (e) corresponding DF image; (f) high-magnification BF image showing the microstructural relationship between the B2 matrix and the B19' martensite; (g) corresponding DF image; (h) high-magnification view of the B19' martensite; and (i) HRTEM image of the region marked in (h).

Distinct from the XY plane, the XZ plane exhibits a more complex microstructure with a markedly higher density of martensite variants, which can be attributed to the steep thermal gradients and severe thermal stresses along the building direction during the LPBF process. Figure 4a presents a low-magnification bright-field TEM image of the XZ plane, revealing a complex microstructure consisting of a B2 matrix interspersed with plate-like B19' martensite variants. The B19' martensite exhibits a characteristic lamellar morphology and is densely distributed within the B2 matrix, indicating an enhanced degree of martensitic transformation compared with the XY plane (Figure 3a). This microstructure also displays pronounced lattice distortion and a higher apparent dislocation

density, reflecting the more severe thermal–mechanical history experienced along the building direction.

An enlarged bright-field TEM image of the B2 matrix is shown in Figure 4b. The corresponding selected-area electron diffraction (SAED) pattern (inset) can be indexed to the B2 phase along the [010] zone axis, confirming the retention of the parent austenitic structure at this scale. Nanoscale precipitates embedded within the B2 matrix are further revealed in Figure 4c. The SAED pattern obtained from the circled region contains additional diffraction spots that can be indexed to the Ni_4Ti_3 phase, viewed along the [001] zone axis, indicating the formation of coherent or semi-coherent Ni_4Ti_3 precipitates. This observation is consistent with the results obtained for the XY plane (Figure 3d–e), confirming that Ni_4Ti_3 precipitation occurs in both orientations. However, because TEM probes limited local regions, the present images cannot be used to establish a statistically meaningful difference in precipitate density between the XY and XZ planes.

Figure 4d shows the coexistence of the B2 matrix and B19' martensite at a finer length scale. The corresponding SAED pattern (inset) contains diffraction spots from both phases, indicating a specific crystallographic orientation relationship between the parent B2 phase and the B19' martensite. A bright-field image with enhanced contrast is shown in Figure 4e, where densely packed lamellar features are observed throughout the matrix. These lamellae are primarily associated with the B2 phase and are attributed to strain-induced contrast and lattice modulation arising from the martensitic transformation and the high residual stress state [34]. A high-resolution HRTEM image taken from the B2/B19' interfacial region is shown in Figure 4f. Well-defined lattice fringes corresponding to the $(001)_{\text{B19}'}$ planes, with an interplanar spacing of approximately 0.459 nm, are clearly resolved. Adjacent regions exhibit lattice fringes with a spacing of ~ 0.213 nm, which can be indexed to the $(0\bar{1}1)_{\text{B2}}$ planes. The FFT patterns obtained from regions A, B, and C further confirm the coexistence of B2 and B19' phases and indicate the presence of a semi-coherent B2/B19' interface.

The local coexistence of the B2 matrix and B19' martensite is further illustrated in Figure 4g, where diffraction spots from both phases are simultaneously observed in the corresponding SAED pattern. Figure 4h highlights well-developed B19' martensite plates containing parallel internal lamellae, indicative of an organized martensitic substructure. The boxed region marked “i” was selected for high-resolution analysis. The HRTEM image of this region (Figure 4i) reveals periodic lattice fringes with varying orientations. The measured angles between adjacent lamellae, ranging from approximately 58° to 62° , are consistent with the presence of multiple B19' martensite variants accommodated through internal twinning and variant interaction. Such variant-rich martensitic substructures are characteristic of NiTi alloys subjected to high residual stresses and complex thermal histories.

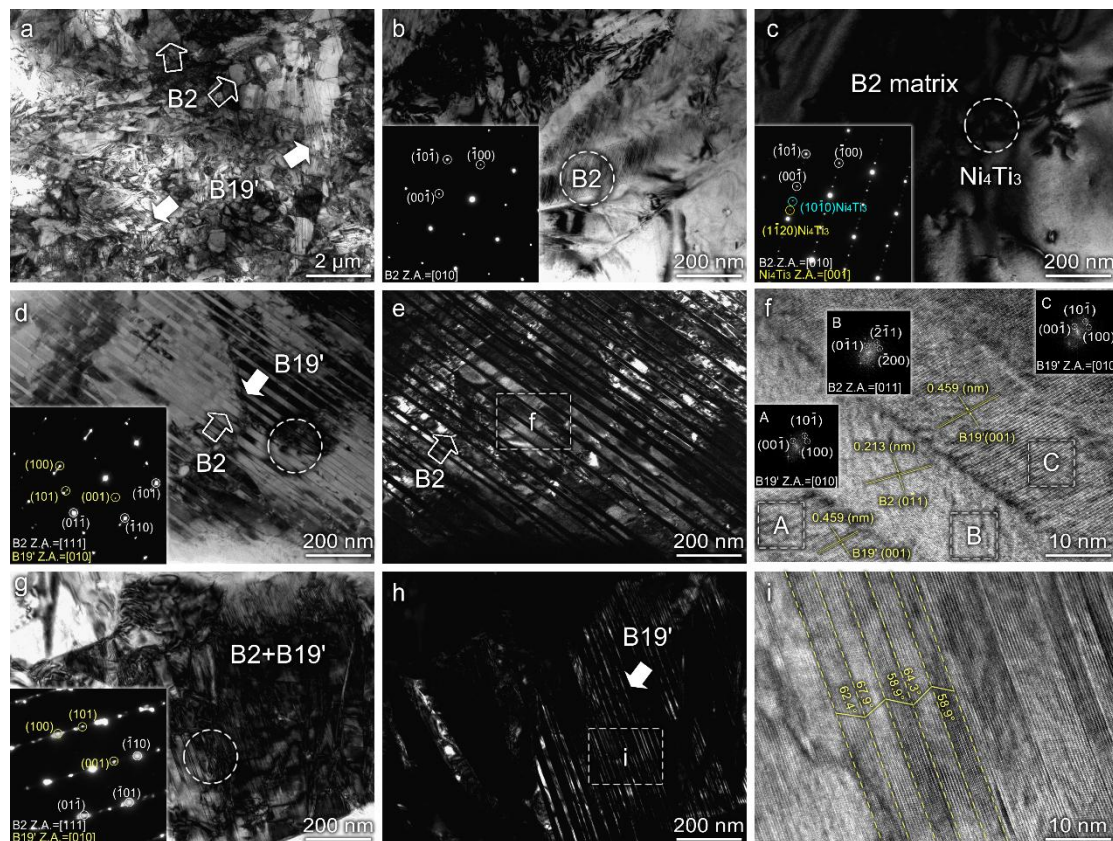


Figure 4. TEM characterization of the XZ-plane microstructure in the LPBF-fabricated NiTi alloy: (a) low-magnification bright-field (BF) image showing the overall microstructure; (b) BF image of the B2 matrix; (c) BF image showing a Ni_4Ti_3 precipitate embedded in the B2 matrix; (d) high-magnification BF image revealing the microstructural relationship between the B2 matrix and the B19' martensite; (e) DF image corresponding to (d); (f) HRTEM image taken from the rectangular region marked in (d); (g) another high-magnification BF image showing the coexistence of the B2 matrix and the B19' martensite; (h) DF image corresponding to (g); and (i) HRTEM image taken from the rectangular region marked in (h).

Compared with the XY plane, the XZ plane exhibits a markedly different microstructural feature. In the XY plane, the microstructure is dominated by a relatively stable B2 matrix containing dispersed Ni_4Ti_3 precipitates, while the B19' martensite appears only locally and shows limited spatial continuity. By contrast, the XZ plane shows a more spatially continuous distribution of plate-like B19' martensite in the examined regions, which is densely packed and extends over larger regions with well-developed lamellar substructures. The coexistence of B2 and B19' phases in the XZ plane is therefore more pronounced, accompanied by clearer crystallographic orientation relationships and extensive internal twinning within the B19' martensite. These differences indicate that the martensitic transformation is more advanced in the XZ plane, whereas in the XY plane the transformation is effectively restrained by the stability of the B2 matrix.

Ni_4Ti_3 precipitation may influence the surrounding NiTi matrix through both compositional redistribution and coherency strain. Because Ni_4Ti_3 is Ni-rich relative to the near-equiatomic matrix, its formation can locally deplete Ni from the adjacent B2 phase, modify the stability of B2 and B19', and generate elastic strain fields that may facilitate martensitic transformation [32]. These effects could partly contribute to local variations in the B2/B19' microstructure. Nevertheless, Ni_4Ti_3 precipitates were identified in both the XY and XZ planes, and their number density, size distribution, and volume fraction were

not quantified in the present study. Therefore, no orientation-dependent contribution of Ni_4Ti_3 precipitation is inferred from the current TEM observations.

3.3. Hardness

Figure 5 shows that the XZ plane exhibits a higher average hardness (271 HV) than the XY plane (244 HV). This result demonstrates a plane-dependent difference in the local indentation response of the LPBF-fabricated NiTi alloy. The microstructural characterization reveals several differences that may be relevant to this hardness variation. Semi-quantitative XRD analysis suggests a relatively larger B19' contribution on the XZ plane (Figure 1), while TEM observations show denser lamellar B19' variants and stronger local lattice-distortion and defect contrast in the examined XZ regions (Figure 4). Because B19' martensite generally has lower crystallographic symmetry and a more constrained deformation response than B2 austenite, the observed martensitic morphology is consistent with increased resistance to local indentation [23,35,36]. In addition, Ni_4Ti_3 precipitates were observed in both planes, but their number density and volume fraction cannot be quantitatively compared; therefore, no orientation-dependent strengthening contribution is assigned to these precipitates. Accordingly, the present results mainly establish a correlation between the higher hardness of the XZ plane and its denser lamellar B19' morphology and locally observed lattice-distortion contrast.

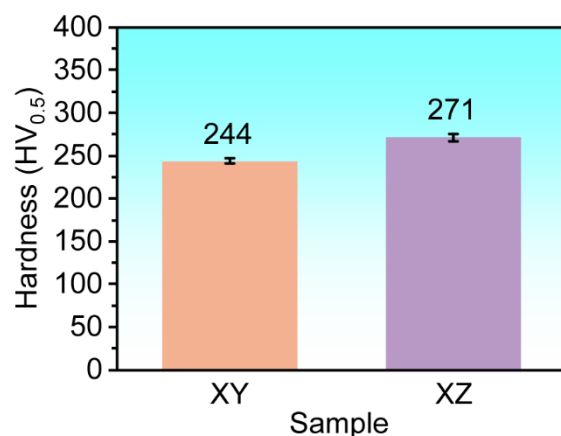


Figure 5. Vickers hardness values of the LPBF-fabricated NiTi alloy at the XY and XZ planes.

3.4. Electrochemical Response After OCP

After OCP stabilization, the spectra obtained from both orientations and at all investigated pH values exhibit one dominant depressed capacitive loop in the Nyquist plots and one broad relaxation region in the Bode phase-angle plots, as shown in Figure 6. The corresponding fitting parameters are summarized in Table 1. The Nyquist plots were fitted using an equivalent electrical circuit (EEC) model with an $R(QR)$ configuration (insets in Figure 6a,c), where R_s corresponds to the solution resistance, R_{ct} represents the charge transfer resistance at the alloy/electrolyte interface [37] and Q denotes a constant phase element (CPE) describing the non-ideal capacitive response of the alloy/passive-film/electrolyte interface [38]. Because only one relaxation process is spectrally resolved at this stage, the contributions from the passive film and the electrochemical double layer cannot be separated unambiguously and are therefore represented by a combined interfacial CPE. The R_s values remain nearly constant at approximately $20 \Omega \text{ cm}^2$, for all conditions, indicating stable electrolyte conductivity during the measurements. As shown in Figure 6, the diameter of the capacitive loops in the Nyquist plots decreases with decreasing pH for both planes, suggesting a gradual degradation of the passive films under acidic conditions. At pH 7, the R_{ct} of the XY plane ($109.1 \pm 7.1 \text{ k}\Omega \text{ cm}^2$) is approximately 32%

lower than that of the XZ plane ($143.9 \pm 9.6 \text{ k}\Omega \text{ cm}^2$), indicating inferior corrosion resistance. This trend persists across all pH values, with the XZ plane consistently exhibiting higher R_{ct} values than the XY plane.

Notably, when the pH decreases from 7 to 3, the R_{ct} of the XY plane drops by about 50.0% (from 109.1 to $54.6 \pm 7.4 \text{ k}\Omega \text{ cm}^2$), whereas the XZ plane shows a comparatively smaller reduction of 38.4%, demonstrating a higher stability of the passive film on the XZ plane in acidic environments. The CPE exponent n exceeds 0.9 under all conditions (Table 1), indicating predominantly capacitive behavior and relatively limited interfacial dispersion. However, the CPE exponent alone does not provide direct information on the chemical composition or physical compactness of the passive film [39].

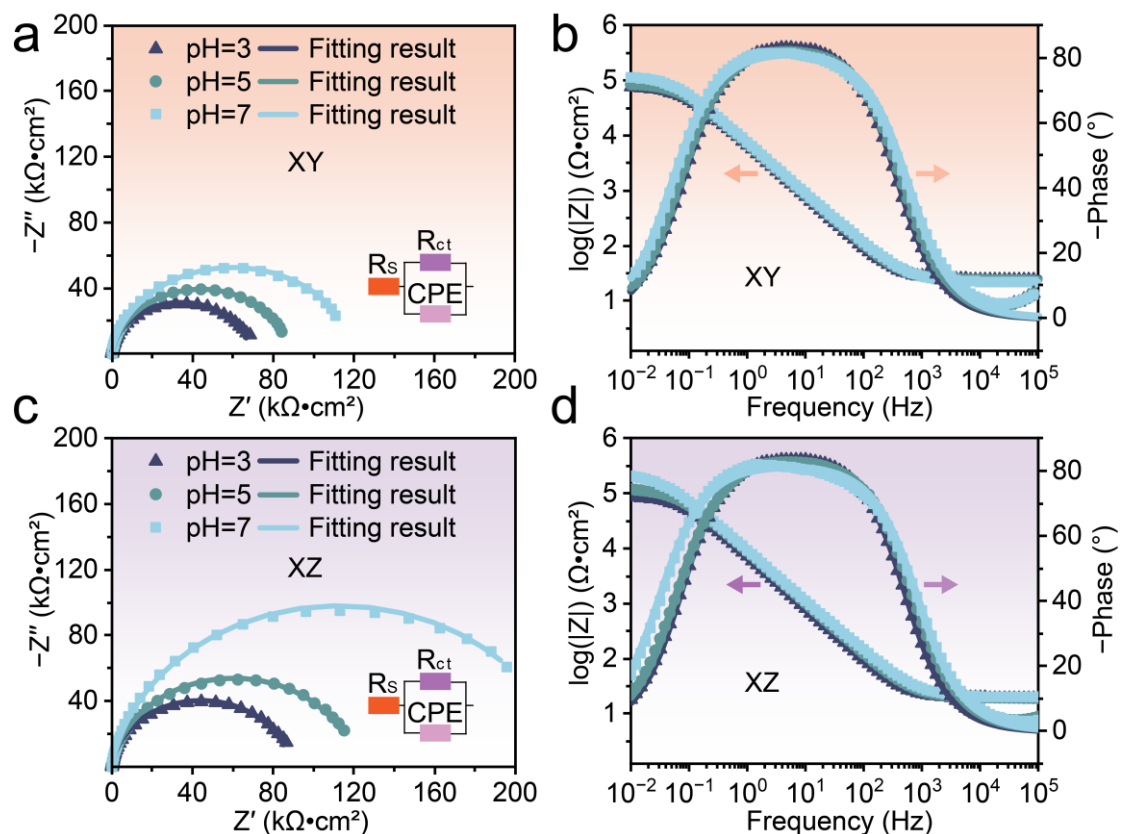


Figure 6. Electrochemical impedance spectra of the LPBF-fabricated NiTi alloy after open-circuit potential stabilization in Hank's solution at pH values of 3, 5, and 7: (a) and (b) Nyquist and Bode plots for the XY plane and (c) and (d) Nyquist and Bode plots for the XZ plane.

Table 1. Fitted electrochemical impedance spectroscopy parameters corresponding to Figure 6, where R_s is solution resistance, R_{ct} is the charge transfer resistance, CPE denotes the constant phase element, n is the CPE exponent, and χ^2 is the goodness-of-fit parameter.

Plane	pH	$R_s (\Omega \text{ cm}^2)$	$\text{CPE} \times 10^{-5} (\Omega \text{ S}^n \text{ cm}^2)$	n	$R_{ct} (\text{k}\Omega \text{ cm}^2)$	$\chi^2 \times 10^4$
XY	7	22.8 ± 1.1	2.290 ± 0.17	0.91 ± 0.01	109.1 ± 7.1	3.23
	5	24.1 ± 0.9	2.435 ± 0.19	0.93 ± 0.02	84.3 ± 6.6	2.01
	3	23.8 ± 1.2	2.890 ± 0.21	0.94 ± 0.03	54.6 ± 7.4	8.63
XZ	7	20.5 ± 1.5	1.980 ± 0.18	0.91 ± 0.04	143.9 ± 9.6	7.54
	5	19.5 ± 1.3	1.940 ± 0.22	0.93 ± 0.05	106.6 ± 8.7	6.14
	3	19.2 ± 0.9	2.470 ± 0.21	0.94 ± 0.02	88.7 ± 5.6	8.15

Figure 7 presents the Tafel polarization curves of the XY and XZ planes obtained after the OCP stabilization. Two clear trends can be identified. First, under identical pH conditions, the XY plane consistently exhibits a more positive corrosion potential (E_{corr}) than the XZ plane. Second, for both planes, decreasing the pH leads to a positive shift of E_{corr} . However, E_{corr} should be interpreted as a mixed potential rather than as a direct measure of corrosion resistance [40]. According to mixed-potential theory, E_{corr} is established at the potential where the total anodic oxidation current is balanced by the total cathodic reduction current [41]. Its position therefore depends on the relative kinetics of both partial reactions and may shift in the positive or negative direction without a corresponding decrease or increase in the net corrosion rate.

The more positive E_{corr} of the XY plane may partly reflect orientation-dependent differences in the anodic dissolution and cathodic reduction kinetics associated with its phase constitution and surface state. The B2-rich microstructure may contribute to a more positive mixed potential because B2 and B19' exhibit different local electrochemical activities [42]. Consequently, NiTi alloys with a higher fraction of the B2 phase generally exhibit higher E_{corr} values under identical corrosive environments. Nevertheless, the present polarization data do not separate the individual anodic and cathodic contributions, and the E_{corr} difference should therefore not be interpreted solely as evidence that the XY plane is more corrosion resistant. Similarly, the positive shift of E_{corr} with decreasing pH reflects a change in the balance between the anodic and cathodic reactions, potentially influenced by proton concentration and lactic-acid-related adsorption, rather than an improvement in corrosion resistance [43].

At pH 7, the E_{corr} of the XY plane is -0.381 ± 0.021 V, which is nobler than that of the XZ plane (-0.415 ± 0.027 V). Although the XY plane shows the more noble mixed potential, this result must be considered together with the corrosion current density and impedance response. In fact, the simultaneous positive shift of E_{corr} and increase in I_{corr} with decreasing pH further demonstrates that a more positive corrosion potential does not necessarily correspond to a lower corrosion rate.

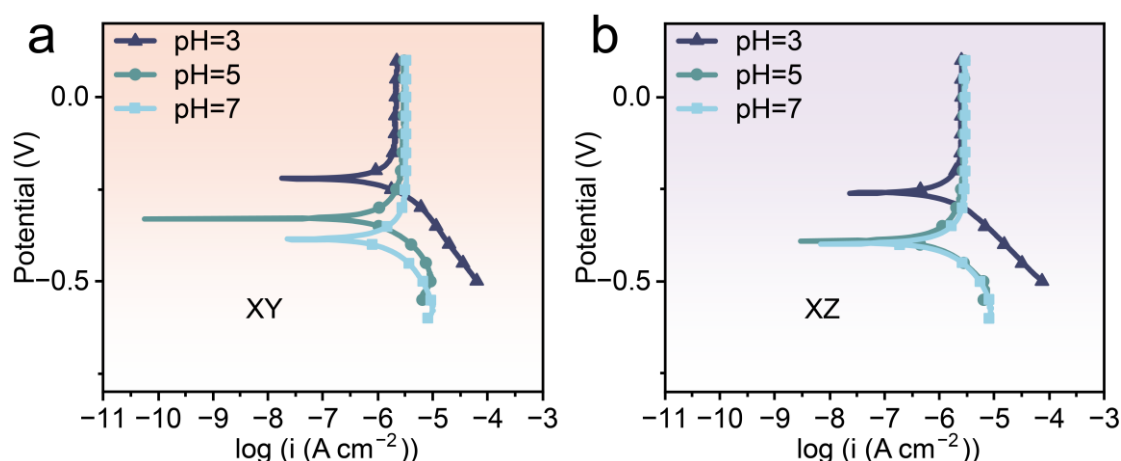


Figure 7. Tafel polarization curves of the LPBF-fabricated NiTi alloy after OCP tests in Hank's solution at pH = 3, 5, and 7: (a) XY and (b) XZ planes.

The fitted corrosion current densities (I_{corr}) are listed in Table 2. At pH 7, the XY plane exhibits a significantly higher I_{corr} ($0.599 \pm 0.055 \mu\text{A cm}^{-2}$) than the XZ plane ($0.231 \pm 0.077 \mu\text{A cm}^{-2}$), indicating inferior corrosion resistance. Because I_{corr} reflects the net rate of the coupled anodic and cathodic reactions at E_{corr} , it provides a kinetic measure of the corrosion rate [44]. The higher R_{ct} obtained for the XZ plane from EIS is consistent with its lower I_{corr} , indicating slower interfacial charge-transfer kinetics (Table 1).

With decreasing pH, the increased H^+ concentration accelerates the chemical dissolution of the passive film, resulting in a progressive increase in I_{corr} for both planes. Even at pH 3, the XY plane still shows a higher I_{corr} ($0.732 \pm 0.156 \mu A cm^{-2}$) than the XZ plane ($0.460 \pm 0.123 \mu A cm^{-2}$). This increase indicates accelerated corrosion kinetics under acidic conditions, despite the simultaneous positive shift in E_{corr} . Therefore, the apparently different trends of E_{corr} and corrosion resistance are not contradictory: E_{corr} reflects the mixed-potential position determined by the balance of partial reactions, whereas I_{corr} and R_{ct} characterize the rate of the corrosion process. On this kinetic basis, the XZ plane exhibits better overall corrosion resistance across the investigated pH range.

Table 2. Fitted electrochemical parameters obtained from Tafel curves in Figure 7, where I_{corr} denotes corrosion current density and E_{corr} denotes corrosion potential.

Sample	pH	I_{corr} ($\mu A cm^{-2}$)	E_{corr} (V)
XY	7	0.599 ± 0.055	-0.381 ± 0.021
	5	0.646 ± 0.092	-0.331 ± 0.022
	3	0.732 ± 0.156	-0.220 ± 0.011
XZ	7	0.231 ± 0.077	-0.415 ± 0.027
	5	0.318 ± 0.069	-0.398 ± 0.025
	3	0.460 ± 0.123	-0.263 ± 0.015

3.5. Electrochemical Response After Immersion Within 72 h

To evaluate the long-term electrochemical response of the XY and XZ planes, immersion tests were conducted in Hank's solution at pH 7 and pH 3 for 24, 48, and 72 h, as shown in Figure 8. After immersion in Hank's solution at pH 7, the EIS spectra become more complex than those obtained immediately after OCP stabilization. Broadening or partial separation of the phase-angle response indicates the presence of two overlapping relaxation processes. Accordingly, an R(QR(QR)) EEC was employed to fit the EIS data (insets in Figure 8a,b) because it provided a better description of both the high- and low-frequency impedance responses than the single-time-constant model. In this EEC model, R_s corresponds to the solution resistance. The high-frequency branch (R_f/CPE), is assigned phenomenologically to the electrochemical response associated with the surface film and any adsorbed or deposited species. The low-frequency branch, (R_{ct}/CPE), represents the non-ideal double-layer response and charge-transfer process at the underlying electrochemical interface. The occurrence of two-time constants demonstrates the presence of two distinguishable electrochemical relaxation processes within the experimental frequency range. The element R_f represents the resistive contribution associated with the high-frequency surface-layer response. Because this response may include contributions from the passive oxide, adsorbed species, surface deposits, and local film heterogeneity, R_f should not be interpreted as a direct measurement of film thickness, chemical stability, or dissolution rate. The element R_{ct} provides a more direct indication of the resistance to interfacial charge-transfer reactions. Throughout all immersion durations, the Nyquist plots of the XZ plane consistently exhibit larger capacitive loop diameters than those of the XY plane, in agreement with the short-term EIS results. The corresponding fitted parameters are summarized in Table 3.

Compared with the initial EIS results obtained after OCP tests (Table 1), the R_{ct} values of both planes increase markedly after immersion, indicating the enhanced protectiveness of the passive film with time. The continuous increase in R_{ct} with immersion duration is consistent with the time-dependent evolution and stabilization of the surface film. Nevertheless, EIS does not independently quantify the physical thickness or chemical composition of the oxide layer. The formation of passive films on NiTi alloys is a dy-

dynamic process governed by the competition between film growth and dissolution, eventually reaching a quasi-steady equilibrium state [45]. During immersion, dissolved metal ions tend to precipitate as hydroxide species near the surface, which impede charge transport and are therefore represented by an additional R_f /CPE element in the EEC.

Throughout all immersion durations, the XZ plane consistently exhibits higher R_{ct} values and lower R_f values than the XY plane. These trends are not contradictory because the two parameters describe different electrochemical relaxation processes. R_f characterizes the effective high-frequency response of the surface-associated layer, whereas R_{ct} reflects the resistance to the low-frequency interfacial charge-transfer reaction that more directly controls the corrosion kinetics. After 72 h of immersion, the R_{ct} of the XZ plane ($648 \pm 48 \text{ k}\Omega \text{ cm}^2$) is approximately 31% higher than that of the XY plane ($495 \pm 54 \text{ k}\Omega \text{ cm}^2$), whereas the R_f value of the XZ plane ($457 \pm 21 \text{ }\Omega \text{ cm}^2$) is about 57% lower than that of the XY plane ($1071 \pm 59 \text{ }\Omega \text{ cm}^2$). These results demonstrate that the XZ surface maintains a higher long-term electrochemical barrier response in Hank's solution.

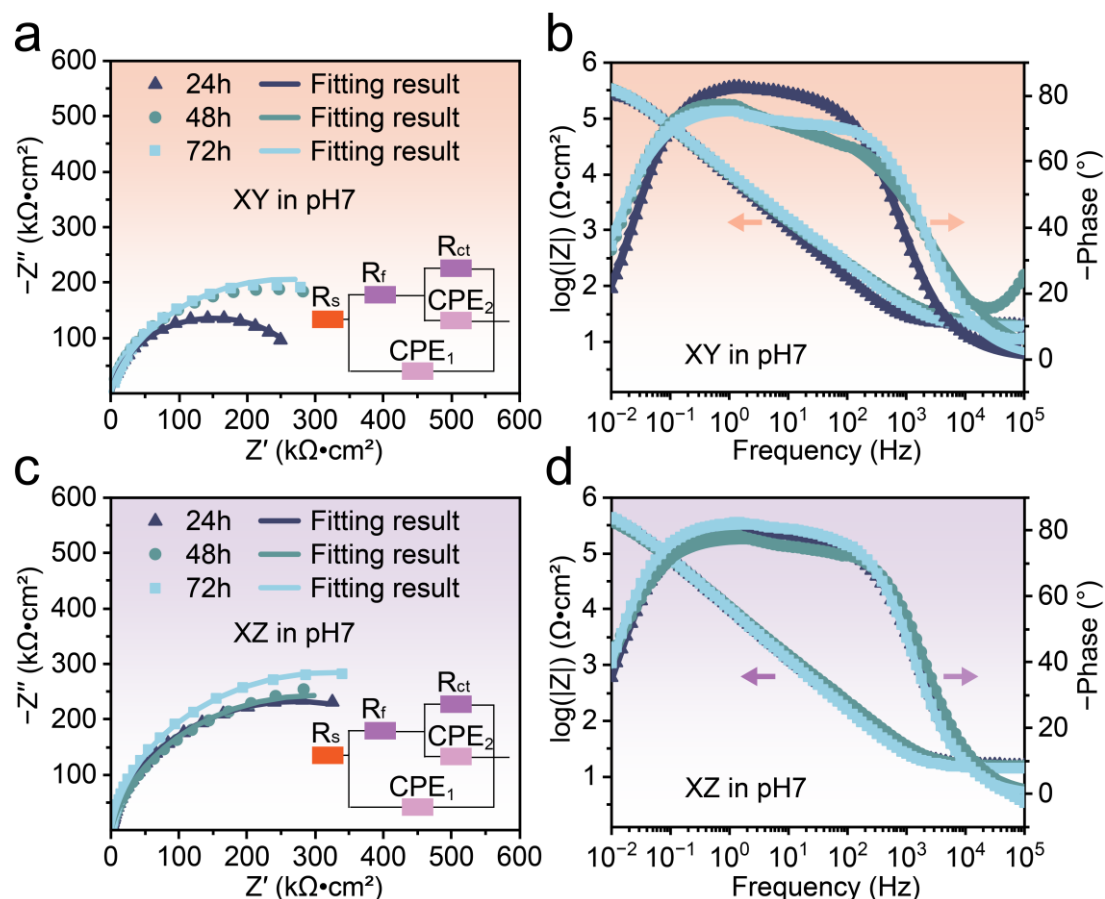


Figure 8. Electrochemical impedance spectra of the LPBF-fabricated NiTi alloy after immersion for 24, 48, and 72 h in Hank's solution at pH = 7: (a) and (b) Nyquist and Bode plots of the XY plane, and (c) and (d) Nyquist and Bode plots of the XZ plane.

Table 3. Fitted electrochemical impedance spectroscopy parameters corresponding to Figure 8, where R_s is solution resistance, R_f is the effective resistance associated with the high-frequency surface-layer response, R_{ct} is the charge transfer resistance, CPE denotes the constant phase element, n is the CPE exponent, and χ^2 is the goodness-of-fit parameter.

Sample	Duration	R_s ($\Omega \text{ cm}^2$)	$\text{CPE}_1 \times 10^{-5}$ ($\Omega \text{ S}^n \text{ cm}^2$)	n_1	R_f ($\Omega \text{ cm}^2$)	$\text{CPE}_2 \times 10^{-5}$ ($\Omega \text{ S}^n \text{ cm}^2$)	n_2	R_{ct} ($\text{k}\Omega \text{ cm}^2$)	$\chi^2 \times 10^4$
XY	24 h	19.5 ± 2.0	0.874 ± 0.11	0.64 ± 0.02	264 ± 25	1.93 ± 0.11	0.94 ± 0.01	300 ± 39	1.87
	48 h	17.6 ± 1.1	0.219 ± 0.21	0.59 ± 0.01	496 ± 33	2.02 ± 0.16	0.90 ± 0.02	446 ± 43	5.31
	72 h	18.5 ± 1.9	0.127 ± 0.18	0.75 ± 0.02	1071 ± 59	1.95 ± 0.15	0.87 ± 0.04	495 ± 54	7.22
XZ	24 h	15.8 ± 1.7	0.366 ± 0.19	0.76 ± 0.03	149 ± 13	1.78 ± 0.13	0.90 ± 0.02	544 ± 89	7.53
	48 h	15.3 ± 2.1	0.937 ± 0.15	0.94 ± 0.02	245 ± 11	1.86 ± 0.19	0.87 ± 0.06	598 ± 67	7.95
	72 h	14.3 ± 1.5	0.592 ± 0.13	0.77 ± 0.04	457 ± 21	1.85 ± 0.21	0.92 ± 0.05	648 ± 48	2.65

In certain clinical scenarios, local pH levels may decrease owing to postoperative inflammation or bacterial infection [23]. Therefore, it is crucial to evaluate the long-term stability of passive films under acidic conditions to ensure the reliability of LPBF-fabricated NiTi alloys during service. As shown in Figure 9, the EIS spectra obtained after immersion in Hank's solution at pH 3 exhibit a single capacitive loop throughout the entire immersion period. The (R(QR)) circuit was therefore selected as the simplest model that adequately reproduces both the Nyquist and Bode responses. Under these acidic conditions, any surface-film-related and charge-transfer responses are not sufficiently separated within the investigated frequency range to justify the use of two independent time constants. The use of a single-time-constant model should not be interpreted as direct evidence for the formation of a physically single-layer passive film. Rather, it indicates that only one effective interfacial relaxation process can be resolved electrochemically under the present measurement conditions. The corresponding fitted parameters are summarized in Table 4. Under these acidic conditions, the passive films formed on the XY plane consistently exhibit lower R_{ct} values than those on the XZ plane, indicating that the reduction in pH does not alter the intrinsic corrosion susceptibility trend between the two orientations. After 72 h of immersion in pH 3 Hank's solution, the R_{ct} of the XZ plane ($241 \pm 34 \text{ k}\Omega \text{ cm}^2$) remains nearly twice that of the XY plane ($126 \pm 21 \text{ k}\Omega \text{ cm}^2$). Notably, compared with its value at pH 7 ($648 \pm 48 \text{ k}\Omega \text{ cm}^2$), the R_{ct} of the XZ plane decreases by 62.8%, whereas the R_{ct} of the XY plane at pH 3 is comparable to that obtained after the OCP test. These results demonstrate that acidic environments significantly inhibit passive film growth; nevertheless, the XZ plane retains a relatively high charge transfer resistance, thereby providing more effective protection against alloy corrosion [46].

Table 4. Fitted electrochemical impedance spectroscopy parameters corresponding to Figure 9, where R_s is solution resistance, R_{ct} is the charge transfer resistance, CPE denotes the constant phase element, and χ^2 is the goodness-of-fit parameter.

Sample	Duration	R_s ($\Omega \text{ cm}^2$)	$\text{CPE} \times 10^{-5}$ ($\Omega \text{ S}^n \text{ cm}^2$)	n	R_{ct} ($\text{k}\Omega \text{ cm}^2$)	$\chi^2 \times 10^4$
XY	24 h	21.6 ± 1.7	3.01 ± 0.13	0.95 ± 0.02	76 ± 11	6.99
	48 h	21.6 ± 1.8	3.19 ± 0.15	0.95 ± 0.03	97 ± 13	4.80
	72 h	20.1 ± 2.0	2.82 ± 0.17	0.94 ± 0.01	126 ± 21	2.07
XZ	24 h	18.5 ± 1.9	2.04 ± 0.11	0.93 ± 0.03	158 ± 17	6.77
	48 h	19.4 ± 2.1	2.35 ± 0.14	0.94 ± 0.01	197 ± 19	4.46
	72 h	16.6 ± 2.3	2.34 ± 0.16	0.93 ± 0.03	241 ± 34	8.85

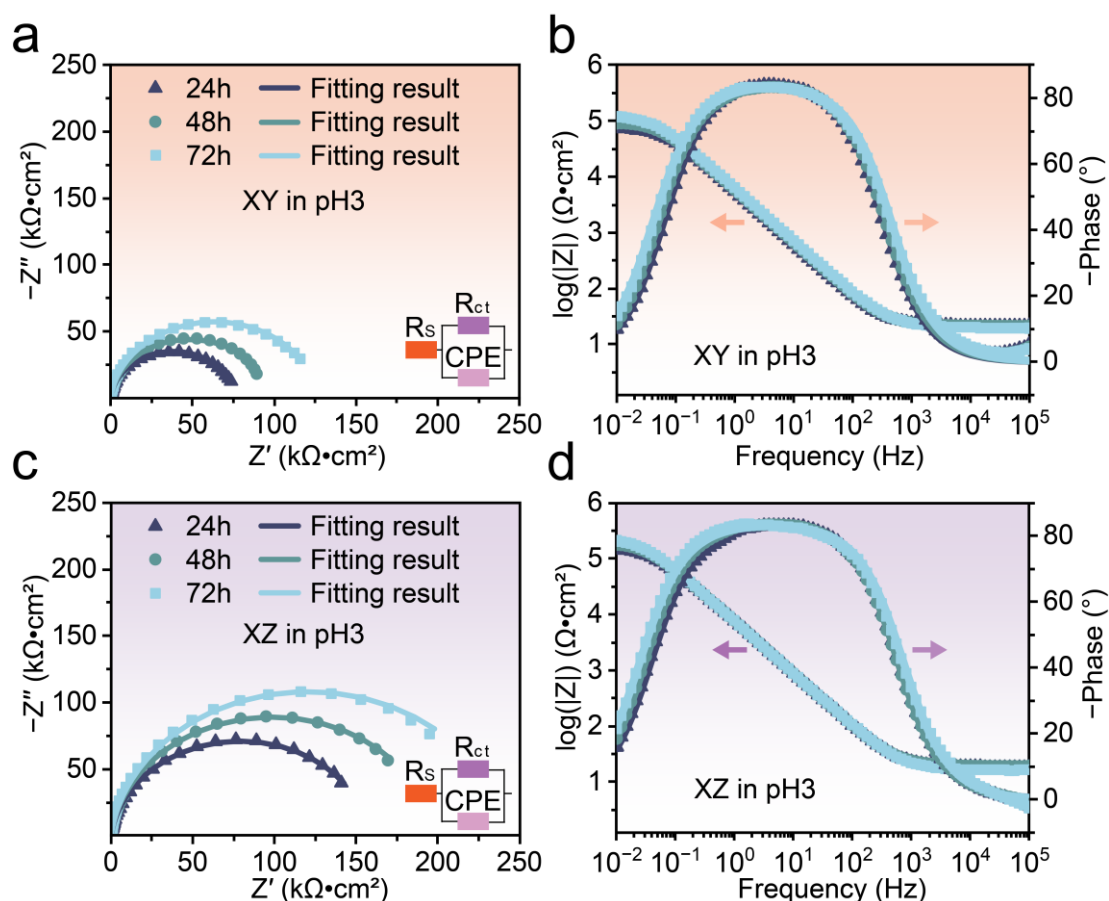


Figure 9. Electrochemical impedance spectra of the LPBF-fabricated NiTi alloy after immersion for 24, 48, and 72 h in Hank's solution at pH = 3: (a) and (b) Nyquist and Bode plots of the XY plane, and (c) and (d) Nyquist and Bode plots of the XZ plane.

3.6. Mott–Schottky Tests

To further elucidate the point defect chemistry and electronic structure of the passive films, Mott–Schottky (M–S) measurements were conducted. As illustrated in Figure 10, the C^{-2} vs. E plots for both the XY and XZ planes exhibit positive linear slopes within the potential range of -0.6 to 0.0 V, indicating that the surface films exhibit an n-type semiconducting response. In passive films formed on Ti-containing alloys, such behavior is commonly associated with electrically active donor-type defects. Oxygen vacancies are frequently invoked as one possible donor species within point-defect descriptions of Ti-containing oxides [47]. However, M–S analysis cannot independently identify the chemical composition of the film or the specific atomic defects responsible for the measured electronic response.

The space-charge capacitance is influenced by the electronic defect response and the width of the space-charge region. As illustrated in Figure 10a,b, a moderate upward shift in the C^{-2} curves is observed for both planes with increasing immersion time from 24 to 72 h at pH 7. Within the assumptions of the Mott–Schottky model, this shift corresponds to a decrease in capacitance and may reflect changes in the space-charge width and/or the electrochemically active film thickness [48]. However, the protective performance of a passive film is governed not only by its thickness but also by its point defect density. At a given potential, a higher capacitance generally implies a higher concentration of charge carriers (i.e., oxygen vacancies in n-type TiO_2), which facilitates ionic transport through the film and undermines its long-term stability [49].

A pronounced divergence in electrochemical behavior emerges when the environment is acidified to pH 3 (Figure 10c,d). For the XY plane, the C^{-2} plots exhibit not only a pronounced upward shift but also a substantial reduction in the slope of the linear region with prolonged immersion, corresponding to an increase in the apparent donor density calculated under the assumptions of the M–S model (Figure 10c). This result indicates a larger population of electrically active donor-type defects in the surface film. In contrast, the XZ plane maintains remarkable stability even under acidic conditions (Figure 10d). The slopes of its C^{-2} plots remain relatively constant and are consistently steeper than those of the XY plane throughout the 72 h immersion period. Accordingly, the XZ plane exhibits a lower apparent donor density. This behavior is consistent with a comparatively lower defect-mediated electronic response and reduced charge transport through the surface film.

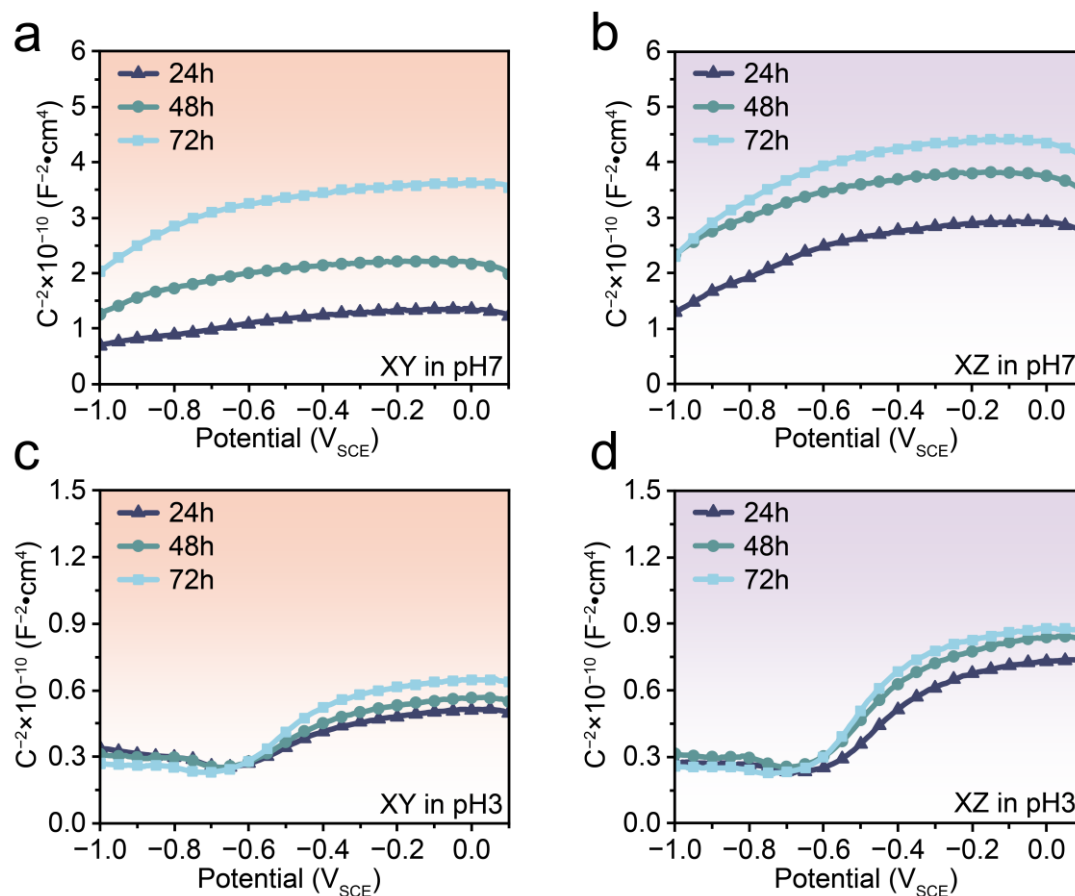


Figure 10. Mott–Schottky plots of the LPBF-fabricated NiTi alloy after immersion for 24, 48, and 72 h in Hank’s solutions at pH 7 and 3: (a) XY plane at pH 7, (b) XZ plane at pH 7, (c) XY plane at pH 3, and (d) XZ plane at pH 3, illustrating the space-charge capacitance behavior of the passive films.

To provide a quantitative assessment of the defect chemistry within the passive films, the donor density (N_D) was calculated from the slopes of the linear regions in the Mott–Schottky plots (Figure 10) according to the following relation [50]:

$$N_D = \frac{2}{\epsilon \epsilon_0 e A^2} \left[\frac{1}{d(C^{-2})/dE} \right] \quad (1)$$

where e is the elementary charge, ϵ_0 is the vacuum permittivity, ϵ is the relative dielectric constant of the passive film (assumed to be 60 for TiO₂-based films), and A is the exposed surface area. The calculated N_D values for both planes under various immersion conditions are summarized in Figure 11.

Under neutral conditions (pH 7), both the XY and XZ planes exhibit relatively low N_D values throughout the 72 h immersion period (Figure 11a). After 24 h of immersion, the fluctuations in N_D become negligible, indicating that the passive films progressively reach a state of dynamic equilibrium. This observation is in good agreement with the EIS results discussed previously (Figure 8), which also suggested the formation of a stable interfacial structure after the initial 24 h. At 72 h, the N_D values of the XY plane ($5.77 \times 10^{29} \text{ cm}^{-3}$) remain higher than those of the XZ plane ($4.41 \times 10^{29} \text{ cm}^{-3}$). This difference establishes an orientation-dependent variation in the M–S response.

Under acidic conditions (pH 3), the N_D values of both planes increase markedly with prolonged immersion. According to the point defect model (PDM), Ti atoms at the alloy/film interface are oxidized and undergo stepwise valence transitions from Ti^{2+} to Ti^{4+} as they migrate toward the film/solution interface [50]:



Within the PDM, the incorporation or migration of lower-valence metal species in Ti-containing oxides may require charge compensation by donor-type defects, which are frequently represented as oxygen vacancies [50,51]. Equations (2)–(4) are therefore used here as a conceptual framework for interpreting the M–S trends. Accordingly, the increase in apparent donor density under acidic conditions is interpreted as evidence of a more defect-rich electronic response rather than as direct proof of oxygen-vacancy accumulation or selective dissolution of a specific oxide layer.

Specifically, the N_D of the XY plane reaches a maximum value of $19.45 \times 10^{29} \text{ cm}^{-3}$ after 24 h of immersion at pH 3. Such a high apparent defect density is consistent with enhanced defect-mediated transport of aggressive species (e.g., Cl^-) through the surface film, thereby contributing to accelerated substrate oxidation and film degradation. In contrast, the XZ plane maintains considerably lower and more stable N_D values throughout immersion at pH 3, decreasing from ($10.03 \times 10^{29} \text{ cm}^{-3}$) at 24 h to ($7.38 \times 10^{29} \text{ cm}^{-3}$) at 72 h. Under the assumptions of the M–S model, these values indicate a lower concentration of electrically active donor defects than on the XY plane [52]. These values are consistent with a lower concentration of electrically active donor-type defects and reduced defect-mediated transport.

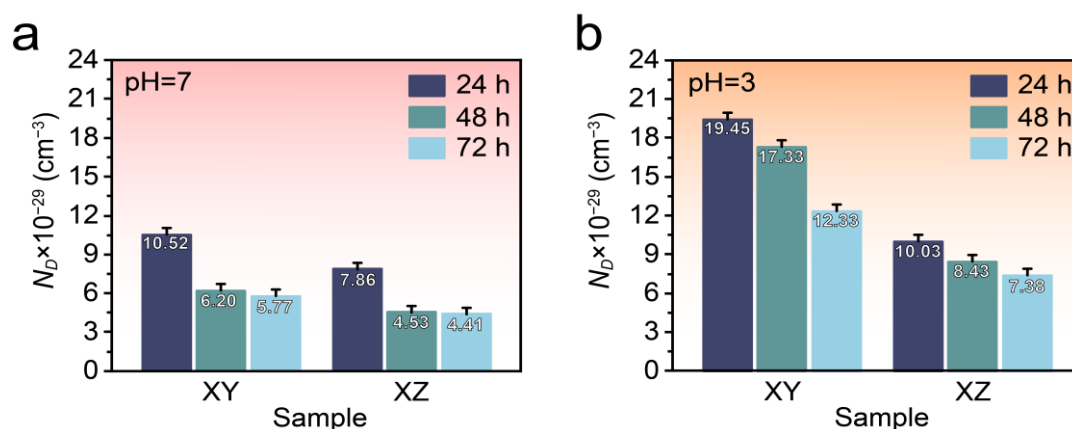


Figure 11. Donor density (N_D) of passive films formed on the LPBF-fabricated NiTi alloy after immersion for 24, 48, and 72 h in Hank's solutions at (a) pH 7 and (b) pH 3, comparing the evolution of defect density on the XY and XZ planes.

4. Discussion

4.1. Integrated Interpretation of the Orientation-Dependent Responses

The results collectively demonstrate that the XY and XZ planes exhibit correlated but distinct microstructural, indentation, and electrochemical responses. The XY plane is characterized mainly by polygonal B2 grains and a relatively limited spatial distribution of B19' martensite, whereas the XZ plane contains elongated epitaxial B2 grains together with a denser and more spatially continuous lamellar B19' morphology. Semi-quantitative XRD further suggests a relatively larger B19' contribution on the XZ plane. These observations are consistent with the directional thermal gradients and repeated thermal cycles associated with LPBF processing.

The average hardness of the XZ plane is approximately 11.1% higher than that of the XY plane. However, the simultaneous occurrence of a denser B19' morphology and higher hardness should be interpreted as a correlation rather than as evidence of a single dominant strengthening mechanism. Texture, residual stress, crystallographic orientation, local defect structure, and indentation direction were not independently separated in the present work. Similarly, the occurrence of higher hardness and better corrosion resistance on the XZ plane does not imply that hardness directly controls corrosion behavior. To integrate the electrochemical results quantitatively, the anisotropy ratio was defined as the value measured on the XZ plane divided by that measured on the XY plane. For hardness and R_{ct} , ratios greater than unity indicate higher values on the XZ plane. For I_{corr} and apparent donor density, ratios lower than unity indicate lower values on the XZ plane. The derived ratios are summarized in Table 5.

Table 5. Quantitative summary of the plane-dependent hardness and electrochemical responses obtained in the present work. The anisotropy ratio is defined as the ratio of the value in the XZ plane to that in the XY plane.

Response Parameter	Condition	XY Plane	XZ Plane	Anisotropy Ratio
Vickers hardness	As fabricated	244 HV	271 HV	1.11
R_{ct} after OCP	pH 7	109.1 k Ω cm ²	143.9 k Ω cm ²	1.32
R_{ct} after OCP	pH 5	84.3 k Ω cm ²	106.6 k Ω cm ²	1.26
R_{ct} after OCP	pH 3	54.6 k Ω cm ²	88.7 k Ω cm ²	1.62
I_{corr} after OCP	pH 7	0.599 μ A cm ⁻²	0.231 μ A cm ⁻²	0.39
I_{corr} after OCP	pH 5	0.646 μ A cm ⁻²	0.318 μ A cm ⁻²	0.49
I_{corr} after OCP	pH 3	0.732 μ A cm ⁻²	0.460 μ A cm ⁻²	0.63
R_{ct} after immersion	pH 7, 24 h	300 k Ω cm ²	544 k Ω cm ²	1.81
R_{ct} after immersion	pH 7, 48 h	446 k Ω cm ²	598 k Ω cm ²	1.34
R_{ct} after immersion	pH 7, 72 h	495 k Ω cm ²	648 k Ω cm ²	1.31
R_{ct} after immersion	pH 3, 24 h	76 k Ω cm ²	158 k Ω cm ²	2.08
R_{ct} after immersion	pH 3, 48 h	97 k Ω cm ²	197 k Ω cm ²	2.03
R_{ct} after immersion	pH 3, 72 h	126 k Ω cm ²	241 k Ω cm ²	1.91
Apparent donor density	pH 7, 72 h	5.77×10^{29} cm ⁻³	4.41×10^{29} cm ⁻³	0.76
Apparent donor density	pH 3, 72 h	12.33×10^{29} cm ⁻³	7.38×10^{29} cm ⁻³	0.60

At the initial electrochemical stage, the XZ plane exhibits higher R_{ct} values at all investigated pH levels. The ratios of R_{ct} values of the XY and XZ planes are 1.32, 1.26, and 1.62 at pH 7, 5, and 3, respectively. The corresponding XZ/XY ratios of I_{corr} are 0.39, 0.49, and 0.63, respectively, indicating consistently lower corrosion current densities on

the XZ plane. Thus, although acidification accelerates corrosion on both planes, the XZ plane retains slower overall corrosion kinetics throughout the investigated pH range. The immersion results further confirm the persistence of the electrochemical anisotropy. At pH 7, the ratio of R_{ct} values of the XY and XZ planes decreases from 1.81 after 24 h to 1.31 after 72 h. This reduction indicates that the electrochemical response of the XY plane improves substantially during immersion, although its R_{ct} remains lower than that of the XZ plane. Under the more aggressive pH 3 condition, the corresponding ratios remain between 1.91 and 2.08 throughout the 72 h period, demonstrating a more persistent orientation-dependent difference under acidic conditions. The lower apparent donor density of the XZ plane after prolonged immersion is consistent with this higher charge-transfer resistance, although Mott–Schottky analysis does not directly identify the chemical composition or atomic defect species within the passive film.

4.2. Mechanistic Implications and Limitations

The orientation-dependent grain morphology observed in the present work is consistent with previous studies of LPBF-fabricated NiTi. Liu et al. [24] showed that changes in processing conditions modify the passive-film characteristics and corrosion resistance of LPBF NiTi. Chmielewska et al. [25] found that the fabrication route influences passive-layer protectiveness in phosphate-buffered saline. Perumal et al. [27] further demonstrated that both volume energy density and observation plane influence the corrosion response of LPBF-fabricated NiTi. In this work, both XY and XZ planes have a mixed B2/B19' microstructure, but have different fractions. From a phase perspective, the B2 austenite and B19' martensite exhibit intrinsically distinctive corrosion behavior [42]. Chen et al. [26] reported that the B2 phase shows a more noble potential (−222 to −204 mV) compared with the B19' phase (−270 to −230 mV). Such a potential difference may generate local electrochemical heterogeneity near B2/B19' interfacial regions and thereby influence the spatial distribution of the initial oxidation and passivation reactions. However, an increased interfacial density is not intrinsically beneficial to corrosion resistance [53]. The lattice distortion, chemical heterogeneity, and local potential gradients associated with such interfaces may provide preferential pathways for ionic transport and localized dissolution or may establish micro-galvanic coupling between the adjacent phases [54]. Conversely, the same high-energy interfacial regions may also facilitate initial oxidation and provide abundant sites for passive-film nucleation [23]. The electrochemical role of B2/B19' interfaces should therefore be understood as a competition between interface-assisted passivation and interface-related degradation.

In the present work, semi-quantitative XRD analysis and TEM observations indicate a relatively greater contribution of lamellar B19' and more extensive B2/B19' interfacial regions on the XZ plane. The XZ plane consistently exhibits higher R_{ct} , lower I_{corr} , and lower apparent donor density than the XY plane under the investigated pH and immersion conditions (Figures 6, 7 and 11). This combination suggests that interface-related localized dissolution or rapid transport does not dominate the macroscopic electrochemical response of the XZ surface under the present test conditions. Instead, the observed behavior is consistent with a net balance in which interface-assisted oxidation and passivation may outweigh interface-associated micro-galvanic and transport effects. Nevertheless, local current distributions, interface-specific dissolution kinetics, and passive-film chemistry were not directly characterized. Therefore, the B2/B19' interfaces are not identified as independently beneficial features, but rather as one possible microstructural contributor to the orientation-dependent passivation response.

However, corrosion resistance is not only dictated by phase fraction alone, but also depends on the spatial distribution of phases and the density of phase boundaries exposed to the electrolyte. In the XY plane, the microstructure is relatively homogeneous (Figures

2 and 3), which can be attributed to the fact that this plane is constructed parallel to the build platform during the additive manufacturing process and therefore experiences relatively small thermal gradients [55]. In contrast, the XZ plane exhibits plate-like or lamellar B19' martensite that is densely packed and extends over larger regions with well-developed substructures (Figure 4), thereby significantly increasing the areal density of phase boundaries intersecting the surface. According to interface-controlled corrosion and micro-galvanic theories [56,57], these interfaces act as preferential sites for localized electrochemical activity and point defect injection during passivation. The interface-mediated passivation mechanism is therefore presented as a possible interpretation that is consistent with the combined microstructural and electrochemical observations (Figures 6, 8 and 9).

The Ni_4Ti_3 precipitates observed in both planes may also influence local electrochemical behavior. Their Ni-rich composition, the associated Ni depletion of the surrounding matrix, and the coherency strain at the precipitate/matrix interface can modify local oxidation kinetics and introduce electrochemical heterogeneity. Such interfaces may act as preferential sites for initial oxidation or passivation, but they may also promote local micro-galvanic activity, depending on the precipitate chemistry, interfacial structure, and electrolyte conditions [54,58]. Therefore, the net effect of Ni_4Ti_3 on localized corrosion cannot be assigned as exclusively beneficial or detrimental based on the present data. Because Ni_4Ti_3 was detected locally in both planes and no statistically reliable difference in its density was established, it is regarded here as a possible secondary microstructural factor rather than a demonstrated origin of the corrosion anisotropy. The orientation-dependent corrosion response is consequently interpreted primarily from the experimentally observed differences in B19' morphology, phase-boundary distribution, and passive-film donor density.

Beyond phase-dependent corrosion behavior, the oxidation thermodynamics of the constituent elements play a decisive role in passivation [59]. Ti exhibits a significantly stronger affinity for oxygen than Ni, as reflected by the much more negative standard Gibbs free energies of formation for TiO and TiO_2 compared to NiO at 25 °C (-495 and -889.5 kJ mol⁻¹ versus -211.7 kJ mol⁻¹) [60]. This thermodynamic preference leads to selective oxidation of Ti and destabilization of NiO , which tends to dissolve during film evolution. Consequently, previous investigations have commonly reported that the passive film on NiTi alloys adopts a bilayered configuration, featuring a TiO_2 -rich outer layer and an inner layer composed of mixed Ti- and Ni-containing oxides [23,60].

Since the highest oxidation state of Ni is limited to +2, the incorporation of Ni^{2+} into the TiO_2 -rich passive film requires charge compensation and, according to the electroneutrality principle, leads to the formation of oxygen vacancies [50]. As Ni oxides are preferentially located within the inner layer of the passive film, dissolution of the outer oxide layer under acidic conditions exposes this vacancy-rich region, thereby giving rise to a pronounced increase in N_D (Figure 11). It is challenging to directly capture the evolution of defect chemistry within the passive film during the 72 h immersion period, as this process inherently spans both spatial and temporal scales. For NiTi alloys, the rapid formation of Ti oxides effectively hinders the ingress of oxygen ions and other oxidizing species, thereby limiting further oxidation of the substrate beneath the passive film [28]. Within the point-defect framework, variations in oxide valence state and cation incorporation may generate electrically active donor defects that are commonly associated with oxygen vacancies. The present M-S results show that the XZ plane develops a lower apparent donor density than the XY plane under identical immersion conditions (Figure 11). Owing to the reduced density of oxygen vacancies within the passive film, charge transport across the film/electrolyte interface is effectively suppressed, resulting in a higher charge transfer resistance, as demonstrated in Figures 6, 8 and 9. In summary, the

present results establish orientation-dependent differences in corrosion kinetics and passive-film donor density in LPBF-fabricated NiTi. The correlation between these electrochemical differences and the spatial arrangement of B2/B19' phases is consistent with a possible phase- and interface-mediated passivation mechanism.

5. Conclusions

This work systematically investigates the microstructural features associated with corrosion anisotropy in LPBF-fabricated NiTi alloys by correlating plane-dependent microstructure, hardness response, and electrochemical behavior. The surfaces perpendicular to the building direction (XY plane) and parallel to the building direction (XZ plane) were investigated. The main conclusions are summarized as follows:

1. Pronounced microstructural anisotropy is observed between the XY and XZ planes. The XY plane is dominated by polygonal B2 grains with a small fraction of B19' phase, whereas the XZ plane exhibits epitaxial grain growth along the building direction and a higher fraction of lamellar B19' martensite. Semi-quantitative peak-area analysis suggests a modestly larger B19' contribution on the XZ plane, while TEM provides direct qualitative evidence of more spatially continuous B19' variants and more extensive B2/B19' interfacial regions.
2. Corrosion anisotropy is demonstrated in Hank's solution over a wide pH range (3–7). After OCP tests at pH 7, the XZ plane exhibits a significantly higher charge transfer resistance ($R_{ct} \approx 143.9 \text{ k}\Omega \text{ cm}^2$) than the XY plane ($\approx 109.1 \text{ k}\Omega \text{ cm}^2$), accompanied by a lower corrosion current density ($0.231 \text{ vs. } 0.599 \mu\text{A cm}^{-2}$), indicating superior corrosion resistance.
3. After 72 h immersion at pH 7, the R_{ct} of the XZ plane reaches $648 \pm 48 \text{ k}\Omega \text{ cm}^2$, which is $\sim 31\%$ higher than that of the XY plane ($495 \pm 54 \text{ k}\Omega \text{ cm}^2$). Even under acidic conditions (pH 3), the XZ plane maintains nearly twice the R_{ct} of the XY plane after 72 h immersion.
4. Mott–Schottky analysis shows n -type semiconductor behavior for all passive films. Under neutral conditions, both planes exhibit relatively low donor densities; however, the XY plane consistently shows higher N_D ($5.77 \times 10^{29} \text{ cm}^{-3}$ at 72 h) than the XZ plane ($4.41 \times 10^{29} \text{ cm}^{-3}$). Under acidic conditions, the N_D of the XY plane increases sharply to $12.33 \times 10^{29} \text{ cm}^{-3}$ after 72 h, whereas the XZ plane remains significantly lower ($7.38 \times 10^{29} \text{ cm}^{-3}$ at 72 h). These results indicate fewer electrically active donor defects and reduced defect-mediated transport on the XZ surface; they do not independently determine passive-film composition or morphology.
5. These findings highlight the critical role of additive manufacturing-induced anisotropy in governing the corrosion performance of NiTi alloys. Controlling build orientation and microstructural architecture provides an effective strategy for optimizing the corrosion resistance of biomedical NiTi components operating in complex physiological environments.
6. Future work should quantitatively separate the individual contributions of crystallographic texture, residual stress, phase-boundary topology, Ni_4Ti_3 precipitation, and passive-film chemistry to the observed corrosion anisotropy. Long-term immersion, ion-release, corrosion-fatigue, and component-level tests on architected NiTi structures are also needed to evaluate whether the plane-dependent corrosion response observed in this work can be translated into reliable design guidelines for biomedical LPBF-fabricated NiTi devices.

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