

Temperature-mediated chelation chemistry in organic acid-based slurry for dynamic interfacial control surface processing of Ti-6Al-4V

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ABSTRACT

The exceptional specific strength of Ti-6Al-4V (TC4) with the high hardness and low density, renders it a critical structural material for aerospace systems. However, its adoption in high-precision applications is severely constrained by the intrinsically poor as-built surface. To address this limitation, a unique slurry constructed by silica sol and organic acid is designed under controllable temperature. Under the influence of lactic acid, the TC4 via chemical mechanical polishing (CMP) obtained a high surface quality of surface roughness (Sa) 0.323 ± 0.039 nm at $50 \times 50 \mu\text{m}^2$ area. The achieved material removal rate (MRR) via acetic acid was about 4301 nm/min, representing an enhancement over conventional abrasive-based polishing methods. Combinatorial analyses by Molecular Dynamics (MD) calculations, electrochemical, surface characterization demonstrate the slurry enables dual functionality, which leads to highly efficient defect planarization via controlled mechanical delamination of the reaction layer, and dynamic modulation of interfacial reactivity at the solid–liquid interface through organic acid-regulated oxide dissolution and ligand-assisted Ti^{4+} complexation. Specifically, Lactic acid plays three key roles: (i) keeping the acidity at pH 4.0 to sustain H_2O_2 -driven oxide formation, (ii) supplying lactate anions that chelate with Ti^{4+} sites to stabilize dissolved species and prevent redeposition and (iii) allowing temperature control over complex stability for reliable performance from 25 to 40°C. This work establishes a scalable, chemistry-guided slurry design strategy specifically tailored for the precision finishing of TC4 parts.

1. Introduction

In the realm of advanced surface treatment technologies, a multitude of methods have been developed to refine and enhance the surface characteristics of TC4 titanium alloy, have facilitated its widespread application [1] across various domains, including aerospace, automotive manufacturing, and medical implants [2–4]. The unique high hardness and chemical stability of TC4 are among the reasons why they are difficult to polish [5]. Thus, CMP operates through a synergistic combination of chemical reactions and friction arises, stands out as a particularly effective and versatile process [6]. This dual-action method of CMP ensures precision and minimizes surface damage, crucial for high-performance applications, achieving nano-scale smoothness. Given that the effectiveness of polishing predominantly hinges on both the

polishing process and the polishing slurry [7,8], and considering that the polishing process itself is primarily shaped by the equipment utilized and the operational scheme employed, it becomes more practical to focus on the design of the polishing slurry [9–12].

Slurry serves as a multifunctional medium, fulfilling two essential roles: providing frictional resistance and facilitating chemical dissolution [13]. Economically viable alternatives are highly sought to ensure cost-effectiveness and sustainability in large-scale applications [14]. Silica sol is identified as a prime candidate for delivering the requisite frictional resistance in slurry formulations due to its abundant availability, relatively low cost, and excellent abrasive properties [15]. Its hardness and durability render it suitable for a diverse range of abrasive processes, effectively wearing down surfaces while minimizing wear on the equipment itself [16].

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Furthermore, acidic solutions are favored for their ability to impart chemical dissolution properties to the slurry [17]. The choice of an appropriate acidic solution depends on the specific application and the target material intended for dissolution, with organic acids identified as promising candidates [18–20]. Critical factors in the selection process include reactivity, safety, and environmental impact. To ensure that the chemical reactions of the slurry involving organic acids achieve equilibrium with the mechanical removal processes, the temperature of the slurry is regulated to enhance the reaction rate [21–23]. This study aims to develop a slurry formulation that optimally balances frictional resistance and chemical dissolution capabilities by incorporating economically viable colloidal silica with a carefully selected acidic solution. Such a formulation is intended to enhance the efficiency and effectiveness of industrial processes reliant on slurry-based operations.

Thus, this research developed a green, three-component polishing slurry consisting solely of silica sol, an organic acid, and hydrogen peroxide. The effects of various organic acids on the polishing performance of TC4 at different temperatures were systematically investigated. Furthermore, Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), electrochemical characterization and MD simulation were employed to gain a profound understanding of the complex interaction mechanisms between the slurry components and the TC4 surface. This study serves as a valuable reference for leveraging organic acid in green chemical polishing, paving the way for their successful implementation in industrial processing environments.

2. Experimental section

2.1. Materials and slurry preparation

The TC4 alloy utilized in the experiment, with dimensions of 10 mm × 10 mm × 3 mm, was sourced from Hefei Shushan Wenhui Metal Materials Co., Ltd. The chemical reagents employed in this study comprised hydrogen peroxide (H₂O₂, supplied by Sinopharm Chemical Reagent Co., Ltd) and silica sol (provided by Dezhou Crystal Fire Technology Glass Co., Ltd.). The organic acids utilized, specifically oxalic acid, lactic acid, tartaric acid, malic acid, acetic acid, and citric acid, were of analytical grade and procured from Sinopharm Chemical Reagent Co., Ltd. All chemicals were utilized as received, without any further purification. Here, we would like to remind you that the H₂O₂, deionized water, silica sol and organic acids used in this work are all non-toxic and harmless products.

The base polishing slurry was formulated to a total mass of 500 g per batch. In a typical preparation procedure, 33.3 g of 30 wt% H₂O₂ solution (equivalent to a measured volume of 30 mL, based on a density of 1.11 g/cm³) was first introduced into a beaker. Subsequently, 187.5 g of the 40 wt% colloidal silica (equivalent to a measured volume of 144 mL, based on a density of 1.30 g/cm³) was added. The mixture was then diluted with 279 mL of deionized water to achieve the targeted total mass. The resulting suspension was continuously agitated using a magnetic stir for 120 min and ultrasound for 10 min to ensure thorough homogenization. The ultrasound equipment has a power of 700 W. To investigate the influence of organic acid additives, six distinct slurry groups were prepared. The initial pH of the base slurry was recorded using pH meter, with an accuracy of 0.01. The 0.01 mol/L aqueous solution of the respective organic acid was then titrated dropwise into the vigorously stirred slurry. Following each incremental addition and a brief equilibration period under stirring for 60 min, his titration process was meticulously repeated until a final, stable pH value of 4.0 was attained for each of the six slurry formulations. It notes that during the use of the slurry, it should be constantly stirred, and the temperature of the slurry should be controlled using a water bath, which should be maintained at 25, 30, 35 and 40 °C.

2.2. CMP testing

The samples were uniformly mounted on the periphery of a 180 mm diameter aluminum disk using molten paraffin wax. Subsequently, all samples were ground on a precision polishing machine (UNIPOL-1200S, Shenyang Kejing Auto Instrument Co., Ltd.). The rough polishing process lasts for 5 min using sandpapers with grit sizes of 1000# to complete the initial surface preparation.

Prior to the precision polishing process, three samples were uniformly fixed at three equally spaced positions along the periphery of an aluminum disc using molten paraffin to ensure uniform force distribution during polishing. The polishing experiments were carried out on a precision polishing machine (UNIPOL-1200S, Shenyang Kejing Auto Instrument Co., Ltd., China). The polishing pad was purchased from SHEN YANG KEJING E-SHOP. It is a suede polishing pad with a diameter of 300 mm and a thickness of 10 mm. It also comes with a backing adhesive, which is water-resistant, oil-resistant and has stable adhesion. During CMP, the down pressure was maintained at 10.16 kPa, the platen rotation speed was set to 60 rpm, the slurry flow rate was controlled at 5 (mL/min), and the polishing time was 30 min. Throughout the polishing process, the slurry was continuously supplied onto the polishing pad to ensure sufficient chemical reaction and mechanical abrasion at the pad/workpiece interface, thereby enabling effective material removal and improving the surface quality of the TC4 alloy. After polishing, the samples were rinsed thoroughly with deionized water and dried with compressed air.

To systematically evaluate the influence of different organic acids on the CMP performance of TC4, this study first employed a Two-factor experimental approach. A two-factor experiment was conducted to investigate the effects of organic acid type and polishing temperature. Six organic acids (Citric, Oxalic, Lactic, Acetic, Tartaric, and Malic acid) were selected as the first factor, while temperature served as the second factor. All other process parameters were held constant. The detailed experimental layout is presented in Table 1. Each experimental group underwent nine replicated experiments to ensure the elimination of experimental contingency.

For CMP, the MRR (nm/min) is an important index to test the polishing effect, thus the MRR was calculated according to Formula (1) [24]. The formula for calculating MRR is presented as follows:

Table 1

Experimental design for evaluating the effects of organic acid type and polishing temperature on TC4 alloy CMP performance.

No.	Temperature	H ₂ O ₂	Abrasive	pH	Acid
1	25°C	2 wt%	15 wt% SiO ₂	4	Citric acid
2	30°C	2 wt%	15 wt% SiO ₂	4	Citric acid
3	35°C	2 wt%	15 wt% SiO ₂	4	Citric acid
4	40°C	2 wt%	15 wt% SiO ₂	4	Citric acid
5	25°C	2 wt%	15 wt% SiO ₂	4	Lactic acid
6	30°C	2 wt%	15 wt% SiO ₂	4	Lactic acid
7	35°C	2 wt%	15 wt% SiO ₂	4	Lactic acid
8	40°C	2 wt%	15 wt% SiO ₂	4	Lactic acid
9	25°C	2 wt%	15 wt% SiO ₂	4	Acetic acid
10	30°C	2 wt%	15 wt% SiO ₂	4	Acetic acid
11	35°C	2 wt%	15 wt% SiO ₂	4	Acetic acid
12	40°C	2 wt%	15 wt% SiO ₂	4	Acetic acid
13	25°C	2 wt%	15 wt% SiO ₂	4	Tartaric acid
14	30°C	2 wt%	15 wt% SiO ₂	4	Tartaric acid
15	35°C	2 wt%	15 wt% SiO ₂	4	Tartaric acid
16	40°C	2 wt%	15 wt% SiO ₂	4	Tartaric acid
17	25°C	2 wt%	15 wt% SiO ₂	4	Malic acid
18	30°C	2 wt%	15 wt% SiO ₂	4	Malic acid
19	35°C	2 wt%	15 wt% SiO ₂	4	Malic acid
20	40°C	2 wt%	15 wt% SiO ₂	4	Malic acid
21	25°C	2 wt%	15 wt% SiO ₂	4	Oxalic acid
22	30°C	2 wt%	15 wt% SiO ₂	4	Oxalic acid
23	35°C	2 wt%	15 wt% SiO ₂	4	Oxalic acid
24	40°C	2 wt%	15 wt% SiO ₂	4	Oxalic acid

$$MRR = \frac{(\Delta m)}{(\rho \times A \times t)} \times 10^7 \quad (1)$$

Where Δm represents the mass difference (g) of TC4 before and after CMP measured using an ultra-precision electronic balance. The density of TC4 is 4.51 g/cm³ labeled as ρ . The surface area (A) of TC4 was estimated at 1.0 cm². Then, t represents the CMP time (min). Since the calculated value of $\Delta m/(\rho A t)$ has a unit of cm/min, the factor 10^7 was introduced to convert the final result into nm/min.

2.3. Characterization

An optical microscope (MX 40, Olympus, Japan) was utilized to investigate scratches on the polished surfaces. The three-dimensional surface topography and S_a were evaluated using a White-light interferometer (WLI) (ContourX-200, Bruker, Germany). Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) were performed using a Hitachi 4800 field-emission scanning electron microscope. Furthermore, Nuclear Magnetic Resonance (NMR) (Avance II 400, Bruker, Germany) was used to provide chemical information of slurry. FTIR analysis was performed with a Thermo Fisher Scientific Nicolet iS20 instrument (USA) to examine the surface functional groups and potential interactions between the organic acid and the TC4 surface. The analysis employed the attenuated total reflection (ATR) mode, spanning a wavenumber range from 400 cm⁻¹ to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. To quantitatively analyze the surface chemistry of the samples, XPS was conducted using a Thermo Scientific K-Alpha system (USA). High-resolution spectra were obtained for the Ti 2p, O 1s, and Al 2p regions to ascertain their specific elemental states and bonding configurations. The surface of the TC4 alloy following CMP was examined via Raman spectroscopy using a Horiba LabRAM Odyssey system (Japan) with a 532 nm laser source. Spectra were collected across the 400–2500 cm⁻¹ range to qualitatively assess the phase composition and crystallinity of the oxide layer, thereby providing insights into the reaction mechanisms involved in the polishing process. Dynamic light scattering (DLS) and electrophoretic light scattering (Zeta potential) are employed to analysis information of slurry.

2.4. Electrochemical property measurements

Electrochemical tests were performed using an electrochemical workstation. A three-electrode system was configured, utilizing a TC4 alloy sample (10 × 10 × 3 mm) as the working electrode, an Ag/AgCl (saturated KCl) electrode as the reference electrode, and a platinum wire (diameter 0.5 mm) as the counter electrode. Electrochemical impedance spectroscopy (EIS) was employed to investigate the electrochemical behavior of TC4 alloy in 0.2 M Na₂SO₄ solutions containing different organic acid systems. The EIS measurements were conducted at open circuit potential (OCP) with a 5 mV amplitude over a frequency range of 0.1 Hz to 10⁶ Hz. The obtained spectra were fitted to determine the solution resistance (R_s), capacitance of the adsorbed layer (C), and charge transfer resistance (R_{ct}). Potentiodynamic polarization curves were subsequently recorded at a scan rate of 1 mV/s, over a potential range from −0.2 V vs. open circuit potential to +0.4 V vs. OCP, to evaluate the corrosion resistance. To deconvolve the individual and synergistic effects of the polishing solution constituents, potentiodynamic polarization measurements were performed. Each component from the optimized formulation was sequentially introduced into a 0.2 M Na₂SO₄ base solution, and the corresponding polarization curves for the TC4 alloy were recorded. This approach enabled the analysis of how each component influences the corrosion behavior, both individually and in combination. Linear sweep voltammetry (LSV) was performed at a scan rate of 10 mV/s to evaluate the anodic reaction and passivation behavior of TC4 in the different organic-acid-containing slurries. Before each measurement, the OCP was recorded for 400 s. The polarization resistance (R_p) was determined by performing an LSV

scan within ±15 mV of the stabilized OCP and linearly fitting the potential-current density data. For single-step chronoamperometry (CA), the potential was stepped from the stabilized OCP to an acid-specific passivation potential ($E_{\text{passivation}}$), selected from the passivation region identified by the corresponding LSV curve, and maintained for 1000 s. For two-step CA, the potential was first stepped to the corresponding $E_{\text{passivation}}$ and maintained for 300 s to allow passive-film growth, and was then stepped to −1.0 V vs. Ag/AgCl and maintained for another 300 s to investigate the oxide-reduction/removal-related electrochemical response.

2.5. Statistical analysis

A balanced two-factor full-factorial design was employed to examine the main effects of organic acid type (six levels) and temperature (four levels), as well as their two-way interaction, on the response variable. This design yielded 24 unique independent polishing slurry batches, each replicated nine times, resulting in a total sample size of 216. Fixed-effects two-way analysis of variance (ANOVA) was conducted to assess statistical significance at $\alpha = 0.05$. All ANOVA computations were performed using OriginPro (version 2023b), and statistical power for each effect was estimated post hoc using PASS 2025 (version 25.0.2). Effect sizes were quantified using partial eta-squared (η^2), calculated as $SS_{\text{effect}}/(SS_{\text{effect}} + SS_{\text{error}})$. Crucially, this study implemented the complete 6×4 factorial structure—rather than a fractional or orthogonal design (e.g., Taguchi L-series), ensuring unbiased estimation of all main effects and interactions with maximal precision and generalizability.

2.6. Molecular dynamics simulation

All molecular dynamics (MD) simulations were performed using the BIOVIA Materials Studio software package, specifically employing the Forcite module. A tri-layer laminated interface model was constructed, consisting (from bottom to top) of a TC4 surface layer, an organic acid interlayer (containing oxalic acid, acetic acid, tartaric acid, malic acid, citric acid, lactic acid, respectively), and an amorphous silica (SiO₂) abrasive layer. Initial energy minimization was carried out using the Smart Minimizer algorithm (a hybrid of steepest descent, conjugate gradient, and Newton-Raphson methods). To overcome high energy barriers and locate the global minimum energy configuration, a Forcite Anneal task was executed under the NVT ensemble (Nosé-Hoover thermostat). The final Total Energy of each fully equilibrated and sheared tri-layer system was extracted from the last frame of the trajectory.

3. Results and discussion

3.1. CMP experiment analysis

In order to find the simplest, cheapest and most efficient polishing slurry for TC4, we developed a facile and versatile organic acid-assisted strategy at a specific temperature for the construction of a polishing slurry, based on the specific interfacial interaction between TC4 and organic acid. The slurry was composed of silica sol, hydrogen peroxide, and organic acids (citric acid, lactic acid, acetic acid, tartaric acid, malic acid, oxalic acid). Subsequently, each batch of slurry was sonicated, stirred, and preheated to its respective temperature (ranging from 25 to 40°C) before being dropped onto a polishing disc. The CMP experiments were conducted on the setup illustrated in Fig. 1, in which the TC4 samples were mounted on a holder disk and polished against a 300 mm suede leather pad. The polishing parameters were set as follows: down pressure 10.16 kPa, platen rotation speed 60 rpm, slurry flow rate 5 mL/min, and polishing time 30 min. After polishing for 30 min, a smooth TC4 sample was peeled off the objective table. Upon completion of the experiments, the samples were immediately rinsed with deionized water to remove any residual slurry. During the polishing process, Al₂O₃ and

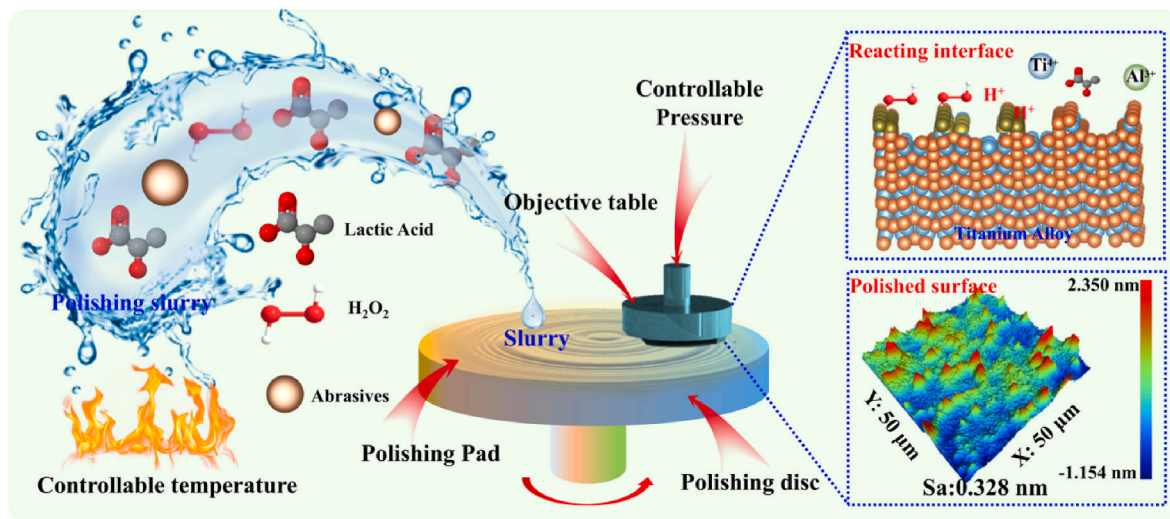


Fig. 1. Schematic of the polishing of TC4 with developed slurry.

TiO₂ were in situ-formed from TC4 via H₂O₂ as an oxidizing agent, and the organic functional groups effectively coordinated with unsaturated bonds, enabling the removal of defects from TC4. Therefore, a smooth TC4 surface was obtained.

This section examines the influence of two key experimental variables, such as temperature and organic acid type on the Sa and MRR of polished TC4 samples in a factorial design. Experimental results are summarized in Figs. 2 and 3 and Table 2. Fig. 2 presents three-dimensional surface topographies, acquired via WLI, for TC4 specimens polished with six organic acid-based slurries across four temperatures. Each row corresponds to a distinct acid system (acetic, lactic, oxalic, malic, tartaric, and citric acid, respectively), and each column represents a polishing temperature (25, 30, 35, and 40°C). Specifically, panels (a–d), (e–h), (i–l), (m–p), (q–t), and (u–x) correspond to the acetic, lactic, oxalic, malic, tartaric, and citric acid systems. The results demonstrate that the influence of temperature on Sa is highly dependent on the organic acid type, indicating that the CMP behavior of TC4 is governed by the synergistic interplay between acid chemistry and thermal activation—not by temperature in isolation. In the acetic acid-based slurry system (Fig. 2a–d), Sa exhibited pronounced non-monotonic variation with temperature. Specifically, the Sa value—measured over a 50 × 50 μm² area, increased from 0.572 nm at 25°C (Fig. 2a), rose further to 0.748 nm at 30°C (Fig. 2b), decreased to 0.493 nm at 35°C (Fig. 2c), and then surged to 1.070 nm at 40°C (Fig. 2d). Specifically, Fig. 2d reveals pronounced surface pitting and deep valleys, indicating a substantial increase in Sa at 40°C. This pronounced topographic variation suggests that the etching action of acetic acid is highly temperature-sensitive. At relatively low temperatures, surface reaction kinetics may be insufficient to induce significant morphological change; conversely, at excessively high temperatures, chemical dissolution may proceed too rapidly or non-uniformly, leading to localized over-etching.

In contrast, the lactic-acid-based slurry (Fig. 2e–h) demonstrated superior thermal responsiveness. The Sa decreased from 0.588 nm (measured over a 50 × 50 μm² area, Figs. 2e and 25°C) to 0.323 nm (same scan area, Figs. 2f and 30°C), suggesting that a moderate temperature elevation facilitates a more synergistic chemical–mechanical interaction. Upon further heating, Sa increased to 0.527 nm at 35°C (Figs. 2g and 35°C) and 0.468 nm at 40°C (Fig. 2h). Although the surfaces in Fig. 2g and h remained relatively smooth, neither exhibited lower Sa values than that in Fig. 2f (0.328 nm). Thus, under the present experimental conditions, 30°C represents the optimal temperature for surface smoothing using the lactic-acid-based slurry. The oxalic-acid-based slurry (Fig. 2i–l) yielded Sa values of 0.492, 0.560, 0.520, and

0.509 nm—each measured over a 50 × 50 μm² area (Fig. 2i–l, corresponding to 25, 30, 35, and 40°C, respectively). The narrow variation (±0.034 nm around the mean) indicates minimal topographic sensitivity to temperature, with no evidence of morphological degradation across the tested range. Consequently, the oxalic acid system demonstrates robust thermal stability and consistent polishing performance. For the malic-acid-based slurry (Fig. 2m–p), a distinct temperature dependence emerged: Sa decreased modestly from 0.628 nm at 25°C (Fig. 2m) to 0.583 nm at 30°C (Fig. 2n), then rose slightly to 0.622 nm at 35°C (Fig. 2o), before declining markedly to 0.468 nm at 40°C (Fig. 2p, same scan area). This non-monotonic trend suggests that malic acid's chemical activity, particularly its chelating and proton-donating capacity, is thermally activated, with full efficacy realized only near the upper limit of the investigated temperature range.

For the tartaric-acid-based slurry (Fig. 2q–t), the Sa increased progressively from 0.571 nm (50 × 50 μm², Figs. 2q and 25°C) to 0.691 nm (Figs. 2r and 30°C), remained elevated at 0.661 nm (Figs. 2s and 35°C), and rose further to 0.782 nm (Figs. 2t and 40°C). The observed monotonic upward trend suggests that increased temperatures consistently deteriorate the surface finish within the tartaric acid system, likely due to the promotion of non-uniform dissolution or the suppression of mechanical planarization efficiency. Similarly, the citric-acid-based slurry (Fig. 2u–x) exhibited no systematic improvement with temperature: Sa values were 0.732 nm (Figs. 2u and 25°C), 0.705 nm (Figs. 2v and 30°C), 0.804 nm (Figs. 2w and 35°C), and 0.681 nm (Figs. 2x and 40°C), all measured over identical 50 × 50 μm² areas. Under all experimental conditions, the citric acid system produced surfaces with significantly greater roughness compared to both the lactic acid and oxalic acid systems, thereby underscoring its relatively lower efficacy in polishing. Collectively, the WLI data reveal that temperature exerts acid-specific effects on TC4 surface topography. The smoothest surface (Sa = 0.328 nm) was achieved with the lactic-acid-based slurry at 30°C (Fig. 2f), whereas the roughest (Sa = 1.070 nm) occurred with the acetic-acid-based slurry at 40°C (Fig. 2d). The results highlight that the polishing performance on TC4 is determined not solely by temperature, but by the synergistic interaction among the molecular structure of the acid, the strength of chelation, the availability of protons, and the kinetics of thermal activation. In this context, temperature primarily acts as a modulator of interfacial reaction pathways rather than serving as a universal accelerator of material removal.

Analysis of data from 24 independent polishing slurry batches indicates that heating the acetic acid-based slurry to 35°C yields a MRR of 4301 nm/min (Fig. 3b). This enhanced polishing performance enables effective mitigation of macro-scratches and surface defects on TC4

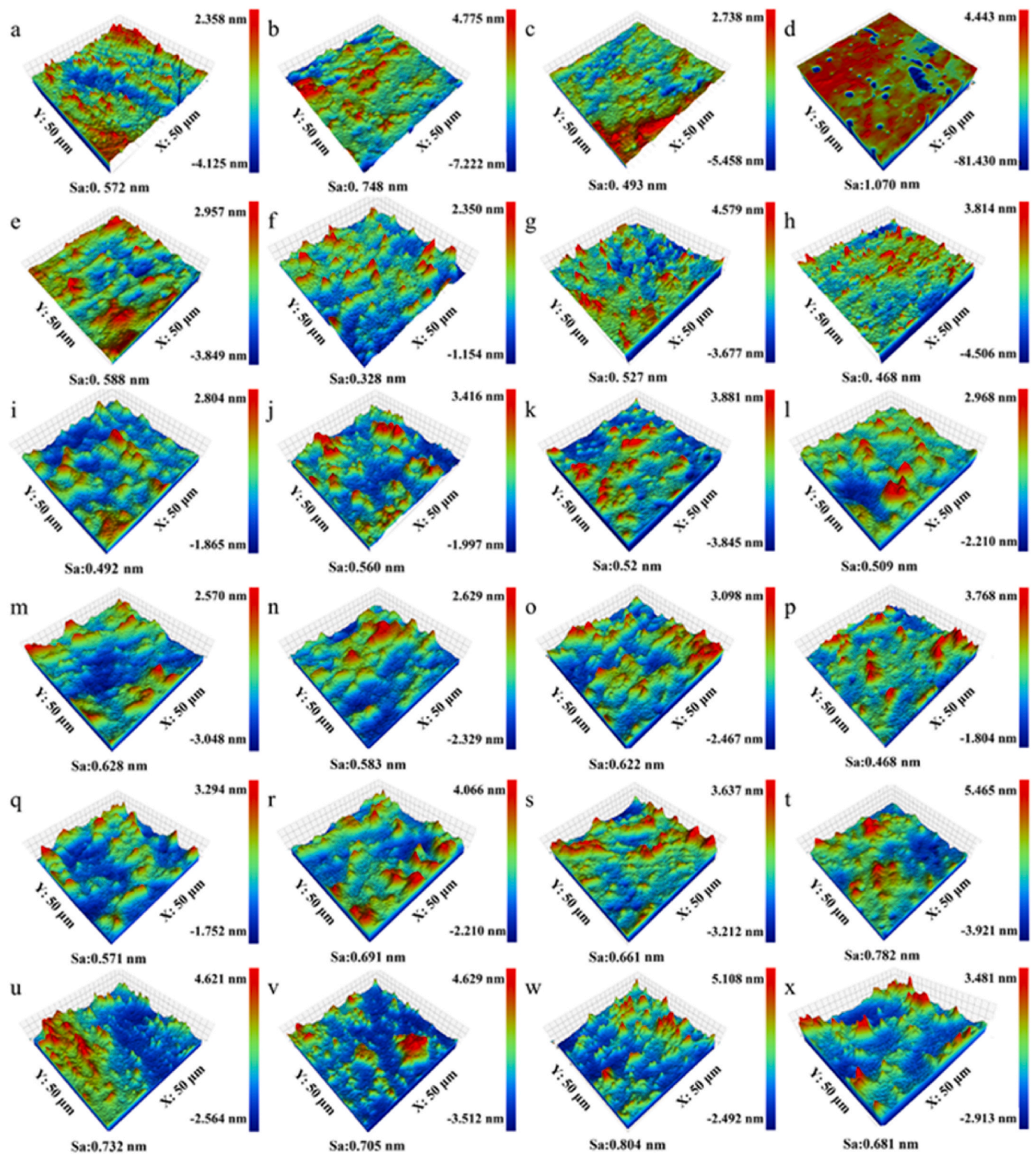


Fig. 2. WLI three-dimensional surface morphologies of polished TC4 under different acid-based CMP slurries at different temperatures. From left to right, the polishing temperatures are 25, 30, 35, and 40°C, respectively. From top to bottom, the acids are acetic acid, lactic acid, oxalic acid, malic acid, tartaric acid, and citric acid, respectively.

substrates. In detail, for citric acid-based slurries, the MRR is approximately 580–750 nm/min of the slurry temperature to the range of 30–40°C. The MRR attained using lactic acid-based slurries demonstrates minimal sensitivity to variations in slurry temperature, maintaining stability within the range of 600 to 1100 nm/min. Acetic acid is

the most corrosive constituent in the slurry. With increasing temperature, the MRR exhibits a marked decline: it stabilizes at approximately 4301 nm/min at 35°C and decreases to approximately 1773 nm/min at 40°C. This reduction is primarily attributable to the thermal evaporation of acetic acid [25], which lowers its effective concentration in the slurry.

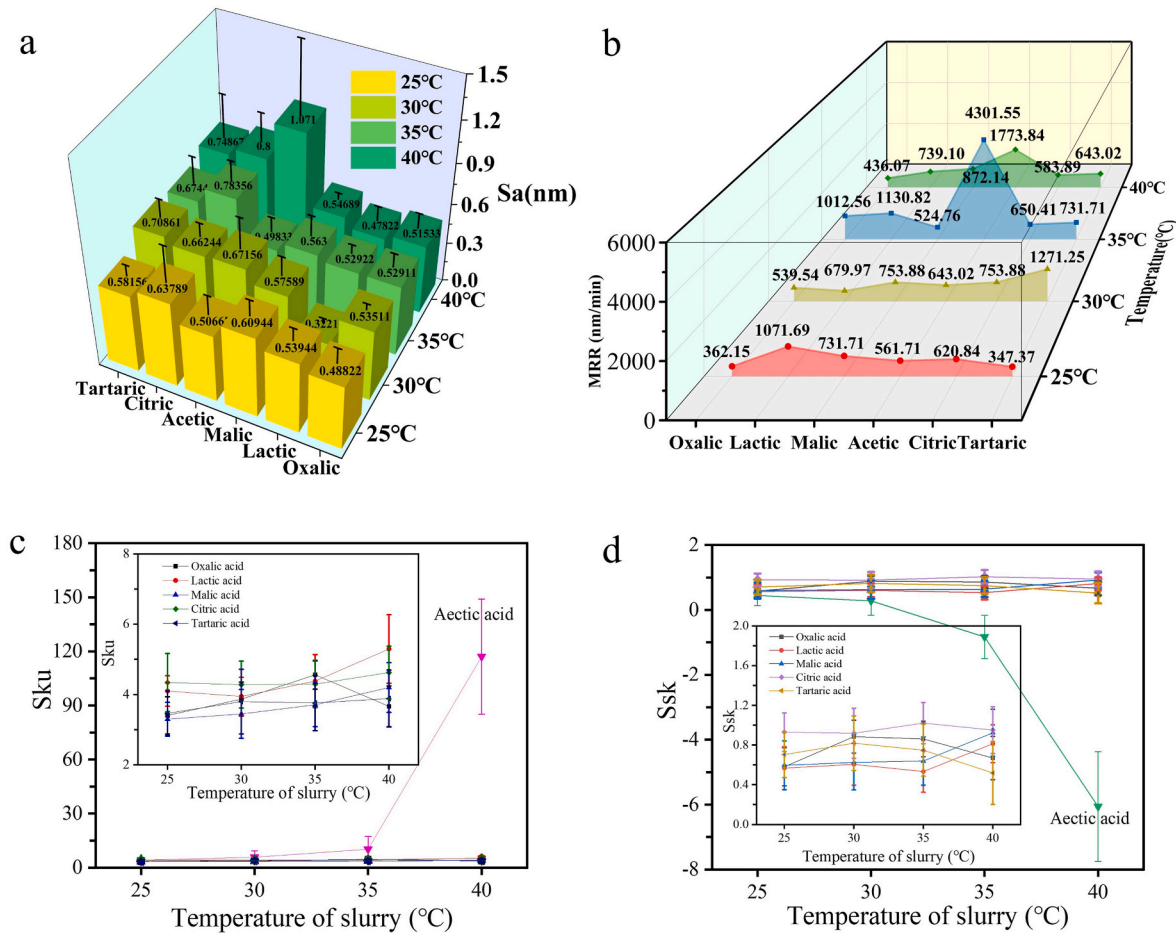


Fig. 3. (a) The obtained Sa value of the polished TC4 with different slurry. (b) The MRR value of the polished TC4. (c) The obtained Sku value and (d) Ssk value of the polished TC4 with different slurry.

Table 2

The Sa and MRR of TC4 alloy under different organic acid and temperature conditions.

No.	Temperature	Acid	Sa (nm)	MRR (nm/min)
1	25°C	Citric acid	0.638 ± 0.269	620.84
2	30°C	Citric acid	0.662 ± 0.101	753.88
3	35°C	Citric acid	0.784 ± 0.145	650.41
4	40°C	Citric acid	0.800 ± 0.214	583.88
5	25°C	Lactic acid	0.539 ± 0.095	1071.69
6	30°C	Lactic acid	0.323 ± 0.039	679.97
7	35°C	Lactic acid	0.529 ± 0.068	1130.82
8	40°C	Lactic acid	0.478 ± 0.110	739.11
9	25°C	Acetic acid	0.507 ± 0.144	561.71
10	30°C	Acetic acid	0.671 ± 0.230	643.02
11	35°C	Acetic acid	0.498 ± 0.109	4301.55
12	40°C	Acetic acid	1.071 ± 0.514	1773.84
13	25°C	Tartaric acid	0.582 ± 0.082	347.37
14	30°C	Tartaric acid	0.709 ± 0.134	1271.25
15	35°C	Tartaric acid	0.674 ± 0.199	731.71
16	40°C	Tartaric acid	0.749 ± 0.318	643.02
17	25°C	Malic acid	0.609 ± 0.120	731.71
18	30°C	Malic acid	0.576 ± 0.142	753.88
19	35°C	Malic acid	0.563 ± 0.152	524.76
20	40°C	Malic acid	0.547 ± 0.051	872.14
21	25°C	Oxalic acid	0.488 ± 0.116	352.15
22	30°C	Oxalic acid	0.535 ± 0.048	539.54
23	35°C	Oxalic acid	0.529 ± 0.103	1012.56
24	40°C	Oxalic acid	0.515 ± 0.115	436.07

For tartaric acid, malic acid, and oxalic acid, the MRR remains within the range of 300–1300 nm/min under isothermal conditions. Although

temperature exerts a measurable influence on the removal rate, its effect is comparatively modest relative to other factors. Collectively, these findings demonstrate that the choice of organic acid and thermal conditions constitute the two dominant parameters governing defect removal efficiency in the slurry system.

The surface kurtosis (Sku) and surface skewness (Ssk) of the polished TC4 via developed slurry were investigated (Fig. 3c and d). Sku is used to describe whether the extreme peaks or deep valleys in the surface height distribution are prominent. The obtained Sku is greater than 3.0, it indicates that abnormal peaks and deep pits exist on the sample surface. Except for the fact that the Sku value obtained by polishing via acetic acid at 30–40°C is relatively high, indicating that the surface defects of the sample are severe, the Sku values of the other pastes remain around 4.0. Ssk is used to determine whether the surface height distribution is biased towards “convex peaks” or “valleys”. The Ssk values of all slurries is greater than 0, the surface is mainly composed of protrusions and sharp peaks, and there may be protrusions or local areas that have not been fully removed. Analogously, the surface quality is the worst under acetic acid at 30–40°C range. All these observations highlight the key role that the slurry acetic acid at 30–40°C can severely damage the surface of titanium alloys, which is also one of the main reasons for its high MRR.

Experimental results demonstrate that Formulation No. 6 delivered the lowest Sa value (0.323 nm) among all evaluated CMP slurries. Consequently, the optimal composition and process parameters for the ternary green polishing slurry are established as follows: 2 wt% H₂O₂, 15 wt% colloidal SiO₂, a polishing temperature of 30°C, and pH adjustment to 4.0 using lactic acid. Surface topography of the TC4 alloy

was characterized pre-and post-CMP via 3D optical profilometry ($50 \times 50 \mu\text{m}^2$ scan area) and 2D optical microscopy. As illustrated in Fig. 4a, the as-received surface demonstrates significant height variations and pronounced groove-like features, resulting in Sa value of 473 nm, which is indicative of considerable microscale roughness. This observation is corroborated by the 2D optical micrograph (Fig. 4c), which reveals a high density of elongated scratches and localized plastic deformation zones. Following polishing with the optimized ternary slurry, Fig. 4b shows marked planarization and improved uniformity. Concurrently, the WLI image (Fig. 4d) displays a homogeneous, scratch-free surface morphology. This Sa has been reduced from 473 nm to 0.323 nm ($50 \times 50 \mu\text{m}^2$ scan area). Collectively, these complementary metrological analyses confirm that the developed CMP process effectively mitigates surface asperities and eliminates mechanical damage, resulting in a significant enhancement of TC4 alloy surface quality.

What's more, the statistical validation (two-way ANOVA, interaction plots, confidence intervals, or p-values) has been performed to establish the significance of the observed trends. The full factorial model was highly significant ($F(23, 192) = 21.64$, $p < 0.0001$) and explained 72.2% of the total variance in the dependent variable (adjusted $R^2 = 0.698$). By analysis, conducted at Significance level (α) = 0.05, indicated near-perfect statistical power (1.000) for detecting all reported effects, reflecting the robustness of the design and sample size (Table 3). Two-way ANOVA revealed statistically significant main effects of organic acid type ($F(5, 192) = 41.61$, $p < 0.0001$, $\eta^2 = 0.520$) and temperature ($F(3, 192) = 21.45$, $p < 0.0001$, $\eta^2 = 0.251$), as well as a significant organic acid type $\times$ temperature interaction ($F(15, 192) = 15.01$, $p < 0.0001$, $\eta^2 = 0.540$) (Table 4). The substantial interaction effect indicates that the influence of temperature on the

Table 3

Statistical power analysis for the balanced two-factor full-factorial design.

Parameter	Organic acid type (A)	Temperature (B)	A $\times$ B interaction
Levels/combinations	6	4	24 combinations
Numerator degrees of freedom (df_1)	5	3	15
Denominator degrees of freedom (df_2)	192	192	192
Group sample size	9	9	9
Total sample size	216	216	216
Standard deviation of means/effects	0.08935	0.04970	0.09297
Residual Standard deviation	0.09104	0.09104	0.09104
Standardized effect size	0.98143	0.54588	1.02114
α	0.05	0.05	0.05
Statistical power	1.000	1.000	1.000

Note: Statistical power was calculated using PASS 2025 (version 25.0.2) for a fixed-effects 6×4 factorial design at $\alpha = 0.05$. The standardized effect size was calculated as the standard deviation of the factor-level means or interaction effects divided by the residual standard deviation. Power values of 1.000 are rounded values reported by PASS.

response variable was not uniform across organic acid types. The magnitude of temperature effects depended on the specific organic acid employed.

It's worth noting that, the developed slurries with lactic acid or acetic acid obtained the values for Sa and MRR that are 0.323 ± 0.039 nm, 679.97 nm/min and 0.498 ± 0.109 nm, 4301.55 nm/min respectively.

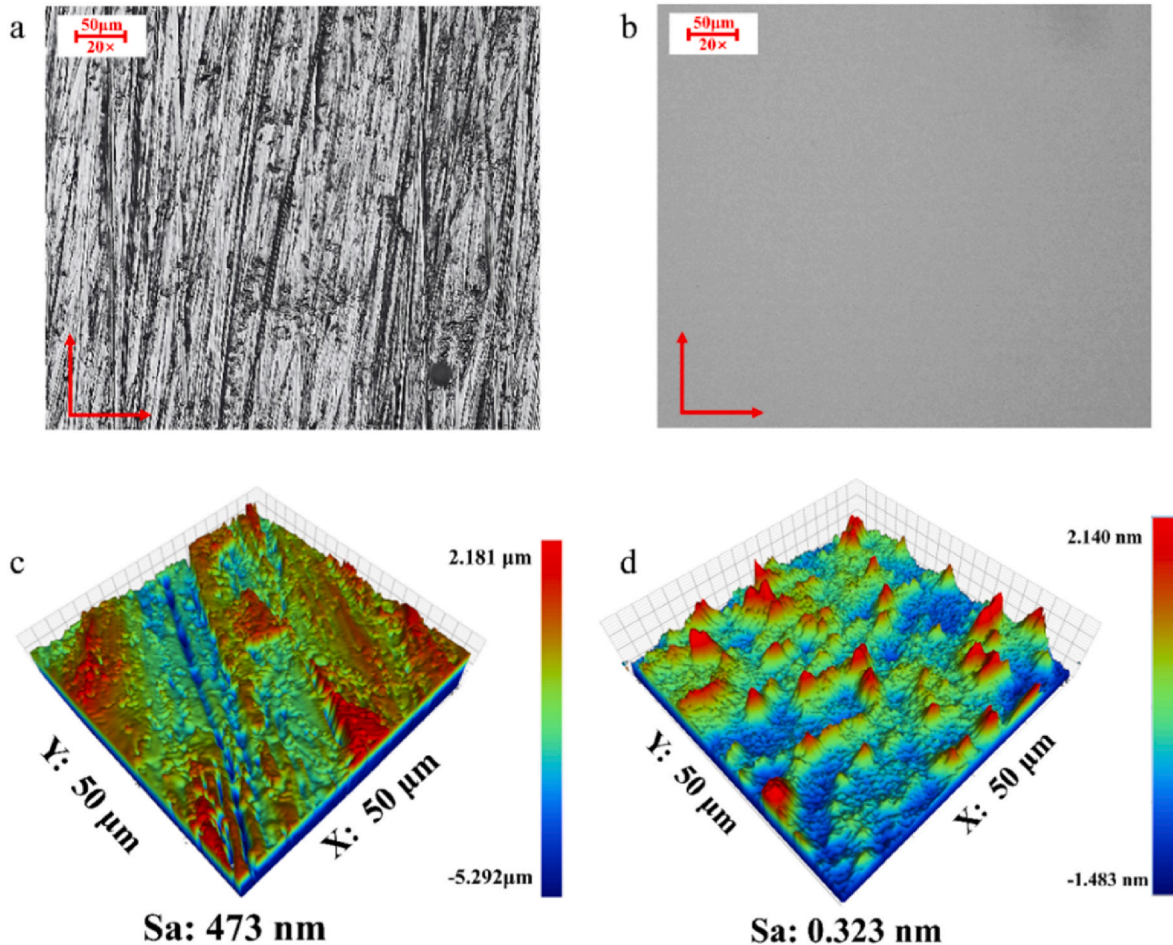


Fig. 4. The Surface information of TC4. Optical picture of original TC4 (a) and polished TC4 (b). The WLI images of original TC4 (c) and polished TC4 (d).

Table 4

Two-way ANOVA for the effects of organic acid type and temperature.

Source of variation	df	Sum of squares	Mean square	F value	p value	Partial η^2
Organic acid type (A)	5	1.72443	0.34489	41.60793	<0.0001	0.520
Temperature (B)	3	0.53351	0.17784	21.45473	<0.0001	0.251
A $\times$ B interaction	15	1.86685	0.12446	15.01473	<0.0001	0.540
Model	23	4.12479	0.17934	21.63586	<0.0001	0.722
Error	192	1.59148	0.00829	—	—	—
Corrected total	215	5.71627	—	—	—	—

Note: Partial η^2 was calculated as $SS_{\text{effect}}/(SS_{\text{effect}} + SS_{\text{error}})$. The analysis included 24 independent polishing slurry batches and nine observations per combination ($N = 216$). “—” indicates not applicable.

Comparing the reported literature, the temperature-regulated slurry can provide excellent offer superior polishing quality and efficiency, as listed in Table S1. This work provides new insight into the rational design of efficient slurry, which can be used for the polishing of TC4 in ultra-precision parts.

The hydrodynamic diameter and surface charge characteristics of the slurry of silica sol and different organic acid-modified slurry were systematically investigated via DLS and Zeta potential, respectively. The average diameter exhibited a pronounced dependence on the molecular structure of the incorporated acid. The pristine silica sol slurry presented a well-dispersed nanoscale population with a mean diameter of 16.3 nm. Upon the introduction of organic acids, a substantial increase in the

aggregated particle size was observed (Fig. 5a), following the sequence: Tartaric acid (99.0 nm) < acetic acid (124.4 nm) < oxalic acid (125.7 nm) < malic acid (165.9 nm) < lactic acid (178.7 nm) < citric acid (272.7 nm). The marked enlargement induced by organic acid suggests a strong bridging flocculation effect, which is the appropriate aggregation of abrasive particles helps to enhance the polishing effect.

Complementary to the size evolution, the Zeta potential measurements provided critical insights into the electrical double-layer (EDL) stability (Fig. 5b). The slurry with silica sol displayed a negative surface charge of -19.36 mV, indicative of stable electrostatic repulsion due to deprotonated silanol groups. However, the addition of organic acids distinctly altered the surface potential. Notably, acetic acid induced a charge reversal, yielding a positive Zeta potential of $+32.79$ mV, that is attributed to significant surface protonation and specific adsorption of acetate cations. Conversely, the remaining organic acids maintained a negative surface potential, with values ranging from -6.7 mV (tartaric acid) to -22.97 mV (citric acid). While citric acid endowed the slurry with the strongest negative charge (-22.97 mV), its largest particle size (272.7 nm) suggests that electrostatic stabilization alone is insufficient to counteract the substantial van der Waals attraction and polymeric bridging effects imposed by the polydentate citrate ligands. The tartaric acid system, despite having a Zeta potential close to the aggregation threshold (-6.7 mV), implying that the stability of the slurry is poor, which is the reason for the poor polishing quality. In order to further reveal the stability of slurry with lactic acid, the static experiment of the slurry was provided in Fig. S3. After 168 h, the lactic acid slurry remained stable, but the other slurries had basically formed gels and could no longer be utilized.

The flow characteristics of the slurries were evaluated by steady-

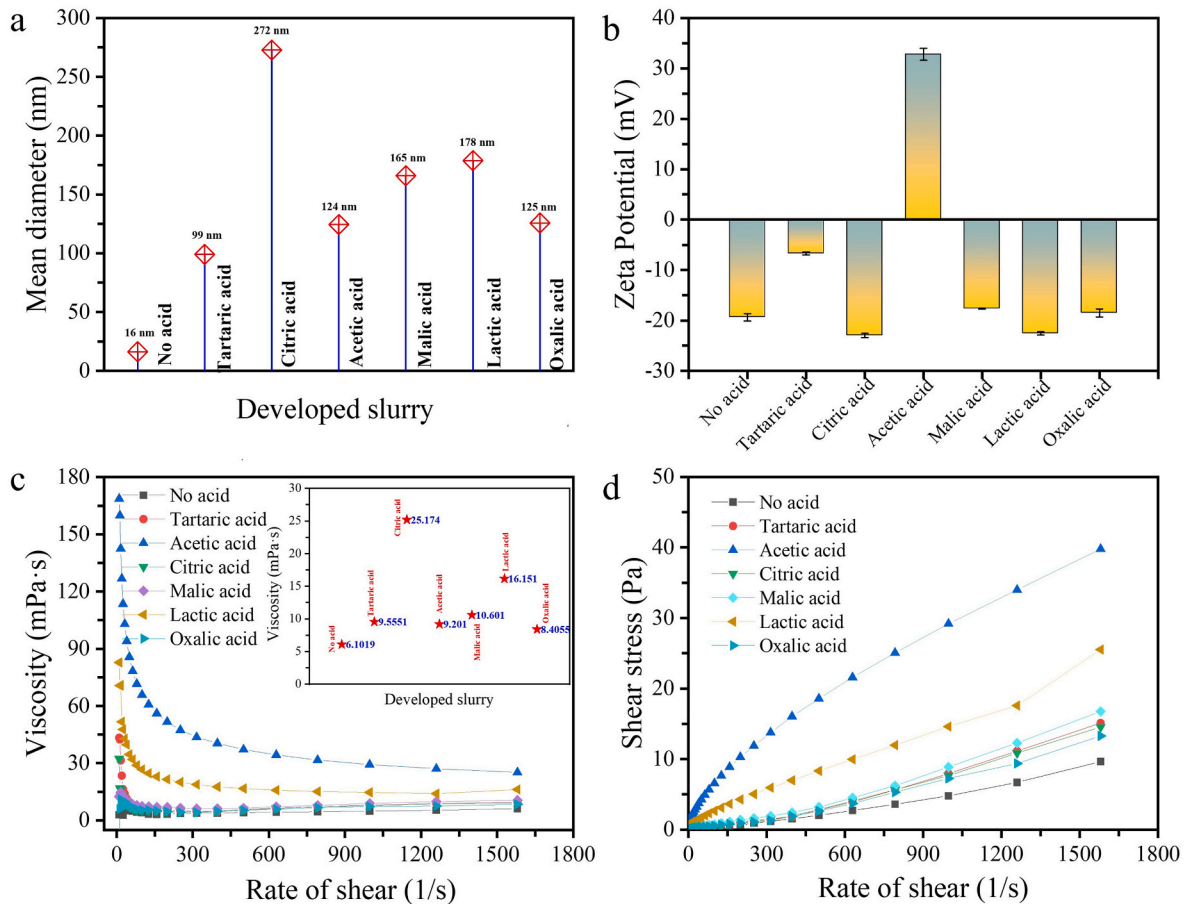


Fig. 5. (a) The average hydrodynamic diameter of slurry. (b) The Zeta potential of slurry. (c) Shear rate and viscosity curve of slurry. (d) Shear rate and shear stress curve of slurry.

state shear measurements, covering the evolution of both shear stress and apparent viscosity as a function of shear rate (Fig. 5c and d). All seven slurries exhibited a quasi-linear increase in shear stress with increasing shear rate. The slurry of silica sol registered the lowest terminal shear stress (9.641 Pa) and viscosity (6.102 mPa s), confirming a well-dispersed, non-interacting suspension with minimal interparticle friction. The viscosities and shear stresses were arranged in the intermediate order: Malic acid (10.601 mPa s; 16.749 Pa) > acetic acid (9.201 mPa s; 14.538 Pa) > tartaric acid (9.555 mPa s; 15.097 Pa) > oxalic acid (8.406 mPa s; 13.281 Pa). However, the citric acid-modified slurry demonstrated the most substantial resistance, with the highest terminal shear stress (39.776 Pa) and viscosity (25.174 mPa s). The lactic acid system followed as the second most viscous formulation (16.151 mPa s; terminal stress 25.519 Pa). The results show that the lactic acid slurry provided the best shear force and friction during the polishing process, which is consistent with the obtained lowest Sa.

Fig. 6 shows a representative SEM and correspond EDS mapping images of the polished and immersed TC4. The polished TC4 is smooth without particles (Fig. 6a) and the immersed TC4 in developed slurry appear non-dense layer and irregular particles (Fig. 6c). EDS was then performed to investigate the spatial distribution of the elements. Comparison of the polished and immersed TC4, the elemental mapping of the polished TC4 reveals the homogeneous loading of the N, Ti, Al and V on the alloy structure (Fig. 6b). During the immersion process, the formed layer nanoparticles is consisting of C, N, O, Ti, Al, and V (Fig. 6d). In surprise, the enhanced oxygen signal is evidence of the oxidation reaction on the TC4 surface.

3.2. Electrochemical experimental analysis

To elucidate the electrochemical role of individual components in the polishing system, potentiodynamic polarization (Tafel) measurements were performed on TC4 alloy in various electrolyte formulations. Corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were extracted from the linear Tafel regions of the polarization curves. As illustrated in Fig. 7a and b, the base electrolyte—comprising solely

0.2 M Na_2SO_4 as supporting electrolyte, that yielded a relatively low E_{corr} of 0.183 V vs. Ag/AgCl and the highest I_{corr} of $3.50 \times 10^{-5} \text{ A cm}^{-2}$, indicating rapid spontaneous dissolution of the titanium surface. Upon addition of 2 wt% H_2O_2 , I_{corr} decreased markedly to $1.38 \times 10^{-6} \text{ A cm}^{-2}$, accompanied by a slight negative shift in E_{corr} to 0.148 V vs. Ag/AgCl. As a potent oxidant, H_2O_2 drives surface oxidation of Ti, promoting the formation of a compact, protective TiO_2 -rich passive film. This film alters the mixed potential of the electrode/electrolyte interface and substantially suppresses anodic dissolution kinetics. Further incorporation of colloidal SiO_2 (15 wt%) resulted in the most negative E_{corr} among all tested formulations (0.124 V vs. Ag/AgCl and the second lowest I_{corr} ($7.46 \times 10^{-7} \text{ A cm}^{-2}$), reflecting enhanced corrosion resistance relative to the H_2O_2 -only system. This synergistic inhibition is attributed to the adsorption of silica nanoparticles onto the TiO_2 passive layer [26,27], which partially passivates surface active sites and increases interfacial charge-transfer resistance. Furthermore, the adsorbed silica layer hinders the mass transport of reactive species, such as H_2O_2 , H^+ , and dissolved Ti^{4+} ions, at the solid-liquid interface [28], consequently further slowing the rates of electrochemical reactions. Crucially, this electrochemical passivation behavior contrasts with the mechanical function of SiO_2 in CMP: under polishing conditions, colloidal SiO_2 particles act primarily as abrasives that mechanically disrupt and remove the H_2O_2 -induced oxide layer, sustaining the cyclic oxidation-abrasion-removal mechanism essential for controlled material removal [29].

Upon addition of lactic acid, the corrosion potential shifts markedly in the noble direction ($E_{\text{corr}} = 0.333 \text{ V}$ vs. Ag/AgCl), while the corrosion current density decreases modestly to $6.35 \times 10^{-7} \text{ A cm}^{-2}$. This electrochemical response signifies enhanced interfacial stability and suppressed anodic dissolution kinetics. As an α -hydroxy carboxylic acid, lactic acid exhibits strong chelating affinity for Ti^{4+} ions via synergistic coordination through its α -hydroxyl and carboxylate functional groups [30,31], forming stable, water-soluble titanium-lactate complexes. This complexation facilitates selective dissolution of the H_2O_2 -generated TiO_2 layer and inhibits redeposition of hydrolyzed titanium species onto the surface. Concurrently, adsorbed lactate anions contribute to passive film stabilization. It is likely by occupying oxygen vacancy sites or

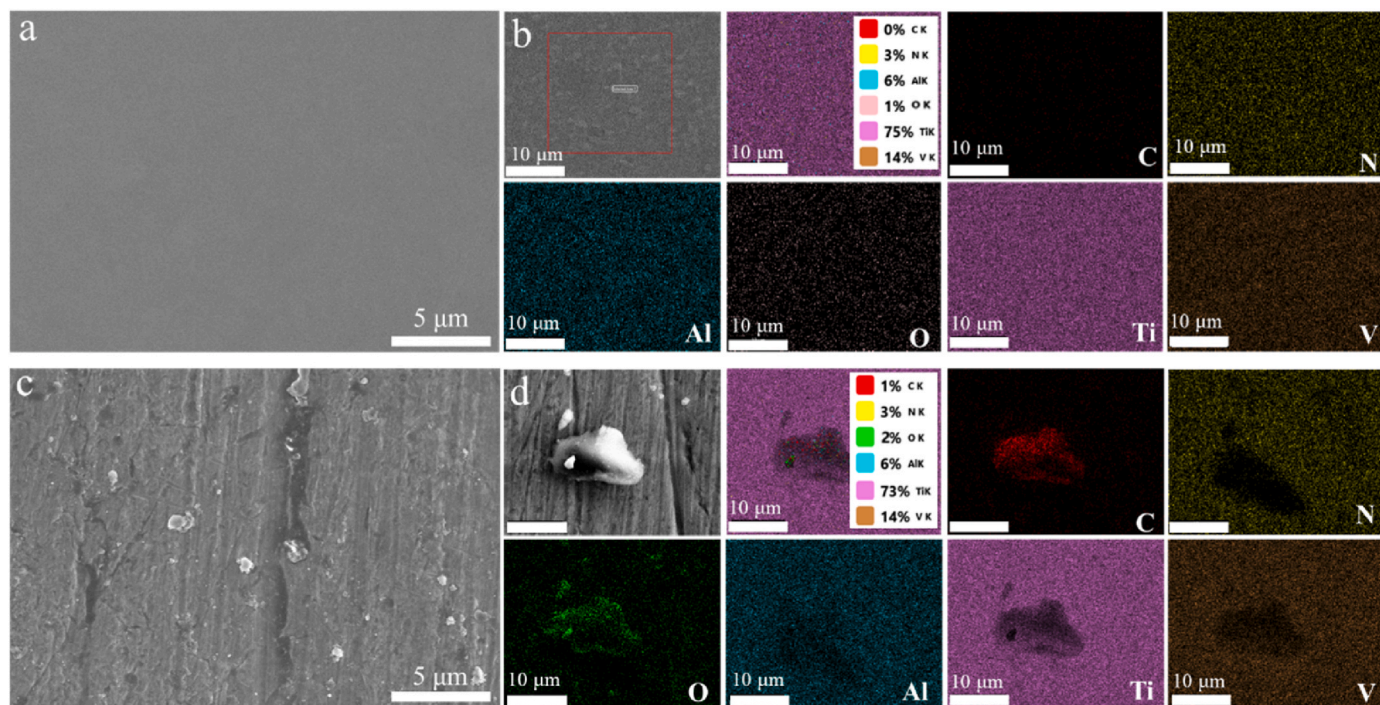


Fig. 6. SEM images of the polished (a) and immersed TC4 (c). EDS elemental mappings of the polished (b) and immersed TC4 (d).

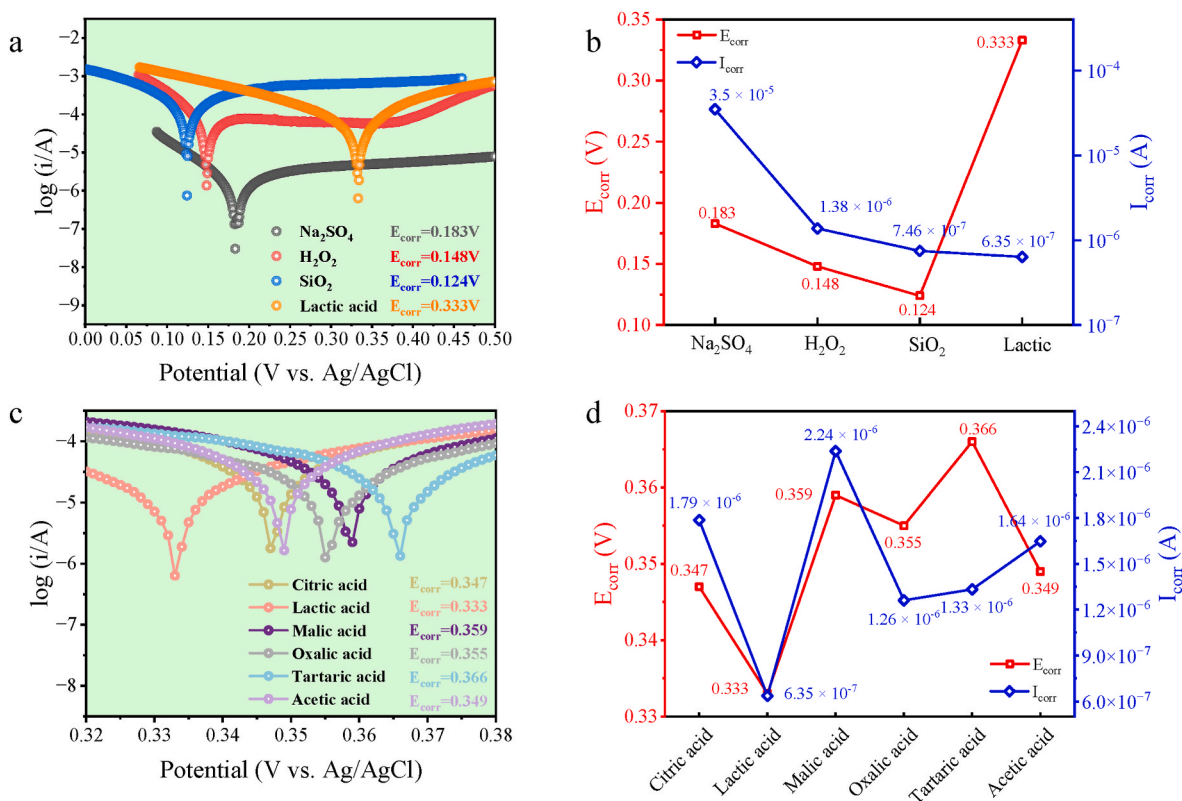


Fig. 7. (a) Tafel analysis of TC4 in various components, and (b) the corresponding corrosion current and corrosion voltage curves. (c) Tafel analysis of TC4 in different organic acids, and (d) the corresponding corrosion current and corrosion voltage curves.

modifying surface charge distribution, thereby elevating the mixed potential and inducing the observed positive E_{corr} shift. Collectively, these effects establish a dynamic equilibrium between oxide formation (driven by H_2O_2) and ligand-assisted oxide dissolution (mediated by lactate), which underpins the controllability and uniformity of material removal in the CMP process. To systematically compare the modulating effects of organic acids on interfacial electrochemistry, additional Tafel measurements were performed across a representative set of α -hydroxy and dicarboxylic acids. As shown in Fig. 7c and d, lactic acid yields both the lowest I_{corr} ($6.35 \times 10^{-7} \text{ A cm}^{-2}$) and the most noble E_{corr} (0.333 V vs. Ag/AgCl) among all tested formulations—indicating superior passivation capability and the most thermodynamically stabilized electrode interface under polishing-relevant conditions.

The adsorption behavior of organic acids on the TC4 surface was further probed via ex situ EIS. Fig. 8a displays the Nyquist plots acquired in electrolytes containing equimolar concentrations (10 mM) of respective organic acids. The smallest capacitive arc radii are observed for the blank Na_2SO_4 electrolyte and the acetic acid-containing solution, indicating minimal interfacial resistance and relatively unimpeded charge transfer kinetics. On the contrary, markedly enlarged semicircles appear in the presence of polycarboxylic acids, particularly tartaric and oxalic acids. It suggests the formation of highly resistive, adsorbate-derived interfacial layers that impede faradaic processes at the TC4/electrolyte interface.

The EIS data were fitted to the equivalent circuit depicted in Fig. 8b, comprising: R_s , C , R_{ct} , and Warburg impedance associated with diffusion-controlled mass transport (W). Fitted parameter values are summarized in Fig. 8c. R_s remains essentially invariant (9.00–11.54 Ω) across all formulations, confirming that organic acid addition does not appreciably alter the bulk ionic conductivity of the 0.2 M Na_2SO_4 supporting electrolyte. Conversely, R_{ct} exhibits pronounced sensitivity to organic acid structure. Relative to the blank Na_2SO_4 system ($R_{\text{ct}} = 1379 \Omega$), all organic acids elevate R_{ct} , with values following the

descending order: tartaric acid (20,053 Ω) > oxalic acid (14,787 Ω) > citric acid (11,420 Ω) > malic acid (7963 Ω) $\approx$ lactic acid (7900 Ω) > acetic acid (2275 Ω). This systematic increase in R_{ct} provides direct electrochemical evidence that organic acid molecules adsorb onto the TC4 surface and form compact, passivating interfacial layers that suppress electron transfer across the oxide–electrolyte boundary [32]. Surface adsorption capacity was further quantified using the surface adsorption rate (SCR), calculated from R_{ct} values as $\text{SCR} = 1 - (R_{\text{p,Non-e}}/R_{\text{p,Inhibitor}})$ [33]. As shown in Fig. 8d, SCR follows a nearly identical trend: tartaric acid (93.1%) > oxalic acid (90.7%) > citric acid (87.9%) > malic acid (82.7%) > lactic acid (82.5%) > acetic acid (39.4%). Collectively, these results demonstrate that polycarboxylic acids, owing to their multiple carboxylate groups enabling multidentate chelation with surface Ti^{4+} sites, achieve adsorption layers on the native TiO_2 film compared to monocarboxylic analogues [34]. This mechanistic understanding underpins the critical role of organic acids as key functional additives in CMP slurries engineered for TC4 materials characterized by high hardness, low chemical reactivity, and inherent resistance to conventional etching and abrasion.

LSV were employed to evaluate the anodic reaction and passivation behaviors of TC4 in different slurry. The curves were divided into apparent activation, passivation and over passivation regions (Fig. S4). The overall activation range of all the slurries remained within the voltage range of 0.5 to 0.8 V. As the applied voltage increases, the passivation region of oxalic acid, tartaric acid, malic acid, lactic acid, acetic acid, citric acid. Electrolyte began to form in the near of 0.84, 0.74, 0.80, 0.82, 0.87, 0.90 V vs. Ag/AgCl, respectively. From the passivation platform hereafter, it enters the over-passive state, its reaction became very active. Therefore, it is important to understand the oxidizing reaction of TC4 at various states of the I-V curve in order to evaluate the optimal process parameters for the CMP application.

At the same time, we recorded the OCP for 400 s in the six organic-acid-containing slurries. As shown in Fig. 9a, all systems exhibited an

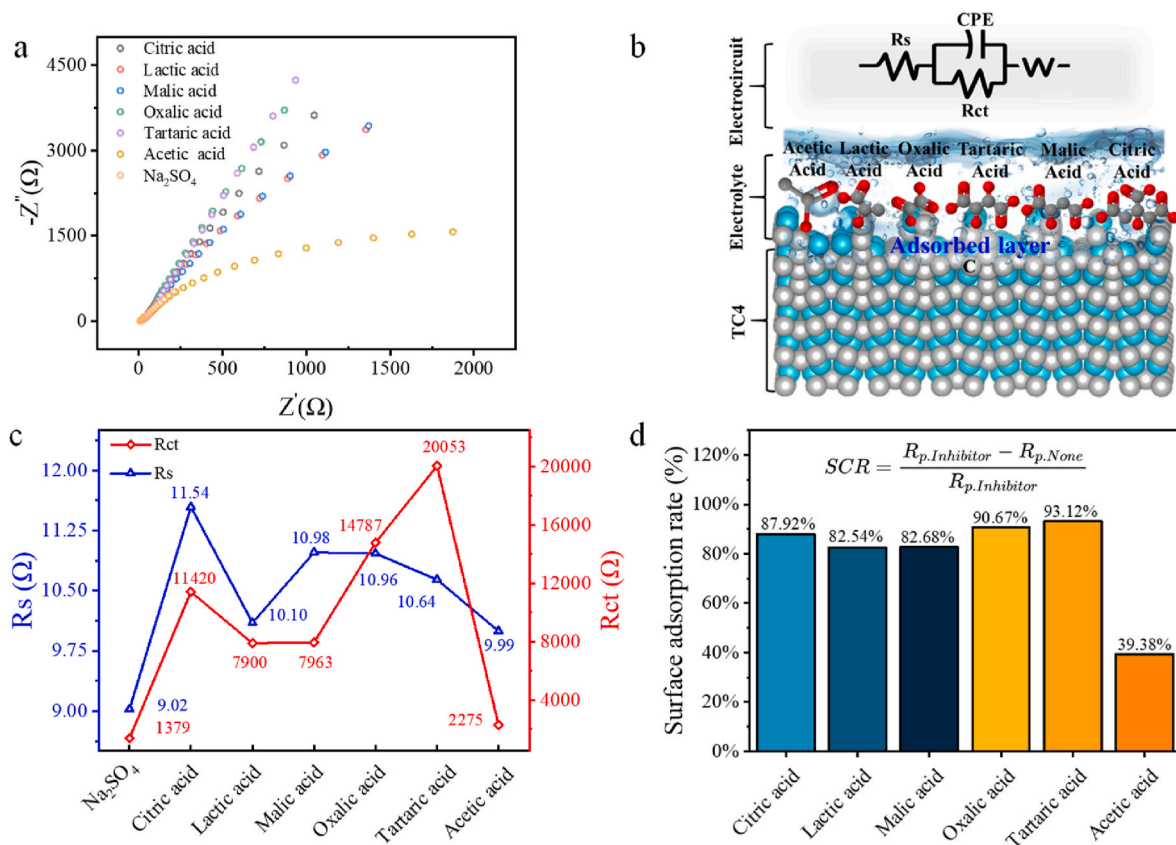


Fig. 8. Electrochemical impedance analysis of molecules adsorption behavior on TC4 surface. (a) Nyquist plots, (b) the equivalent circuit for resistance fitting, (c) calculated equivalent resistance, and (d) surface adsorption rate of the titanium alloys treated with different inhibitors. $R_{p,Inhibitor}$ represents polarization resistance of TC4 in the presence of inhibitor, and $R_{p,None}$ represents the polarization resistance in the absence of inhibitor.

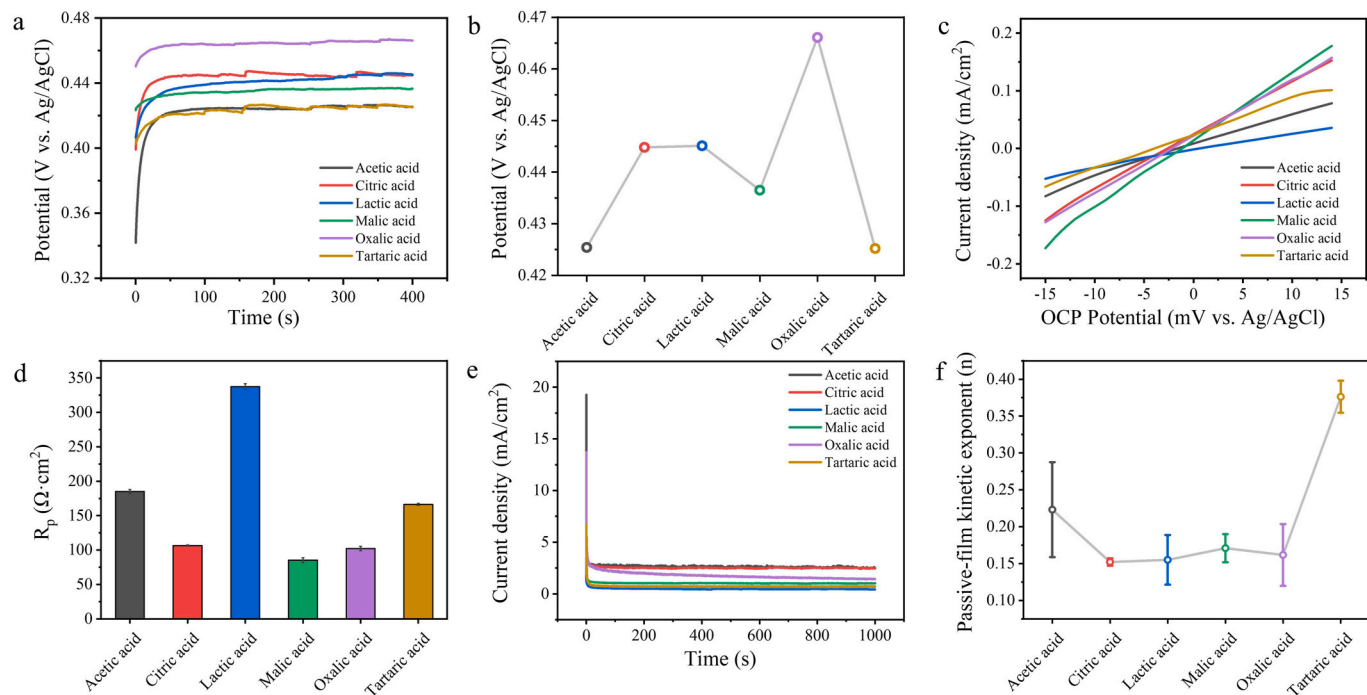


Fig. 9. (a) OCP curves of the different slurries and (b) The corresponding stable voltage. (c) The linear fitting curves of current and voltage and (d) the calculated R_p values. (e) CA curves of the different slurries during potential of passivation. (f) The calculated n values (Passive-film kinetic exponent) of each acid slurries.

initial positive shift in OCP and subsequently approached quasi-steady values. The final OCP values followed the order oxalic acid

(0.4661 V) > lactic acid (0.4451 V) $\approx$ citric acid (0.4448 V) > malic acid (0.4365 V) > acetic acid (0.4254 V) $\approx$ tartaric acid (0.4252 V) (Fig. 9b). The different thermodynamic tendency towards surface oxidation and/or stabilization of an oxidized surface layer were proved. The R_p was determined by performing a linear potential sweep within ± 15 mV of the stabilized open-circuit potential and linearly fitting the potential-current density data (Fig. 9c and d). The measured R_p values followed the order lactic acid ($337.5 \Omega \text{ cm}^2$) > acetic acid ($185.0 \Omega \text{ cm}^2$) > tartaric acid ($166.3 \Omega \text{ cm}^2$) > citric acid ($106.5 \Omega \text{ cm}^2$) > oxalic acid ($102.2 \Omega \text{ cm}^2$) > malic acid ($85.3 \Omega \text{ cm}^2$). A higher R_p indicates greater resistance to interfacial electrochemical polarization, whereas a lower R_p indicates a more electrochemically active interface and a greater tendency towards static electrochemical dissolution. Accordingly, the lactic-acid-containing slurry exhibited the strongest suppression of interfacial electrochemical reactions. The malic-acid-containing slurry exhibited the greatest static electrochemical dissolution tendency.

Besides, the passive-film growth kinetics were investigated using single-step CA model. To quantitatively compare the passive-film growth behavior (Fig. 9e and f), we analyzed the CA current transients using a power-law current-decay model Formula (2). After transformation to the double-logarithmic form Formula (3). The obtained n values are approximate order tartaric acid (0.376) > acetic acid (0.223) > malic acid (0.171) > oxalic acid (0.162) > lactic acid (0.155) > citric acid (0.152). The higher the kinetics, the faster the current decays, and the faster the passivation surface state is established. Therefore, these results demonstrate that the organic-acid chemistry strongly affects the kinetics of passivated state.

$$j = Kt^{-n} \quad (2)$$

$$\log_{10} j = \log_{10} K - n \log_{10} t \quad (3)$$

Where the selected linear region of each $(\log_{10} j) - (\log_{10} t)$ plot was fitted, and (n) was obtained as the negative value of the fitted slope. j is the current density (mA/cm^2), t is time (s), K is a proportionality constant, and n is the passivation kinetic exponent.

Furthermore, the oxide dissolution/removal-related kinetics were

investigated using two-step CA (Fig. 10a). For each electrolyte, the baseline current density was estimated as the median current density measured between 360 and 600 s. Because the current density immediately following the second step was more cathodic than the baseline current density, a positive background-corrected excess current density was defined by Formula (4) and (5), as shown in Fig. 10b. Moreover, the j_{excess} was integrated over the interval from 0 to 2 s followed Formula (6) [35–38], as shown in Fig. 10c. For a standardized comparison among the organic-acid solutions, the value accumulated over the first 2 s of the second potential step was extracted through Formula (7) and is displayed in Fig. 10d. The q_{excess} followed the order of acetic acid ($6.630 \text{ mC}/\text{cm}^2$) > oxalic acid ($1.57 \text{ mC}/\text{cm}^2$) > citric acid ($0.750 \text{ mC}/\text{cm}^2$) > tartaric acid ($0.536 \text{ mC}/\text{cm}^2$) > lactic acid ($0.465 \text{ mC}/\text{cm}^2$) > malic acid ($0.235 \text{ mC}/\text{cm}^2$). Previous ellipsometric and coulometric measurements have demonstrated that cathodic polarization of anodically formed titanium oxide in acidic media results in film thinning and reductive dissolution to soluble Ti^{3+} , with the dissolved TC4 amount and film-thickness change depending on the applied cathodic charge. Accordingly, the q_{excess} was assigned to the oxide-reduction/removal-related electrochemical response. Under otherwise identical experimental conditions, a larger q_{excess} therefore represents a larger integrated relative response.

$$j_{ss} = \text{med}\{j(t) : t \in [360, 600]\} \quad (4)$$

$$j_{\text{excess}} = j_{ss} - j \quad (5)$$

$$q = \int_0^t j_{\text{excess}} \cdot dt, t \in [0, 2] \quad (6)$$

$$q_{\text{excess}} = q(2) = \int_0^2 j_{\text{excess}} \cdot dt \quad (7)$$

Where, j_{ss} is the baseline current density (mA/cm^2). j_{excess} represents the positive baseline-corrected excess current density (mA/cm^2). q is the charge density (mC/cm^2). q_{excess} is the excess charge (mC/cm^2).

Motivated by the exponential current decay predicted for a simple irreversible surface-confined electrochemical process, j_{excess} was fitted

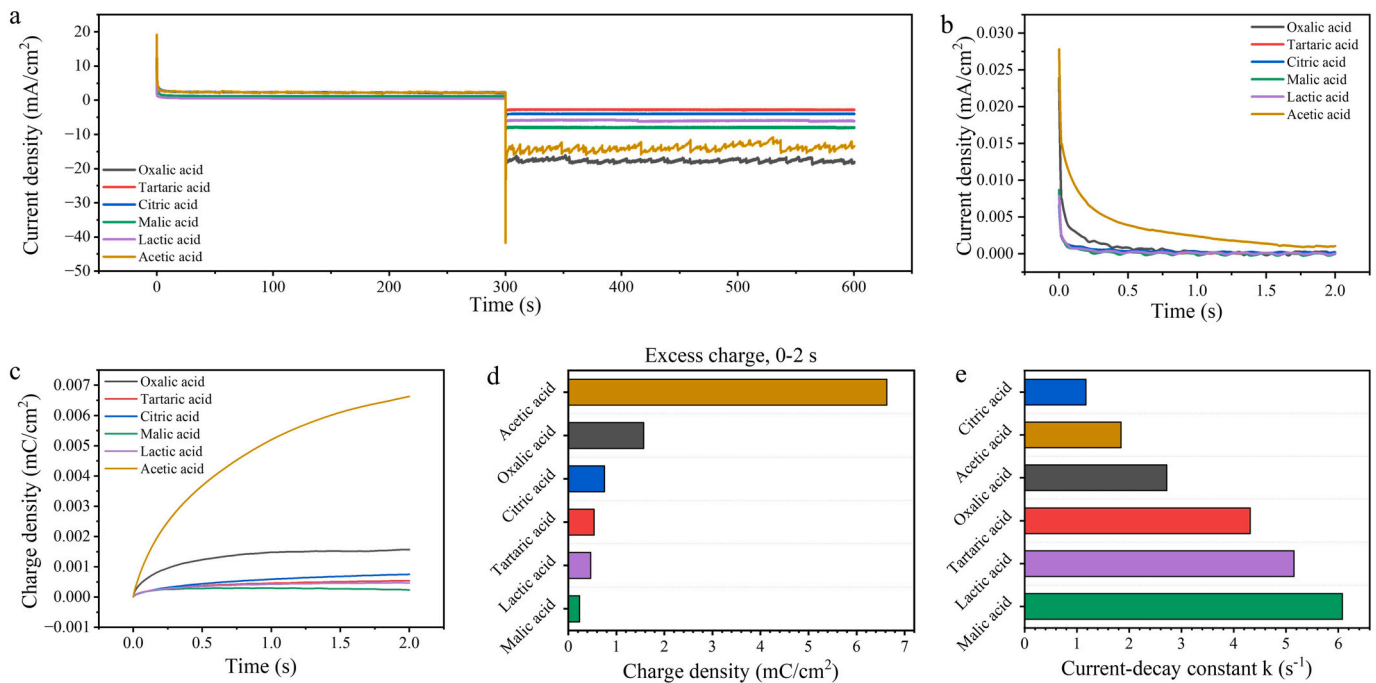


Fig. 10. (a) Two-step CA curves. (b) The obtained current density curve via Formula (5). (c) The integral curve of charge density-time. (d) The calculated charge value for 2 s. (e) The current-decay constant k for each acid.

using Formula (8) [39–41] and was further transformed to the natural double-logarithmic form Formula (9). The k followed the order of malic acid (6.078 s^{-1}) > lactic acid (5.152 s^{-1}) > tartaric acid (4.316 s^{-1}) > oxalic acid (2.72 s^{-1}) > acetic acid (1.844 s^{-1}) > citric acid (1.172 s^{-1}) (Fig. 10e). The current-decay constant k proves the bigger value in malic and lactic acids, whereas acetic acid produced the smallest current-decay constant. A larger k indicates faster fractional decay of the remaining excess current. In this sense, a higher current attenuation rate correlates with reduced oxide dissolution. The experimentally determined k value for acetic acid closely aligns with the q_{excess} value, thereby substantiating its comparatively stronger oxidative dissolution capacity.

$$j_{\text{excess}}(t) = A \cdot e^{-kt} \quad (8)$$

$$\ln j_{\text{excess}}(t) = \ln A - k \cdot t \quad (9)$$

Where A is the fitted transient amplitude (mA/cm^2) and k is the current-decay constant (s^{-1}). Where the selected linear region of each $(\ln j_{\text{excess}}) - (t)$ plot was fitted, and (k) was obtained as fitted slope.

With these collected observables in mind, lactic acid slurry exhibits a pronounced inhibitory effect on the interfacial electrochemical reaction. In contrast, the formation of the passivated surface state proceeds gradually. Acetic acid demonstrates superior oxidative dissolution capability. Consequently, the electrochemical analyses including polarization resistance, passive film growth kinetics, and oxide dissolution kinetics are in agreement with the experimentally determined trends in MRR and Sa.

In molecular mechanics, the Total Energy (Potential Energy at 298 K)

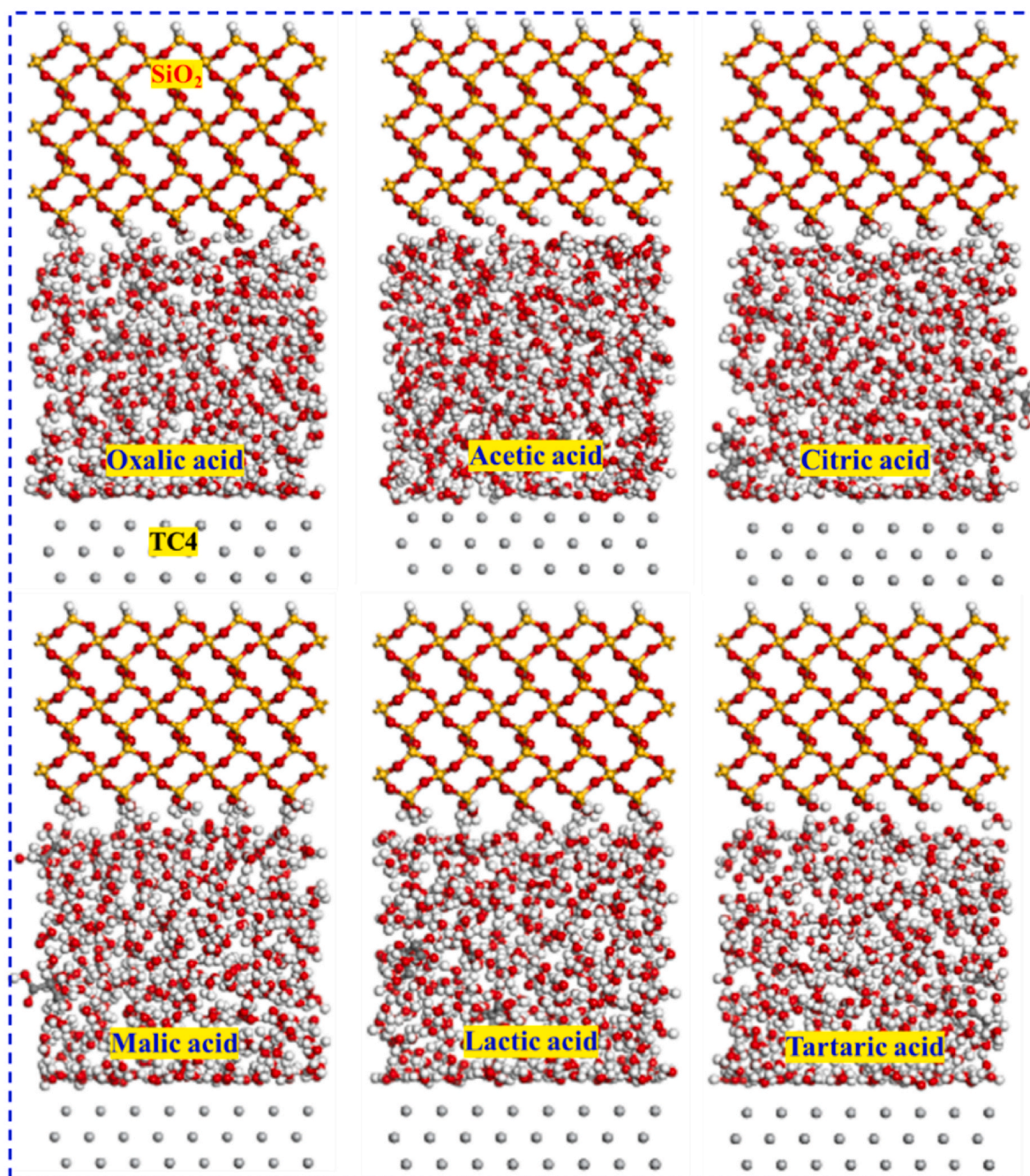


Fig. 11. MD simulation of polishing process on SiO_2 /slurry (oxalic acid/acetic acid/citric acid/malic acid/lactic acid/tartaric acid)/TC4 interface.

directly reflects the thermodynamic favorability of the assembled interface system. A lower (more negative) value indicates a more stable composite structure under the given forcefield parameters. In demonstrated Fig. 11, tartaric acid exhibits the lowest total energy (-14531.48 kcal/mol), indicating it forms the most thermodynamically stable tri-layer interface. Malic acid (-14329.32 kcal/mol) and lactic acid (-14433.71 kcal/mol) show comparable stability, trailing tartaric acid by a negligible margin (~ 100 – 200 kcal/mol). Citric acid yields a slightly higher energy (-13684.12 kcal/mol), suggesting that although it has multiple carboxyl groups, its bulkier tertiary structure may introduce steric hindrance at the confined interface, slightly destabilizing the system. Acetic acid shows a significantly higher energy (-7653.95 kcal/mol), roughly 50% less stable than the polyhydroxy acids. This is attributed to its single functional group, which provides limited anchoring sites to bridge the TC4 and SiO_2 surfaces [42,43]. Comparing tartaric acid, malic acid, citric acid, and lactic acid, all four contain hydroxyl (-OH) groups in addition to carboxyl (-COOH) groups. This multi-dentate configuration allows them to form strong coordination bonds with Ti atoms on the alloy surface (via -COOH) and extensive hydrogen-bond networks with silanol (-SiOH) groups on the SiO_2 surface (via -OH) [44,45]. Tartaric acid (with two -OH and two -COOH groups) provides the densest network of these interactions, leading to its superior stability. Citric acid, despite having three -COOH groups, has fewer flexible -OH groups available for SiO_2 hydrogen bonding, explaining its lower relative stability compared to tartaric acid/lactic acid.

Based on the Forcite MD simulations (GeomOpt, Anneal, and Confined Shear) using the COMPASS II forcefield, the following conclusions are drawn regarding the binding of organic acids to Ti-alloy and SiO_2 abrasives. TA, LA and MA demonstrate the most negative total system energies, identifying them as the most effective interface stabilizers. Their dual functional groups (-COOH and -OH) provide synergistic bridging between the metallic substrate and the oxide abrasive. AA is far less effective due to its monofunctional nature, lacking the hydroxyl groups necessary for strong secondary interactions with the silica surface. OA is entirely unsuitable for this tri-layer system. Its rigid, strain-free conformation fails to accommodate the spatial constraints of

the confined interface, leading to massive repulsive strain (positive energy).

3.3. Surface chemical environment analysis of TC4

All XPS peak deconvolution and spectral fitting were conducted using established binding energy references and validated literature data [46]. XPS was employed to characterize chemical state evolution at the immersed and polished TC4 alloy surface. Core-level assignments for C 1s, O 1s, Ti 2p, and Al 2p spectra were rigorously anchored to characteristic binding energies reported for titanium alloys and adsorbed organic species, ensuring full consistency with benchmark surface science studies. Fig. 12a presents the high-resolution C 1s spectra, deconvoluted into three chemically distinct components: adventitious C-C (284.78 eV), ether-type C-O-C (286.38 eV), and carboxylate O-C=O (288.28 eV) [47]. In the as-received sample, the O-C=O contribution is negligible, and the C-O-C signal is undetectable—indicating that surface carbon is predominantly adventitious hydrocarbon contamination. Following immersion in the ternary slurry, the relative intensities of oxygenated carbon species (C-O-C and O-C=O) increase substantially, confirming chemisorption and oxidative functionalization of adsorbed organic moieties. As shown in Fig. 12b, the Ti 2p spectra exhibit a dominant peak at 458.4 eV in both pristine and polished samples, unambiguously assigned to Ti^{4+} in stoichiometric TiO_2 [48]. Critically, the polished sample shows a significantly enhanced metallic Ti^0 component at 453.8 eV relative to the as-received surface [49], providing direct spectroscopic evidence that mechanical abrasion during CMP partially removes the native/passive oxide layer and exposes underlying metallic Ti. The immersed (non-polished) sample exhibits pronounced attenuation of both Ti 2p signals, indicative of a thick, organic-inorganic hybrid adsorption layer that effectively masks the substrate elemental signature.

Fig. 12c displays the high-resolution O 1s spectra, revealing pronounced chemical state redistribution upon immersion in the ternary slurry. The O 1s signal was deconvoluted into three chemically resolved components: lattice oxygen (O_L) in $\text{TiO}_2/\text{Al}_2\text{O}_3$ at 530.0 eV, hydroxyl

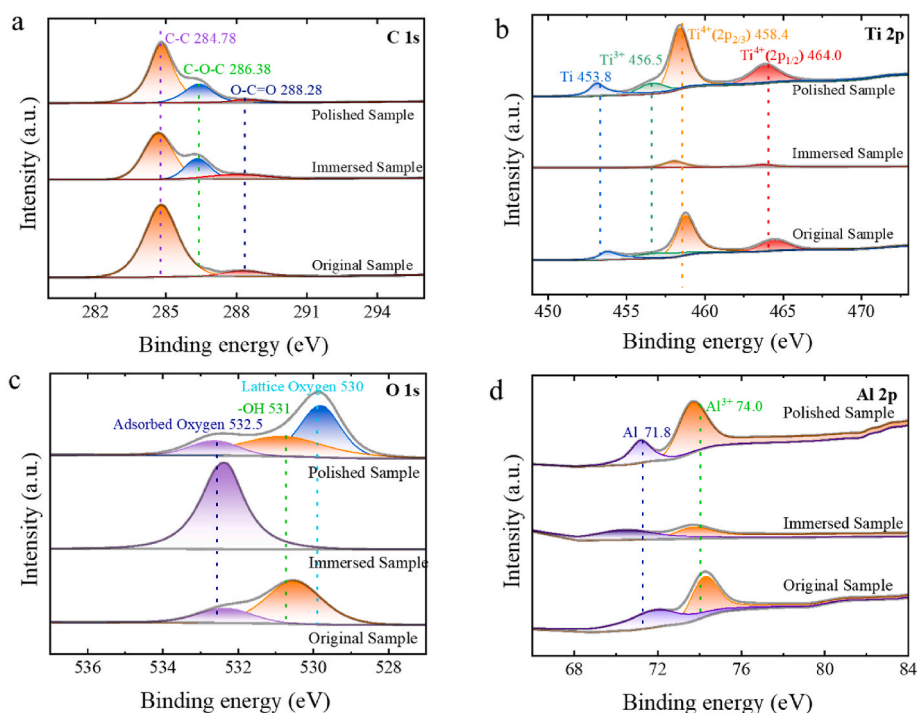


Fig. 12. The surface information of the immersed, original and polished TC4. (a) C 1s high-resolution XPS spectrum. (b) Ti 2p high-resolution XPS spectrum. (c) O 1s high-resolution XPS spectrum. (d) Al 2p high-resolution XPS spectrum.

oxygen (O–OH) associated with surface hydroxides or hydrogen-bonded water at 531.5 eV, and adsorbed oxygen species (O_{ads}), including chemisorbed H_2O , carboxylate, or ether functionalities at 532.8 eV [50]. Critically, the immersed sample exhibits a dramatic intensification of the O_{ads} component, which becomes the dominant spectral feature, directly evidencing extensive surface adsorption of oxygen-containing species, including hydration layers and organic ligands during immersion. Collectively, these complementary XPS observations confirm the formation of a thick, adsorption-enriched surface overlayer that effectively masks the underlying TC4 alloy matrix. This conclusion is further corroborated by the O 1s evolution shown in Fig. 12b, which demonstrates parallel increases in O_{ads} and O–OH intensities, indicating synergistic adsorption of both aqueous and organic oxygen donors. Fig. 12d presents the high-resolution Al 2p spectra, deconvoluted into metallic Al^0 (71.8 eV) and Al^{3+} in oxidized states (74.0 eV) [51]. In both the as-received and polished samples, the Al^{3+} component dominates, confirming that aluminum resides predominantly in its thermodynamically stable oxide form (Al_2O_3) on the TC4 surface. The immersed sample exhibits significantly reduced overall Al 2p intensity alongside a relative enhancement of the Al^0 contribution—suggesting that the adsorption overlayer not only attenuates total signal yield but also modifies the effective sampling depth, thereby increasing the apparent proportion of near-surface metallic Al due to differential attenuation of the deeper-lying oxide signal.

High-resolution XPS spectra were acquired to quantitatively assess surface chemical state evolution, with the relative atomic percentages of deconvoluted components summarized in Fig. 13. For the C 1s region (Fig. 13a), three chemically distinct contributions were resolved at 284.78 eV (adventitious C–C/C–H), 286.38 eV (ether-type C–O–C), and 288.28 eV (carboxylate O–C=O) [52]. The polished sample exhibits 70.99% C–C/C–H, 24.92% C–O–C, and 4.90% O–C=O, indicating persistence of ambient carbon contamination alongside newly introduced oxygenated functionalities derived from slurry constituents. The as-received sample is dominated by C–C/C–H (92.27%), with negligible

C–O–C and O–C=O signals. Upon immersion, the proportion of C–C/C–H bonds decreases to 65.11%, whereas the O–C=O component increases to 10.68%. This change indicates oxidative functionalization of the adsorbed carbon species, likely facilitated by carboxylation or carbonate formation mediated by lactic acid and H_2O_2 .

The O 1s spectra (Fig. 13b) were deconvoluted into three principal components: lattice oxygen (O_L , $Ti^{4+}-O^{2-}/Al^{3+}-O^{2-}$) at 530.0 eV, hydroxyl oxygen (O–OH) at 531.5 eV, and adsorbed oxygen species (O_{ads}), including chemisorbed H_2O , carboxylates, and ether linkages at 532.8 eV [53]. In the polished sample, O_L constitutes 45.56%, O–OH accounts for 38.36%, and O_{ads} represents 16.08%, demonstrating coexistence of bulk oxide lattice integrity and surface hydroxylation/adsorption. The as-received sample shows no discernible O_L peak; instead, O–OH (50.01%) and O_{ads} (49.99%) dominate, indicating that detected oxygen arises solely from physisorbed/chemisorbed surface species, with no contribution from the underlying oxide lattice. Critically, the immersed sample exhibits O_{ads} as the overwhelming majority (72.41%), with O_L reduced to 12.85% and O–OH at 14.74%, providing direct spectroscopic evidence for formation of a thick, organic–inorganic hybrid adsorption overlayer that substantially attenuates signal from the substrate oxide lattice.

The Ti 2p spectra (Fig. 13c) resolve multiple titanium oxidation states [54]. In the polished sample, Ti^{4+} constitutes the dominant species (59.75% Ti 2p_{3/2}, 24.53% Ti 2p_{1/2}), with minor contributions from Ti^{3+} (7.44%) and Ti^0 (8.28%), confirming that mechanical abrasion preserves the bulk oxide lattice while exposing limited subsurface metallic regions. The as-received sample exhibits a comparable Ti^{4+} fraction (66.78% Ti 2p_{3/2}, 22.16% Ti 2p_{1/2}), but with significantly lower Ti^{3+} content (0.80%) and a marginally higher Ti^0 proportion (10.26%), consistent with a native oxide layer of moderate thickness and low defect density. In stark contrast, the immersed sample displays near-exclusive Ti^{4+} character (67.79% Ti 2p_{3/2}, 32.21% Ti 2p_{1/2}), with no resolvable Ti^{3+} or Ti^0 signals—indicating complete surface passivation and absence of metallic substrate exposure under immersion.

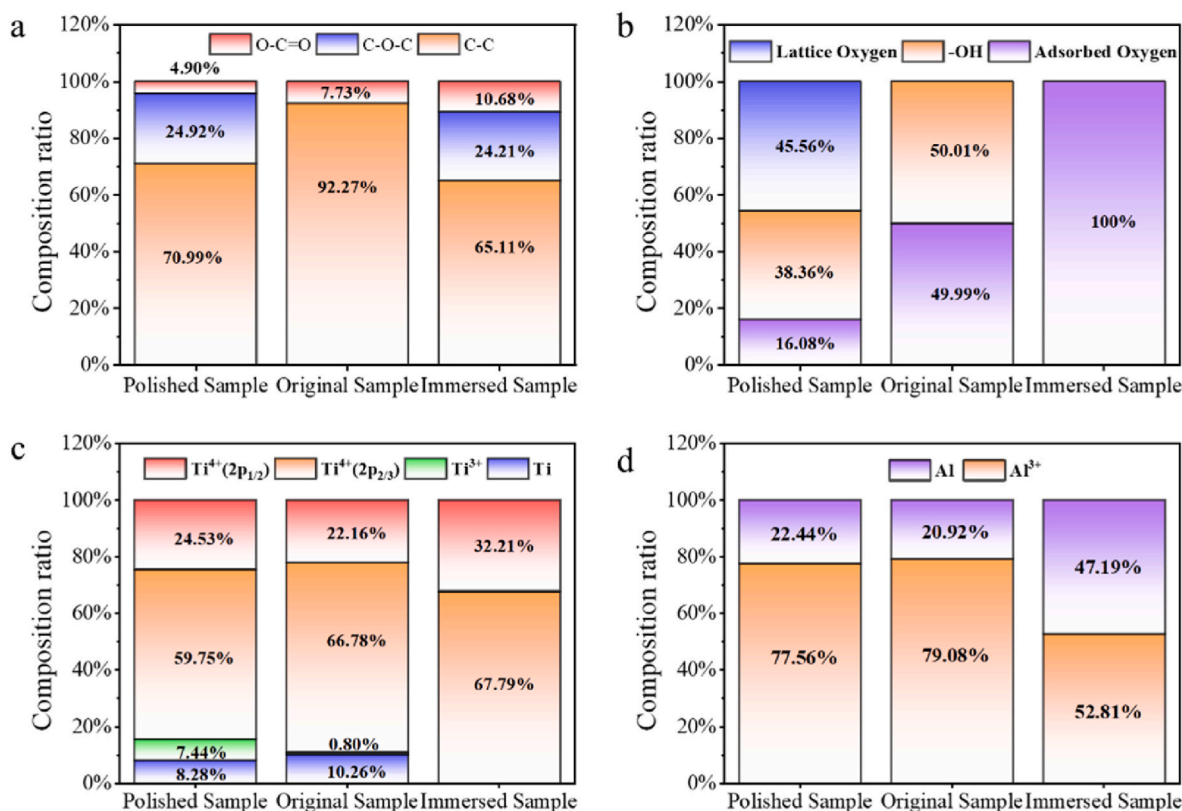


Fig. 13. The content of elements on the surface of the TC4 by XPS analysis. The component content of C (a), O (b), Ti (c), and Al (d).

conditions.

The Al 2p spectra (Fig. 13d) were deconvoluted into two principal components: metallic Al⁰ at 71.8 eV and Al³⁺ in Al₂O₃ at 74.0 eV [55]. For both the polished and as-received samples, Al³⁺ dominates (77.56% and 79.08%, respectively), confirming aluminum's thermodynamic preference for oxidation as a stable Al₂O₃ layer. The residual Al⁰ signal arises from the underlying alloy matrix. Conversely, the immersed sample exhibits a marked shift toward metallic Al⁰ (47.19%) and reduced Al³⁺ (52.81%). This inversion is not attributable to actual dissolution of Al₂O₃, but rather to differential attenuation of the Al³⁺ signal by the thick organic–inorganic adsorption overlayer. This is consistent with the pronounced O_{ads} dominance and O_L suppression observed in the O 1s spectra—thereby increasing the apparent Al⁰/Al³⁺ intensity ratio.

Raman spectroscopy was employed to probe the vibrational structure and phase evolution of surface oxides on the as-received TC4 alloy. Spectra were normalized to unit integrated area to enable quantitative comparison, as shown in Fig. 14a. The as-received sample exhibits low overall Raman intensity and features three broad, low-intensity bands centered at 801, 1171, and 1879 cm⁻¹. The 801 cm⁻¹ band is assigned to Ti–O stretching vibrations in amorphous or highly disordered titanium oxide (TiO_{2-x}), consistent with the native, ultrathin oxide layer typical of air-exposed titanium alloys [56]. The weak feature at 1171 cm⁻¹ falls within the spectral region associated with C–H bending or carboxylate deformation modes. Following immersion in the CMP slurry, the Raman spectrum undergoes a dramatic intensification and spectral sharpening. A dominant, narrow peak emerges at 607 cm⁻¹, matches the A_{1g} phonon of stoichiometric rutile TiO₂ that belongs to Ti–O coordination environments, exhibiting intensity enhancement relative to the as-received spectrum [57]. However, the lack of other crystalline TiO₂ signatures (e.g., B_{1g} at 801 cm⁻¹), confirms that the immersed surface does not host long-range rutile crystallinity. Collectively, the characteristic peaks on the surface of the immersed samples disappeared, indicating that a chemical decomposition reaction occurred between the slurry and TC4 surface.

FTIR spectroscopy was conducted to probe molecular-level surface functionalization on the TC4 alloy, with spectra acquired in ATR mode and normalized to unit absorbance for comparative analysis (Fig. 14b). The immersed sample exhibits distinct absorption bands at 2922 cm⁻¹ (asymmetric C–H stretch) and 2852 cm⁻¹ (symmetric C–H stretch), characteristic of alkyl chains in adsorbed organic ligands—consistent with the presence of lactic acid and its titanium–lactate complexes identified by XPS and electrochemical analysis. A pair of intense, well-resolved bands appears at 1553 cm⁻¹ (asymmetric –COO⁻ stretch) and 1402 cm⁻¹ (symmetric –COO⁻ stretch), with a Δν (COO⁻) separation of 151 cm⁻¹. According to the Deacon–Phillips criterion, Δν values greater than approximately 200 cm⁻¹ are generally associated with monodentate coordination, values below approximately 100–110 cm⁻¹ with

chelating bidentate coordination, and intermediate values around 140–200 cm⁻¹ with bridging coordination [58]. Accordingly, the measured Δν of 151 cm⁻¹ is most consistent with a bridging bidentate carboxylate coordination mode involving surface Ti⁴⁺ sites [59]. This spectral signature provides direct vibrational evidence for chemisorption of lactate anions and formation of inner-sphere titanium–carboxylate surface complexes. Furthermore, a broad absorption feature spanning 1120–1030 cm⁻¹, centered at ~1075 cm⁻¹, is assigned to Si–O–Si asymmetric stretching vibrations of adsorbed colloidal silica nanoparticles [60], corroborating the EIS- and XPS-derived conclusion that silica forms a persistent interfacial layer on the TC4 surface during immersion.

The ¹H NMR spectra of the slurry with acetic acid and lactic acid are provided in Figs. S5 and S6. Upon the addition of the Ti⁴⁺ species to the acetic acid, we observed significant downfield shifts for –CH_{3c} (from 2.098 to 1.86), accompanied by distinct peak broadening of the protons adjacent to the carboxylate groups (Fig. S5). For NMR spectra of slurry with lactic acid, the quadruple peaks of the –CH– showed significant changes during the treatment of TC4 (Fig. S6). These changes are direct indicators of electron density redistribution and ligand exchange dynamics at the coordination site [61,62].

The mechanistic framework of the developed CMP slurry is schematically illustrated in Fig. 15. Prior to slurry-based polishing, TC4 samples underwent pre-conditioning via mechanical abrasion in deionized water for 5 min—sufficient to remove the native air-formed oxide layer and expose a chemically active metallic surface. During subsequent polishing in the acidic ternary slurry (pH ≈ 4.0), electrochemical oxidation by H₂O₂ generates a dynamic TiO₂/Al₂O₃-rich reaction layer, while concurrent protonation (H⁺) weakens the Ti–O/Al–O lattice bonds, facilitating interfacial dissolution. Organic acids—particularly lactic acid—adsorb onto the hydrated oxide surface and form soluble titanium–carboxylate chelates via multidentate coordination, thereby thermodynamically stabilizing dissolved Ti⁴⁺/Al³⁺ species and preventing redeposition. Colloidal silica nanoparticles simultaneously adsorb onto this modified interface, forming a protective yet mechanically labile overlayer that modulates interfacial shear stress. Under applied mechanical shear, this composite reaction–adsorption layer is selectively removed, exposing fresh metal for cyclic re-oxidation, while simultaneously planarizing surface topography by preferentially eroding asperities. Crucially, material removal is governed by a tightly coupled chemical–mechanical synergy: the rate of oxide formation (H₂O₂-driven), ligand-assisted dissolution (organic acid-mediated), and mechanical delamination (SiO₂-abrasive-induced) are dynamically balanced to achieve atomic-level surface smoothing without subsurface damage.

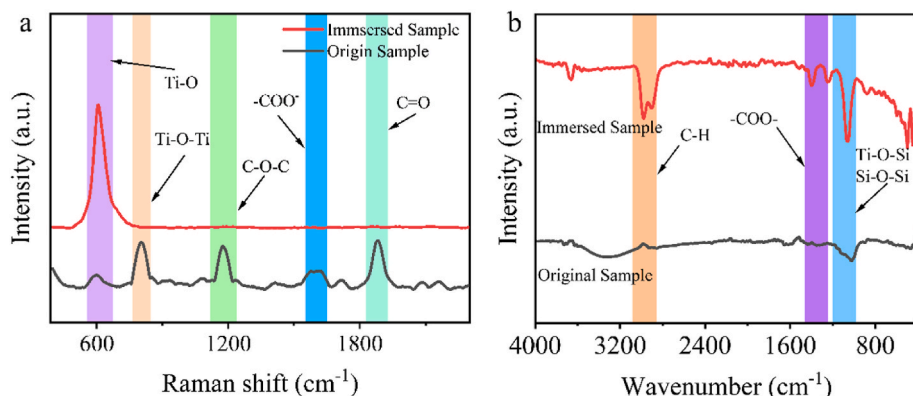


Fig. 14. (a) Raman spectra of the original and immersed samples. (b) FTIR spectra of the original and immersed samples.

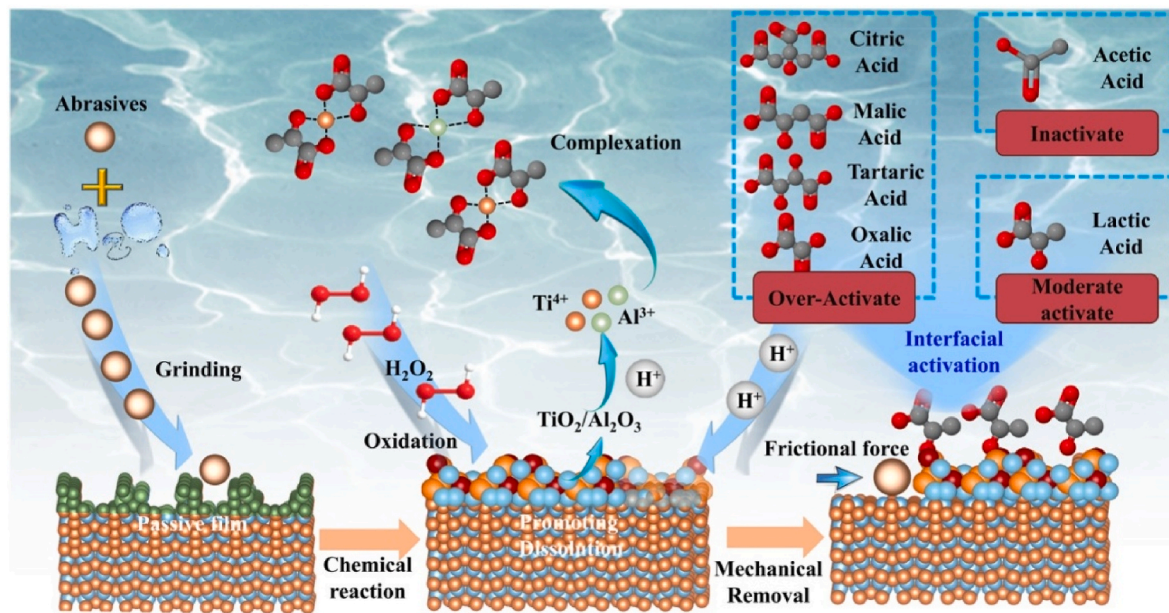


Fig. 15. Schematic diagrams of the CMP mechanism of TC4 via the developed optimal CMP slurry containing organic acids and hydrogen peroxide.

4. Conclusion

In summary, we have developed a CMP slurry for atomic-precision surface finishing of TC4. The optimized slurry formulation comprises 2.0 wt% H_2O_2 (oxidant), 15 wt% silica sol (abrasive), and organic acid, with deionized water as the continuous phase. This slurry with lactic acid at 30°C delivers exceptional planarization performance, yielding an atomically smooth surface with Sa of 0.323 ± 0.039 nm over a $50 \times 50 \mu\text{m}^2$ scan area. The maximum MRR of 4301 nm/min was achieved using acetic acid as the organic additive under optimized slurry conditions (35°C). The slurry involving lactic acid exhibits outstanding dispersibility, stability, physical viscosity and chemical activity. Using key evidence of MD simulations and surface characterization, LA demonstrate the most negative total system and energies, identifying it as the most effective interface stabilizers. Their dual functional groups (-COOH and -OH) provide synergistic bridging between the metallic substrate and the oxide abrasive. In particular exploring passive film growth kinetics, and oxide dissolution kinetics, q_{excess} (0.465 mC/cm^2) and k (5.152 s^{-1}) of lactic acid have been monitored to further demonstrate that lactic acid can achieve the appropriate chemical reaction rate, which is in balance with mechanical removal. Our work demonstrates that controlling the chemical rate and synergistic bridging of the organic acid present in a CMP slurry is an effective route to simultaneously regulate temperature and compose to design efficient polishing of TC4.

CRediT authorship contribution statement

Zhihui Wang: Writing – original draft, Investigation, Formal analysis, Conceptualization. **Chunjing Shi:** Validation, Resources, Investigation, Formal analysis. **Baolu Zhang:** Investigation, Formal analysis. **Zhuoqun Liu:** Writing – review & editing, Supervision. **Jing Ni:** Supervision, Resources, Funding acquisition. **Lu Liu:** Writing – review & editing, Supervision. **Mingjun Wu:** Investigation, Formal analysis. **Fanning Meng:** Software, Investigation. **Chun Cao:** Investigation, Conceptualization. **Ying Yang:** Resources, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wear.2026.207012>.

Data availability

Data will be made available on request.

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