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Corrosion behavior of dental metallic alloys

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ABSTRACT

Dental metallic alloys undergo electrochemical degradation in the oral environment, which compromises structural integrity and surface functionality. Ionic dissolution can activate hypersensitivity and potential cytotoxic or genotoxic effects; therefore, released ion levels must remain within defined safety limits. Corrosion also accelerates fatigue, fretting fatigue, and tribocorrosion, increasing the risk of deformation and fracture.

This review consolidates methodologies for immersion and galvanic corrosion testing, presents the electrochemical background required for study design and data interpretation, and identifies the physiological variables that govern intraoral degradation, including saliva composition and pH cycling, proteins and biofilms, mechanical loading, temperature fluctuations, and fluoride exposure. Evidence on the corrosion behavior of dental alloys is summarized across in vitro, in situ, and in vivo contexts. In addition, surface engineering approaches are examined, including passivation strategies, surface modification, and protective coatings, with the aim of reducing ion release, improving corrosion resistance, and extending clinical service life.

Keywords: biocompatibility, tribocorrosion, passivation, implant materials, electrochemical testing, biomaterials degradation.

1. Introduction

Dental metallic materials contact oral tissues and physiological fluids, either temporarily or permanently, to restore or replace structures compromised by ageing, disease, or trauma (Anusavice et al. 2012, Black and Hastings 2013). To function safely and durably in this setting, they must provide biocompatibility, resistance to corrosion in chloride- and protein-containing media, adequate strength and toughness under cyclic loading, long service life, and an elastic modulus compatible with load transfer to surrounding tissues (Niinomi 2008, Niinomi et al. 2012). In parallel, biocompatibility is routinely assessed according to ISO 10993-5:2009, which specifies in-vitro cytotoxicity assays that capture cellular viability and morphological changes in response to degradation products.

For complex restorations operating in an aggressive oral environment, the combined strength, toughness, and wear resistance of metals remain unmatched by alternatives, which makes metallic systems indispensable (Pilliar 2009, Geetha et al. 2009). Important limitations persist. The elastic modulus of many alloys exceeds that of bone or dentin, which may promote stress shielding; exposure to biofluids drives electrochemical degradation and ion release with potential local or systemic effects in susceptible patients; and disruption of passive films by micromotion and tribological contacts increases dissolution and debris generation (Aksakal et al. 2004, Hanawa 2003, Hanawa 2012, Eliaz 2019, Upadhyaya et al. 2006). Methodological variability across media, loading, and standards, for example ISO 10271, complicates comparison between in vitro, in situ, and in vivo findings. These factors frame the present review, which synthesizes corrosion test methodologies, intraoral degradation drivers, and surface strategies to mitigate ion release and extend service life.

Within current clinical practice, titanium and titanium alloys predominate for endosseous implants because they couple high corrosion resistance and favorable biocompatibility with comparatively low stiffness that facilitates load transfer to bone; their spontaneous TiO_2 surface film exhibits bioactive behavior that supports osseointegration (Niinomi 2008, Niinomi et al. 2012; Geetha et al. 2009, Eliaz 2019). Cobalt–chromium alloys are employed where high strength and wear resistance are required, including frameworks and components exposed to significant contact stresses (Anusavice et al. 2012; Geetha

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et al. 2009). Stainless steels are used more selectively for long-term intraoral components because of lower corrosion resistance in chloride-containing media and concerns related to nickel hypersensitivity (Aksakal et al. 2004, Anusavice et al. 2012). In all systems, disruption of the passive film by friction and micromovements exposes the substrate to biofluids, which may increase ion release and particulate generation; therefore, identifying the species and concentrations released from the implant surface remains central to evaluating local and systemic biological responses (Hanawa 2012, Eliaz 2019, Upadhyaya et al. 2006).

Hundreds of commercial dental alloys are available and can be organized by primary constituent elements and by clinical use. A practical classification by primary constituents and clinical use is provided in Table 1.Listed elements are typical; commercial compositions vary and may include proprietary additions. Note that NiTi commonly exhibits a TiO_2-enriched surface with minimal detectable Ni at the outer film under passive conditions, and trade names, if used, are indicated at first mention only (Anusavice 1996, Anusavice et al. 2012).

Table 1. Typical components of dental alloys (de Matos et al. 2021, Anusavice 1996).

Crowns and bridges:
Gold-based: Au, Ag, Cu, In, Pd, Pt, Zn
Palladium-based: Pd, Ag, Cu, Ga
Silver-based: Ag, Pd
Cobalt-based: Co, Cr, Mo, Fe, C, Si, Mn
Nickel-based: Ni, Co, Mo, Fe, C, Be, Mn
High-palladium alloys: Pd, Ga, In, Sn, Ru
Orthodontics / endodontics_
Titanium–vanadium: Ti, V, Cr, Al, Sn
Stainless steel (Fe-based): Fe, Ni, Cr, C
Nickel–titanium (Nitinol®): Ni, Ti
Co–Cr–Ni (Elgalloy®): Co, Cr, Ni, Mo, Mn, Be, C, Fe
β-titanium alloys: Ti, Mo, Zr, Sn
Implants:
Commercially pure titanium (cp-Ti): Ti, O, N, C, Fe, H
Ti-6Al-4V: Ti, Al, V, O, N, C, Fe, H
316 stainless steels: Fe, Ni, Cr, C, Si, Mn, P, Co, Mo
Cobalt–chromium (Vitallium®): Co, Cr, Mo, Fe, C, Si, Mn
Additively manufactured Co–Cr: Co, Cr, Mo, W (minor)

Accordingly, this review is organized to move from fundamentals to application. Section 2 systematizes corrosion modes encountered in the oral environment (uniform, localized, and galvanic), and consolidates immersion and electrochemical test methodologies with attention to test media, loading, and data interpretation, so that results from in vitro, in situ, and in vivo studies can be compared on a common basis. Polarization analysis and potential–pH (Pourbaix) concepts are introduced to link kinetic rates and thermodynamic feasibility to clinically relevant conditions. Section 3 examines the chemistry, structure, and dynamics of surface oxides on the principal dental alloys, including repassivation times and implications for ion release, with cross-alloy comparison. Section 4 translates these principles into practice by analyzing host–implant interfacial phenomena and surveying surface-engineering strategies that couple osteogenic support with bacteriostatic or bactericidal function, with notes on tribocorrosion and biofilms. The review concludes by integrating methodological guidance with criteria for material and surface selection in dentistry and by outlining priorities for harmonizing test standards and improving clinical relevance in corrosion–wear studies.

2. Corrosion of dental metallic alloys

Corrosion is a physicochemical interaction between a metal and its environment that results in changes to the material and may impair function. In the oral cavity, corrosion is clinically relevant because degradation products can compromise biocompatibility and mechanical reliability of devices in service. The predominant corrosion mechanisms in the oral cavity are localized, since metallic biomaterials generally exhibit high resistance to uniform attack due to the presence of passive films. Breakdown of these films under the action of chloride ions, combined with micromotion and cyclic loading, favors pitting, crevice, and tribocorrosion processes that are most often observed in vivo.

Classical texts describe the principal forms of corrosion encountered in metallic systems; in dentistry the most relevant include uniform corrosion, galvanic (active–noble) coupling, crevice and pitting corrosion, intergranular corrosion, dealloying, erosion–corrosion, hydrogen damage, and environmentally induced cracking (stress-corrosion cracking, corrosion fatigue, and hydrogen-assisted cracking) (Figure 1) (Fontana 1987, Jones 1996). Manufacturing and processing history materially influence performance through composition control, microstructure, inclusions, and residual stresses. For example, heat treatment associated with burnout of prefabricated stainless-steel posts has been reported to reduce corrosion resistance (Sorensen et al. 1990).

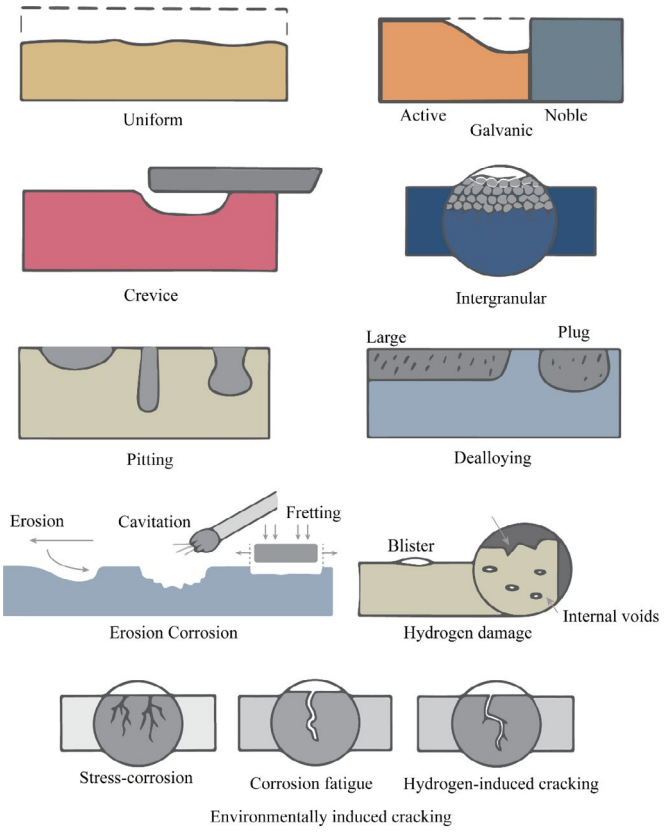


Fig. 1. Representative forms of corrosion relevant to dental alloys (schematic after Fontana and Jones, 1987).

From a mechanistic standpoint, it is useful to distinguish purely chemical corrosion from electrochemical corrosion. Chemical corrosion refers to direct reaction without ionic conduction and is uncommon under intraoral conditions. Electrochemical corrosion is sustained by anodic metal dissolution and cathodic reactions in conductive media and is often intensified by micro-galvanic cells that arise from compositional or microstructural inhomogeneities. Galvanic coupling can also occur between dissimilar alloys in mixed restorations or implants, accelerating attack of the more active member of the couple (Amine et al. 2022).

Oral-specific drivers modulate both thermodynamics and kinetics: salivary composition and buffering, biofilm formation, temperature and oxygen gradients, pH excursions, and exogenous agents such as fluoride. Synergistic action with mechanical stimuli is common. Tribocorrosion—material degradation due to the combined action of

mechanical wear and electrochemistry—disrupts passive films and increases ion and debris release at contacts such as abutment–implant interfaces (De Stefano et al. 2022, Kheder et al. 2021, Gaur et al. 2022). Fluoride, particularly at low pH, can destabilize titanium oxide films and increase corrosion rates, which is relevant for prophylaxis and home-care regimens (Kheder et al. 2021).

Because reported corrosion rates and ion-release data depend strongly on test media and methodology, comparability requires standardized protocols. ISO 10271:2020 specifies immersion and electrochemical methods for dental metallic materials and is frequently referenced in materials specifications; awareness of its scope and limitations is essential when interpreting literature values and designing experiments.

2.1. *Immersion tests - evaluation of chemical corrosion*

Immersion tests remain the most widely used experimental method for quantifying the chemical corrosion of dental metallic materials. These procedures measure the dissolution of metallic ions from an alloy surface into a test solution, either gravimetrically by weight loss or, more sensitively, by solution analysis techniques such as inductively coupled plasma–optical emission spectrometry (ICP-OES), inductively coupled plasma–mass spectrometry (ICP-MS), or atomic absorption spectrometry (AAS). The primary standard governing these tests for dental alloys is ISO 10271:2020, which prescribes immersion conditions in artificial saliva to assess corrosion behavior and metal ion release from metallic materials in dentistry. Other relevant standards, such as BS EN 1811 and JIS T 0304, provide guidance on nickel release testing, particularly relevant for Ni-containing alloys.

The selection of the immersion medium is central to the relevance of results. Physiologically relevant solutions aim to approximate the ionic composition and pH of human body fluids, although no single medium perfectly replicates the oral cavity. Commonly employed test solutions include saline (0.9% NaCl), phosphate-buffered saline (PBS), Ringer's solution, Hank's solution, serum, culture media, and formulations of artificial saliva. Among these, PBS is generally favored because its buffering capacity stabilizes pH during extended immersion, minimizing artifacts caused by acidification or alkalization. For accelerated corrosion studies, 0.1 mol L^{-1} lactic acid or 0.1 mol L^{-1} hydrochloric acid solutions are frequently used; these are not physiologically representative but provide insight into alloy stability under extreme acidic conditions.

Test conditions typically include a temperature of 310 K (37 °C) to reflect human physiology, with immersion periods of at least seven days to ensure measurable ion release. Longer durations may be necessary for alloys with high corrosion resistance, such as Ti-based systems. The pH of test solutions must be measured before and after immersion, as changes can indicate the extent of metal dissolution and the buffering response of the medium.

While inorganic components dominate solution design, it is increasingly recognized that minor constituents of physiological fluids—such as proteins, amino acids, bicarbonates, phospholipids, and cholesterol—play important roles in modulating corrosion and passivation. For example, sodium citrate, routinely added to blood as an anticoagulant, has been shown to destabilize the passive films on Co–Cr–Mo alloys and stainless steels. Some studies therefore substitute serum for whole blood to avoid artifacts related to anticoagulants. Similarly, proteins and amino acids can adsorb to alloy surfaces, altering oxide film chemistry, while sulfur-containing species may promote crevice corrosion of stainless steels.

Comparative compositions of natural fluids and simulated body fluids (SBFs) illustrate the variability of the testing environment. Table 2 lists typical ionic and organic constituents of interstitial fluid, synovial fluid, and serum, while Table 3 provides representative formulations of SBFs commonly employed in immersion experiments. The absence of proteins in simple SBFs highlights a key limitation, as adsorption and biofilm formation significantly influence corrosion kinetics *in vivo*.

Another limitation arises from hydrodynamics. Most *in vitro* tests are static, whereas *in vivo* environments involve continuous fluid movement. Blood flow, saliva circulation, and masticatory forces create dynamic mass-transport conditions that accelerate localized corrosion relative to static laboratory setups. For example, diffusion-limited conditions in stagnant saline may underestimate the pitting susceptibility of stainless steels or Co–Cr alloys compared with dynamic *in vivo* exposure.

Table 2. Typical ionic and protein compositions of selected body fluids (mg L^{-1}) (Eliaz 2019, Manivasagam et al. 2010)

Component	Interstitial Fluid	Synovial Fluid	Serum
Na^+	3280	3127	3265
K^+	156	156	156
Ca^{2+}	100	60	100
Mg^{2+}	24	—	24
Cl^-	4042	3811	3581
HCO_3^-	1892	1880	1648
HPO_4^{2-}	96	96	96
SO_4^{2-}	48	48	48
Organic acids	245	—	210
Protein	4144	15,000	66,300

Footnotes: — = not reported. Values vary with donor characteristics, sampling technique, and physiological state.

Table 3. Composition of commonly used simulated body fluids (g L^{-1}) (Upadhyaya et al. 2006, Nagay et al. 2022)

Component	PBS	Ringer's	Hank's
NaCl	8.00	8.60	8.00
$CaCl_2$	—	0.33	0.14
KCl	0.20	0.30	0.40
$MgCl_2 \cdot 6H_2O$	—	—	0.10
$MgSO_4 \cdot 7H_2O$	—	—	0.10
$NaHCO_3$	—	—	0.35
NaH_2PO_4	1.15	—	—
$Na_2HPO_4 \cdot 12H_2O$	—	—	0.12
KH_2PO_4	0.20	—	0.06
Phenol red	—	—	0.02
Glucose	—	—	1.00

Footnotes: — = not included in the formulation. Formulations differ across laboratories; listed compositions represent common baseline recipes. pH buffering capacity and ionic strength may vary depending on preparation method.

Accelerated immersion tests in lactic acid or HCl provide valuable data on alloy stability under extreme acidity, simulating conditions such as peri-implant inflammation or biofilm metabolism, where localized pH may drop to <4. However, extrapolation from accelerated media to clinical performance must be approached cautiously, since these tests overemphasize aggressive dissolution pathways not representative of normal saliva (Fontana 1987, Jones 1996).

Physiological immersion, by contrast, seeks to replicate the complex milieu of saliva or serum. Artificial saliva compositions vary widely across studies, reflecting a lack of consensus on a "true" formulation. Some researchers recommend simple saline as a baseline control (Solar 2005), while others stress the importance of calcium and phosphate species to mimic remineralization conditions in the oral cavity. A systematic review concluded that the absence of standardized artificial saliva formulations remains a major barrier to cross-study comparability (Nagay et al. 2022).

Despite these limitations, immersion tests provide critical baseline information on ion release profiles of dental alloys. Data generated from such tests inform risk assessment for local and systemic exposure to nickel, cobalt, and other potentially allergenic or toxic ions (Di Spirito

et al. 2024). They also serve as a preliminary screen for evaluating modifications in alloy composition, casting quality, or surface treatments prior to more complex electrochemical or tribocorrosion tests (Amine et al. 2022, Fagaia et al. 2024). In this context, immersion tests form the foundation of corrosion evaluation, but they should be interpreted alongside electrochemical, mechanical, and biological assays for comprehensive assessment (ISO 10271:2020). Moreover, even if standardized immersion media are used, intraoral conditions vary significantly: saliva pH is not constant across individuals and is influenced by factors such as systemic disease, dietary habits, and smoking, all of which can accelerate or mitigate corrosion processes.

2.2. *Galvanic (electrochemical) corrosion*

When two dissimilar metals are in electrical contact within the same electrolyte, the one with the more negative potential in the galvanic series acts as the anode and preferentially corrodes, while the more noble metal serves as the cathode. This process, known as galvanic or bimetallic corrosion, can proceed significantly faster than the uniform corrosion of a single metal under the same conditions (Eliaz 2019, Jones 1996). In dental practice, this phenomenon is clinically relevant when different metallic restorations or implants coexist in the oral cavity; for example, titanium abutments in contact with Co–Cr frameworks or amalgam adjacent to gold alloys.

The actual electrode potential E of a metal is determined not only by its intrinsic standard potential but also by the ion concentration (or activity) in the electrolyte. This relationship is described by the Nernst equation:

$$E = E^0 - \frac{RT}{nF} ln\, a_{M^{n+}} \quad (1)$$

where E^o is the standard electrode potential (V), R is the universal gas constant (8.314 J·mol^{-1}·K^{-1}), T is the absolute temperature (K), n is the number of electrons transferred, F is Faraday's constant (96,487 C·mol^{-1}), and a_M^{n+} is the activity of the dissolved metal ion.

Galvanic action is not limited to dissimilar metals; inhomogeneities within a single alloy can also generate localized micro-galvanic cells. As shown in Figure 2a, a crack may act as an anode relative to the surrounding matrix, while Figure 2b illustrates how grain boundaries can behave anodically compared to grain interiors. These micro-galvanic cells drive preferential dissolution, which can progress into crevice corrosion, intergranular attack, or, under cyclic loading and stress, environmentally induced cracking.

Several factors modulate the severity of galvanic corrosion: (i) the potential difference between metals; (ii) the ratio of cathodic to anodic surface areas, with small anodes coupled to large cathodes being most vulnerable; (iii) the conductivity and composition of the electrolyte, particularly chloride concentration and pH; and (iv) the presence of proteins, fluoride, or biofilms, which can destabilize passive films and alter kinetics (Amine et al. 2022, Nagay et al. 2022).

Gold, platinum, and silver are traditionally classified as noble metals due to their resistance to corrosion. However, the effective "order of nobility" observed clinically may differ from thermodynamic predictions. This divergence arises because many base metals form protective oxide films that passivate the surface, or because the dissolution reactions are kinetically hindered, requiring activation overpotentials. Thus, corrosion resistance depends on the balance between thermodynamics, passivation stability, and local electrochemical conditions.

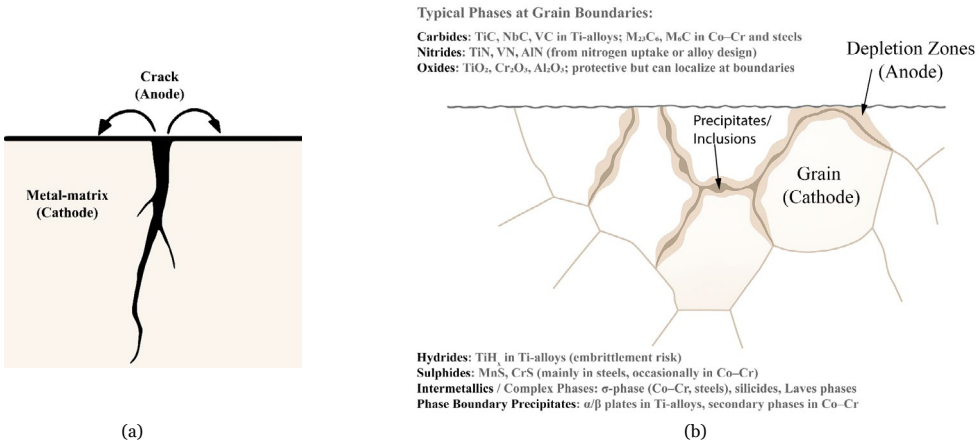
2.2.1 Electrochemical Aspects

The corrosion tendency of metals can be expressed in terms of their standard electrode potential, as defined in the electrochemical series (Table 4). These potentials, measured relative to the standard hydrogen electrode (SHE), reflect the thermodynamic driving force for metal oxidation under standard conditions (298 K, 1 mol L^{-1} ionic activity, pH = 0).

Table 4. Standard electrode potential of elements relevant to metallic biomaterials (298 K) (Revie and Uhlig 2025)

Electrode reaction	Standard electrode potential, E^o (V vs. NHE*)
$Mg \leftrightarrow Mg^{2+} + 2e^-$	−2.36
$Al \leftrightarrow Al^{3+} + 3e^-$	−1.66
$Ti \leftrightarrow Ti^{2+} + 2e^-$	−1.63
$H_2 + 2OH^- \leftrightarrow 2H_2O + 2e^-$	−0.8281
$Cr \leftrightarrow Cr^{3+} + 3e^-$	−0.744
$Fe \leftrightarrow Fe^{2+} + 2e^-$	−0.440
$Co \leftrightarrow Co^{2+} + 2e^-$	−0.277
$Ni \leftrightarrow Ni^{2+} + 2e^-$	−0.250
$H_2 \leftrightarrow 2H^+ + 2e^-$	±0.000
$Ag \leftrightarrow Ag^+ + e^-$	0.799
$Pd \leftrightarrow Pd^{2+} + 2e^-$	0.987
$Pt \leftrightarrow Pt^{2+} + 2e^-$	1.188
$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^-$	1.229
$Au \leftrightarrow Au^{3+} + 3e^-$	1.498

Note: *The equilibrium potential of elements in the standard state is called the standard electrode potential, which is expressed relative to the standard hydrogen electrode (SHE or NHE).*



(a) (b)

Fig. 2. Micro-corrosion: (a) localized crevice corrosion arising from an oxygen-deficient zone at a crack, with the crack interior acting as anode and the surrounding matrix as cathode, and (b) intergranular corrosion schematized as anodic grain boundaries (or depletion zones - precipitation removes alloying elements from the surrounding solid solution) relative to cathodic grain centers.

However, direct correlation between standard potentials and *in vivo* corrosion rates is limited. First, the electrochemical series does not account for passivation. For instance, titanium ($E^0 \approx -1.63$ V) is thermodynamically active but exhibits outstanding corrosion resistance due to the rapid formation of a stable TiO_2 passive film. Similarly, chromium and aluminum form adherent oxides that reduce corrosion rates far below what their standard potentials suggest (Milošev and Strehblow 2003).

Second, actual implant performance occurs in complex electrolytes at near-neutral pH, not under the acidic, high-ionic-activity conditions used to define the standard series. Therefore, open-circuit potentials (OCP) measured in simulated body fluids or saliva often deviate from E^0 values. These potentials are dynamic, influenced by chloride concentration, dissolved oxygen, proteins, and flow conditions. Reviews of orthopedic and dental implant materials have emphasized that corrosion resistance is not solely governed by electrode potentials but is critically dependent on passive film stability and interactions with biological species *in vivo* (Saji and Choe 2009).

2.2.2 Pourbaix Diagrams

Pourbaix diagrams, also known as potential–pH maps, graphically represent the thermodynamic stability of metals in aqueous environments. By plotting electrode potential against pH, these diagrams delineate regions of immunity (where the metal remains stable), passivation (where a protective oxide is favored), and active dissolution (corrosion). Originating from equilibrium thermodynamics and the Nernst equation, Pourbaix diagrams serve as a valuable conceptual tool for understanding corrosion behavior in biomaterials (Pourbaix 1966, Revie 2008).

In Figure 3, a Pourbaix diagram for chromium is depicted with overlays corresponding to the pH and potential ranges of relevant bodily fluids; including saliva, interstitial fluid, and gastric fluid. Chromium's presence within the passivation domain near neutral pH explains its capacity to form a stable, protective oxide in oral environments.

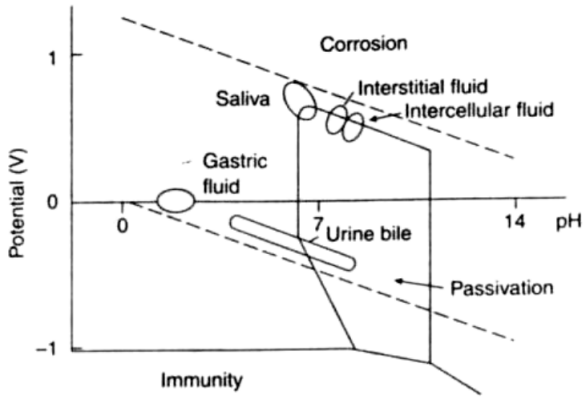


Fig. 3. Pourbaix diagram for chromium: thermodynamic domains of immunity, passivation, and corrosion overlaid with physiological fluid conditions (Modified from Black 2005).

Figures 4a and 4b contrast the behavior of a noble metal (gold) and a passive metal (titanium). Gold remains in the immunity region across a broad pH range, which explains its inertness in dental and physiological settings. In contrast, titanium exhibits an expansive passivation region around neutral pH (due to formation of stable titanium oxide layers), which underlies its exceptional durability as an implant material despite a thermodynamically active standard potential.

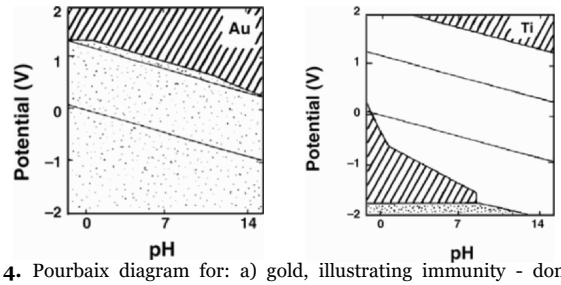


Fig. 4. Pourbaix diagram for: a) gold, illustrating immunity - dominated behavior across a wide pH range; and b) titanium, showing a prominent passivation domain near physiological pH (Modified from Black 2005).

Pourbaix diagrams also encapsulate water stability boundaries: the upper "oxygen line" marks the onset of oxygen evolution, and the lower "hydrogen line" indicates proton reduction. Corrosion is possible only between these lines. Importantly, many physiological fluids (such as saliva and interstitial fluid) occupy regions close to the oxygen line, indicative of oxidizing conditions that favor passive-film formation rather than dissolution.

Despite their utility, Pourbaix diagrams have limitations when extrapolated to in vivo behavior. First, they are purely thermodynamic, neglecting kinetic factors such as film growth rates, breakdown potentials, and repassivation dynamics. Many metals that appear immune under equilibrium may corrode due to film disruption or metastability under real-world conditions. Second, these diagrams assume pure chemical systems and do not account for aggressive species like chloride ions or proteins, which can destabilize passive films and provoke localized corrosion even within the theoretical passivation zone. Third, in vivo environments are often dynamic. Local pH, oxygen tension, and mechanical stress — particularly at implant interfaces — frequently fluctuate due to inflammation, loading, and biofilm activity, potentially shifting the effective local "operating point" into corrosion-prone regions.

2.2.3. Corrosion rates and polarization curves

While Pourbaix diagrams indicate whether a metal is thermodynamically stable, passive, or prone to corrosion, they do not provide information about how quickly corrosion will occur. To evaluate corrosion kinetics, polarization curves are employed, which plot current density as a function of electrode potential. These curves, illustrated in Figure 5, reveal how a material behaves under anodic and cathodic polarization and provide quantitative estimates of corrosion rates. From such measurements, it is possible to calculate the flux of metal ions released into the environment and the depth of metal loss over time. Complementary approaches, such as gravimetric tests that track weight loss of a specimen during immersion, provide similar insights into long-term degradation.

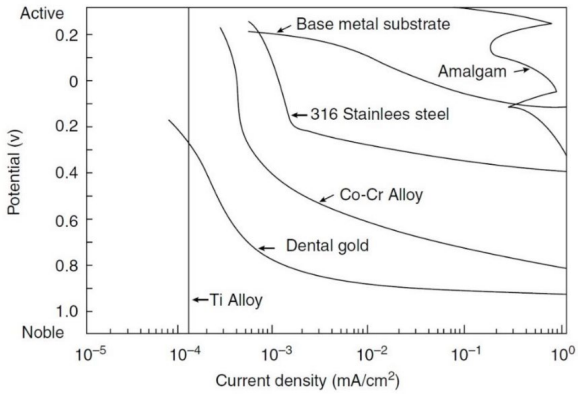


Fig. 5. Potential–current density curves for selected dental biomaterials, including titanium alloy, dental gold, Co–Cr alloy, stainless steel, and amalgam (Greener et al. 1972)

The polarization response of dental metallic materials differs markedly. Titanium alloys and noble metal systems (e.g., dental gold) exhibit wide passive ranges and high pitting potentials, which explain their excellent in vivo reliability. By contrast, Co–Cr alloys, stainless steels, and amalgams often show lower pitting potentials and narrower passive ranges, indicating a greater risk of localized breakdown in chloride-containing media. It is important to note that these electrochemical measurements primarily capture uniform corrosion. In physiological environments, localized forms of attack (pitting, crevice corrosion, or galvanically coupled dissolution) often dominate, making simple extrapolations from uniform rates insufficient. For such cases, alternative metrics, including pit density, pit depth, or time to passive film breakdown, become more relevant than average current density. Susceptibility to pitting is better characterized by the potential at which metastable and stable pits initiate, and by the difference between the pitting potential (E_{pit}) and the corrosion potential (E_{corr}), rather than by corrosion current density alone.

A key question for biomaterials is what constitutes an "acceptable" corrosion rate. This depends on the specific clinical application, the functional requirements of the device, and patient safety considerations. For implants, a commonly cited threshold is less than 1 μm per year of penetration (≈0.0394 mils per year). Rates above this value increase the risk of premature structural degradation, excessive ion release, and adverse tissue responses. The corrosion penetration rate (CPR) is typically reported in units of micrometers per year or in mils per year (mpy), where 1 mil = 25.4 μm, providing a convenient engineering metric for material comparison.

In practice, the corrosion rate of metallic biomaterials is rarely determined solely by electrochemical factors. Mechanical influences are highly significant, creating synergistic effects that accelerate degradation. In corrosion fatigue, cyclic stresses in a corrosive medium increase both the rate of passive film rupture and the propagation of microcracks, leading to early failure. Fretting corrosion occurs at interfaces subject to micromotion, such as the contact between a screw and a bone plate, where mechanical rubbing continuously disrupts the protective passive film and exposes fresh metal to the electrolyte. Pitting corrosion, particularly in stainless steels, concentrates attack in small regions, leading to deep penetration and potentially catastrophic failure. Grain boundaries, which are energetically less stable, may preferentially dissolve, promoting intergranular corrosion. Similarly, restricted geometries such as crevices create differential aeration and chemical gradients that enhance localized corrosion.

Since the *in vivo* environment combines physiological loading with chemically aggressive fluids, corrosion testing of candidate implant materials must account for both electrochemical and mechanical influences. For example, fatigue experiments are best conducted in Ringer's solution at body temperature to approximate realistic service conditions. Only by coupling electrochemical methods with mechanical testing can researchers accurately predict the durability and safety of metallic dental and orthopedic materials.

3. Surface oxide film on metallic biomaterials in the human environment: passivation and its breakdown

The initiation of corrosion in metallic biomaterials begins with oxidation of the metal surface to a stable valence state, typically followed by the formation of corrosion products whose solubility and adherence determine long-term behavior. In alloys such as titanium, aluminum, and chromium, corrosion products consolidate into dense, adherent oxides that confer protection by limiting further dissolution. In contrast, steel and other less noble alloys produce porous oxides that permit ongoing attacks. Remarkably, films only a few nanometers thick (3 nm for stainless steel and 5 nm for aluminum) can provide effective protection when continuous and stable, as confirmed by spectroscopic studies (Fontana 1987, Jones 1996).

The structural and chemical composition of these passive films varies across biomaterials. Titanium alloys typically exhibit TiO_2-rich layers containing mixed valence states (Ti^{2+}, Ti^{3+}, Ti^{4+}), while stainless steels develop thinner, hydroxyl-rich multilayers enriched in Fe, Cr, Ni, and Mo. Co–Cr alloys display Cr- and Co-dominated oxides, sometimes with Mo less evident at the outer surface. Alloying elements such as vanadium in Ti–6Al–4V may not be detectable in surface films, while Zr additions can increase oxide thickness and stability. These compositional differences have direct implications for corrosion resistance and ion release (Hanawa 2003, Eliaz 2019). Table 5 summarizes oxide film characteristics across major dental metallic biomaterials.

Disruption of the passive film (by micromotion, fretting, or aggressive ions such as fluorides) exposes the underlying metal to dissolution. The ability of an alloy to restore its protective oxide layer, known as repassivation, is therefore critical. Kinetic studies indicate that Ti–6Al–4V re-establishes its protective film within minutes, while stainless steel requires substantially longer regeneration times, leading to prolonged ion release. This difference highlights one reason for the superior in vivo performance of titanium alloys over stainless steels. Repassivation times for common biomaterials are summarized in Table 6 (Hanawa 2012).

Table 5. Surface oxide film characteristics of selected metallic biomaterials (Eliaz 2019)

Biomaterial	Surface oxides	Surface analysis / descriptive features
cp-Ti	Ti^{2+}, Ti^{3+}, Ti^{4+} species	The oxide film contains suboxides near the metal interface (Ti^{2+}, Ti^{3+}), which gradually transform into TiO_2 (Ti^{4+}) at the outermost layer. This stratified structure improves stability, and the film is thin but strongly adherent.
Ti–6Al–4V	TiO_2	The passive film is dominated by TiO_2, with trace Al_2O_3 and hydroxyl groups; vanadium is usually undetectable. The oxide is highly protective and supports osseointegration, though its repassivation kinetics are crucial in tribological conditions.
NiTi	TiO_2-based oxide	A TiO_2-enriched outer surface forms spontaneously, leaving minimal Ni detectable at the interface. This explains why, despite bulk Ni content, the alloy exhibits relatively low Ni ion release under passive conditions.
Ti–56Ni	TiO_2 with minor NiO	In addition to TiO_2, small amounts of Ni and NiO can be detected, together with hydroxyl species. The presence of Ni at the surface increases corrosion susceptibility under low-pH or protein-rich conditions.
Ti–Zr	Mixed Ti and Zr oxides	Ti and Zr oxides are evenly distributed; oxide thickness increases with Zr concentration, enhancing passivation. The film is dense, continuous, and improves corrosion resistance in chloride environments.
316L stainless steel	Fe, Cr, Ni, Mo, Mn oxides	The film is ~3–4 nm thick, with hydroxides and adsorbed water. The outer layer is enriched in Fe oxides, while the inner region contains Cr, Ni, Mo, and Mn oxides, which control stability and repassivation.
Co–36.7Cr–4.6Mo	Co and Cr oxides (little Mo)	The ~2–3 nm thick oxide contains Cr and Co oxides with significant hydroxylation, forming a hydrate/oxyhydroxide structure. Mo is usually absent or minimal in the passive layer but contributes indirectly to corrosion resistance.

Table 6. Repassivation times of surface oxide films on selected metallic biomaterials. (Values from in vitro electrochemical studies; times vary with medium and test method)

Alloy	Regeneration time (min)
SUS316L	35.3
Ti-6A1-4V	8.2
Co-28Cr-6Mo	12.7
Zr-2.5Nb	13.8

The biological consequences of metal ion release are complex. Nickel is strongly associated with allergic contact dermatitis and hypersensitivity reactions (Thyssen and Menné 2010); cobalt has systemic effects through interference with iron metabolism (Leyssens et al. 2017); chromium exists in multiple oxidation states with different toxicological profiles (Dayan and Paine 2001); and aluminum (Kawahara and Kato-Negishi 2011), vanadium, and molybdenum have all been linked, at higher doses, to neurological or metabolic disturbances (Barceloux 1999). While normal exposure levels from well-functioning dental alloys are typically low, disruption of oxide films and accelerated corrosion can elevate systemic burdens. Table 7 summarizes the main biological effects of selected ions relevant to dental alloys (Bhat 2002, Black and Hastings 2013, Eliaz 2019).

3.1. *Formation of an oxide layer on the titanium surface*

Titanium is highly reactive and spontaneously forms a thin protective oxide film when exposed to air or aqueous environments. Within milliseconds, a ~1 nm film develops, and within the first minute, the oxide layer can reach ~10 nm in thickness. Surface analyses show that the passive layer is stratified, with inner suboxides (TiO, Ti_2O_3, Ti_3O_5) and an outer TiO_2-rich zone, with typical total thicknesses of 5–12 nm (Hanawa 2003, Eliaz 2019). Figure 6a schematically illustrates the initial oxide film on pure titanium.

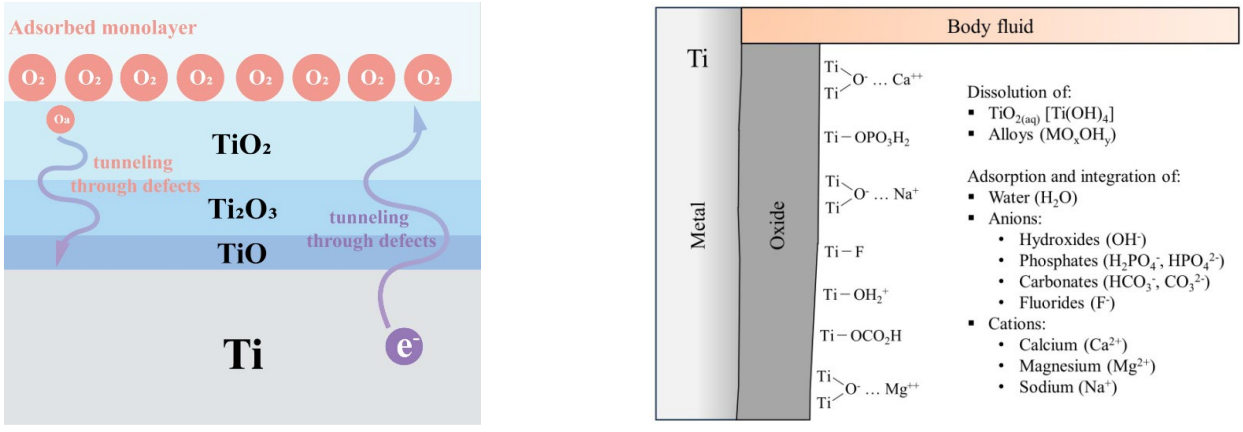
Even after passivation, the titanium surface remains chemically reactive due to hydroxylation. Hydroxyl groups form within tens of milliseconds upon contact with water vapor, imparting a pH-dependent surface charge. This behavior is described by the isoelectric point (IEP), defined as the pH at which net surface charge is zero. For TiO_2, IEP values differ between crystalline phases, at ~5.3 for rutile and ~6.2 for anatase. In solutions below the IEP, surfaces carry a net positive charge, while at higher pH values, they become negatively charged. Such charge reversal influences protein adsorption, bacterial adhesion, and the binding of calcium and phosphate species essential for osseointegration. Comparative IEP values for common oxides are summarized in Table 8.

In vivo and *in vitro* analyses further show that the composition of titanium oxide layers evolves after implantation. Calcium, phosphorus, and sulfur are readily incorporated into the surface film, and rapid precipitation of calcium phosphate contributes to the excellent tissue integration of titanium alloys. Simulated biological tests confirm this behavior: immersion in Hank's solution leads to calcium phosphate deposition, while cellular environments may additionally yield sulfur-containing compounds (Hanawa 2003). Figure 6b illustrates how electrolytes interact with the titanium oxide surface, emphasizing its ability to adsorb and integrate ions such as Ca^{2+}, Mg^{2+}, Na^{+}, phosphates, and fluorides. Compared with stainless steels and Co–Cr alloys, titanium exhibits faster calcium phosphate nucleation and more favorable Ca/P ratios, which partly explains its superior clinical biocompatibility (Geetha et al. 2009, Eliaz 2019).

Importantly, the stability of this oxide film is not absolute. Mechanical disruption from mastication, micromotion at implant–bone interfaces, or bacterial biofilm activity can damage the passive layer, initiating transient increases in ion release. This phenomenon,

Table 7. Biological effects of selected metallic ions released in vivo due to corrosion (Summarized from Bhat 2002, Black and Hastings 2013, Eliaz 2019).

Metal	Biological effects
Nickel (Ni)	A leading cause of allergic contact dermatitis; threshold of ~0.5 $mg \cdot cm^{-2} \cdot week^{-1}$ from skin contact may trigger reactions in sensitive individuals. At higher levels, Ni exhibits cytotoxicity, damages bone cell cultures, and may contribute to carcinogenic risk. Normal blood levels are ~5 $\mu g \cdot L^{-1}$.
Cobalt (Co)	Biologically essential only as part of vitamin B_{12}. Excess Co can inhibit iron absorption, induce anemia, and contribute to neurological symptoms or ulcer formation. High systemic levels have been linked to cardiotoxicity.
Chromium (Cr)	Cr(III) is poorly absorbed and stored in the reticuloendothelial system, whereas Cr(VI) readily crosses membranes and is highly toxic. Elevated Cr may contribute to oxidative stress and cytotoxicity; typical blood values are ~2.8 µg per 100 g tissue.
Aluminum (Al)	Linked to epileptic symptoms and potential association with Alzheimer's disease. Normally not essential in metabolism, and accumulation in tissues raises neurotoxicity concerns.
Vanadium (V)	Toxic in elemental state; in ionic form it interferes with enzymatic activity and can impair bone cell viability.
Molybdenum (Mo)	An essential trace element with highest concentrations in the liver (1–3 ppm). Required for key enzymes (ceruloplasmin, cytochrome oxidase, etc.), but excessive intake causes diarrhea, metabolic disruption of Ca and P, and multi-organ toxicity.



a) b)

Fig. 6. a) Schematic illustration of oxide film formation mechanism on pure titanium; b) Schematic illustration of electrolyte–oxide interactions, showing adsorption and incorporation of ionic species relevant to oral and physiological fluids.

Table 8. Isoelectric points (IEP) of selected oxides (Hanawa 2003, Eliaz 2019).

Oxide	IEP value	Notes
SiO_2	2.0–3.7	Highly negative surface charge at physiological pH; poor protein adsorption.
SnO_2	4.7–5.3	Moderately negative above neutral pH.
TiO_2 rutile	5.3	Neutral around weakly acidic saliva; surface chemistry supports Ca^{2+} binding.
TiO_2 anatase	6.2	Closer to physiological pH; favorable for protein adsorption and cell adhesion.
Fe_2O_3	6.6–6.7	Stable but less bioactive than TiO_2.
Cr_2O_3	7.0	Maintains neutrality near physiological pH.
Al_2O_3	9.0	Positively charged at physiological pH; influences protein adsorption differently from TiO_2.

known as tribocorrosion, is particularly relevant in dentistry because the oral cavity imposes combined mechanical and chemical challenges. The ability of an alloy to rapidly reform its oxide layer, its repassivation kinetics, becomes critical under these conditions. Comparative studies show that Ti-6Al-4V repassivates in ~8 minutes, Co–Cr–Mo in ~12 minutes, whereas stainless steels require >30 minutes (Hanawa 2012). Faster repassivation limits the accumulation of toxic or allergenic ions such as Ni^{2+} and Cr^{3+} in surrounding tissues, reinforcing the clinical preference for Ti alloys. Thus, titanium's corrosion resistance derives from the presence of stable passive oxide, and from its ability to regenerate this film rapidly after disruption.

Although titanium spontaneously forms a protective TiO_2 film, this layer is thin and often porous, and therefore susceptible to localized breakdown. Current surface engineering strategies focus on increasing the thickness, stability, and biological activity of this passive film. Anodic oxidation, in particular, has emerged as a highly effective approach: anodized cp-Ti shows markedly improved corrosion stability in NaCl solution and enhanced biocompatibility, as evidenced by increased mitochondrial activity and upregulation of adhesion-related genes in human gingival fibroblasts (Popović et al. 2025)

4. Elements of surface engineering for dental metallic biomaterials

4.1. Host–implant interactions

Dental metallic biomaterials are continuously exposed to a complex physiological environment composed of aqueous electrolytes (≈0.9% NaCl), amino acids, proteins, and circulating cells such as leukocytes, macrophages, and platelets. Under normal conditions, the pH of body fluids is close to 7.4, but can decrease to 4–5 in inflamed or infected tissue, while temperature (37 °C) and hydrostatic pressure (≈0.1 MPa) remain relatively constant (Anusavice et al. 2012, Hanawa 2003). These variations in fluid chemistry, particularly pH and protein composition, directly influence oxide stability and the repassivation kinetics of metallic implants.

At the moment of implantation, biomaterial surfaces are rapidly covered by a layer of water, ions, and proteins, which defines the initial host–implant interaction. Protein adsorption can mediate both beneficial cell adhesion and adverse reactions such as inflammation or hypersensitivity (Di Spirito et al. 2024). Other biological risks include hemolysis, coagulation, cytotoxicity, and even mutagenic or carcinogenic outcomes in extreme cases (Nagay et al. 2022). Thus, understanding the surface–fluid interface is essential to predict corrosion, ion release, and long-term performance.

The physiological environment is chemically and mechanically aggressive. The reduced oxygen partial pressure *in vivo* compared to air slows the regeneration of protective passive films, leaving alloys more vulnerable to localized corrosion (Hanawa 2012). Mechanical stresses further amplify this effect: cyclic loading contributes to corrosion fatigue, while micromotion at screw–plate or bone–implant contacts promotes fretting corrosion by disrupting the oxide film. These processes accelerate metal ion release and debris generation, often visible as tissue darkening and metallosis in orthopedic cases (Aksakal et al. 2004, Eliaz 2019).

The biological consequences of released metal ions depend strongly on their reactivity. Highly reactive ions such as Ti, Zr, Nb, and Ta rapidly form oxides, hydroxides, or salts in solution, limiting their persistence and reducing their likelihood of biomolecular binding. This partially explains their favorable biocompatibility (Hanawa 2012). In contrast, ions such as Ni or Cu remain longer in solution, increasing the probability of binding with proteins or nucleic acids, which can trigger hypersensitivity, cytotoxicity, or systemic transport to organs such as the kidney or liver (Di Spirito et al. 2024, Amine et al. 2022). Thus, four factors must be considered when assessing toxicity:

(i) alloy corrosion resistance,
(ii) the type and quantity of ions released,
(iii) the chemical activity of these ions in body fluids, and
(iv) the intrinsic toxicity of the ions themselves.

4.2. Strategies to enhance osteointegration and antimicrobial performance

The long-term success of dental metallic implants is frequently compromised by two major challenges: insufficient bone–implant integration and implant-associated infections. The initial response of tissues to the implant is dictated by the biointerface, the zone where

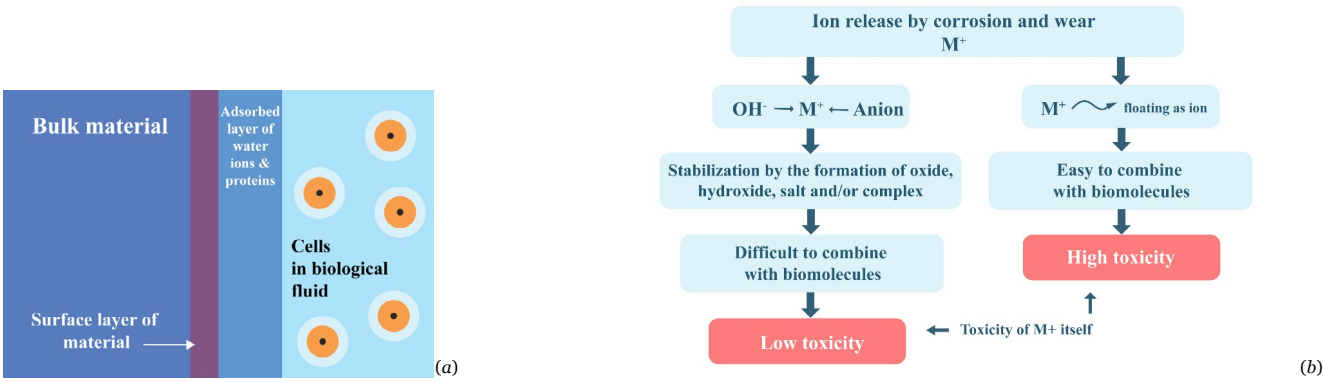


Fig. 7. (a) Dynamic layers at the surface of dental metallic biomaterials, including oxide, hydration/protein layer, and adjacent cells in biological fluid; (b) pathways of metal ion stabilization (low toxicity) or biomolecule interaction (high toxicity).

cells, proteins, and biomolecules interact with the engineered surface. Effective surface design must therefore reconcile the requirements of both osteogenesis and infection control (Panseri et al. 2016, Na et al. 2020).

Surface engineering has emerged as a versatile approach to optimize this biointerface. Modifications may involve altering the original surface topography and chemistry (e.g., anodization to produce TiO_2 nanotubes, grit blasting, acid etching), or depositing additional layers that introduce bioactive or antibacterial functionalities (e.g., hydroxyapatite, bioactive glass, Ag- or Cu-based coatings). These strategies can be further combined to achieve hierarchical, multiscale structures, which improve osteoblast adhesion and proliferation while simultaneously reducing bacterial colonization (Durner et al., 2022).

One promising direction is the development of multifunctional coatings capable of releasing therapeutic ions or molecules. For example, calcium- and phosphate-enriched coatings promote mineralized bone matrix deposition, while the controlled release of silver or copper ions suppresses bacterial growth without impairing osteoblast activity. Other approaches integrate drug-delivery functions, where antimicrobial peptides or anti-inflammatory agents are incorporated within degradable surface layers to provide localized, sustained release (Na et al., 2020). By tailoring such multifunctional surfaces, it is possible to simultaneously enhance osteointegration and mitigate the risk of peri-implantitis.

The conceptual framework of surface engineering is illustrated in Figure 8. By systematically altering surface composition, topography, and chemistry, one can direct specific biological outcomes, including protein adsorption, stem cell behavior, angiogenesis, and antibacterial resistance. These advances indicate that future dental metallic biomaterials will be designed less as passive structures and more as active, multifunctional platforms for biological modulation.

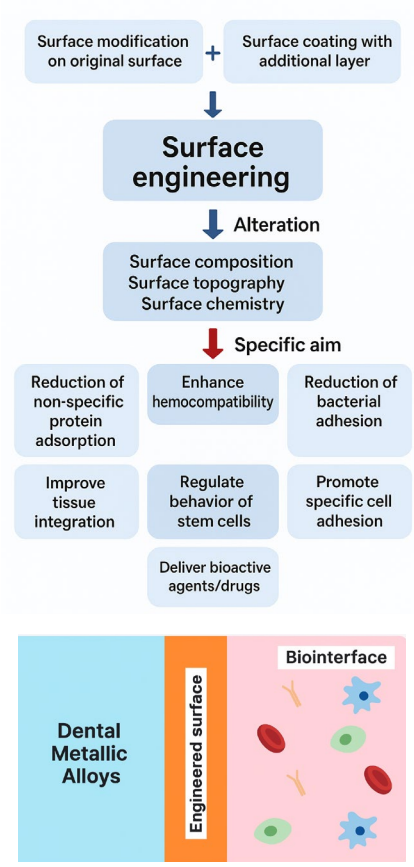


Fig. 8. Conceptual scheme of dental metallic alloy surfaces and their engineered biointerface and schematic of surface engineering strategies for multifunctional dental implants

Conclusion

Dental metallic biomaterials remain indispensable in restorative and implant dentistry due to their superior mechanical strength, toughness, and wear resistance compared to non-metallic alternatives. Nevertheless, the clinical performance of dental metallic materials remains limited by corrosion, tribocorrosion, and ion release, which can undermine both structural integrity and biological safety. The formation of protective passive oxide films, particularly on titanium and its alloys, is crucial for regulating dissolution and maintaining long-term biocompatibility. Yet, the instability of these films under dynamic oral conditions underscores the necessity for alloy optimization and advanced surface engineering. The development of multifunctional coatings that enhance osteointegration while simultaneously reducing microbial colonization represents a promising path toward improved clinical outcomes. Accordingly, future progress in alloy design and bioactive surface modification must integrate electrochemical stability with biological functionality to ensure durable, safe, and patient-centered results in dental practice.

Future research should focus on harmonizing *in vitro* testing standards with *in vivo* conditions, particularly through improved artificial saliva formulations, corrosion protocols, and multi-scale evaluation of implant surfaces. Advances in nanostructured coatings, antimicrobial agents, and biofunctional surface modifications will likely play a central role in addressing both osteointegration and infection challenges. Further, incorporating computational approaches, such as machine learning and multi-scale modeling, could accelerate the optimization of alloy composition and surface treatment strategies. Collaboration between materials science, dentistry, and clinical research will be essential for developing the next generation of dental metallic biomaterials with predictable long-term performance.

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