

## INFLUENCE OF RADIATION ON THE CORROSION RESISTANCE OF TITANIUM ALLOYS IN SPACE ENVIRONMENT

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**Abstract:** Titanium alloys are widely used in aerospace applications due to their exceptional strength-to-weight ratio and inherent corrosion resistance. However, the harsh space environment characterized by intense radiation and vacuum conditions poses unique challenges to their long-term durability. This review article systematically examines the impact of space radiation on the corrosion behavior of titanium alloys. It explores the fundamental mechanisms by which high-energy particles alter the microstructure and surface chemistry of these alloys, leading to changes in the protective oxide layer and overall corrosion resistance. Experimental studies and theoretical models addressing radiation-induced defects, phase transformations, and electrochemical behavior under radiation exposure are analyzed. The efficacy of alloying strategies and advanced surface coatings, including nanostructured and oxidation-based films, in mitigating radiation-enhanced corrosion is also discussed. By consolidating current knowledge and identifying gaps, this work aims to provide a foundation for developing titanium-based materials with improved reliability for extended space missions. The review underscores the critical need for integrated research combining radiation physics, materials science, and corrosion engineering to optimize titanium alloys for the extreme conditions encountered in space.

## ВЛИЯНИЕ НА РАДИАЦИЯТА ВЪРХУ УСТОЙЧИВОСТТА НА ТИТАНОВИТЕ СПЛАВИ КЪМ КОРОЗИЯ В КОСМИЧЕСКА СРЕДА

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**Ключови думи:** титанови сплави, космическо лъчение, корозия, радиационно увреждане, оксиден слой, повърхностни покрития, космическа среда, разграждане на материали

**Резюме:** Титановите сплави се използват широко в аерокосмическите приложения поради изключителното си съотношение между якост и тегло и присъщата им устойчивост на корозия. Въпреки това, суровата космическа среда, характеризираща се с интензивна радиация и вакуумни условия, поставя уникални предизвикателства пред тяхната дългосрочна издръжливост. В тази обзорна статия се разглежда систематично въздействието на космическата радиация върху корозионното поведение на титановите сплави. Изследват се основните механизми, чрез които високоенергийните частици променят микроструктурата и повърхностната химия на тези сплави, което води до промени в защитния оксиден слой и общата корозионна устойчивост. Анализират се експериментални изследвания и теоретични модели, които разглеждат дефектите, предизвикани от радиацията, фазовите превръщания и електрохимичното поведение при излагане на радиация. Обсъжда се и ефективността на стратегиите за легиране и усъвършенстваните повърхностни покрития, включително наноструктурни и оксидационни филми, за смекчаване на радиационно ускорената корозия. Чрез консолидиране на настоящите знания и идентифициране на пропуските, тази работа има за цел да предостави основа за разработване на материали на титанова основа с подобрена надеждност за продължителни космически мисии. Прегледът подчертава критичната необходимост от интегрирани изследвания, комбиниращи радиационна физика, материалознание и корозионно инженерство, за оптимизиране на титановите сплави за екстремните условия, срещани в космоса.

## Introduction

The expansion of human and robotic presence into space, encompassing long-duration missions, orbiting stations, and lunar/planetary habitats, is critically dependent on the structural integrity and longevity of materials. Among these, titanium alloys, particularly Ti-6Al-4V, are cornerstone materials in aerospace engineering. Their popularity stems from an unparalleled combination of high specific strength, excellent fracture toughness, and superb corrosion resistance in terrestrial and aqueous environments [1–5]. This corrosion resistance is primarily attributed to a stable, adherent, and self-healing passive oxide layer (2–10 nm thick predominantly TiO<sub>2</sub>) that forms spontaneously on the alloy surface [6].

However, the space environment presents a unique and aggressive combination of challenges not found on Earth, including ultra-high vacuum, extreme temperature cycles, atomic oxygen (in LEO), micrometeoroid impacts, and, most pertinently for this review, intense and continuous radiation. The space radiation spectrum includes galactic cosmic rays (GCRs), solar particle events (SPEs), and trapped particles in planetary magnetospheres (e.g., electrons and protons in the Van Allen belts) [2]. These high-energy particles can impart significant damage to a material's lattice structure [7].

When radiation exposure intersects with the requirement for corrosion resistance, a complex and potentially synergistic degradation pathway emerges [8, 9]. Energetic particles can disrupt the protective TiO<sub>2</sub> layer, generate defects and dislocations in the underlying metal, and even induce phase transformations [6, 10–12]. This microstructural damage can create pathways for corrosive species, alter electrochemical potentials, and compromise the self-passivating ability of the alloy, potentially leading to enhanced corrosion rates, stress corrosion cracking, or pitting in the presence of contaminants [13–16].

Existing literature confirms that radiation generates point defects (e.g., oxygen vacancies) and amorphous domains in metal oxides [17], but the specific mechanisms by which these changes degrade the corrosion resistance of titanium alloys in space-relevant conditions are fragmented and often inferred from non-space analogs. Crucially, the synergy between radiation, atomic oxygen (in LEO), adsorbed moisture from outgassing, and thermal cycling is rarely addressed in a unified framework.

While the individual effects of radiation on mechanical properties or corrosion in isolated environments have been studied [18, 19–24], a comprehensive understanding of their interplay in the context of space applications is lacking. This review, therefore, aims to systematically consolidate and critically evaluate the current body of literature on the influence of radiation on the corrosion resistance of titanium alloys. Specifically, it seeks to:

- elucidate the fundamental mechanisms of radiation-induced damage in titanium alloys and their passive films;
- analyze reported changes in electrochemical and corrosion behavior post-irradiation;
- evaluate proposed mitigation strategies, including alloying and surface engineering;
- identify critical knowledge gaps and propose future research directions to ensure material reliability for next-generation space missions.

## Methods

A structured search was conducted across electronic databases including Scopus, Web of Science, NASA Technical Reports Server (NTRS), and Google Scholar using the following Boolean query: (“titanium alloy” OR “Ti-6Al-4V” OR “CP-Ti”) AND (“space radiation” OR “proton irradiation” OR “heavy ion irradiation”) AND (“corrosion resistance” OR “passive film” OR “electrochemical behavior”).

The search spanned publications from January 1990 to June 2025. Inclusion criteria were:

- peer-reviewed journal articles, conference proceedings (e.g., AIAA SciTech, MRS Spring), or official technical reports (NASA, ESA);
- experimental or modeling studies involving irradiation of titanium alloys with space-relevant particles (protons: 0.1–200 MeV; heavy ions: e.g., Fe, Kr, Xe at 10–1000 MeV);
- reporting of corrosion-related outcomes (e.g.: polarization curves, impedance spectra, oxide composition, pitting susceptibility).

Excluded were studies focusing solely on mechanical degradation, non-titanium materials, or terrestrial corrosion without radiation exposure.

Data were extracted and thematically synthesized into three categories:

- radiation-induced microstructural and surface modifications;
- electrochemical and corrosion behavior under irradiation;
- performance of mitigation strategies with emphasis on nanostructured coatings.

Critical appraisal focused on radiation relevance (fluence, energy, dpa), environmental realism (e.g. presence of electrolytes, AO), and methodological consistency across studies.

## Results

Radiation exposure influences titanium alloys through defect formation, oxide modification, and changes in corrosion behavior (see Table 1). At low radiation doses, oxide densification can enhance corrosion resistance, while high doses lead to oxide disorder and increased corrosion rates.

Table 1. Summary of radiation type, dose, effects, and corrosion trends

| Radiation type              | Dose / Fluence                                | Key effect                      | Corrosion trend                       | Representative alloys              |
|-----------------------------|-----------------------------------------------|---------------------------------|---------------------------------------|------------------------------------|
| Proton / Ion                | $\sim 10^{14} - 10^{16}$ ions/cm <sup>2</sup> | Defect formation, oxide damage  | Increased corrosion rate at high dose | Ti-6Al-4V, Ti-5Al-2.5Sn            |
| Heavy Ion                   | $10^{13} - 10^{16}$ ions/cm <sup>2</sup>      | Oxide amorphization, sputtering | Passivity loss, film cracking         | Ti-Al-V-Mo                         |
| Electron / $\gamma$         | Up to $10^9$ Gy                               | Bulk defect formation           | Minimal surface change                | Ti-6Al-4V                          |
| UV / VUV                    | $10^2 - 10^3$ J/cm <sup>2</sup>               | Photochemical oxidation         | Slight improvement                    | CP-Ti, TiO <sub>2</sub> -coated Ti |
| Combined Radiation + Vacuum | -                                             | Synergistic degradation         | Significant loss of protection        | Ti-6Al-4V, Ti-Nb-Zr                |

Below is a structured synthesis of findings from the reviewed literature, organized by mechanistic domain.

### Radiation-induced microstructural changes

Radiation (ions, protons, neutrons) introduces point defects (vacancies, interstitials), defect clusters, dislocation loops, and in some cases phase transformations. In Ti-6Al-4V and Ti-5Al-2.5Sn irradiated with protons or ions at fluences of  $10^{14} - 10^{16}$  ions•cm<sup>-2</sup>, TEM and other techniques reveal defect clustering and dislocation loops [19, 25–27].

In newer alloys, [28] report that Ti-15V-3Cr-3Sn-3Al exhibits enhanced radiation resistance, attributed to higher displacement threshold energy and defect tolerance.

Swift heavy ion irradiation experiments on Ti-6Al-4V show dense damage tracks, local amorphization, and defect-rich zones, depending on ion species and energy [29].

Analyses of irradiation in titanium alloys confirm that swelling and void formation are limited below  $\sim 500$  °C, making titanium more resistant to volumetric radiation damage than many steels [30].

These structural alterations set the stage for altered diffusion paths, stress fields, and local electrochemical heterogeneity, all of which influence corrosion.

### Radiation effects on oxide layers

The passive TiO<sub>2</sub> (and related mixed oxides) layer is the key protective barrier in titanium alloys. Radiation interacts with this film by generating defects (oxygen vacancies, cation interstitials), modifying stoichiometry, and causing structural disorder or amorphization.

At low-to-moderate doses, some studies report radiation-assisted oxide densification: defects facilitate oxygen diffusion and allow the densification or slight growth of the oxide, potentially improving passivity.

At higher doses, oxide degradation dominates: partial amorphization, increased defect concentration, and the emergence of sub-oxide phases (TiO<sub>x</sub>,  $x < 2$ ) have been observed, reducing barrier continuity and increasing conductance.

Coatings (e.g., TiN, Al<sub>2</sub>O<sub>3</sub>, TiAlN) have been shown to degrade under high-fluence irradiation: microcracks, delamination, or phase segregation reduce their protective function over time.

In pulsed ion beam treatments of Ti-6Al-4V, irradiated surfaces exhibit changes in wear and corrosion behavior, attributed to modified surface microstructure and oxide stability [31, 32]. Also, the work “Wear and corrosion resistance of Ti6Al4V alloy irradiated by high-intensity pulsed ion beam” reports relevant data.

Thus, radiation modifies both the structure and chemistry of oxide films, often degrading their passive behavior under aggressive environments.

## **Corrosion performance post-irradiation**

The ultimate metric is how corrosion behavior (electrochemical parameters, breakdown potential, corrosion current) changes after radiation exposure.

In many experiments, low-dose irradiation yields slight reduction of passive current densities ( $i_{\text{pass}}$ ) and marginal improvements in corrosion potential, likely due to densified oxide layers.

At higher irradiation doses, more common effects include:

- decrease in corrosion potential ( $E_{\text{corr}}$ );
- increase in passive current or leakage current;
- earlier breakdown of passivity and sometimes pitting or localized corrosion.

The effect is environment-dependent: in vacuum or low-pressure oxygen, oxide growth is suppressed and degradation effects dominate; in humid or aqueous electrolytes, radiation-enhanced ionic transport often accelerates corrosion.

Some alloys demonstrate better tolerance: Ti-Nb-Zr and Ti-Mo-based alloys form more stable mixed oxides that better resist radiation-induced degradation. For example, “Corrosion Behavior of TiMoNbX (X = Ta, Cr, Zr) Refractory” [33] explores corrosion properties of multicomponent mixtures under harsh conditions.

Overall, the data show a dose-dependent transition: low-level irradiation may temporarily strengthen passivity; beyond a threshold, damage overwhelms protection and corrosion accelerates.

## **Discussion**

### **Mechanistic interpretation**

The evidence supports a dual-regime model: initial beneficial effects (oxide densification) at low doses give way to net degradation at higher doses. This is consistent with the notion that radiation enhances diffusion (especially at defect sites) but simultaneously accumulates damage that weakens structural integrity.

Radiation-induced point defects and clusters increase the mobility of oxygen and metal ions, modifying oxide growth kinetics. As defects accumulate, the oxide lattice becomes disordered or amorphous, sub-oxide regions appear, and conduction paths emerge. These changes reduce the barrier function of the film, increase electronic leakage, and facilitate electrochemical attack.

Alloying plays a critical role: elements such as Nb, Mo, Zr, and Ta tend to stabilize mixed oxides under radiation, suppressing vacancy clustering or preferential diffusion. Conversely, Al- and V-rich alloys are more prone to oxide destabilization under radiation. Thus, alloy design is a key strategy.

Additionally, coatings must be evaluated not just for static performance but for radiation durability: microstructural integrity under ion/particle flux is essential for sustained protection.

### **Limitations and challenges**

Heterogeneous experimental conditions (radiation types, energies, doses, environments) make cross-study comparison difficult.

Short exposure durations (hours to days) limit insight into cumulative long-term behavior over mission lifetimes.

Many studies do not simulate all space-relevant stressors (vacuum, atomic oxygen, UV, temperature cycling) concurrently.

Advanced alloy/coating systems under radiation–corrosion coupling remain underexplored.

Predictive modeling is sparse: few studies tie atomistic radiation damage simulations with corrosion kinetics.

### **Practical and theoretical implications**

For spacecraft designers, these results suggest that conventional titanium alloys (e.g. Ti-6Al-4V) may gradually lose corrosion resistance in radiation-rich orbits. Alloying with radiation-tolerant elements and using robust, radiation-hardened coatings are promising mitigation routes [34–38].

From a theoretical perspective, the coupling between radiation defect physics and electrochemical kinetics must be better integrated. Predictive models that link damage accumulation, diffusion, oxide corrosion stability, and behavior would empower materials design.

## Hypothesis validation

The central hypothesis is supported: radiation exposure can degrade corrosion resistance in titanium alloys through microstructural damage and modification of the passive oxide film. While the degree of degradation depends on dose, alloy composition, and environment, the core mechanism is consistently observed across studies.

## Future research directions

1. Perform integrated irradiation–corrosion experiments under real space-like environments (vacuum, atomic oxygen, thermal cycling).
2. Use in-situ diagnostics (e.g. EIS, XPS) during irradiation to observe dynamic changes in oxide films.
3. Develop multiscale modeling frameworks to predict performance under coupled radiation–corrosion effects.
4. Explore novel alloy systems (e.g., Ti-Nb-Zr, high-entropy titanium blends) for radiation resilience.
5. Investigate radiation-resistant coatings (nanolayers, self-healing oxides) explicitly under particle flux.
6. Standardize test protocols and build open data repositories on radiation–corrosion performance.

## Conclusion

Space-relevant radiation demonstrably degrades the corrosion resistance of titanium alloys by introducing defects and amorphization in the protective TiO<sub>2</sub> layer, increasing ionic conductivity and susceptibility to localized attack.

This review establishes that corrosion performance in space cannot be extrapolated from terrestrial data; radiation must be considered a primary degradation driver for passive alloys.

Nanoengineered coatings - particularly ALD-grown nanolaminates and doped oxides – offer a near-term solution to enhance the durability of titanium components in high-radiation zones of spacecraft, supporting mission success for Artemis, Lunar Gateway, and Mars missions.

Critical unknowns include the long-term evolution of radiation-corrosion synergy under real spacecraft conditions, the role of spacecraft outgassing products, and the development of self-monitoring self-healing surfaces that respond dynamically to radiation damage.

Optimizing titanium alloys for deep space requires an integrated research paradigm that unites radiation physics, nanoscale surface science, and electrochemical engineering - ensuring that the materials enabling humanity's expansion into space are as resilient as the missions they support.

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