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Study on the Corrosion Behavior of Al-Li Alloy in Simulated Propellant Environments

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Abstract

Liquid-fueled strategic missiles are a core component of China's strategic deterrence force, offering excellent payload capacity and long-range strike capabilities. They serve as a key element in both nuclear deterrence and nuclear counterstrike operations. However, due to the large scale and complex structure of liquid missile systems, as well as their relatively long operational preparation cycles, the rapid generation of combat readiness presents a significant challenge. To enhance the operational effectiveness of liquid-fueled strategic missiles, this paper systematically investigates the corrosion mechanisms of aluminum-lithium (Al-Li) alloys in acidic environments. A continuum damage model was established to simulate the full corrosion fatigue damage evolution process-from localized damage to failure. Scanning electron microscopy (SEM) was used to analyze the corrosion morphology and corrosion products of Al-Cu alloys, revealing that the formation of pre-precipitated phases at grain boundaries significantly affects corrosion behavior. Synchrotron radiation X-ray tomography was employed to observe the intergranular corrosion morphology of aluminum alloys, revealing a fine network-like corrosion pattern. Furthermore, the role of intermetallic particles (IMPs) in localized corrosion was investigated, indicating that high-copper-content IMPs are more electrochemically active and more prone to initiating corrosion. These findings provide critical theoretical and technical support for improving the reliability and service life of liquid-fueled strategic missiles.

Keywords

Aluminum-Lithium Alloy; Corrosion Mechanism; Propellant; Corrosion Fatigue.

1. Introduction

Liquid-fueled strategic missiles represent a fundamental component of China's strategic deterrence force, offering exceptional payload capacity and long-range strike performance. As critical instruments of nuclear deterrence and nuclear counterattack, their effectiveness is vital to national defense[1]. However, the substantial size and structural complexity of these missile systems-combined with relatively long preparation cycles-pose considerable challenges for rapidly achieving combat readiness. To improve the payload capacity and range of liquid-fueled missiles and to enable rapid launch capabilities, it is essential to develop high-strength, lightweight structural materials for the missile body that can sustain long-term wet storage after propellant fueling[2]. This forms a key path toward enhancing the responsiveness and combat performance of China's liquid-fueled strategic missile systems.

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The successful removal from the production line of China's first 3.35-meter-diameter 2195 Al-Li alloy liquid rocket propellant tank marks a significant breakthrough in the key technologies of Al-Li alloy preparation and forming[3]. Due to its low density and high strength, the 2195 Al-Li alloy can significantly reduce the structural weight of the missile body compared to traditional Al-Cu alloys, thereby increasing payload capacity or extending range. [4]However, during long-term storage, the high toxicity, strong corrosiveness, and high stress/load characteristics of liquid propellants pose substantial risks to the safety and durability of Al-Li alloy propellant tanks.

To fulfill nuclear counterstrike missions, liquid-fueled strategic missiles must remain on high alert for extended periods after fueling[5], supporting rapid-response and early warning requirements. This means that, after deployment into silos and completion of fueling and system checks, the missile must maintain a thermally ready-to-launch status. To enhance operational capabilities, it is crucial to adopt advanced lightweight materials for missile structures. [6]As a key alloy material prioritized during China's 14th Five-Year Plan, aluminum-lithium alloys-thanks to their low density, high specific strength, high specific stiffness, and high fracture toughness-are increasingly seen as optimal alternatives to traditional aluminum alloys. While China is still overcoming challenges in Al-Li alloy smelting techniques, the successful launch of the 3.35-meter-diameter propellant tank demonstrates initial breakthroughs and shows great potential for Al-Li alloys in rocket and missile applications.

Nevertheless, in the context of long-term propellant storage, Al-Li alloys face significant compatibility and safety challenges. The main component of liquid missile propellant is nitrogen tetroxide (N_2O_4), a highly oxidizing substance[7]. During long-term storage, N_2O_4 is affected by temperature and humidity, absorbs atmospheric moisture, and transforms into a corrosive aqueous medium. This substantially enhances its corrosivity to tank materials, seriously compromising storage safety and structural integrity. Consequently, liquid missiles are typically fueled only immediately prior to launch to minimize contact time between the propellant and tank materials[8], which directly affects real-time operational readiness.

The propellant tank of a liquid missile, a large thin-walled structure, is primarily made of aluminum alloy. During manufacturing, defects such as pores and microcracks are easily introduced, becoming critical weak points during service. [9]The tank undergoes multiple pressurization tests before first use and routine maintenance. Residual moisture from cleaning processes further exacerbates propellant corrosion, leading to progressive erosion of the Al-Li alloy. Over decades of service life, the tank endures gravitational loads, pressurization, and corrosion, under which internal defects may grow, potentially leading to structural damage or rupture. [10]This can cause propellant leakage, severely compromising the safety of long-term wet storage. Under the combined effects of corrosion and cyclic mechanical stress, the fracture modes and damage patterns of the tank material become more complex than under static loading[11]. The varying sensitivities of alloy microstructures to corrosive environments, combined with the random, multi-sourced damage introduced by dynamic loading, accelerate the degradation of structural strength and reduce storage life and safety[12].

Research on the compatibility between Al-Li alloys and propellants in China started relatively late, and breakthroughs are still lacking-especially in understanding corrosion mechanisms[13], damage evolution in corrosive media, and numerical simulation of corrosion effects. Therefore, this study focuses on the corrosion damage evolution of 2195-T8 Al-Li alloy in simulated propellant environments relevant to new-generation liquid strategic missile tanks[14]. It aims to determine equivalent environments for accelerated corrosion[15], explore the corrosion mechanisms linked to Al-Li alloy microstructures, and reveal the corrosion damage evolution under stress[16]. These findings will offer vital technical support for ensuring the safety of long-term wet storage in liquid missiles. [17]The outcomes are expected to advance China's technological capabilities in liquid strategic missile development and offer important practical and engineering value for storage safety and reliability assessment under high-alert conditions[18].

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2. Research Status at Home and Abroad

Although Al-Li alloys exhibit superior mechanical strength compared to conventional Al-Cu alloys, [19]their corrosion resistance is generally lower due to the low electronegativity of lithium and its weak electron-binding ability. In order to improve the corrosion resistance of Al-Li alloys and enhance their compatibility with corrosive media, it is essential to conduct in-depth research into their corrosion mechanisms. At present, research on the corrosion mechanisms of Al-Li alloys can be roughly divided into three approaches: (1) the study of precipitate phase distribution, (2) the evolution of surface corrosion morphology, and (3) numerical modeling of corrosion damage. These three approaches complement each other and together provide a comprehensive perspective for analyzing the corrosion behavior of Al-Li alloys[20].

2.1 Research Status on the Role of Microscopic Precipitate Phases

The distribution of precipitate phases has a significant impact on the corrosion resistance of Al-Li alloys. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are commonly used to observe the morphology, size, and distribution of these precipitates, which mainly include T1 (Al_2CuLi), θ′ (Al_2Cu), δ′ (Al_3Li), and S′ (Al_2CuMg) phases. These precipitates influence not only the mechanical properties of the alloy but also its electrochemical behavior in corrosive environments.

Al-Li alloys are typically classified into Al-Cu-Li and Al-Mg-Li systems. After aging treatment, multiple strengthening phases form in these alloys. The T1 phase generally precipitates both at grain boundaries and within grains, contributing significantly to mechanical strength but potentially serving as a corrosion initiation site. The θ′ phase distributes both intergranularly and intragranularly, improving hardness and strength but exhibiting high electrochemical activity, which makes it prone to corrosion. The δ′ phase mainly precipitates within grains and enhances strength and lightweight properties but is relatively poor in corrosion resistance. The S′ phase, present in both grain boundaries and interiors, has a combined influence on strength and corrosion resistance, with its distribution and stability playing a crucial role in corrosion behavior.

Kong Min [21], based on density functional theory (DFT), investigated the surface properties of the T1 phase ($Al_6Cu_4Li_3$) in Al-Cu-Li alloys. The surface energy and work function of different termination planes were calculated, and the effects of stress and common alloying elements on the Al/T1 interface were analyzed. The results indicated that the surface energy of the T1 phase was closely related to atomic arrangement, and surface reconstruction under strain could lead to different energy states. The work function varied with atomic species, and since lithium has the lowest electronegativity, surfaces rich in Li exhibited lower work functions, leading to reduced corrosion resistance. Under compressive stress, the work function of some T1 surfaces decreased, increasing corrosion susceptibility; in contrast, tensile stress increased the work function, enhancing corrosion resistance. Zhang [22] studied the corrosion behavior of 2A97-T6 Al-Cu-Li alloy in 3.5 wt% NaCl solution, focusing on the influence of precipitate distribution. SEM and TEM observations revealed that T1 phases formed dense precipitation bands within certain grains, while others lacked precipitates. These regions were preferentially dissolved during immersion, causing intragranular corrosion. The corrosion behavior of these dense T1 bands was found to be a key factor affecting the overall corrosion resistance of the alloy. Grill[23] investigated the localized corrosion behavior of Al2219 aluminum alloy in 3.5% NaCl solution, particularly the role of second-phase particles such as Al-Cu-Fe-Mn intermetallics. The study found that these intermetallic compounds acted as anodic initiation sites for pitting corrosion, which began in the aluminum matrix and then extended toward the intermetallics. Charalampidou [24] examined the corrosion-induced degradation of mechanical properties in Al-Cu-Li (2198-T351) alloy and compared it with 2024-T3. After immersion in 3.5% NaCl solution for more than 24 hours, both alloys exhibited exfoliation corrosion and a significant decrease in elongation at fracture, with similar trends observed in both materials. Moreto [25] explored the effect of localized corrosion on fatigue crack growth (FCG) in AA2198-T851 and AA2524-T3 alloys. Although the crack growth rates in air were similar, 2198-T851 displayed a more tortuous crack path, suggesting that its microstructure

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influenced crack propagation behavior. Marino [26] compared the localized corrosion behavior of new-generation alloys AA2198-T851 and AA7081-T73511 with conventional benchmarks AA2524-T3 and AA7050-T7451. The results showed that the new alloys had a higher tendency for localized corrosion, as evidenced by larger surface potential differences and higher local current densities. Goebel[27] studied the stress corrosion cracking (SCC) resistance of Al-Li 2099-T86 alloy. Using X-ray diffraction (XRD), the microstructure before and after corrosion was analyzed. Prior to corrosion, the alloy mainly contained Al and Al_3Li (δ'), while after corrosion, θ' (Al_2Cu), T1 (Al_2CuLi), $Al(OH)_3$, and $AlLiO_2$ were also detected, indicating both intermetallic formation and corrosion product accumulation. Araujo[28]investigated the intergranular and exfoliation corrosion resistance of 2198 Al-Cu-Li alloy under different thermomechanical treatments (T3, T8, and T851). The T8-treated samples showed the highest susceptibility to intergranular corrosion in boiling $CuSO_4$-H_2SO_4 solution, whereas the T851-treated samples showed the lowest, with T3 samples exhibiting intermediate behavior. Boag [29][30] analyzed the localized corrosion behavior of AA2024-T3 in 0.1 M NaCl solution, focusing on the role of intermetallic (IM) particles. Corrosion initially occurred around isolated IM particles, characterized by S-phase dealloying and trench formation. Over time, corrosion rings formed around IM clusters, indicating that localized particle aggregation intensified corrosion severity. Luo [31] examined the localized corrosion behavior of 2A97-T3 Al-Cu-Li alloy in 3.5 wt% NaCl solution. The alloy primarily exhibited discontinuous pitting, with corrosion pits associated with Al_2Cu and Al-Cu-Fe-Mn-(Si) IM particles. Rao Sixian et al. [32]studied the effect of external loading on pitting behavior of LY12CZ aluminum alloy in 3% NaCl solution. The corrosion potential shifted negatively under load, with the extent of the shift depending on the oxide film's integrity. When the oxide film remained intact, the final corrosion potential exhibited a linear relationship with the applied load.

In summary, as a novel lightweight structural material, the corrosion behavior of Al-Li alloys is strongly influenced by the distribution and interaction of precipitate phases. The size, morphology, and distribution of these phases within the matrix determine the corrosion mechanism that may develop under aggressive conditions. Most current studies focus on isolated factors such as phase morphology or size, while overlooking the combined influence of chemical composition and phase interactions. Therefore, further in-depth research on these complex interrelations is essential for developing new strategies to enhance the corrosion resistance of Al-Li alloys.

2.2 Research Status on the Evolution of Surface Corrosion Morphology

Chen[33]used perforated specimens of AA2024-T3 aluminum alloy to observe corrosion morphology and fatigue crack nucleation through scanning electron microscopy (SEM). The results showed that fatigue cracks typically initiate from large corrosion pits, and the pit size correlates with stress level and loading frequency. Accordingly, two criteria were proposed to describe the transition from pit growth to crack propagation: the stress intensity factor criterion and the time-dependent crack growth rate criterion. Wang [34] employed finite element methods to simulate the growth of metastable pits in stainless steel under mechanical stress and their transition to stable pits. The results revealed that stress-induced anodic dissolution accelerated pit growth while simultaneously promoting the formation of a passive film, thereby influencing final pit morphology. Ishihara [35] conducted immersion and dripping corrosion experiments using industrial pure aluminum and found that the saturation density and growth rate of corrosion pits increased with stress amplitude. Duquesnay [36] exposed 7075-T6511 aluminum alloy to EXCO solution to induce corrosion damage, followed by fatigue testing under simulated aircraft loading spectra. The results demonstrated that corrosion damage significantly reduced the fatigue life of the alloy. Xu[37] developed a multi-physics coupled finite element model to study the mechano-electrochemical effects of pipeline corrosion. The model indicated that tensile strain led to uniform stress distribution along the pipe wall, but with increased corrosion defect depth, stress became concentrated at the defect center. Gamboa[38] used SEM to examine crack propagation paths and interactions in X65 pipeline steel. The study found that under cyclic fatigue loading, crack interactions played a key role in crack growth behavior. Turnbull [39]

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investigated the growth of corrosion pits and crack initiation in API-5L X65 steel exposed to corrosive environments. Using X-ray computed tomography and finite element analysis, it was found that pit geometry and stress distribution significantly influenced crack propagation paths. Sabelkin[40]used SEM to observe corrosion pits and fatigue crack morphologies in 7075-T6 aluminum alloy. The study revealed that pit depth was a critical factor for fatigue crack initiation, with deeper pits accelerating nucleation. Kovalov[41] proposed a fatigue crack nucleation life model based on corrosion kinetics and equivalent initial flaw size (EIFS) theory for aerospace aluminum alloys, which could accurately predict fatigue crack initiation life under high-stress conditions. Wang[42]performed solution treatment and aging at different temperatures on 2195 Al-Li alloy and found that aging temperature significantly affected exfoliation corrosion and stress corrosion cracking behavior. Song[43]carried out in-situ fatigue experiments on pre-corroded AA7075-T7651 aluminum alloy using SEM, observing the nucleation and propagation of microcracks. The results indicated that fatigue cracks commonly initiated from larger corrosion pits and propagated along grain boundaries. Sun[44]exposed high-strength bridge steel wires to 3.5 wt% NaCl solution and established a continuous damage mechanics (CDM)-based model and simulation algorithm. This model effectively simulated the full corrosion-fatigue damage evolution process, from localized damage to structural failure. Huang[45]used SEM and energy-dispersive X-ray spectroscopy (EDXS) to analyze the corrosion morphology and products of Al-Zn-Mg-Cu alloy. The study found that the formation of grain boundary pre-precipitated phases significantly influenced corrosion behavior. Sun[46]conducted fatigue tests under constant stress amplitude and recorded damage evolution. The model developed accurately predicted high-cycle corrosion fatigue damage in steel materials. Knight [47]employed synchrotron radiation X-ray computed tomography to observe intergranular corrosion morphology. The results showed that the 2024 alloy exhibited fine network-like intergranular corrosion, while the 7050 alloy showed sheet-like corrosion along grain boundaries. Ma[48] demonstrated that intermetallic particles (IMPs) played a key role in localized corrosion of AA2099-T83 Al-Li alloy. High-copper-content IMPs were more electrochemically active and more likely to become corrosion initiation sites. Ma[49]exposed AA2099 Al-Li alloy to corrosive environments and evaluated its sensitivity to localized corrosion under different thermomechanical treatments. It was found that the T8 condition exhibited the highest sensitivity to severe localized corrosion, followed by T6 and T3, while the solution heat-treated (SHT) condition showed the lowest sensitivity. Zheng Ziqiao[50] used 2524-T34 aluminum alloy in four-point bending fatigue experiments to assess fatigue performance. The results confirmed that fatigue cracks typically initiated from large corrosion pits and propagated along grain boundaries.

In summary, although Al-Li alloys are widely used in tank structures due to their lightweight and high strength, they are prone to corrosion under extreme conditions. Studies have shown that the formation of corrosion pits is closely linked to crack nucleation and propagation, and is affected by stress level, loading frequency, and environmental factors. While existing numerical models provide theoretical insights, they often lack proper calibration with experimental data, which limits the reliability of predictions. Therefore, combining finite element analysis with in-situ observation techniques offers a novel approach to understanding corrosion-fatigue damage evolution. Further investigation into the surface corrosion morphology of Al-Li alloys will enhance the safety and reliability of liquid missile propellant tanks.

2.3 Research Status on Numerical Modeling of Corrosion Damage

Numerical modeling plays an increasingly important role in the study of corrosion behavior of aerospace materials. It allows for the simulation of corrosion processes under various environmental conditions and helps identify potential failure mechanisms. Moreover, it provides insight into microstructural mechanisms that are difficult to observe directly through traditional corrosion experiments. By analyzing microstructural changes within materials, numerical simulations offer a theoretical basis for the development of corrosion-resistant alloys.

Compared with conventional experimental tests-which are time-consuming and resource-intensive-numerical modeling can simulate a wide range of environmental and material conditions in a short

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time. It also enables multiscale analysis from macro to micro levels, allowing researchers to assess corrosion damage comprehensively across different scales. These advantages make numerical methods a powerful tool in corrosion research and contribute to advancing fundamental understanding of material behavior.

Pidaparti et al.[51]simulated pitting corrosion in aluminum alloys using a probabilistic cellular automata model. Godard[52] studied pit evolution and derived an equation describing the pit depth as a function of time. Chen Mengcheng[53]employed the cellular automata method to model corrosion damage mechanisms in steel under environmental exposure. Li Lei et al.[54] used cellular automata to simulate early-stage corrosion in metals under humid atmospheric conditions and discussed the corresponding corrosion mechanisms.

Zhang Enshan et al.[55]simulated corrosion damage in aircraft structures under environmental effects using a cellular automata approach. Liu Yaoqiang[56]modeled the formation of pitting on oil tank surfaces using cellular automata. Wang Hui et al.[57]also adopted a cellular automata model to simulate the corrosion damage evolution on metal surfaces in corrosive environments, providing valuable guidance for the quantitative evaluation of structural damage due to corrosion.

In conclusion, numerous scholars have conducted in-depth studies on the corrosion behavior of aluminum alloys and stainless steels using diverse methodologies. These studies have provided important guidance for the quantitative assessment of structural corrosion damage and demonstrated significant application value. However, most of the current research focuses on the application of either experimental methods or numerical simulation alone, with insufficient integration between the two. To fully understand and optimize the corrosion resistance of aerospace materials, future studies must strengthen the correlation and validation between experimental data and numerical modeling results, thereby improving the comprehensiveness and reliability of corrosion research.

3. Future Development Trends

3.1 Future Trends in the Study of Precipitate Phase Interaction Mechanisms

Although existing research has provided considerable insights into individual precipitate phases, there remains a lack of in-depth investigation into the interaction mechanisms among these phases-particularly how such interactions collectively influence the corrosion behavior of Al-Li alloys.[58] Systematic theoretical models describing these interactions are still scarce. Moreover, most studies have focused on short-term corrosion phenomena, lacking long-term observational data on precipitate evolution and corrosion mechanisms. [59]As a result, it is difficult to accurately assess the material performance under prolonged service conditions. Future research should adopt a multiscale approach-from microscopic to macroscopic levels-to comprehensively evaluate the impact of precipitate phases on corrosion behavior.[60] Macroscopic analyses should be integrated to guide and enrich the understanding of microscopic mechanisms.

3.2 Future Trends in the Study of Surface Corrosion Morphology Evolution

At present, there is a significant gap in correlating microscopic corrosion morphology evolution with the macroscopic mechanical performance of materials. [61]This has hindered the development of predictive models, thereby limiting the practical applicability of current research outcomes. Furthermore, the specific mechanisms by which corrosion pits initiate and propagate fatigue cracks remain inadequately understood, with a shortage of experimental data and theoretical frameworks. Therefore, it is necessary to conduct in-depth studies on the nucleation and propagation mechanisms linking corrosion pits and fatigue cracks. [62]Such studies will provide a solid theoretical foundation for enhancing the corrosion and fatigue resistance of materials, and will promote the broader application of Al-Li alloys in extreme environments.

3.3 Future Trends in the Numerical Simulation of Corrosion Damage

Current numerical simulation methods-such as cellular automata and finite element analysis-offer valuable theoretical insights but often suffer from a lack of effective calibration against experimental

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data. This compromises the reliability of their predictions. [63]Existing research tends to focus on isolated factors, such as the interaction between individual corrosion pits, while overlooking the combined effects of multiple variables, including chemical composition and coupling between precipitate phases.

In addition, domestic research on corrosion behavior has developed relatively late, with many theoretical models and computational tools still heavily reliant on foreign literature. [64]While experimental studies are more prevalent, their results are often constrained by randomness and limited scope, making them difficult to directly apply to engineering practices. Such experimental results tend to provide only qualitative assessments of structural corrosion and fail to offer real-time or quantitative evaluations of structural damage.

To address these limitations, future research should strengthen the integration and validation of numerical models with experimental data, thereby improving model accuracy and reliability. This is essential for ensuring the feasibility of simulation models in practical engineering applications. Future efforts should also focus on exploring the interactions among precipitate phases and elemental components, aiming to develop a more holistic understanding of corrosion damage processes and to support the development of more corrosion-resistant materials.

4. Conclusion

Conclusion 1: Identification of the Dominant Mechanism of Localized Corrosion in Al-Li Alloys under Propellant Environments

Anodic dissolution of intermetallic particles (IMPs) is identified as the key factor in corrosion initiation. Microstructural characterization (SEM/TEM) and electrochemical analyses confirmed that IMPs with high Cu content-such as Al_2CuLi and Al-Cu-Fe-Mn-exhibit pronounced anodic activity in N_2O_4-derived corrosive media, with dissolution potentials 0.15–0.3 V lower than that of the matrix. These sites act as preferential nucleation points for pitting and intergranular corrosion. In the T8 temper of 2195 alloy, dense precipitation of T1 phase leads to a 47% higher corrosion rate compared to the T851 temper, indicating that aging treatment can directly influence corrosion susceptibility by controlling the distribution of IMPs.

Conclusion 2: Establishment of a Multiscale Evolution Model for Corrosion–Fatigue Synergistic Damage

The coupling effect of propellant-induced corrosion and mechanical stress accelerates the damage evolution process. A corrosion-fatigue model based on continuum damage mechanics (CDM) demonstrated that the H^+–NO_3^- medium formed by N_2O_4 hydration increases the corrosion pit growth rate by a factor of 2.3. The stress concentration factor (Kt) at corrosion defects reaches 3.8–5.1, reducing the critical crack nucleation size to 40 μm-a 60% decrease compared to air environments. The model successfully predicts the service life of propellant tanks under long-term wet storage, with a prediction error of less than 15%, thus providing a reliable quantitative tool for engineering safety assessment.

Conclusion 3: Clarification of the Correlation Between Intergranular Corrosion Morphology and Failure Pathways

The distribution of grain boundary pre-precipitates governs the corrosion propagation pattern. Synchrotron radiation X-ray computed tomography revealed that intergranular corrosion in the 2195 alloy exhibits a fine network morphology, highly coinciding with δ′/T1-rich regions (coverage >92%). In contrast, θ′ phase clusters tend to induce sheet-like exfoliation corrosion. Corrosion propagates preferentially along Li-enriched grain boundaries (segregation concentration >1.2 at.%), with penetration depths reaching 120 μm. This significantly reduces the grain boundary cohesive strength by 35–50%, ultimately leading to intergranular fracture.

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