



High-Temperature Oxidation and Corrosion of Alloys: Kinetics, Scale Formation, and Protective Coatings

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Article info

Article info

Received: 14.05.2026

Accepted: 27.07.2026

Available Online: 30.07.2026

Checked for Plagiarism: Yes

Keywords:

High-temperature oxidation, parabolic kinetics, oxide scale formation, protective coatings, high-entropy alloys

ABSTRACT

High-temperature oxidation and corrosion represent critical degradation mechanisms that severely impair the service life of metallic components across aerospace, power generation, and energy sectors, with turbine inlet temperatures in modern engines now routinely exceeding 1500°C. This comprehensive review systematically examines the fundamental principles governing high-temperature oxidation, from thermodynamic foundations and diffusion-controlled kinetics to the protective characteristics of oxide scales. The parabolic rate law, derived from Wagner's theory of diffusion-controlled growth, provides the framework for predicting oxidation kinetics, with rate constants increasing exponentially with temperature as demonstrated by activation energies ranging from 171 kJ/mol for Ti-based refractory alloys to higher values for alumina-forming systems. The formation of protective oxide scales primarily α -Al₂O₃ and Cr₂O₃ depends critically on alloy composition, with critical concentrations of Al (>5 wt.%) and Cr (>20 wt.%) required for continuous scale formation. Non-protective oxides with Pilling-Bedworth ratios substantially deviating from unity lead to rapid, often catastrophic, degradation through linear kinetics. Surface coating technologies, including thermal spray processes (HVOF, plasma spraying), diffusion coatings, and emerging high-entropy alloy coatings, have emerged as the primary engineering solution, with MCrAlY coatings forming stable α -Al₂O₃ scales and high-entropy alloy coatings demonstrating exceptional thermal stability and oxidation resistance through their unique core effects. The review concludes that effective high-temperature corrosion management requires integrated approaches combining mechanistic understanding, advanced coating technologies, and real-time monitoring.

Introduction

High-temperature oxidation and corrosion constitute one of the most significant and enduring challenges confronting metallic materials across critical industrial applications [1]. From gas turbine blades in aerospace engines and power generation systems to boiler tubes in thermal power plants and structural components in nuclear reactors, materials routinely exposed to extreme temperatures, aggressive gaseous environments, and complex thermomechanical loading conditions [2].

The degradation of metallic components through high-temperature oxidation not only compromises structural integrity and operational safety but also imposes substantial economic burdens through unplanned shutdowns, maintenance, and premature component replacement [3]. The fundamental challenge of high-temperature oxidation arises from the thermodynamic instability of metals in oxidizing environments. At elevated temperatures, all metals possess a negative Gibbs free energy of formation for their oxides, rendering oxidation thermodynamically spontaneous. The critical

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distinction between a metal's utility and its rapid destruction lies in the nature of the oxide scale formed during initial exposure. Protective oxide scales principally α -Al₂O₃, Cr₂O₃, and SiO₂ provide diffusion barriers that dramatically reduce oxidation rates when continuous, adherent, and slow-growing. Conversely, non-protective scales with poor adhesion or excessive growth stresses lead to rapid, often catastrophic, degradation through linear kinetics and oxide spallation [4-10]. The engineering significance of high-temperature oxidation has intensified dramatically with advancing operational requirements. In modern gas turbines, inlet temperatures now routinely exceed 1500°C, far surpassing the temperature capabilities of even advanced nickel-based superalloys [11-20]. Thermal barrier coating systems, comprising a ceramic top coat and a metallic bond coat, have become essential to bridge this performance gap, enabling turbine entry temperatures 150-250°C above substrate limits. Similarly, in utility boilers, co-firing of biomass and waste-derived fuels has introduced complex corrosive environments involving chlorides, sulfides, and molten salts that accelerate degradation beyond conventional oxidation mechanisms [21-30]. This comprehensive review aims to synthesize current understanding of high-temperature oxidation and corrosion across three interconnected domains: the fundamental kinetics and thermodynamics governing oxidation, the mechanisms of protective and non-protective oxide scale formation, and the state-of-the-art protective coating technologies. Particular emphasis is placed on emerging high-entropy alloy coatings and the integration of additive manufacturing techniques that promise transformative improvements in high-temperature corrosion resistance [31].

Literature Review

Historical Foundations and Fundamental Principles:

The scientific investigation of high-temperature oxidation traces its origins to the early 20th century with the pioneering work of Wagner, who established the theoretical framework for understanding diffusion-controlled oxidation kinetics [32-40]. Wagner's theory demonstrated that the growth of compact, adherent oxide scale proceeds through diffusion of ions and electrons across the growing scale, resulting in parabolic kinetics where the square of the scale thickness increases linearly with time. This foundational insight transformed the understanding of oxidation from an empirical observation to a quantitative, predictive science. The thermodynamic framework for oxidation was established through the Ellingham diagram, which provides the Gibbs free energy of formation for oxides as a function of temperature. These diagrams reveal several critical insights: the

stability of oxide scales varies dramatically with temperature, with more noble metals forming less stable oxides; the relative stability of Al₂O₃ versus Cr₂O₃ versus SiO₂ determines the selective oxidation behavior of alloys; and the competition between elements for available oxygen governs the composition and structure of the developing oxide scale [41-50]. The Pilling-Bedworth ratio the volume ratio of oxide to consumed metal has emerged as a crucial predictive parameter for oxide protectiveness. Values between 1 and 2.5 indicate compressive stresses in the scale favorable for protectiveness, while values substantially deviating from unity generate tensile stresses that promote cracking and spallation.

Oxidation Kinetics: Parabolic, Linear, and Logarithmic Behavior:

Oxidation kinetics describes the rate at which oxidation proceeds and provides the quantitative basis for predicting component lifetimes. The three fundamental kinetic laws logarithmic, parabolic, and linear reflect the rate-determining step in the oxidation process. Parabolic kinetics represents the ideal behavior for engineering alloys, where the rate of oxide formation continuously decreases with time, reflecting the increasing diffusion path length through the growing scale [51-60]. According to Wagner's theory, parabolic kinetics follows $x^2 = k_p t$, where x is the scale thickness, k_p is the parabolic rate constant, and t is time. The parabolic rate constant exhibits Arrhenius temperature dependence: $k_p = A \exp\left(\frac{-Q}{RT}\right)$, where A is a pre-exponential factor, Q is the activation energy for the rate-limiting diffusion process. Experimental studies have reported activation energies ranging from approximately 150-250 kJ/mol for chromia-forming systems to 300-400 kJ/mol for alumina-forming systems [61-70]. Linear kinetics represents catastrophic behavior where the oxide scale provides no effective protection, often due to cracking, spallation, or porous, non-protective scale formation. The oxidation proceeds at a constant rate, leading to rapid metal consumption. Identification of linear kinetics in service conditions signals imminent component failure requiring immediate intervention. Logarithmic kinetics is observed at low temperatures or for noble metals, where extremely slow oxidation occurs after an initial fast reaction due to electron tunneling or space-charge-limited transport mechanisms.

Protective and Non-Protective Oxide Scales:

The protectiveness of an oxide scale is governed by its composition, structure, adhesion, and growth mechanisms. The most effective protective scales are α -Al₂O₃ and Cr₂O₃, which exhibit low defect concentrations, slow cation and anion diffusion, and thermodynamically stable microstructures [71-80]. The transition from formation of non-protective

oxides (FeO, NiO, TiO₂) to protective scales (Al₂O₃, Cr₂O₃, SiO₂) represents the fundamental design principle of oxidation-resistant alloys. Alumina-forming alloys (FeCrAl, NiCrAl, CoCrAl) are employed for the most demanding high-temperature applications (>900 °C) due to the exceptional properties of α -Al₂O₃. This oxide exhibits extremely low growth rates, high thermodynamic stability, and excellent adherence when promoted by reactive element additions such as Y, Hf, or Zr [81-90]. The critical Al concentration for continuous Al₂O₃ scale formation depends on the alloy system and operating conditions, typically requiring 5-8 wt.% Al. Chromia-forming alloys provide excellent oxidation resistance up to approximately 900°C, after which volatile CrO₃ formation limits their effectiveness [91-100]. The critical Cr concentration for continuous Cr₂O₃ scale formation is approximately 20 wt.%, though this threshold depends on temperature and oxygen partial pressure.

Non-protective oxides typically result from insufficient concentrations of protective-scale-forming elements, leading to the formation of fast-growing, porous, or poorly adherent scales. The oxidation process follows linear kinetics, providing no effective long-term protection [101-111]. In advanced boiler environments, the interplay between oxidation, sulfidation, and chlorination creates complex multi-factor corrosion that conventional oxide scales struggle to resist.

High-Temperature Corrosion in Industrial Environments:

The complexity of industrial high-temperature environments extends well beyond simple oxidation, encompassing sulfidation, chlorination, hot corrosion, and multi-factor coupled degradation. Sulfidation corrosion arises from sulfur-containing gases (SO₂, SO₃, H₂S) produced during fuel combustion. Sulfate-type corrosion initiates from alkali metal sulfate deposits that dissolve protective oxide scales, allowing sulfur to diffuse into the substrate and form metal sulfides. Sulfides typically possess high defect concentrations, enabling rapid inward oxygen and sulfur diffusion [112-122]. The Ni-Ni₃S₂ low-melting-point eutectic constitutes a critical failure mechanism for nickel-based alloys in sulfur-rich environments.

Chlorine-induced corrosion has become increasingly prevalent with the co-firing of biomass and waste-derived fuels containing alkali metal chlorides. The "active oxidation" mechanism, where chlorine forms volatile metal chlorides that subsequently oxidize to deposit non-protective oxides, accelerates corrosion rates substantially beyond conventional oxidation.

Hot corrosion involves the interaction of alloys with molten salts at high temperatures, particularly vanadates and sulfates from fuel impurities. The molten salts dissolve protective oxide scales and

accelerate degradation through fluxing mechanisms, with conventional thermal barrier coatings particularly susceptible to CMAS (calcium-magnesium-aluminum-silicate) attack.

Protective Coating Technologies:

Surface coating technologies have emerged as the primary engineering solution for high-temperature corrosion protection, enabling cost-effective protection of conventional alloys through deposition of corrosion-resistant layers. MCrAlY coatings (M=Ni, Co, NiCo) represent the mature standard for high-temperature protection, forming stable α -Al₂O₃ scales through selective oxidation of aluminum. The presence of reactive elements (Y, Hf, Zr) critically influences scale adhesion and growth kinetics, with optimized Y distributions substantially improving thermal cycling performance. High-entropy alloy coatings have emerged as promising next-generation materials, offering exceptional thermal stability, oxidation resistance, and compositional flexibility through their unique core effects: high configurational entropy, sluggish diffusion, severe lattice distortion, and the cocktail effect. Al-containing high-entropy alloys can form stable α -Al₂O₃ scales, while Cr- or Si-containing variants achieve synergistic protection through complex oxide formation. HEA coatings demonstrate CTE compatibility with both ceramic top coats and metallic substrates, mitigating interfacial stresses that drive TGO-induced spalling. Thermal spray processes including high-velocity oxy-fuel (HVOF), plasma spraying, and cold spraying enable deposition of dense, adherent coatings with controlled microstructures. Post-deposition heat treatments optimize oxide scale formation and coating-substrate bonding.

Methodology

This comprehensive review was developed through systematic analysis of peer-reviewed literature indexed in major scientific databases including Scopus, Web of Science, ScienceDirect, and Google Scholar. The search strategy employed combinations of keywords including "high-temperature oxidation," "oxidation kinetics," "parabolic rate constant," "oxide scale," "protective coatings," "MCrAlY," "thermal barrier coatings," "high-entropy alloys," and related terms. Particular emphasis was placed on studies published between 2015 and 2026, while seminal earlier works were included where mechanistically or historically significant. The literature screening process involved identification of peer-reviewed research articles, review papers, and industry reports. Studies were selected based on relevance to the review scope, methodological rigor, completeness of reported experimental conditions, mechanistic significance, and applicability to industrial contexts. Representative studies for comparative analysis

were chosen based on clear presentation of experimental methodology, characterization results, and performance metrics. Quantitative data synthesis focused on oxidation kinetics parameters including parabolic rate constants (k_p), activation energies (Q), and oxide scale characteristics. Performance metrics including mass gain, scale thickness, and coating lifetime were extracted and analyzed. For emerging technologies, specific attention was given to reported mechanisms and development status. Thermodynamic and kinetic

analyses drew upon established principles including Wagner's parabolic growth theory, the Arrhenius relationship, and Pilling-Bedworth ratio calculations. Environmental and industrial context considerations were examined through analysis of application case studies across aerospace, power generation, and oil and gas sectors.

Results

Table 1. Oxidation Kinetics Parameters for Representative Alloy Systems

Alloy System	Temperature (°C)	Parabolic Rate Constant, k_p ($\text{mg}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$)	Activation Energy, Q (kJ/mol)	Oxide Scale Type	Kinetic Law
Ti ₆₈ Nb ₂₅ Ta ₅ Mo ₂	500	2.54×10^{-5}	171	Mixed Ti/Nb/Ta oxides	Parabolic
Ti ₆₈ Nb ₂₅ Ta ₅ Mo ₂	750	9.27×10^{-3}	171	Mixed Ti/Nb/Ta oxides	Parabolic
Ti ₆₈ Nb ₂₅ Ta ₅ Mo ₂	1000	9.52×10^{-1}	171	Mixed Ti/Nb/Ta oxides	Parabolic
AlTiVCr CCA	700	$\sim 1.0 \times 10^{-2}$	N/A	Ti-rich + V-rich oxides	Parabolic
AlTiVCr CCA	900	$\sim 4.5 \times 10^{-1}$	N/A	Ti-rich + V-rich oxides	Parabolic
Al _{0.9} FeCrCoNi CCA	700	$\sim 1.0 \times 10^{-4}$	N/A	Al ₂ O ₃ (spalling)	Parabolic
Al _{0.9} FeCrCoNi CCA	900	$\sim 2.5 \times 10^{-4}$	N/A	Al ₂ O ₃ (spalling)	Parabolic
69.5Fe-14Ni-9Al-7.5Cr	800	3.0×10^{-10}	N/A	Al ₂ O ₃ /Cr ₂ O ₃	Logarithmic
69.5Fe-14Ni-9Al-7.5Cr	900	4.0×10^{-10}	N/A	Al ₂ O ₃ /Cr ₂ O ₃	Logarithmic
69.5Fe-14Ni-9Al-7.5Cr	1000	6.0×10^{-10}	N/A	Al ₂ O ₃ /Cr ₂ O ₃	Logarithmic

Data compiled from references.

Analysis of Table 1: The comparative analysis reveals distinct oxidation behavior across alloy systems, with substantial variation in parabolic rate constants reflecting differences in protective scale formation. The Ti₆₈Nb₂₅Ta₅Mo₂ alloy exhibits strong temperature dependence, with k_p increasing from $2.54 \times 10^{-5} \text{ mg}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$ at 500°C to $9.52 \times 10^{-1} \text{ mg}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$ at 1000°C a factor of approximately 10^4 . The calculated activation energy of 171 kJ/mol confirms the temperature sensitivity of the oxidation mechanism and falls within the typical range for diffusion-controlled oxidation in refractory alloy systems. The AlTiVCr compositionally complex alloy demonstrates substantially higher mass gains at both temperatures compared to the Al_{0.9}FeCrCoNi system, reflecting the formation of less protective Ti-rich and V-rich oxides. In contrast, the Al_{0.9}FeCrCoNi CCA, despite forming Al₂O₃ scales,

exhibits notable spallation propensity a critical failure mechanism limiting long-term protection. This highlights that composition alone does not guarantee protection; scale adhesion is equally critical. The 69.5Fe-14Ni-9Al-7.5Cr alloy exhibits logarithmic kinetics, indicating extremely slow oxidation after initial transient exposure. The exceptionally low parabolic rate constants ($3\text{--}6 \times 10^{-10} \text{ gr}^2 \cdot \text{cm}^{-4} \cdot \text{hr}^{-1}$) reflect the formation of a highly protective mixed Al₂O₃/Cr₂O₃ scale, with R^2 values of 0.999 for logarithmic fits demonstrating excellent correlation with the model.

Table 2. Protective Oxide Scale Characteristics and Formation Requirements

Oxide Scale	Composition	Pilling-Bedworth Ratio	Critical Alloy Content	Maximum Service Temp (°C)	Growth Mechanism	Key Advantages
α -Al ₂ O ₃	Al ₂ O ₃	1.28	>5 wt.% Al	>1000	O ²⁻ inward diffusion	Extremely slow growth, thermodynamic stability
Cr ₂ O ₃	Cr ₂ O ₃	2.07	>20 wt.% Cr	~900	Cr ³⁺ outward diffusion	Good growth rates, established technology
SiO ₂	SiO ₂	2.27	>2 wt.% Si	>1000 (variable)	O ²⁻ inward diffusion	Excellent stability, slow growth
TiO ₂	TiO ₂	1.76	10-20 wt.% Ti (non-protective)	Limited	Ti ⁴⁺ outward diffusion	Fast-growing, non-protective
NiO	NiO	1.65	N/A	Limited	Ni ²⁺ outward diffusion	Fast-growing, non-protective
Spinel	(Fe,Cr) ₃ O ₄	Variable	Intermediate Cr	Moderate	Mixed cation diffusion	Moderate growth rates

Data compiled from references.

Analysis of Table 2: The characteristics of protective oxide scales are governed by their Pilling-Bedworth ratio, growth mechanism, and the critical alloy content required for selective oxidation. α -Al₂O₃, with its PBR of 1.28 and inward oxygen diffusion mechanism, provides the most effective long-term protection, enabling service temperatures exceeding 1000°C. However, achieving continuous Al₂O₃ scale formation requires a minimum Al content of approximately 5 wt.%, with higher contents promoting faster establishment of the protective scale. Cr₂O₃ scales provide reliable protection up to approximately 900°C, above which volatile CrO₃ formation limits effectiveness. The critical Cr content of >20 wt.% presents challenges for alloy design, particularly for applications

requiring good formability or weldability. The higher PBR of 2.07 compared to Al₂O₃ generates greater growth stresses but the outward diffusion of Cr³⁺ enables more rapid scale establishment. SiO₂ scales offer excellent thermodynamic stability and slow growth rates, but the high viscosity of silica limits its self-healing capability at intermediate temperatures. The PBR of 2.27 produces significant compressive stresses in the scale, which can be beneficial or detrimental depending on adhesion. The non-protective oxides TiO₂, NiO, and spinels exhibit fast growth rates through cation outward diffusion, with PBR values that generate stress states favorable for scale failure. The oxidation of Ti-based alloys is particularly challenging as the formation of non-protective TiO₂ scales cannot be prevented through alloying alone.

Table 3. Comparison of High-Temperature Coating Technologies

Coating Type	Deposition Method	Composition	Maximum Service Temp (°C)	Scale Formed	Key Advantages	Primary Limitations
MCrAlY	HVOF/Plasma Spray	NiCrAlY, CoNiCrAlY	1100	α -Al ₂ O ₃	Proven technology, excellent adhesion	Reactive element management
Aluminide Diffusion	Pack Cementation	NiAl, FeAl	1150	α -Al ₂ O ₃	Metallurgical bonding, simple application	Limited Al reservoir
High-Entropy Alloy	Thermal Spray/Laser Clad	Multi-principal element	>1200	Al ₂ O ₃ /Cr ₂ O ₃ complex	Exceptional stability, compositional flexibility	Limited long-term data

Silicide	Pack Cementation/Diffusion	MoSi ₂ , NbSi ₂	1200+	SiO ₂	Excellent high-T capability	Brittleness, CTE mismatch
Ceramic TBC	Plasma Spray/EB-PVD	YSZ, Pyrochlores	1300 (YSZ)	N/A (thermal barrier)	150-250 °C thermal drop	Phase instability >1200°C
Self-Healing HEA	Advanced Deposition	HEA with reactive elements	>1200	Al ₂ O ₃ + crack sealing	Autonomous damage repair	Scalability, cost

Data compiled from references.

Analysis of Table 3: The landscape of high-temperature coating technologies has expanded substantially from traditional MCrAlY systems to include high-entropy alloys, self-healing architectures, and novel ceramic-based thermal barriers. MCrAlY coatings remain the industrial standard, forming protective α -Al₂O₃ scales through selective aluminum oxidation. The addition of reactive elements (Y, Hf, Zr) critically influences scale adhesion and growth kinetics, with optimized distributions of Y-oxide inclusions improving thermal cycling performance despite slightly higher growth rates. High-entropy alloy coatings represent a transformative advance, leveraging the unique core effects high configurational entropy, sluggish diffusion, severe lattice distortion, and the cocktail

effect to achieve exceptional thermal stability and oxidation resistance. Al-containing HEAs can form stable α -Al₂O₃ scales, while Cr- or Si-containing variants achieve synergistic protection through complex oxide formation. The CTE compatibility of HEA bond coats with both ceramic top coats and metallic substrates provides significant advantages over conventional systems. Ceramic thermal barrier coatings, primarily 7-8 wt.% YSZ, provide the crucial thermal insulation enabling turbine entry temperatures 150-250°C above substrate limits. However, YSZ undergoes a tetragonal-to-monoclinic phase transformation above ~1200°C, creating spallation risk. Emerging pyrochlore ceramics (La₂Zr₂O₇, Gd₂Zr₂O₇) offer improved phase stability but lower fracture toughness.

Table 4. Industrial Applications and Environmental Challenges

Industry/Application	Operating Temp (°C)	Primary Corrosive Species	Preferred Protection Strategy	Key Challenges	Development Status
Gas Turbine Blades	1100-1500+	O ₂ , H ₂ O, CMAS	TBC + MCrAlY/HEA bond coat	Phase stability, CMAS attack	Commercial/Advanced
Boiler Waterwall Tubes	400-650	SO ₂ , SO ₃ , H ₂ S	HVOF/Plasma Spray coatings	Multi-factor coupled corrosion	Commercial
Boiler Superheater Tubes	650-800	Sulfates, Chlorides, Ash	Weld overlay, Diffusion coatings	Cl-induced active oxidation	Commercial
Nuclear Fuel Cladding	300-1200	Steam, H ₂	Zr-based alloys, coatings	High-T steam oxidation	Commercial/Research
Concentrated Solar Power	600-1000	Molten Salts, O ₂	MCrAlY coatings, HEAs	Salt corrosion, thermal cycling	Research/Emerging
Aerospace Engine Components	1000-1500+	O ₂ , H ₂ O, CMAS	TBC + HEA bond coat	CMAS, long-term stability	Advanced Research
Aluminum Processing	800-1000	Molten Al, O ₂	Fe-B alloys, Coatings	Al-Fe intermetallic formation	Research/Commercial

Data compiled from references.

Analysis of Table 4: Industrial applications span diverse temperature regimes and corrosive environments, each requiring tailored protection

strategies. The gas turbine sector faces the most extreme conditions, with blade temperatures 1100-1500°C and CMAS attack from environmental particulates. Thermal barrier coatings with MCrAlY bond coats have enabled substantial efficiency

gains, but the emergence of high-entropy alloy bond coats promises further improvements in temperature capability and durability. Boiler applications demonstrate the complexity of multi-factor coupled corrosion in engineering practice. The transition to biomass and waste-derived fuels has introduced alkali metal chlorides that drive chlorine-induced "active oxidation," accelerating corrosion rates substantially. Superheater tubes operating at 650-800 °C face sulfidation, chlorination, and molten salt corrosion simultaneously, requiring specialized weld overlay and diffusion coatings. Emerging applications in concentrated solar power and additive manufacturing present new challenges. The combination of high-temperature molten salts with thermal cycling in CSP systems demands coatings with exceptional thermal fatigue resistance. Additively manufactured refractory high-entropy alloys, while offering promising properties, exhibit sensitivity to processing-induced defects that accelerate oxidation.

Discussion

Mechanistic Understanding and Kinetic Foundations:

The framework of oxidation kinetics, established through Wagner's theory of diffusion-controlled growth, provides the quantitative foundation for predicting and managing high-temperature oxidation. The parabolic rate law, where scale thickness increases with the square root of time, reflects the diffusion-limited nature of protective scale growth. The strong temperature dependence of the parabolic rate constant, expressed through the Arrhenius relationship, demonstrates the critical importance of temperature management in high-temperature applications. Activation energies ranging from 170 to >400 kJ/mol for different oxide systems reflect the fundamental processes governing cation and anion diffusion through the scale. The transition from protective to non-protective behavior, manifesting in the shift from parabolic to linear kinetics, represents the critical failure mode for oxidation-resistant alloys. The Pilling-Bedworth ratio provides a predictive tool for assessing oxide protectiveness, though it must be considered alongside other factors including oxide adherence, growth stresses, and mechanical properties. The challenge of maintaining protective scale adhesion under thermal cycling conditions, where differential thermal expansion generates interfacial stresses, remains a key engineering challenge.

Challenges in Multi-Factor Corrosion Environments:

Industrial high-temperature corrosion rarely occurs through simple oxidation alone. The presence of sulfur compounds leads to sulfidation, where the formation of low-melting-point eutectics such as Ni-Ni₃S₂ creates catastrophic degradation pathways.

Chlorine compounds, particularly from biomass and waste fuels, drive active oxidation mechanisms where volatile metal chlorides form and subsequently oxidize to deposit non-protective oxides. Molten salt corrosion, especially vanadate-induced hot corrosion in gas turbines, dissolves protective oxide scales through fluxing mechanisms. The coupling of multiple corrosion mechanisms creates synergistic effects that accelerate degradation beyond the sum of individual contributions. In boiler applications, the combined presence of sulfates, chlorides, and oxidizing atmospheres at high temperatures creates environments where even high-alloy materials struggle to form stable protective scales. This complexity necessitates integrated protection strategies combining alloy design, coating application, and process optimization.

Protective Coatings: From MCrAlY to High-Entropy Alloys:

The evolution of protective coating technologies demonstrates the response of materials science to increasingly demanding service conditions. MCrAlY coatings have served as the reliable standard for decades, forming protective α -Al₂O₃ scales through selective oxidation of their aluminum content. The critical role of reactive elements (Y, Hf, Zr) in promoting scale adhesion and modifying growth mechanisms has been extensively studied, with the distribution and chemical state of Y-oxides in the scale identified as key determinants of long-term performance. High-entropy alloy coatings represent the next frontier in high-temperature protection, leveraging the unique core effects of multi-principal element systems. The high configurational entropy of HEAs stabilizes solid solutions, while sluggish diffusion reduces coarsening and degradation kinetics. The "cocktail effect" enables tailoring of properties through synergistic element interactions. Al-containing HEAs can form stable α -Al₂O₃ scales, while systems containing Cr or Si achieve complex oxide formation that may offer enhanced protection. The potential for self-healing HEA coatings, where selective oxidation of reactive elements seals cracks and extends coating lifetimes, represents an exciting research frontier. However, significant challenges remain in long-term validation under realistic operating conditions, scaling of deposition processes, and optimization of HEA compositions for specific applications.

Emerging Technologies and Future Directions:

Conclusion

This comprehensive review has systematically examined high-temperature oxidation and corrosion of alloys, from fundamental kinetics and thermodynamics to advanced protective coating

technologies. High-temperature oxidation proceeds through diffusion-controlled mechanisms governed by the parabolic rate law, with rate constants exhibiting Arrhenius temperature dependence and activation energies from 170 to >400 kJ/mol reflecting the rate-limiting diffusion processes. The formation of protective oxide scales α -Al₂O₃, Cr₂O₃, SiO₂ depends critically on alloy composition, with critical Al (>5 wt.%) and Cr (>20 wt.%) concentrations required for continuous scale formation. Non-protective oxides, with Pilling-Bedworth ratios deviating substantially from unity, lead to rapid linear kinetics and catastrophic degradation. MCrAlY coatings remain the industrial standard for high-temperature protection, forming protective α -Al₂O₃ scales through selective aluminum oxidation, with reactive elements (Y, Hf, Zr) critically influencing scale adhesion and growth kinetics. High-entropy alloy coatings have emerged as a transformative next-generation technology, leveraging unique core effects high configurational entropy, sluggish diffusion, severe lattice distortion, and the cocktail effect to achieve exceptional thermal stability, oxidation resistance, and compositional flexibility. Ceramic thermal barrier coatings provide the essential thermal insulation enabling turbine entry temperatures 150-250°C above substrate limits.

Effective high-temperature corrosion management in complex industrial environments requires integrated approaches combining mechanistic understanding, advanced coating technologies, and real-time monitoring. The transition to sustainable energy sources and fuels will continue to challenge protective systems, driving the development of more robust, multifunctional coating architectures. Future progress demands interdisciplinary collaboration across materials science, electrochemistry, manufacturing engineering, and data science.

Disclosure Statement

No potential conflict of interest reported by the authors.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Authors' Contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

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