

Chlorine Corrosion Behavior of $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ high-entropy alloys in an Oxidizing Chlorine-Containing Atmosphere at 700°C

Lingyun Bai

bailingyun12@163.com

Jiangxi Science and Technology Normal University

Longfa Jiang

Technology Center of Nanchang Customs-District

Junhuai Xiang

Jiangxi Science and Technology Normal University

Botao Xiao

Jiangxi Science and Technology Normal University

Xunhu Xu

Jiangxi Science and Technology Normal University

Article

Keywords: $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$, high-entropy alloys, high-temperature chlorine corrosion, thermodynamic calculation, saturation degree

Posted Date: August 18th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10537483/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Chlorine Corrosion Behavior of $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ high-entropy alloys in an Oxidizing Chlorine-Containing Atmosphere at 700°C

Lingyun Bai ^{a,b,*}, Longfa Jiang ^c, Junhuai Xiang ^{a,b}, Botao Xiao ^{a,b}, Xunhu Xu ^{a,b}

^a School of Materials and Energy, Jiangxi Science and Technology Normal University, Nanchang, 330013, China

^b Jiangxi Province Key Laboratory of Surface Engineering, Nanchang, 330013, China

^c Technology Center of Nanchang Customs-District, Nanchang, 330013, China

Corresponding author: E-mail address: bailingyun12@163.com (Lingyun Bai)

Abstract: The cyclic corrosion tests of $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ ($x = 4, 9, 12, 14$ at. %) high-entropy alloys were performed at 700°C for 80 h in a $\text{N}_2 - 9\%\text{CO}_2 - 7\%\text{O}_2 - 0.1\% \text{HCl}$ (mol/mol) atmosphere. Thermodynamic equilibrium calculations were consistent with the XRD phase analysis results of the alloys, validating the reliability of the computational approach. With the exception of Al4 ($\text{Al}_4\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{36}\text{Ni}_{20}$) alloy, all other high-entropy alloys exhibited superior corrosion resistance to Inconel 625. Al9 alloy developed the most continuous and dense corrosion products, achieving a weight gain of merely 5.15% relative to that of Inconel 625. XPS revealed Co/Cr surface reconstruction on Al4 alloy and ultrathin Al_2O_3 layers on Al9 and Al14 alloys. The exceptional corrosion resistance of Al9 alloy is attributed to the synergistic effect of a moderate grain boundary area, an appropriate second-phase content, rapid formation of a dense outer Al_2O_3 layer, and slow growth of an inner Al_2O_3 layer.

Keywords: $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$; high-entropy alloys; high-temperature chlorine corrosion; thermodynamic calculation; saturation degree

1. Introduction

High-temperature chlorine corrosion of metals represents a critical bottleneck restricting the long-term service life of key equipment in energy, chemical, and environmental protection industries, and has attracted extensive attention from researchers worldwide. Unlike conventional high-temperature oxidation, the metal chlorides formed during chlorine corrosion exhibit characteristics of low melting points and high volatility, resulting in loose and porous corrosion product layers lacking protectiveness. Consequently, corrosion rates in chlorine-containing environments are typically one to two orders of magnitude higher than those in purely oxidizing atmospheres. In typical industrial scenarios such as waste-to-energy incineration, biomass combustion, hazardous waste treatment, and coal chemical gasification, beyond enduring temperatures of 600 – 900°C, heat-exposed materials suffer sustained attack from corrosive gases (HCl and Cl_2), which induces severe failure modes: uniform thinning, intergranular corrosion, and stress corrosion cracking. This has become a key technical challenge constraining the green and low-carbon transformation of related industries. Hence, novel materials exhibiting excellent resistance to chlorine corrosion are urgently needed to ensure reliable service and minimize life-cycle costs of critical components in aggressive environments.

High-temperature chlorine corrosion of metals proceeds via the “active oxidation” mechanism and volatilization of metal chlorides, combined with the inward diffusion of Cl_2 through the porous corrosion layer and its enrichment at defects, result in pitting corrosion, under-deposit corrosion, and oxide scale spallation, ultimately leading to rapid material failure. High-temperature chlorine corrosion of alloys belongs to the generalized oxidation, so materials exhibiting excellent performance in the field of high-temperature oxidation may also possess favorable resistance to high-temperature chlorine corrosion. High-entropy alloys (HEAs) are composed of five or more principal elements in equimolar or near-equimolar ratios, characterized by high-entropy, lattice distortion, sluggish diffusion and “cocktail” effects. Owing to the synergistic interaction of passivating elements (such as Cr [2]、Al [3]、Ni [4]、Ti [5, 6]、Mo [7], etc.), dense protective oxide films form on the surface, effectively preventing further corrosion of the matrix. Consequently, HEAs generally exhibit

outstanding passivation behavior, demonstrating tremendous application potential in the field of extreme-environment materials [7-15].

Currently, research on the corrosion of HEAs in Cl-containing environments has primarily focused on electrochemical corrosion and hot corrosion, whereas investigations into high-temperature corrosion behavior in chlorine-containing atmospheres remain relatively scarce [9, 16-18]. As reported by Chu et al. [17], gradient-structured HEA coatings fabricated via high-velocity oxygen-fuel (HVOF) spraying exhibit superior densification and high-temperature chlorine corrosion resistance, with considerable potential for boiler applications. Lv J et al. [9] fabricated a CrMnFeCoNi high-entropy alloy via hot isostatic pressing (HIP) and systematically investigated its high-temperature corrosion behavior in NaCl-KCl molten salts. Thermodynamic calculations revealed that Mn and Cr are highly reactive toward O₂ and Cl₂, leading to the preferential formation of Cr₂O₃- and Mn₂O₃-rich oxide layers initially. Prolonged exposure caused progressive oxide spallation and molten salt penetration, resulting in severe substrate degradation, internal oxidation, and eventual formation of coarse spinel oxides.

Jianming Wang et al. [18] investigated the corrosion performance of as-cast AlCrFeNi₃Mo_x (x = 0, 0.1, 0.2, 0.3, 0.4) HEAs in chloride-containing environments. The results indicated that the Mo-containing HEAs exhibited superior corrosion resistance compared to both the Mo-free high-entropy alloy and 316 L stainless steel. The exceptional anti-corrosion performance of the AlCrFeNi₃Mo_{0.3} HEA was attributed to the formation of a dense Cr₂O₃ and MoO₃ protective film. Furthermore, all HEAs demonstrated micro-galvanic corrosion behavior, with the B2 phase undergoing preferential dissolution. Yang et al. [8] examined the corrosion behavior of NbMoTaWCr coatings in a 75 wt.% Na₂SO₄ - 25 wt.% NaCl molten salt environment at 850°C, wherein the corrosion process involved a complex synergistic interplay of selective oxidation, sulfidation, and chlorination. The results revealed that Cr-enriched Cr₂Nb-type Laves phases precipitated at grain boundaries, which effectively inhibited the formation of porous, non-protective corrosion products and obstructed the penetration of corrosive media along the grain boundaries, thereby enhancing the high-temperature molten salt corrosion resistance of the coatings.

The high-temperature gaseous chlorine corrosion of HEAs has received limited attention to date, restricting the rational design of materials for extreme environments. Accordingly, the present work was conducted to investigate the corrosion mechanisms of HEAs in a synthetic flue gas representative of municipal solid waste incinerators (N₂ - 9% CO₂ - 7% O₂ - 0.1% HCl, mol/mol), with particular emphasis on establishing the influence of Al element on microstructural development and corrosion performance.

2. Materials and Experimental Methods

2.1 Material Preparation

High-purity Al (99.99%), Co (99.99%), Cr (99.99%), Fe (99.99%), and Ni (99.99%) granules were employed as raw materials. Following ultrasonic cleaning in a mixed solution of glacial acetic acid and ethanol at an equal volume ratio and subsequent drying, the raw materials were weighed and blended according to the designed compositions. The Al_xCo₂₀Cr₂₀Fe_(40-x)Ni₂₀ HEAs were subsequently synthesized via non-consumable vacuum arc melting, wherein the values of “x” were determined through calculations using JMat Pro software. The melting process was conducted in a high-purity argon atmosphere at a pressure of 0.5E5 Pa, with the raw materials subjected to six remelting cycles to obtain as-cast HEAs. The obtained alloys were subsequently annealed at 900°C for 24 h to achieve stress relief and compositional homogenization. The annealed alloys were sectioned by wire electrical discharge machining into rectangular specimens with dimensions of 5 × 10 × 2.5 mm³. The specimens were ultrasonically cleaned, dried, and subsequently ground and polished. Their dimensions and mass were then measured using a vernier caliper and an electronic balance with a precision

of 0.01 mg, respectively.

2.2 Corrosion Performance Testing

The high-temperature corrosion tests of the HEAs were conducted in a high-temperature gaseous corrosion apparatus. A cyclic corrosion methodology was adopted to evaluate the temporal evolution of alloy mass, from which the corrosion kinetics curves were derived. Each alloy specimen was placed in an individual quartz crucible to facilitate the collection of potentially spalled corrosion products. The quartz crucibles were subsequently positioned within ceramic boats to enable convenient sampling and placement of the specimens in the horizontal tube furnace. The ceramic boat containing the specimens was introduced into the horizontal tube furnace, and the corrosive gas line was activated. The tube furnace was heated from ambient temperature to 700°C at a rate of 10°C/min, with N₂ flowing at 40 ml/min during the heating stage. Upon reaching 700°C, a simulated corrosive atmosphere representative of waste incinerator conditions, namely N₂ - 9% CO₂ - 7% O₂ - 0.1% HCl (mol/mol), was introduced. Each cyclic corrosion cycle lasted 10 h, after which the corrosive atmosphere was switched to high-purity N₂ at a flow rate of 20 ml/min. The specimens were furnace-cooled to ambient temperature and subsequently removed for weighing. The total corrosion duration was 80 h. The corroded specimens were stored in sealed bags for subsequent analysis of corrosion product composition and morphology. To enable a comparative assessment with currently employed service alloys, concurrent corrosion performance testing of Inconel 625 alloy was also conducted.

2.3 Analytical Methods

The microstructures of the HEAs were examined using optical microscopy. The actual compositions and elemental distributions were determined by energy-dispersive X-ray spectroscopy (EDS, Oxford INCA). The phase compositions of the high-entropy alloy surfaces before and after corrosion were analyzed by X-ray diffraction (XRD, Shimadzu XRD-6100) using continuous scanning mode, with a scanning angle (2 θ) ranging from 20° to 80°, a scanning speed of 4°/min, and tube voltage and current of 40 kV and 30 mA, respectively. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) was employed to characterize the elemental composition, chemical states, and depth distribution of the corrosion product surfaces using a monochromatic Al K α X-ray source (1486.6 eV) with a 400 μ m beam spot, operating at 12 kV and 6 mA under an analysis chamber vacuum better than 5.0E-7 mbar, with survey spectra acquired at a pass energy of 150 eV and a step size of 1 eV, and high-resolution narrow spectra recorded at a pass energy of 50 eV and a step size of 0.1 eV, respectively. The surface and cross-sectional morphologies, compositions, and elemental distributions of the HEAs before and after corrosion were characterized using a field-emission scanning electron microscope equipped with EDS (SEM/EDS, Sigma). By integrating theoretical calculations with experimental results, the high-temperature chlorine corrosion mechanism of the Al_xCo₂₀Cr₂₀Fe_(40-x)Ni₂₀ HEAs was elucidated.

3. Results and Discussion

3.1 Relationship Between Al Content and Alloy Phase Composition

Figure 1 presents the phase composition of Al_xCo₂₀Cr₂₀Fe_(40-x)Ni₂₀ HEAs as a function of Al content, determined by thermodynamic calculations using JMat Pro software (Fig. 1a) and experimental XRD (Fig. 1b) after annealing at 900 °C. As shown in Fig. 1a, at Al contents below 6.77 at. %, the alloy comprised a single austenitic (γ) phase, consistent with the XRD result for the Al₄Co₂₀Cr₂₀Fe₃₆Ni₂₀ (hereafter Al4) alloy in Fig. 1b. In the range of 6.77–16.68 at. % Al, the alloy underwent a transition from single-phase to dual-phase structure, comprising austenite and B2 precipitates (Fe, Ni) Al. With increasing Al content, the austenite fraction decreased linearly while the B2 phase increased proportionally. This prediction agreed with the XRD results for Al9, Al12, and Al14 alloys shown in Fig. 1b. At Al contents exceeding 16.68 at. %, the σ phase emerged; with further Al addition, both σ and B2 phases increased linearly, accompanied by a more

pronounced decline in austenite.

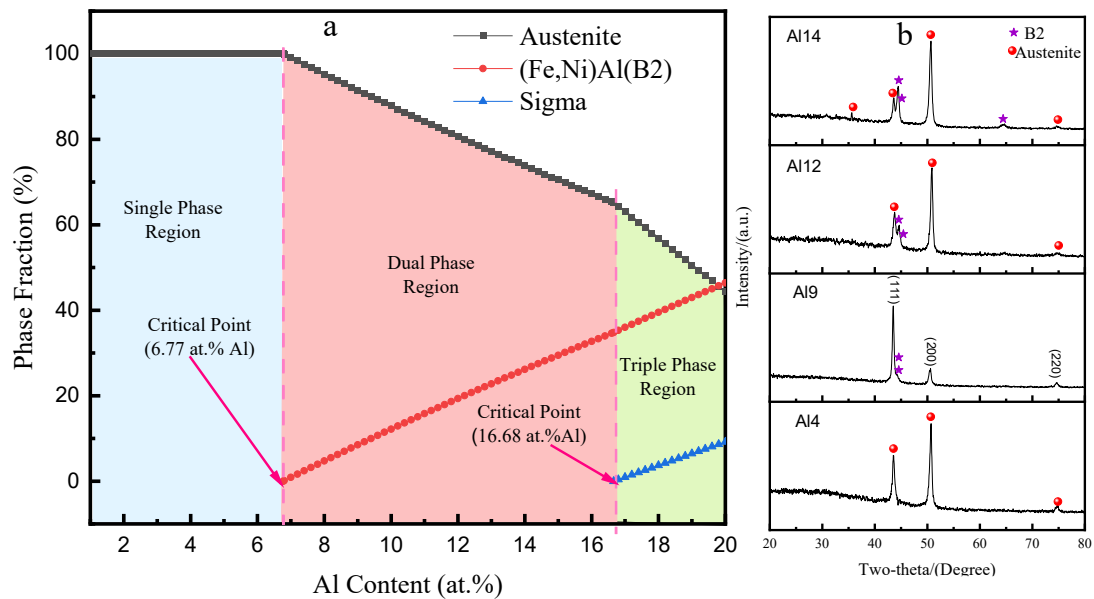


Fig. 1. The theoretical calculation results (Fig. 1a) and experimental XRD test results (Fig. 1b) of the phase composition of $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs as a function of Al content after annealing at 900 °C, wherein the theoretical calculations were performed using JMat Pro software.

Generally, austenitic alloys exhibit favorable corrosion resistance, and moderate secondary phase precipitation can enhance mechanical properties. Furthermore, grain boundary precipitates can impede corrosive element diffusion, thereby improving corrosion resistance. However, σ phase formation is detrimental to overall alloy performance^[19, 20]. Therefore, $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs with Al contents of 4, 9, 12, and 14 at. % were selected to investigate the influence of Al content on corrosion behavior. Table 1 presents the actual alloy compositions, which closely matched the designed values within permissible error margins.

Table 1. The actual composition of the $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs (at. %)

Sample Element concentration	Al	Co	Cr	Fe	Ni
$\text{Al}_4\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{36}\text{Ni}_{20}$ (Al4)	4.39	20.24	20.28	35.74	19.35
$\text{Al}_9\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{31}\text{Ni}_{20}$ (Al9)	9.08	19.70	20.01	31.40	19.81
$\text{Al}_{12}\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{28}\text{Ni}_{20}$ (Al12)	12.16	19.09	19.77	28.14	20.84
$\text{Al}_{14}\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{26}\text{Ni}_{20}$ (Al14)	14.20	19.77	19.53	26.31	20.19

Table 2 lists the thermodynamic parameters of the investigated HEAs. According to HEA phase formation rules, solid solution formation is favored when the mixing entropy (ΔS_{mix}) falls within 11–19.5 J/(mol·K). The mixing enthalpy (ΔH_{mix}) reflects chemical affinity among constituent elements and drives intermetallic compound formation; solid solutions are preferred when $-19 \text{ kJ/mol} \leq \Delta H_{\text{mix}} \leq 5 \text{ kJ/mol}$. The atomic size difference (δ) indicates lattice distortion degree, with values below 6.6% generally required for solid solution stability. The entropy-to-enthalpy ratio (Ω) evaluates the competitive relationship between ΔS_{mix} and ΔH_{mix} , thereby determining solid solution stability at elevated temperatures; stable solid solution formation typically requires $\Omega \geq 1.1$, with larger values indicating greater entropy dominance in suppressing intermetallic compound formation. The calculated parameters confirmed that all investigated compositions fell within the

range for stable solid-solution HEA formation. The valence electron concentration (VEC) predicts solid solution crystal structure: $VEC < 6.87$ favors BCC, $6.87 \leq VEC < 8.0$ favors BCC + FCC mixtures, and $VEC \geq 8.0$ favors FCC. Correspondingly, the Al4 alloy tended to form a single FCC solid solution, whereas the remaining alloys exhibited mixed FCC + BCC structures. These predictions were consistent with both JMat Pro calculations and XRD results.

Table 2. The calculation results of the thermodynamic parameters of $Al_xCo_{20}Cr_{20}Fe_{(40-x)}Ni_{20}$ HEAs

Sample	ΔS_{mix} (J/mol·K)	ΔH_{mix} (kJ/mol)	δ (%)	Ω	VEC	Structure
Al4	12.16	-5.18	2.86	4.28	8.00	FCC
Al9	12.85	-7.65	4.01	2.99	7.75	BCC+FCC
Al12	13.11	-9.03	4.5	2.55	7.60	BCC+FCC
Al14	13.23	-9.91	4.78	2.32	7.50	BCC+FCC

3.2 Microstructure and Elemental Distribution

Figure 2 presents the metallographic microstructures and elemental distribution of the $Al_xCo_{20}Cr_{20}Fe_{(40-x)}Ni_{20}$ HEAs. The Al4 specimen exhibited fine cellular dendritic structures with a characteristic honeycomb pattern, typical of HEA solidification microstructures.

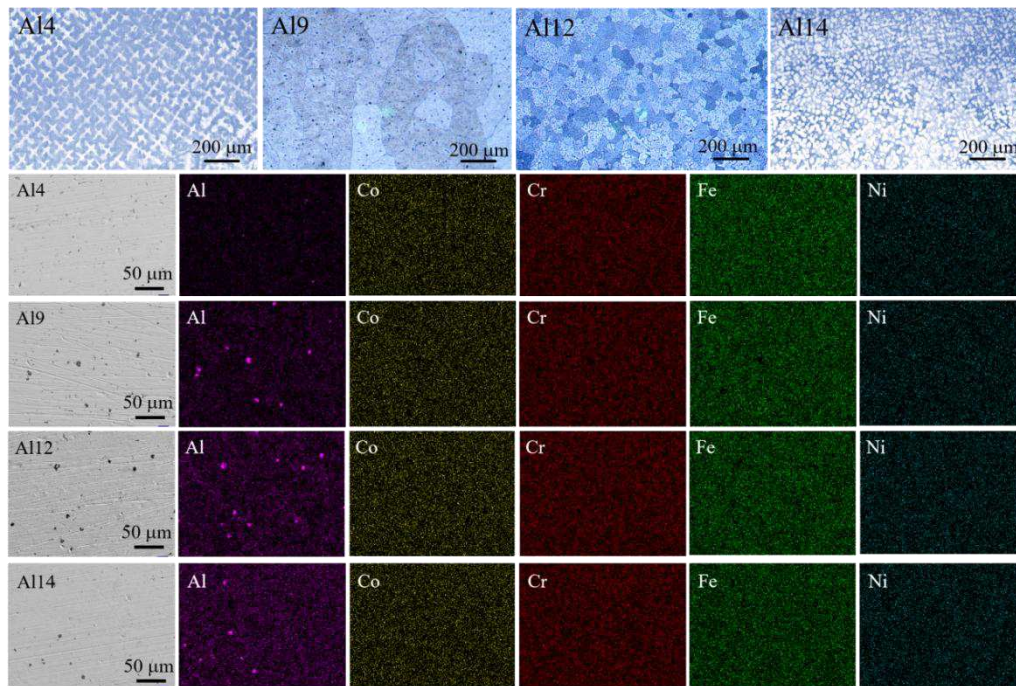


Fig.2. The metallographic microstructures and elemental distribution of the $Al_xCo_{20}Cr_{20}Fe_{(40-x)}Ni_{20}$ HEAs.

The cell dimensions ranged from approximately 20–50 μm , with no secondary phases or grain boundary precipitates, indicating a highly homogeneous microstructure. The Al9 specimen comprised coarse equiaxed grains (~200–500 μm) with dispersed dot-like precipitates both intragranularly and at grain boundaries, constituting an FCC + B2 dual-phase alloy. With increasing Al content, precipitate phases proliferated concurrently with significant grain refinement. The Al12 specimen displayed a non-uniform microstructure, wherein dark B2 phase aggregates (~50–150 μm) were embedded in a lighter matrix. The Al14 specimen exhibited an extremely fine equiaxed grain structure, forming an interwoven two-phase network with grain/phase dimensions of approximately 5–20 μm .

EDS elemental mapping revealed uniform distribution of all elements in the Al4 specimen. At this low Al content (4 at. %), Al was completely dissolved in the FCC matrix. Upon exceeding 9 at. % Al, pronounced Al segregation occurred, accompanied by the emergence of distinct AlN precipitates. Cr remained relatively uniformly distributed, whereas Co was markedly depleted in Al-enriched regions; conversely, Fe and Ni exhibited slight segregation toward these regions.

3.3 Corrosion Kinetics

Figure 3 illustrates the corrosion kinetics of $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs and Inconel 625 exposed to a simulated waste incinerator environment ($\text{N}_2 - 9\% \text{CO}_2 - 7\% \text{O}_2 - 0.1\% \text{HCl}$, mol/mol) at 700 °C for 80 h.

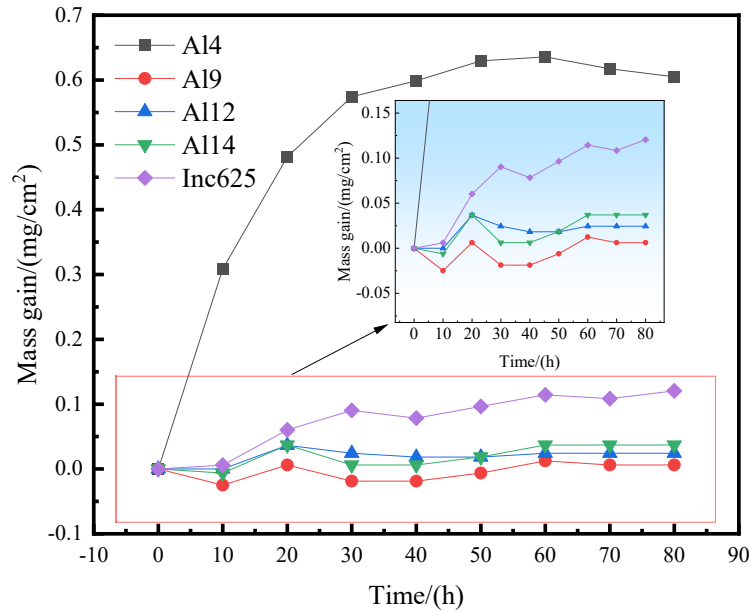


Fig. 3. The corrosion kinetics results for the $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs and Inconel-625 alloy exposed to a simulated waste incinerator environment ($\text{N}_2 - 9\%\text{CO}_2 - 7\%\text{O}_2 - 0.1\%\text{HCl}$ mol/mol) at 700 °C for 80 h.

After corrosion, the mass gains of Al4, Al9, Al12, Al14, and Inconel 625 were 0.60494, 0.00621, 0.02439, 0.02454, and 0.12048 $\text{mg}\cdot\text{cm}^{-2}$, respectively. The Al4 specimen consistently exhibited mass increase throughout the test, with the highest mass gain. During the initial transient oxidation stage, the corrosion mass gain increased rapidly, and the kinetics curve slope was markedly steeper than those of the other specimens; after 30 h, the mass gain trend became relatively gentle. In contrast, the remaining specimens displayed fluctuating kinetics curves, characteristic of typical high-temperature chlorine corrosion, i.e., the coexistence and competition between oxidative mass gain and chlorination-induced mass loss [16]. Simultaneously, the irregular B2/FCC phase interfaces exhibited stress concentration and crevice effects, serving as preferential nucleation sites for pitting and crevice corrosion. During corrosion, the repeated rupture and repair of passive films in these localized regions also contributed to the pronounced fluctuations observed in the kinetics curves [21, 22]. When the Al content exceeded 9 at. %, the corrosion mass gains of all $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs were lower than that of Inconel 625. After 60 h, the kinetics curves of Al9, Al12, and Al14 nearly plateaued, with negligible mass change, whereas Inconel 625 continued to exhibit a steady mass gain trend. Given that high-temperature chlorine corrosion involves the coexistence of mass gain and mass loss, corrosion resistance assessment cannot rely solely on kinetics curves; further analysis of corrosion product morphology and composition was therefore required.

3.4 Surface Composition and Morphology of Corroded Specimens

Figure 4 presents the X-ray diffraction patterns of $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs and Inconel 625 after 80 h of corrosion at 700 °C in a simulated waste incinerator environment ($\text{N}_2 - 9\% \text{CO}_2 - 7\% \text{O}_2 - 0.1\% \text{HCl}$, mol/mol). Distinct diffraction peaks corresponding to the matrix γ phase were detected in all specimens, indicating that the corrosion product layers

formed were relatively thin. The surface corrosion products of the Al4 alloy consisted primarily of Fe and Cr oxides, namely Fe_2O_3 , FeCr_2O_4 , and Cr_2O_3 , with Fe_2O_3 and FeCr_2O_4 being predominant. When the Al content increased to 9 at. % and above, diffraction peaks attributable to the B2 precipitate phase and oxides of Al, Co, Cr, Fe, and Ni emerged at $2\theta \approx 44.6^\circ$ in the XRD patterns; the intensity of these peaks increased markedly with increasing Al content. Correspondingly, the diffraction peaks of Fe_2O_3 and FeCr_2O_4 in the Al4 specimen essentially disappeared. The corrosion products of the Al9, Al12, and Al14 specimens contained a greater variety of oxides, encompassing oxides or mixed oxides of all constituent elements, including Co_2NiO_4 , FeAl_2O_4 , $\text{Fe}(\text{Al}, \text{Cr})_2\text{O}_4$, and Al_2O_3 . Among these, the Cr and Al oxide contents were higher than those of other oxides, and the proportion of Al oxides increased significantly with increasing Al content.

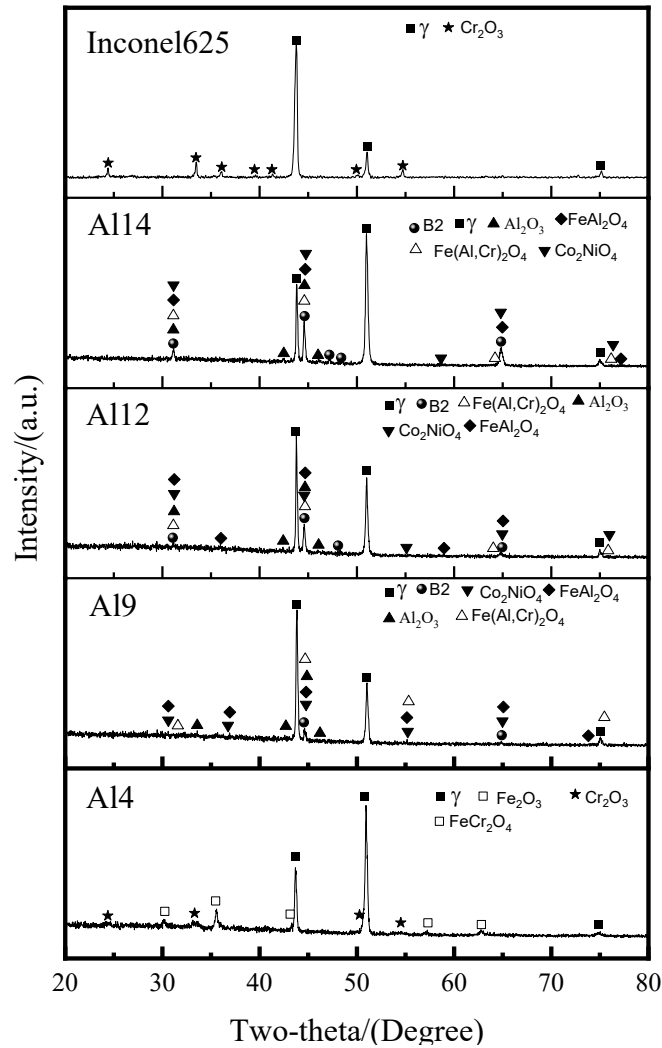


Fig. 4. The X-ray diffraction patterns of the $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs and Inconel 625 alloy after corrosion at 700 °C for 80 h in a simulated waste incinerator environment (N_2 - 9% CO_2 - 7% O_2 - 0.1% HCl mol/mol).

Figure 5 illustrates the surface morphologies and compositional distributions of $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs and Inconel 625 after 80 h of corrosion at 700 °C in the simulated waste incinerator environment. All examined alloys exhibited relatively flat corrosion product surfaces. The Al4 alloy surface comprised primarily flat regions with scattered granular areas. The flat regions consisted mainly of Cr, Fe, and O, with relatively low contents of Al, Co, and Ni; combined with XRD analysis, these regions were identified as predominantly FeCr_2O_4 . Localized high-magnification EDS analysis revealed that the dark flat areas at the bottom exhibited relatively high Al oxide content, with Cl below 0.35 at.%. Numerous polygonal spinel particles, porous Cr_2O_3 particles, and large Fe_2O_3 particles were distributed over these regions.

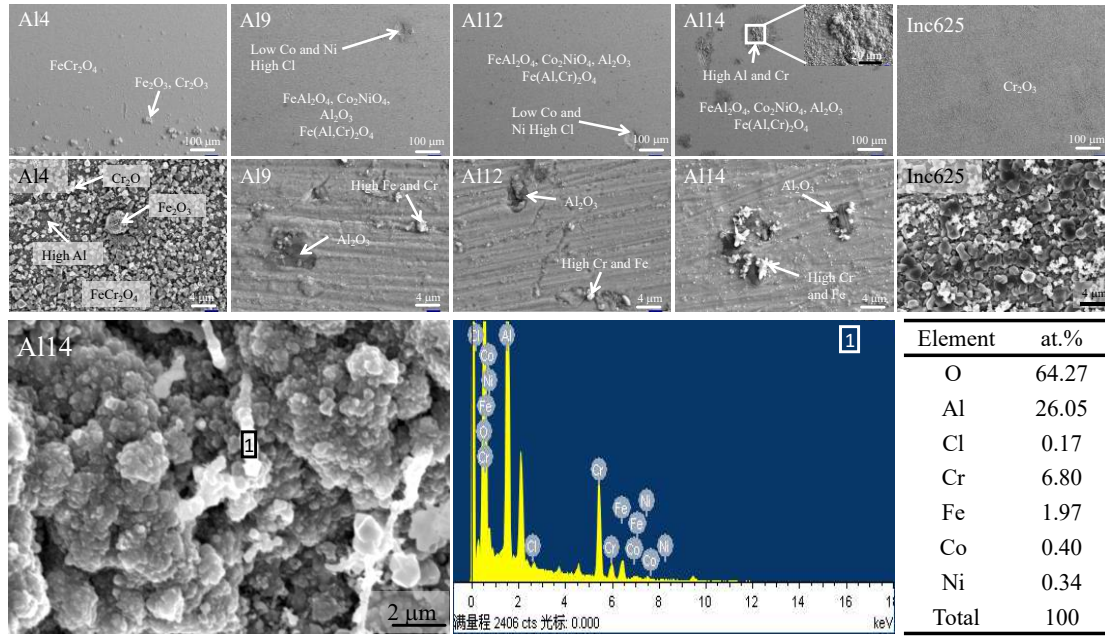


Fig. 5. The surface morphologies and compositional distributions of the $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs and Inconel 625 alloy after corrosion at 700 °C for 80 h in the simulated waste incinerator environment (N_2 - 9% CO_2 - 7% O_2 - 0.1% HCl mol/mol).

Compared with the Al4 specimen, the Al9, Al12, and Al14 alloy surfaces were flatter and denser after corrosion; however, with increasing Al content, an increasing number of pits gradually appeared on the surfaces, originating from the morphological characteristics of the original specimens prior to corrosion. The Co and Ni contents in these pits were lower than those in the flat regions, whereas the Cl content was relatively higher; nevertheless, no severely corroded porous products were observed within the pits. Corresponding to the AlN regions in the initial alloys, dense Al_2O_3 formed on the surfaces after corrosion, while the small granular corrosion products growing at phase boundaries and other grain boundary positions surrounding these regions consisted primarily of Fe and Cr oxides. The Al14 specimen surface exhibited an increased number of dark regions enriched in Al and Cr; compared with other regions, these positions displayed porous, large-sized corrosion product morphologies dominated by Al and Cr oxides. High-magnification examination revealed that whisker-like Al_2O_3 grew within the gaps of the larger nodular Al–Cr mixed oxides, and this product morphology rendered the corrosion products in these regions overall porous. Similarly, corresponding to the AlN-containing regions in the original alloy, flaky Al_2O_3 formed after corrosion; however, due to excessive Al enrichment, the Al_2O_3 formed in this specimen was relatively thick and exhibited cracking. The flaky and acicular Fe–Cr spinel phases at the surrounding phase boundaries grew rapidly, forming large, porous corrosion products that compromised the integrity of the surface product layer, in contrast to the flat regions on the alloy surface. Compared with the HEAs, the Inconel 625 alloy surface formed a flat, single-phase Cr_2O_3 product layer, which was less dense than those of the HEAs and exhibited partially porous Cr_2O_3 products.

Figure 6 presents the surface elemental chemical state distributions of $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs and Inconel 625 after 80 h of corrosion at 700 °C in the simulated waste incinerator environment, following five months of storage in sealed bags.

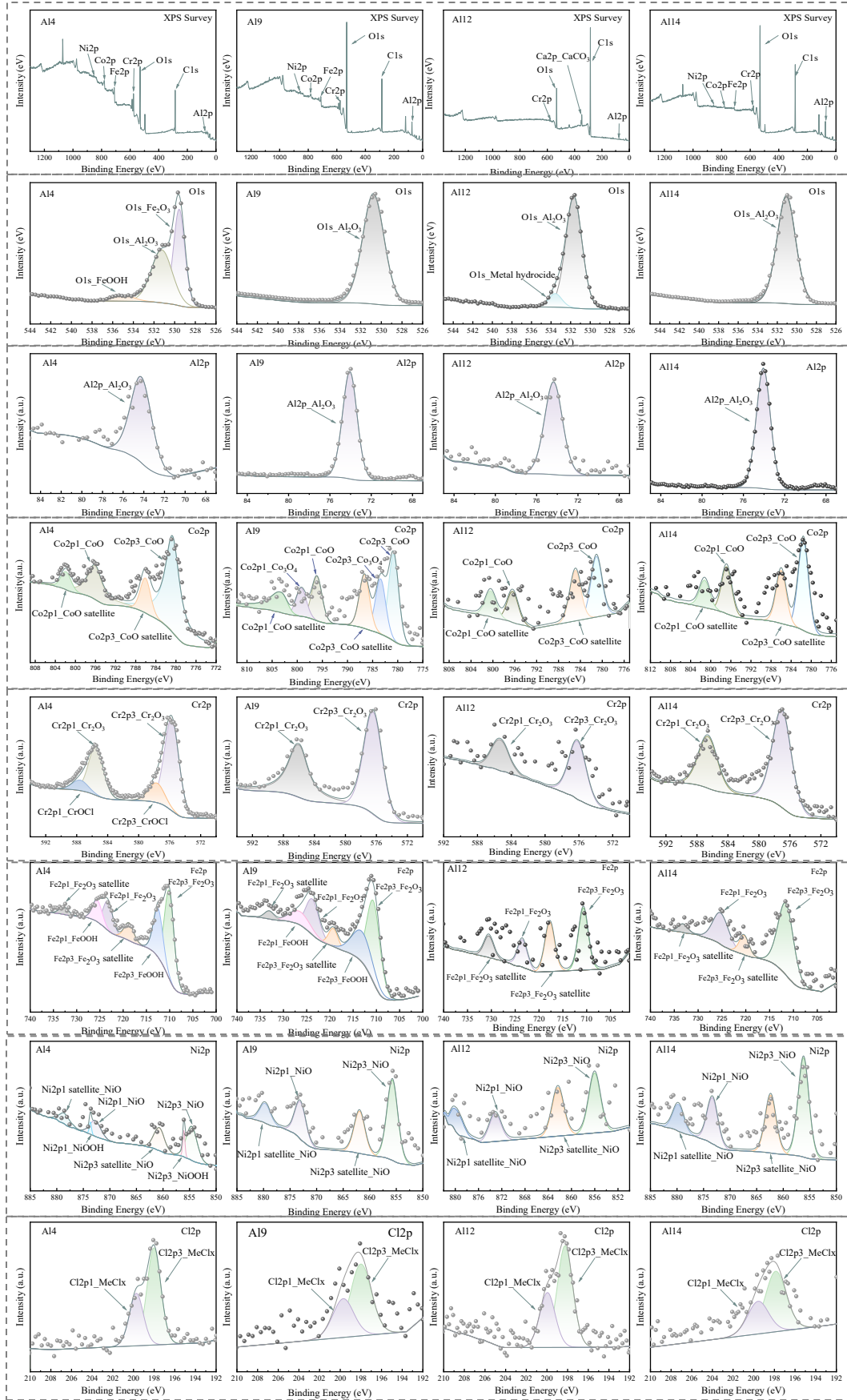


Fig. 6. The surface elemental chemical state distributions of the $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs and Inconel 625 alloy after corrosion at 700 °C for 80 h in the simulated waste incinerator environment, following five months of storage in sealed bags.

Except for the Al12 alloy, photoelectron peaks corresponding to all constituent elements were detected in the XPS survey spectra of the remaining alloys; it was speculated that the Al12 specimen failed to yield complete matrix element signals due to surface coverage or deviation of the tested region during XPS measurement. Al existed exclusively in the Al_2O_3 chemical state in the corrosion products of all alloys. Co existed in both CoO and Co_3O_4 states in the Al9 alloy, whereas it existed solely in the CoO state in the Al4, Al12, and Al14 alloys. Cr existed in both Cr_2O_3 and CrOCl states in the corrosion layer of the Al4 alloy, whereas only the Cr_2O_3 state was present in the Al9, Al12, and Al14 alloys. For the Al4 and Al9 alloys with lower Al contents, Fe existed in both Fe_2O_3 and FeOOH states in the surface corrosion layer; in the Al12 and Al14 alloys, Fe existed solely in the Fe_2O_3 state. With the exception of the Al4 alloy, wherein Ni existed in both NiO and NiOOH states in the surface corrosion layer, Ni existed exclusively in the NiO state in the Al9, Al12, and Al14 specimens. Cl existed in the metal chloride state in all specimens. During storage, the specimens tended to form adsorbed water or corresponding oxyhydroxides with Fe, Ni, and other elements; this phenomenon was particularly pronounced in the Al4 specimen. Regarding the various spinel components detected by XRD, they were not individually labeled in the XPS spectra due to overlap of their photoelectron peak positions with those of the corresponding simple oxides.

Figure 7 presents a comparison of elemental concentrations determined by EDS and XPS fitting on alloy surfaces after corrosion.

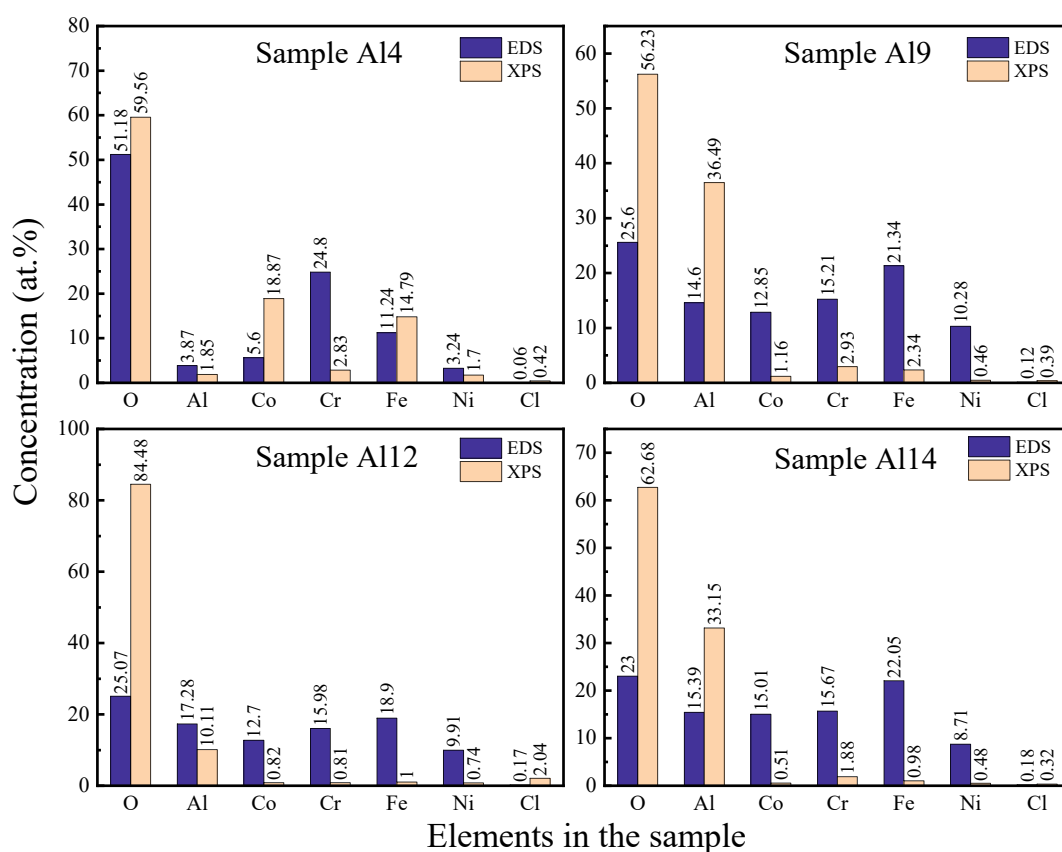


Fig. 7. The comparison of the elemental concentrations obtained from energy-dispersive X-ray spectroscopy (EDS) testing and X-ray photoelectron spectroscopy (XPS) fitting calculations of the $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs surfaces after corrosion at 700 °C for 80 h in the simulated waste incinerator environment (N_2 -9% CO_2 -7% O_2 -0.1% HCl mol/mol).

The O and Cl contents from XPS were relatively high, indicating enrichment of oxides and chlorides at the outermost surface. Notably, the O content of the Al12 alloy was abnormally high (84.48 at. %), which was attributed to contamination during XPS measurement due to improper operation. EDS-determined concentrations of Co, Cr, Fe (except Al4), and Ni

were markedly higher than those from XPS. This discrepancy arose from the substantial difference in detection depths between the two techniques: EDS probes the electron beam-excited region, encompassing the surface oxide layer and partial substrate, and represents the near-surface bulk composition with a typical probing depth of 1–3 μm ; XPS probes the photoelectron escape depth, corresponding to only the outermost several atomic layers, and represents the extremely thin surface layer composition with a probing depth of 1–10 nm. Under pronounced selective oxidation, the elemental composition of the outermost corrosion layer may differ significantly from that of the interior. The EDS and XPS results obtained in this study clearly reflected the variation in elemental distribution within the alloy corrosion product layers, a phenomenon difficult to discern through single XPS or EDS analysis alone.

A noteworthy observation for the Al4 alloy was the pronounced discrepancy in Co and Cr concentrations between the two detection methods: in EDS analysis, the Co and Cr contents were 5.6 at. % and 24.8 at. %, respectively, consistent with the XRD results; in XPS analysis, the Co and Cr contents were 18.87 at. % and 2.83 at. %, respectively, with the concentration ratio essentially reversed. This severe surface–bulk compositional inversion was consistent with the selective oxidation and elemental redistribution mechanisms observed in high-temperature oxidation of HEAs. Garg et al. [23] observed in their study of AlCoCrFeNi oxidation that XPS detected substantial Ni, Co, and Fe oxides, whereas EDS revealed greater enrichment of Al and Cr in the oxide layer; Wang et al. [24] confirmed in their study of early-stage oxidation of CoCrFeMnNi that Co oxides preferentially formed in the outer layer at later stages, covering the Cr-enriched inner layer; Korda et al. [25] found in their investigation of the oxidation behavior of Al_{0.75}CoCrFeNi at 900–1100 °C that the surface oxide layer was enriched in Fe, Co, and Ni, while the inner oxide layer was enriched in Al and Cr. No reports had been published regarding the corrosion products of Al_xCoCrFeNi HEAs in high-temperature chlorine-containing atmospheres; however, these alloys may undergo analogous Cr selective oxidation and chlorination volatilization, resulting in more pronounced surface Co enrichment and Cr depletion. In high-temperature HCl-containing atmospheres, Cr undergoes selective chlorination volatilization,



CrCl₃ volatilized at elevated temperatures, and since XPS detected elemental signals only from the outermost several nanometers, Cr in this surface layer was essentially depleted via chlorination volatilization, resulting in a Cr-depleted surface. Co was relatively stable, with its oxides and chlorides exhibiting low volatility and thus not readily lost from the surface. Consequently, after the volatilization loss of Cr (and partial Al), the surface became relatively enriched in Co and Fe oxides. In contrast to XPS, the EDS signal originated from the lower portion of the oxide layer or from the lower oxide layer plus the substrate (if the corrosion layer was thin); therefore, although Cr in the outermost surface layer had been completely volatilized, substantial Cr was retained in the thicker underlying region, whereas the average concentration of Co in the principal corrosion layer was relatively low. The Cl concentration detected by XPS was seven times that measured by EDS, directly confirming that chlorination corrosion was concentrated within the surface nanoscale layer and that HCl corrosion was considerably more pronounced in the extremely thin surface layer than in the bulk phase. The substantial disparity between the corrosion layer bulk composition detected by EDS (Cr 24.8 at. %) and the surface composition determined by XPS (Cr 2.83 at. %) confirmed that the thickness of this compositional gradient layer lay in the nanometer to sub-micrometer range.

For the Al9 and Al14 specimens, the enrichment of O and Al in the XPS surface detection results was also distinctly observed, with other metallic elements almost completely obscured, further demonstrating the presence of an Al₂O₃-dominated corrosion product layer at the outermost surface of these two alloys—a result rarely reported in the literature. The thickness of the surface Al₂O₃ layer was further estimated using the Beer–Lambert bilayer attenuation model, wherein

the XPS signal intensity decayed exponentially with depth.

$$I(d)=I_0\exp(-\frac{d}{\lambda\cos\theta}) \quad (3.2)$$

wherein d represents the overlayer thickness, λ denotes the inelastic mean free path (IMFP) of Al 2p in Al_2O_3 , taken here as 2.8 ± 0.4 nm, and θ is the emission angle, typically taken as the surface normal with $\cos \theta \approx 1$. The calculation can be performed utilizing the degree of saturation of the Al elemental signal; when the surface is completely covered by Al_2O_3 , the relationship between the detected Al concentration and the Al_2O_3 corrosion layer thickness can be derived from the bilayer attenuation model as follows:

$$C_{Al}^{detected}=C_{Al}^{oxide}[1-\exp(-d/\lambda)]+C_{Al}^{bulk}\exp(-d/\lambda) \quad (3.3)$$

wherein C_{Al}^{oxide} represents the Al content in Al_2O_3 , i.e., 40%, and C_{Al}^{bulk} denotes the near-surface bulk Al content, which is taken as the Al concentration value detected by EDS. By substituting the Al concentration $C_{Al}^{detected}$ calculated from the XPS measurements of valid specimens into the above equation, the thickness d of the Al_2O_3 layer can be obtained. Valid specimens are required to exhibit surface Al enrichment, with $\text{XPS_Al} > \text{EDS_Al}$; $\text{Al/O} > 0.4$; and $50\% < \text{XPS_O} < 65\%$. The Al4 alloy was invalid for calculation due to surface Al depletion, and the Al12 alloy was also invalid due to its abnormally high O content. In addition to the Al_2O_3 layer thickness, its saturation degree (SD) constitutes another parameter capable of reflecting the quality of the Al_2O_3 layer. The saturation degree denotes the contribution proportion of the Al_2O_3 layer to the Al signal detected by XPS, directly reflecting the integrity and shielding capability of the surface Al_2O_3 layer. The term $C_{Al}^{oxide}[1-\exp(-d/\lambda)]$ in Equation (3.3) represents the contribution from the Al_2O_3 layer, while $C_{Al}^{bulk}\exp(-d/\lambda)$ represents the contribution from substrate leakage. By defining the coverage factor $f=1-\exp(-d/\lambda)$, then:

$$C_{Al}^{detected}=C_{Al}^{oxide} \cdot f + C_{Al}^{bulk} \cdot (1-f) \quad (3.4)$$

The saturation degree is defined as the proportion of the signal contribution from the Al_2O_3 layer relative to the theoretical maximum signal, i.e.:

$$SD = f \cdot 100\% = \frac{C_{Al}^{detected} - C_{Al}^{bulk}}{C_{Al}^{oxide} - C_{Al}^{bulk}} \times 100\% \quad (3.5)$$

Table 3 presents the calculated thickness and saturation degree of the outermost Al_2O_3 layer on $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs after corrosion in $\text{N}_2 - 9\% \text{CO}_2 - 7\% \text{O}_2 - 0.1\% \text{HCl}$, mol/mol at 700 °C for 80 h.

Table3 results for the thickness and saturation degree (SD) of the Al_2O_3 layer on the surface of $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs after corrosion

Sample	EDS_Al (at. %)	XPS_Al (at. %)	Al/O Ratio	SD	d (nm)	Error Range	Assessment
Al9	14.60	36.49	0.649	86.2%	5.5	4.7–6.3	Al_2O_3 -dominated
Al14	15.39	33.15	0.529	72.2%	3.6	3.1–4.1	Relatively thick Al_2O_3
Al4	3.87	1.85	0.031	—	—	—	Al-depleted surface
Al12	17.28	10.11	0.120	—	—	—	Abnormally high O (84.5%)

The Al4 alloy failed to form an effective Al_2O_3 protective layer due to an excessively low bulk Al content (3.87%), which was insufficient to sustain selective oxidation; consequently, the surface was dominated by Fe and Co oxides. The Al12 alloy exhibited an anomalous surface state, with an extremely high oxygen content (84.5%) and a very low Al/O ratio,

indicating the presence of substantial non-lattice oxygen likely originating from adsorbed H₂O/OH or carbonates. The Al19 and Al14 alloys successfully formed Al₂O₃ protective films with thicknesses of 3.6–5.5 nm. The Al₂O₃ layer of the Al19 alloy was thicker (5.5 nm) and denser (saturation 86%), whereas that of the Al14 alloy was relatively thinner (3.6 nm) with a greater substrate leakage signal (28%). These calculated results were consistent with the surface morphologies after corrosion (Fig. 5): the Al19 alloy surface was more continuous and denser, while the flaky and acicular high-Cr, high-Fe oxides or spinel structures growing around the Al₂O₃ in the Al14 alloy compromised the integrity of the corrosion layer. Combined with the corrosion kinetics data, it was concluded that the Al19 alloy achieved optimal corrosion resistance through the formation of a continuous, dense Al₂O₃ layer. To further verify the chemical state composition of the corrosion products, the content of each chemical state was calculated using Equation 3.6 based on the total elemental concentrations determined by XPS.

$$\phi_i = \frac{n_i}{\sum_j n_j} \times 100\% = \frac{\frac{C_M^{total} \cdot R_i}{v_M}}{\frac{C_M^{total} \cdot R_j}{v_j}} \times 100\% \quad (3.6)$$

Wherein ϕ_i represents the mole percentage of chemical state C_M^{total} denotes the XPS atomic percentage (total concentration) of element R_i is the relative content of chemical state i (the normalized proportion among various chemical states of the same element), $C_M^{total} \cdot R_i$ is the atomic concentration of element M allocated to chemical state i , v_M is the stoichiometric number of element M in the chemical formula of chemical state i , n_i is the molar equivalent of chemical state i , and $\sum_j n_j$ is the sum of molar equivalents of all target chemical states.

Figure 8 illustrates the contents of various chemical states at the outermost surface of Al_xCo₂₀Cr₂₀Fe_(40-x)Ni₂₀ HEAs and Inconel 625 after 80 h of corrosion at 700 °C in the simulated waste incinerator environment (N₂ - 9% CO₂ - 7% O₂ - 0.1% HCl, mol/mol).

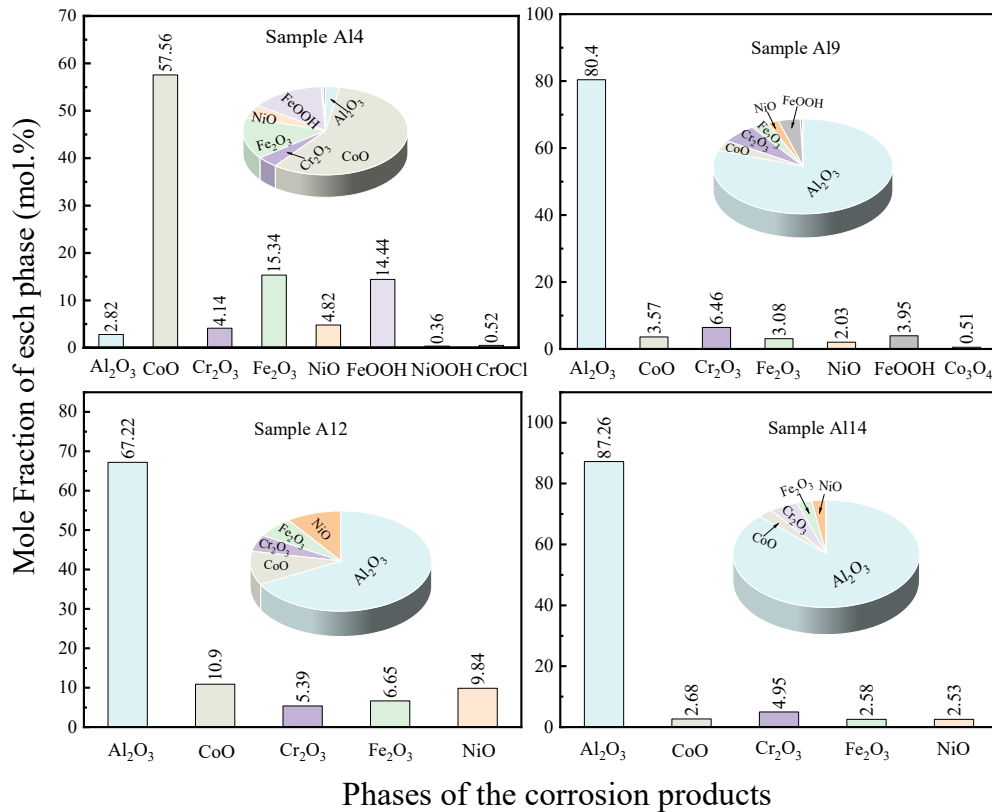


Fig. 8. The contents of various chemical states at the outermost surface of the Al_xCo₂₀Cr₂₀Fe_(40-x)Ni₂₀ HEAs and Inconel 625 alloy after

corrosion at 700 °C for 80 h in the simulated waste incinerator environment (N_2 -9% CO_2 -7% O_2 -0.1% HCl mol/mol).

Since XPS measurements were conducted five months after corrosion, FeOOH was detected in alloys with relatively high surface Fe content, such as Al4 and Al9, primarily formed by moisture adsorption from the sealed bags during storage. The corrosion products at the outermost surface of the Al4 alloy were dominated by CoO, accounting for 57.56 at. %, followed by Fe_2O_3 and FeOOH at 29.78 at.%. The Cl-containing compound CrOCl accounted for 2.07 at. %, representing the highest chloride content among the four alloys, thereby confirming the most severe high-temperature chlorine corrosion. When the Al content exceeded 9 at. %, Al_2O_3 became the predominant corrosion product on the alloy surfaces; the Al_2O_3 contents at the outermost surface of Al9, Al12, and Al14 were 80.4 at. %, 67.22 at. %, and 87.26 at. %, respectively. The higher bulk Al content of the Al14 alloy resulted in a higher Al_2O_3 concentration in the corrosion products; however, as indicated by the aforementioned results, its saturation degree was lower than that of the Al_2O_3 layer on the Al9 alloy. This result further demonstrated that the corrosion resistance of the corrosion layer was not determined by the Al_2O_3 content, but rather by the thickness and saturation degree of the Al_2O_3 layer. No chlorine compounds of Cr or Fe were detected in the corrosion products of Al9, Al12, and Al14. Due to the minimal binding energy difference between Al_2O_3 (74.4 eV) and AlCl_3 (74.7 eV) in the Al 2p spectrum—approximately 0.3 eV—severe peak overlap rendered accurate differentiation difficult; therefore, it was speculated that Cl may exist primarily in the form of AlCl_3 . Nevertheless, given the uncertainty associated with Al 2p peak deconvolution, quantitative analysis of Cl-containing chemical states in the corrosion products of these alloys was not performed.

3.5 Cross-Sectional Morphology and Composition of Corroded Specimens

Figure 9 presents the cross-sectional morphologies and compositional distributions of $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs and Inconel 625 after 80 h of corrosion at 700 °C in the simulated waste incinerator environment (N_2 - 9% CO_2 - 7% O_2 - 0.1% HCl , mol/mol).

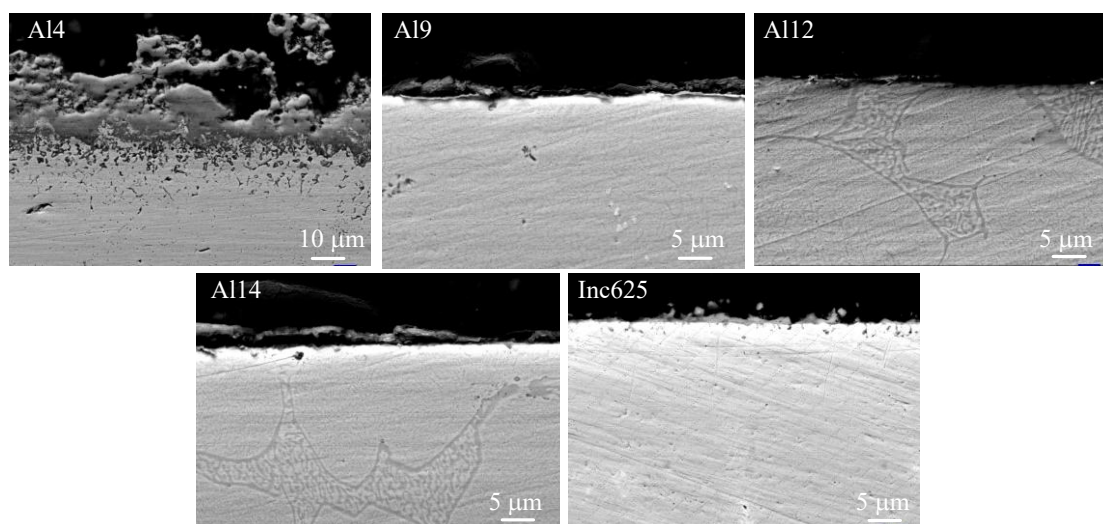


Fig. 9. The cross-sectional morphologies and compositional distributions of the $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs and Inconel 625 alloy after corrosion at 700 °C for 80 h in the simulated waste incinerator environment (N_2 -9% CO_2 -7% O_2 -0.1% HCl mol/mol).

The Al4 alloy exhibited the thickest corrosion product layer, with evident damage; hollow, bubble-like corrosion products were present in the upper layer, characteristic of typical high-temperature chlorine corrosion morphologies. This was attributed to the formation of outer solid oxides via oxidation of volatile gaseous chlorides (FeCl_2 , FeCl_3 , CrCl_3 , etc.) and the voids resulting from evaporation and consumption of volatile metal chlorides within the original solid oxides. The remaining HEA specimens and Inconel 625 exhibited relatively thin corrosion product layers with flat corrosion layer/substrate interfaces. The cross-sectional corrosion product layers of Al9, Al12, and Al14 were extremely thin, while

a continuous thin oxide layer was observed on the surface of Inconel 625. The substrate microstructures observed in the cross-sections indicated that the Al4 and Inconel 625 alloys consisted of a single phase, the Al9 specimen exhibited a fine and uniform microstructure, whereas the Al12 and Al14 specimens displayed evident secondary phase structures. With increasing Al content, the secondary phase content increased, consistent with the JMat Pro calculation results. Further observation revealed that in the Al12 and Al14 alloys, the regions located at the reticulated precipitate phases became preferential corrosion zones.

The following section presents an in-depth analysis of the corrosion products of each alloy in conjunction with EDS results. Figure 10 illustrates the cross-sectional morphologies and elemental distributions of $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs and Inconel 625 alloy after 80 h of corrosion at 700 °C in the simulated waste incinerator environment (N_2 -9% CO_2 -7% O_2 -0.1% HCl mol/mol).

The corrosion product layer of the Al4 alloy exceeded 20 μm in thickness, with a distinct internal oxidation zone. The outer corrosion products were dominated by Fe and Cr oxides, with a relatively high Fe oxide content; toward the gas interface, within the bubble-like corrosion products, and in the relatively porous regions of the corrosion layer, the Fe content was markedly higher than that of Cr. In the corrosion products near the substrate, the Cr_2O_3 content increased significantly, becoming the predominant product; simultaneously, a discontinuous Al_2O_3 layer appeared beneath the Cr_2O_3 , with internal corrosion manifested primarily as punctate or annular Al oxide zones. Selected area scanning results indicated that within the outer range of the corrosion layer, the Cl content was approximately 0.08 at. %, whereas in the inner region, the Cl content reached 0.21 at.%. Although the wet grinding process during cross-sectional specimen preparation may have caused partial dissolution of metal chlorides, the distribution characteristic of Cl was still evident: a significantly higher concentration near the corrosion layer/substrate interface compared to the gas/corrosion layer interface, providing experimental evidence for the active oxidation mechanism induced by Cl.

The Al9 specimen exhibited a flat corrosion layer/substrate interface after corrosion, with relatively pronounced Al enrichment in the corrosion products and a certain degree of Al depletion beneath the Al-rich oxide layer. Selected area scanning results revealed that the corrosion products also contained relatively small amounts of Cr, Fe, and Co oxides. The Cl content detected in the corrosion product layer of the Al9 specimen was 0.84 at. %, markedly higher than that in the surface layer of the Al4 specimen. Meanwhile, no Cl enrichment was observed at the corrosion product/substrate interface, which was attributed to the difficulty of Cl diffusion inward through the dense corrosion product layer, with most Cl retained in the surface layer of the corrosion products.

The Al-containing oxide (Al_2O_3) on the surface of the Al12 alloy after corrosion was more continuous and denser, and no evident Al depletion was observed in the substrate beneath the corrosion layer. This corrosion product layer remained intact and continuous after grinding and polishing, which was related to the high-Al, high-Ni microstructure distributed in a reticulated pattern in the substrate. This microstructure connected with the surface Al_2O_3 , ensuring both the Al source required for Al oxide formation and enhancing the adhesion between the corrosion product layer and the substrate via a pinning effect. Similarly, due to the blocking effect of the dense product layer, diffusion of Cl toward the corrosion layer/substrate interface was suppressed, with the maximum Cl concentration in the corrosion layer reaching 1.49 at. %.

The corrosion product layer of the Al14 alloy was relatively thick, dominated by Al and Cr oxides with small amounts of Co and Ni oxides. The Al_2O_3 product layer exhibited local discontinuities; the Al content was higher in the dense product layer, whereas the Cr content was higher in the thicker, relatively porous regions. This corresponded to the flaky or acicular Cr corrosion products growing around the Al_2O_3 in the surface morphology; this structure compromised the integrity of the corrosion layer, forming channels for inward Cl diffusion. At the corrosion layer/substrate interface in this region, a Cl

content of 0.53 at. % was detected, which was liable to cause further substrate corrosion by Cl, initiating the unfavorable

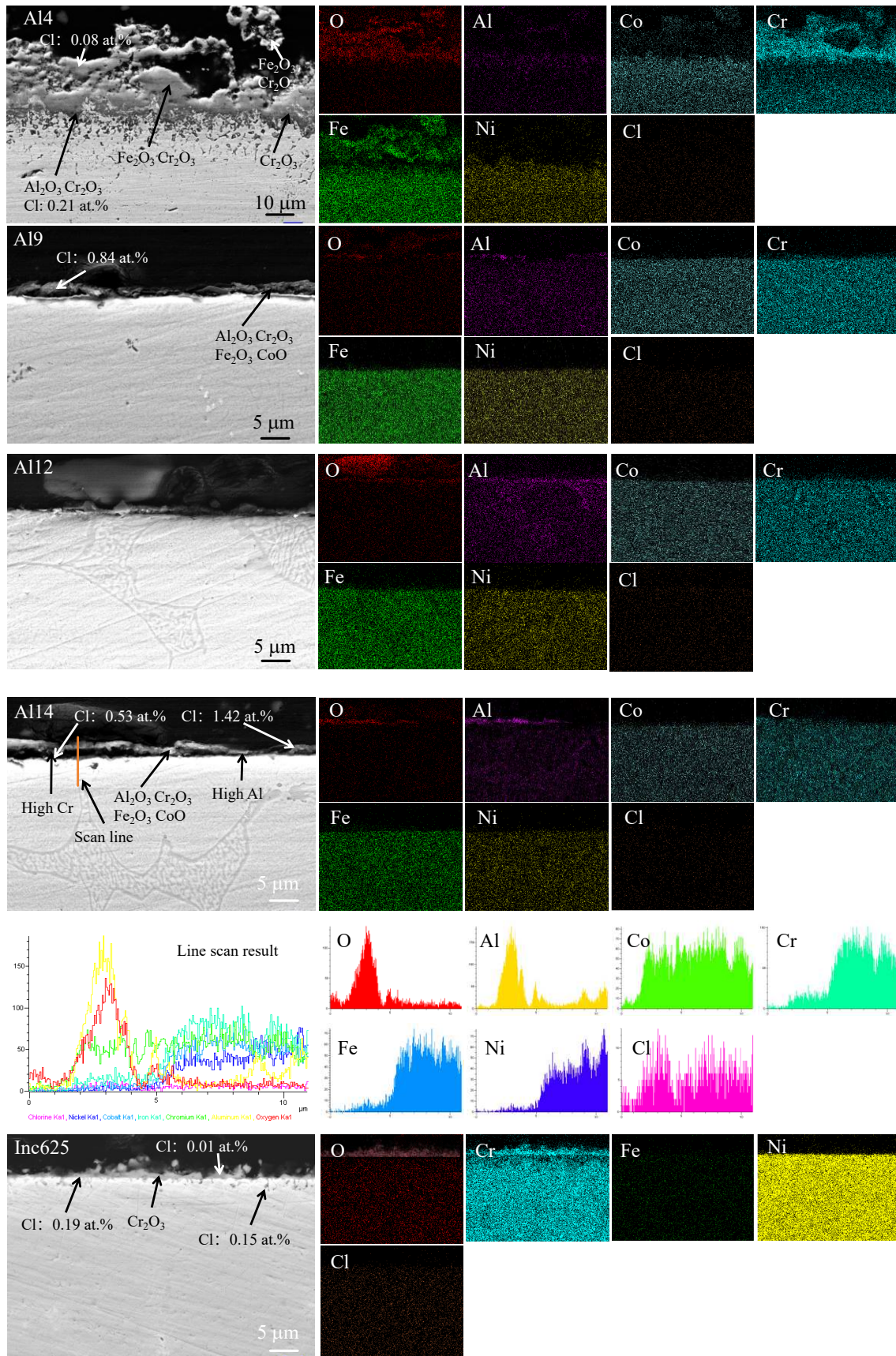


Fig. 10. The cross-sectional morphologies and elemental distributions of the $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs and Inconel 625 alloy after

corrosion at 700 °C for 80 h in the simulated waste incinerator environment (N₂-9% CO₂-7% O₂-0.1% HCl mol/mol).

cycle of active oxidation. In the continuous corrosion product regions with higher Al content, the Cl content reached 1.42 at.%, consistent with the results of the aforementioned alloys, confirming the blocking effect of continuous, dense corrosion product layers on Cl. Line scanning results indicated that the surface corrosion products were dominated by Al and Cr oxides, with a relatively higher Al content, and that Cl enrichment occurred to a certain extent in both the outer corrosion layer and the corrosion layer/substrate interface region, consistent with the active oxidation mechanism.

The corrosion products of Inconel 625 consisted of relatively continuous single-phase Cr₂O₃; due to Cr consumption, a distinct Cr-depleted zone appeared beneath the corrosion layer. Simultaneously, Inconel 625 underwent internal corrosion during the corrosion process, with the corrosion depth comparable to the extent of the Cr-depleted region. Selected area scanning results revealed that the Cl content at the Cr₂O₃ corrosion layer/gas interface was extremely low, merely 0.01 at.%, whereas the Cl concentration at the corrosion layer/substrate interface reached 0.19 at.%, indicating that the locally porous corrosion layer failed to provide adequate blocking of Cl, allowing it to penetrate the corrosion layer and enrich at the interface, thereby inducing the active oxidation process. Cl was also detected in the internal corrosion region, with a concentration of 0.15 at. %, clearly demonstrating that Cl penetrated the corrosion product layer and initiated pitting corrosion of the alloy substrate.

The denseness of the surface corrosion layer played a critical role in suppressing inward Cl diffusion and the formation of porous oxides. Enrichment of Cl in the corrosion product layer and at the corrosion layer/substrate interface was observed in the cross-sectional SEM/EDS results of the corroded specimens. Cl in the corrosion products originated from the initial chlorination reaction of the exposed substrate and subsequent retention via diffusion through the oxide film. If a dense oxide layer formed on the outer surface after the initial reaction, such as the extremely thin, dense Al₂O₃ layer on the Al9 specimen surface, the metal chlorides formed initially might be difficult to volatilize or might be oxidized by inward diffusion of O. Meanwhile, if the corrosion product layer was relatively porous, Cl in the corrosion product layer might be governed by two dynamic processes: inward diffusion penetration and outward volatilization. Therefore, the Cl concentration in the corrosion products could not accurately determine the relative corrosion resistance of the alloys. However, if significant Cl was detected in the internal corrosion zone, it could be definitively concluded that the denseness of the corrosion layer was inadequate, and that internal corrosion of the substrate was caused by Cl and O penetrating the corrosion layer at later stages. Thus, the evident presence of Cl in the internal corrosion zones of the Al4 and Inconel 625 substrates confirmed the suboptimal denseness of their surface corrosion layers.

3.6 Discussion

The high-temperature chlorine corrosion process of alloys differs significantly from high-temperature oxidation. Oxidation relies on the barrier effect of a dense oxide film, whereas chlorine corrosion destroys any protective film attempting to form through a chlorination–volatilization–reoxidation cycle. The former is a passive process controlled by solid-state diffusion, while the latter is an active consumption process driven by gas-phase transport. Consequently, the alloy design strategy for high-temperature chlorine corrosion must prioritize the thermodynamic stability and vapor pressure of elemental chlorides, as well as the chemical homogeneity of the matrix, rather than merely pursuing the ability to form dense oxide films. Accordingly, the discussion in this section first addresses the rationale for selecting the modifying element Al, followed by the influence of Al on the microstructure, corrosion product composition and distribution, and ultimately the corrosion resistance of the HEAs, and finally presents the high-temperature chlorine corrosion mechanism of the Al_xCoCrFeNi HEAs based on the above analysis.

First, in determining the HEA compositions and analyzing the corrosion mechanism in this study, the stability of each elemental oxide in an HCl atmosphere was considered, specifically the Gibbs free energy change (ΔG) for the reaction between the corresponding metal oxide and HCl; a larger value indicates greater stability of the corresponding oxide. Simultaneously, the stability of the metal chlorides corresponding to each element was calculated, namely the magnitude of their saturated vapor pressure and the O_2 partial pressure required for re-oxidation of the chlorides, thereby assessing the volatilization and oxidation extent of the chlorides.

Figure 11 presents the thermodynamic calculation results for possible oxidation, chlorination, and corresponding oxide and chloride reactions of constituent elements in $Al_xCo_{20}Cr_{20}Fe_{(40-x)}Ni_{20}$ HEAs in a high-temperature oxidizing chlorine-containing atmosphere.

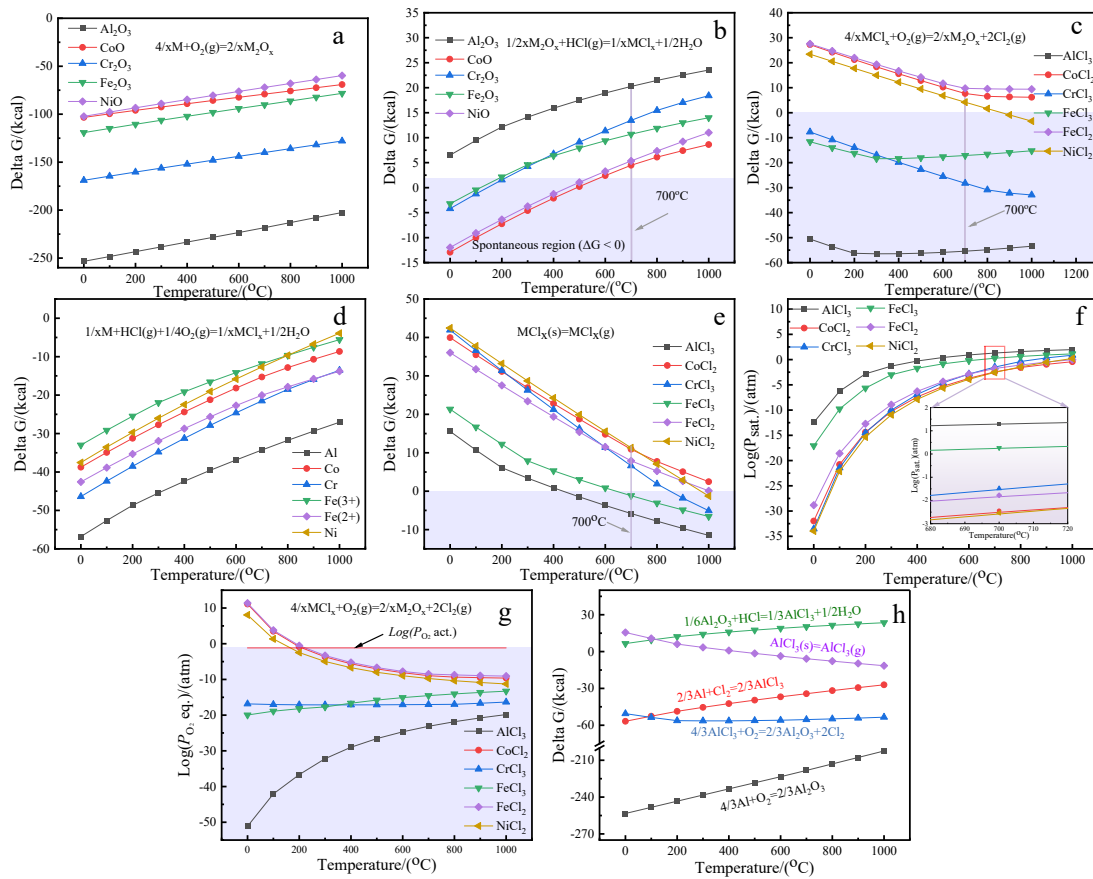


Fig. 11. The thermodynamic calculation results for the possible chemical reactions of oxidation, chlorination, and the corresponding oxides and chlorides of the constituent elements in the $Al_xCo_{20}Cr_{20}Fe_{(40-x)}Ni_{20}$ HEAs in a high-temperature oxidizing chlorine-containing atmosphere.

From the Gibbs free energy changes (ΔG) for elemental oxidation (Fig. 11a) and chlorination reactions (Fig. 11b), the ΔG values for oxidation reactions were markedly lower than those for chlorination reactions, indicating a greater driving force for oxidation and that elements were more prone to undergo oxidation. However, the ΔG values for chlorination reactions of the alloy elements were less than zero, indicating that these reactions could still proceed spontaneously, particularly in the initial stage when the alloy surface was fully exposed to the oxidizing chlorine-containing atmosphere, wherein oxidation and chlorination occurred simultaneously. When a slowly growing, dense protective oxide film formed on the alloy surface (at Al contents above 9 at. %), the opportunity for elemental chlorination reactions increased, i.e., the probability of weight loss due to volatilization of low-boiling-point chlorides increased. The weight loss observed in the Al19, Al12, and Al14 specimens during the first 10 h of corrosion (Fig. 3) accurately corroborated this inference. The

calculation results revealed that the ΔG value for Al oxidation was the lowest among all elements, indicating the greatest driving force for Al oxidation and favoring the formation of protective Al_2O_3 . The ΔG value for the reaction of Al_2O_3 with HCl was the highest among all elements and exceeded zero at 700 °C, indicating that its dissolution by HCl was thermodynamically non-spontaneous and that Al_2O_3 exhibited the highest stability in the corrosive atmosphere. In addition to occurring on the surface during the initial corrosion stage, chlorination reactions of metal elements could also proceed at the corrosion layer/substrate interface due to the strong penetrability of Cl, which could permeate through the corrosion product layer to reach this interface where the oxygen partial pressure was lower, rendering elemental chlorination reactions more favorable. Therefore, the stability of corresponding metal chlorides was considered in the calculations. Accordingly, this study calculated the ΔG values for metal chloride volatilization reactions (Fig. 11e), equilibrium vapor pressures (Fig. 11f), and minimum equilibrium oxygen partial pressures required for re-oxidation (Fig. 11g). The equilibrium Cl_2 partial pressure used in the equilibrium oxygen partial pressure calculation was based on an HCl concentration of 1000 ppm, combined with the chemical reaction equilibrium constant for its oxidation reaction (Equation 3.7) at 700 °C.



The results indicated that Al was the most susceptible to chlorination among all elements, exhibiting the highest saturated vapor pressure of its chloride; however, AlCl_3 was the most prone to oxidation, with the lowest equilibrium oxygen pressure required for its oxidation to Al_2O_3 . Under the actual oxygen partial pressure of the corrosive atmosphere (marked by the red line in Fig. 11g), AlCl_3 was readily oxidized to form stable Al_2O_3 . Furthermore, the saturated vapor pressure results for metal chlorides (Fig. 11f) revealed that the vapor pressure of CoCl_2 was merely approximately one percent of that of CrCl_3 , which also corroborated the compositional redistribution observed on the Al4 alloy surface in the XPS results.

Figure 11g presents the ΔG values for various reactions of Al in the corrosive atmosphere. The positional distribution of each curve from top to bottom reflected the magnitude of the driving force for the corresponding chemical reaction; reactions located lower possessed greater driving force and were thermodynamically more favorable. The calculation results demonstrated that at 700 °C, the oxidation and chlorination reactions of Al, as well as the volatilization and oxidation of the corresponding chloride AlCl_3 , were all spontaneous. Among these, the oxidation reactions of Al and AlCl_3 exhibited greater driving force, indicating that Al was more likely to form metal oxides rather than chlorides under the experimental conditions. This constituted the intrinsic reason why Al could serve as a modifying element to enhance the high-temperature chlorine corrosion resistance of HEAs.

Secondly, the influence of Al content on the microstructure and corrosion resistance of the alloys was analyzed. Existing studies have demonstrated that B2 intermetallic phases rich in Al and Ni can form dense, protective Al_2O_3 films that act as barrier layers to prevent further corrosion[26-29]. At an Al content of 4 at. %, the absence of the B2 phase resulted in a lack of protection and barrier effects from secondary phases. The Al4 alloy exhibited a fine cellular dendritic structure with extremely high grain boundary density; these grain boundaries served as rapid penetration channels for the corrosive medium. Furthermore, although the alloy contained approximately 20 at. % Cr, the Cr was substantially diluted in the cocktail configuration of the five elements, making it difficult to form a complete, continuous Cr_2O_3 passive film. The insufficient Al content also failed to provide supplementary protection via Al_2O_3 films. Consequently, rapid uniform dissolution occurred in the initial corrosion stage, accompanied by preferential grain boundary corrosion, with the protective effect of the passive film remaining weak and the corrosion rate persistently elevated. After 30 h of corrosion, with the formation of an inner continuous Cr_2O_3 and Al-rich oxide layer, the corrosion rate of the alloy was markedly reduced.

The corrosion kinetics of A19 exhibited typical characteristics of passive film growth controlled by diffusion. From the microstructural perspective, A19 lay in the dual-phase FCC + B2 region; with an Al content of 9 at. % exceeding the critical value, ordered B2 phases precipitated during cooling, but these B2 phases were dispersedly distributed as fine particles within the coarse FCC matrix. EDS mapping clearly revealed that Al and Ni were enriched in localized regions to form B2 phases, while Cr was uniformly retained in the FCC matrix. This dual-phase structure engendered a unique synergistic passivation mechanism: the FCC matrix provided the Cr₂O₃ film, and the B2 phase provided the Al₂O₃ film, with both forming a dense composite oxide protective layer on the surface. More critically, the A19 alloy possessed the largest grain size among the several alloys, with the minimum total grain boundary area, thereby substantially eliminating the detrimental effect of grain boundaries as rapid corrosion channels. The B2 phase particle size was less than 5 μm , far below the critical size for inducing large cathodic galvanic corrosion; therefore, it did not induce severe galvanic acceleration effects but instead promoted uniform passivation of the matrix through micro-sacrificial anode behavior [30, 31]. The combined action of these factors rendered the corrosion rate of A19 the lowest and most stable, still exhibiting an advantage over Inconel 625.

When the Al content increased to 12 at.%, the B2 phase precipitate content increased significantly, and the moderate cooling rate of vacuum melting could not suppress diffusion, leading to the aggregation and coarsening of B2 phases into blocky islands of 50–150 μm . EDS data revealed that these large B2 phases were extremely enriched in Al and Ni internally, with Cr almost completely excluded, while the surrounding matrix became Cr-depleted due to supplying the growth of the B2 phases. This microstructural inhomogeneity readily induced galvanic corrosion: the large B2 phases possessed a more positive potential and served as large cathodes, while the surrounding Cr-depleted FCC matrix became a small anode. The anodic current density was proportional to the cathodic area, and the matrix dissolution rate increased dramatically. Therefore, the continued increase in B2 phase content resulting from further Al addition (A114 alloy) elevated the risks of galvanic corrosion, pitting, and crevice corrosion during the corrosion process. In the results of the A114 alloy surface after corrosion (Fig. 5), flaky non-protective oxides rich in Fe and Cr were observed growing at the interface between the dark, slightly protruding Al₂O₃ and the dense, flat oxide layer, which validated the viewpoint that high B2 content increased pitting and crevice corrosion. Simultaneously, the metallographic results indicated that the grain size of the A114 alloy was further refined, with increased grain boundary area providing more channels for rapid diffusion of corrosive elements such as Cl and O. Consequently, compared with the A19 and A112 alloys, the A114 alloy exhibited a higher corrosion mass gain during the corrosion process.

Based on XRD and XPS analyses of corroded surfaces, as well as SEM/EDS analyses of surface and cross-sectional morphologies, it was evident that with increasing Al content, the corrosion products gradually transformed from porous Fe-rich oxides to dense, flat, Al- and Cr-rich oxides. When the Al content exceeded 9 at. %, the denseness of the alloy corrosion product layer was markedly higher than that of Inconel 625. An extremely thin (3.6–5.5 nm) Al₂O₃ layer existed at the outermost surface of the HEA corrosion products. Although the Al₂O₃ chemical state content of the A114 alloy (87.26%) was higher than that of the A19 alloy (80.4%), the denseness of its Al₂O₃ layer (SD = 72.2%) was lower than that of the A19 alloy (SD = 86.2%), consistent with the experimental conclusions.

In summary, the superior corrosion resistance of A19 stemmed from its position within the golden window of the dual-phase region. The Al content exceeded the critical value for B2 phase precipitation, ensuring a dual-phase synergistic passivation mechanism, yet remained far from the critical value for the three-phase region, thereby avoiding the detrimental effects of the σ phase. The coarse grain structure reduced grain boundary corrosion sensitivity, while dispersed B2 phase particles provided strengthening and barrier effects without inducing galvanic acceleration. This coarse-grained dual-phase

synergistic microstructural design maintained the corrosion process in an ideal state of passive film diffusion control, with low and stable kinetics curves, demonstrating corrosion resistance superior to that of the conventional nickel-based alloy Inconel 625. In contrast, Al4 corroded most rapidly due to its single-phase structure with high grain boundary density and insufficient passivation; Al12 exhibited fluctuating and deteriorating corrosion due to severe segregation and galvanic effects induced by large B2 phases; and Al14 experienced exacerbated galvanic and crevice corrosion due to extensive B2 phase precipitation and further grain refinement, which led to continuous degradation of the corrosion resistance of both alloys. This result fully embodies the core design principle of HEAs: compositional regulation governs phase structure, and phase structure determines corrosion kinetics.

Based on the foregoing analysis of the influence of Al content on the microstructure and properties of $\text{Al}_x\text{CoCrFeNi}$ HEAs, the high-temperature chlorine corrosion mechanism of the Al9 alloy, which exhibited optimal performance, is schematically illustrated in Figure 12.

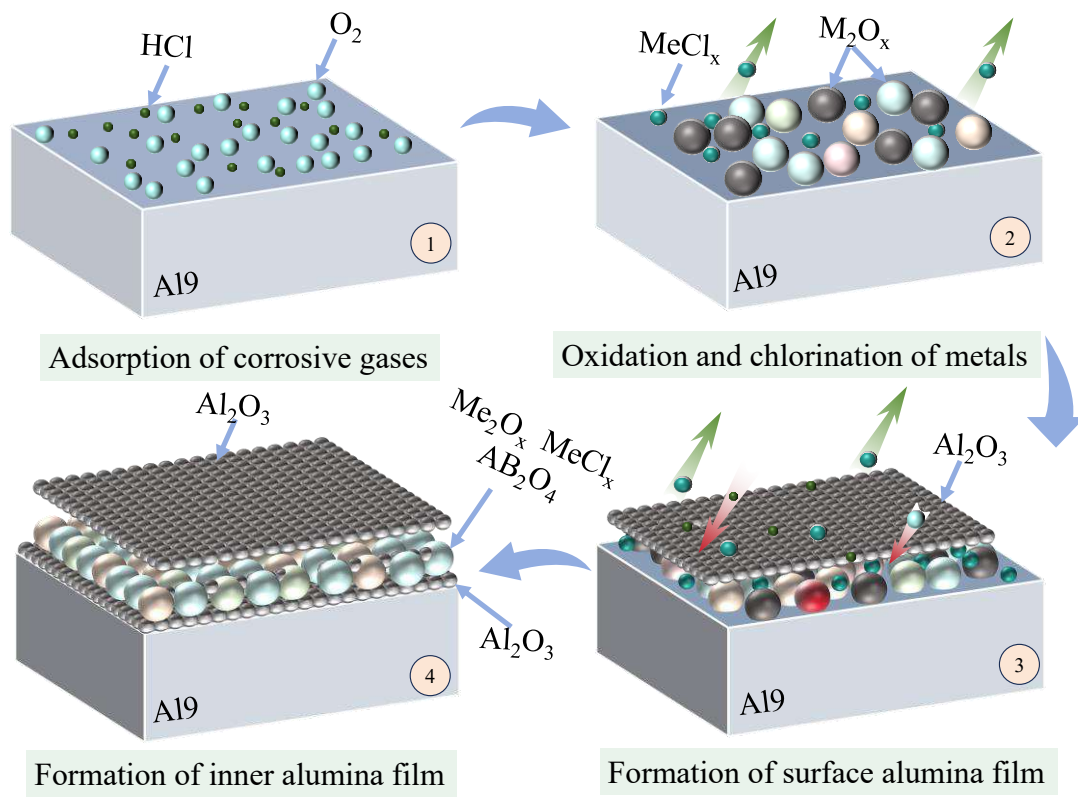


Fig. 12. The high-temperature chlorine corrosion mechanism of the $\text{Al}_9\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{31}\text{Ni}_{20}$ high-entropy alloy, which exhibits optimal performance, corroded at 700 °C in the simulated waste incinerator environment (N_2 -9% CO_2 -7% O_2 -0.1% HCl mol/mol).

Upon initial exposure of the alloy matrix to the oxidizing Cl-containing atmosphere, the constituent elements underwent concurrent oxidation and chlorination reactions, with the former exhibiting greater thermodynamic driving force. However, the chlorides possessed lower boiling points and higher vapor pressures; as they volatilized and escaped from the initial corrosion products, the chlorination reaction proceeded continuously, ultimately causing matrix mass loss. Consequently, during the initial 10 h, the Al9, Al12, and Al14 specimens—all capable of forming dense corrosion products—exhibited a certain degree of weight loss.

Driven by the high driving force of oxidation, the alloy surface was gradually covered by oxides of various elements. Due to the greatest driving force for Al oxidation and the highest stability of Al_2O_3 , Al reduced the oxides of other metal

elements while being oxidized itself, ultimately forming an extremely thin Al_2O_3 layer at the outermost surface of the corrosion products. The subsequent corrosion process was dominated by inward diffusion of O and Cl through this oxide layer, forming a mixed oxide layer of constituent elements below with minor chlorides. With prolonged exposure, the oxides further reacted to form spinel phases. Since the chlorination reactions of oxides were all non-spontaneous at the experimental temperature, chlorination was markedly suppressed, and the corrosion process was dominated by slow oxide growth, manifested as a stable, slow mass gain trend in the corrosion kinetics curves.

When Cl diffused to the corrosion layer/substrate interface, where the oxygen partial pressure was lower, the chlorination reactions of alloy elements continued. The chlorides generated by matrix elements diffused toward the gas/product layer interface due to their high vapor pressures. During this diffusion, as the oxygen partial pressure increased, metal chlorides prone to oxidation (such as AlCl_3 , CrCl_3 , FeCl_3) were re-oxidized to corresponding metal oxides, whereas chlorides corresponding to non-spontaneous oxidation reactions (FeCl_2 , CoCl_2 , NiCl_2) directly escaped from the sample surface, again causing matrix mass loss. This was validated by the fluctuation phenomena observed in the corrosion kinetics curves. O slowly diffused inward through the corrosion product layer, undergoing oxidation reactions with matrix elements and reduction of Al on other metal oxides. Ultimately, a slowly growing continuous Al_2O_3 layer formed at the innermost layer of the corrosion products, substantially suppressing outward diffusion of metal elements and inward diffusion of O, Cl, and other species [28, 32, 33].

Since the metal oxides formed by oxidation of gaseous metal chlorides were relatively porous and generally non-protective [34], and the formation of new oxides within existing oxides inevitably compromised the integrity of the original product layer, the corrosion process could still be accelerated by destruction of the corrosion product layer in the later stages of high-temperature chlorine corrosion if a dense, continuous corrosion product layer failed to form on the alloy surface. For the $\text{Al}_x\text{CoCrFeNi}$ HEAs, the formation of double-layer continuous Al_2O_3 layers at the surface and innermost layers in the later stages (60 h) of corrosion resulted in minimal mass change, particularly when the Al content exceeded 9 at. %, with the kinetics curves essentially exhibiting a flat trend. In contrast, Inconel 625, with Cr_2O_3 of lower stability than Al_2O_3 as its principal corrosion product, exhibited a mass gain trend throughout the entire corrosion cycle. It could thus be concluded that under longer-term corrosion conditions, the HEAs would demonstrate superior high-temperature chlorine corrosion resistance.

4. Conclusions

$\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ ($x = 4, 9, 12, 14$ at. %) HEAs were prepared via vacuum arc melting, and cyclic high-temperature corrosion behavior was investigated at 700 °C for 80 h in a simulated waste incinerator atmosphere (N_2 -9% CO_2 -7% O_2 -0.1% HCl mol/mol).

(1) The relationship between Al content and alloy phase composition was elucidated based on thermodynamic equilibrium calculations, with x values of 4, 9, 12, and 14 at. % determined for the $\text{Al}_x\text{Co}_{20}\text{Cr}_{20}\text{Fe}_{(40-x)}\text{Ni}_{20}$ HEAs. The calculated results were in good agreement with the experimental XRD results, confirming the reliability of thermodynamic equilibrium calculations in determining elemental contents.

(2) Based on combined analysis of corrosion kinetics, surface morphology, elemental chemical state composition and distribution, cross-sectional morphology, and elemental distribution after corrosion, it was established that, with the exception of the Al4 alloy, the corrosion resistance of the remaining HEAs was superior to that of Inconel 625. The Al9 alloy exhibited the most continuous and dense surface corrosion product layer, with a corrosion mass gain after 80 h amounting to merely 5.15% of that of Inconel 625.

(3) Regarding the discrepancy between XPS and XRD results for the surface composition analysis of the Al4 alloy,

the reconstruction phenomenon of Co and Cr elements at the outermost surface of the corrosion layer was clarified based on an analysis of the stability of Co and Cr oxides and chlorides, thereby establishing the application value of Co in high-temperature chlorine-containing atmospheres. Calculations based on the surface chemical state analysis results confirmed the existence of an extremely thin Al_2O_3 layer on the corrosion layer surface, and its thickness and saturation degree were quantified. The analytical results further supported that the Al9 alloy possessed the optimal corrosion product layer structure.

(4) Thermodynamic calculation results demonstrated that Al exhibited a propensity to form stable Al_2O_3 products in high-temperature oxidizing chlorine-containing atmospheres. The synergistic effects of multiple factors—including relatively small grain boundary area, appropriate secondary phase content, rapid formation of a dense Al_2O_3 layer at the outermost surface, and formation of a slowly growing inner Al_2O_3 layer—collectively enabled the Al9 alloy to achieve optimal high-temperature chlorine corrosion resistance.

Acknowledgements:

This study was supported by Jiangxi Province Key Laboratory of Surface Engineering (No. 2024SSY05071) and financially supported by the Doctoral Startup Foundation of Jiangxi Science and Technology Normal University (Grant No. 2023BSQD19) and the General Open Project of Jiangxi Provincial Key Laboratory of Surface Engineering (Grant No. 2025KFJJ07).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Lingyun Bai: Conceptualization and design of the study, Writing-review and editing, Software, Methodology. **Longfa Jiang:** Formal analysis, Data curation. **JunHuai Xiang:** Acquisition of data. **Botao Xiao:** Writing-original draft. **Xunhu Xu:** Data curation.

References

- [1] Li Y Y, Zhang C, Niu X Y, Zhang C Y, Li S, Bao Z B, et al. Chlorine-induced high-temperature corrosion of the Pt-modified aluminide coating in simulated marine environment[J]. Corrosion Science, 2023, 224:111493.
- [2] Gerard A, Kautz, E, Schreiber D, Han J, McDonnell S, Ogle K, et al. The role of chromium content in aqueous passivation of a non-equiatomic $\text{Ni}_{38}\text{Fe}_{20}\text{Cr}_x\text{Mn}_{21-0.5x}\text{Co}_{21-0.5x}$ multi-principal element alloy ($x = 22, 14, 10, 6$ at. %) in acidic chloride solution[J]. Acta Materialia, 2023,245:118607.
- [3] Song H, Feng C, Guan Z, Zhang F, Ma H, Ma Z, et al. Effect of Al/Cr ratio on structure, magnetism, and corrosion resistance of $\text{FeCoNiCr}_{1-x}\text{Al}_x$ high entropy alloys[J]. Journal of Alloys and Compounds, 2025,1010:177415.
- [4] Yu D, Cheng J, Chu Y, Zhang H, Zhou X. An investigation on high temperature corrosion behavior of $\text{FeCr}_{0.5}\text{NiCu}_{0.5}$ high-entropy alloy in waste incineration environments[J]. Anti-Corrosion Methods and Materials, 2025,75(5):702-712.
- [5] Wang J, Guan X, Meng Y, Wu Y, Wang Y, Huang X, et al. Cooperative of Ti and Cr elements on passivation enhancement of FeCoCrNiTi_x HEAs[J]. Corrosion Science, 2025,252:112937.
- [6] Bai L, Peng W, Li W, Shi X, Xiang J, Deng X. Effect of titanium element on high temperature chlorine corrosion [J]. Corrosion Science, 2023,211(110915):1-15.
- [7] Zhu C, Wu J, Pan H, Pan Z, Teng C, Wu L. Study on high temperature oxidation resistance of $\text{MoNbTi}(\text{Al}, \text{Cr})$ refractory high entropy alloys[J]. Materials Today Communications, 2025:112202.
- [8] Yang X, Zhang D, Wang Y, Zhao D, He Z, Dong Y, et al. Investigation on tribological and high-temperature molten-salt corrosion behavior of NbMoTaWCr refractory high-entropy alloy coating[J]. International Journal of Refractory

Metals and Hard Materials, 2026,136:107650.

- [9] Lv J, Liu J, Guo S, Zhang J, Chen C, Zheng C, et al. The corrosion behavior and mechanism of hot isostatically pressed CrMnFeCoNi high-entropy alloy in high-temperature molten salt environments[J]. Intermetallics, 2026,188:109074.
- [10] Lei Y, Yang K, Xu M, Zhang S, Tong B, Liu X, et al. High-temperature wear and hot corrosion mechanisms of nitrided AlCoCrMoNi high-entropy alloy coatings[J]. Surface and Coatings Technology, 2026,520:133014.
- [11] Mei L, Zhang J, Li Q, Tian Q. High-temperature oxidation behavior of high-entropy duplex-phase MnCuNiFeZnCrMoAl alloy[J]. Materials Chemistry and Physics, 2026,349:131802.
- [12] Wu Z, Tan X, Liu Y, Li J. Effect of Yttrium on the high-temperature oxidation resistance of Al_{0.7}CoCrFeNi high-entropy alloy[J]. Journal of Alloys and Compounds, 2026,1050:185712.
- [13] Wang X, Zhou Y, Ren B, Liu J, Jiang A. Effect of sintering temperature on the high-temperature oxidation behavior of TiB₂@Ti/AlCoCrFeNi_{2.1} eutectic high-entropy alloy matrix composites[J]. Intermetallics, 2026,188:109078.
- [14] Sun Y, Miao Q, Liang W, Gupta M, Jia F, Xu J, et al. High temperature oxidation-resistant AlCoCrFeNi high entropy alloy coating on TiAl alloy: Role of pre-diffusion on oxidation resistance[J]. Applied Surface Science, 2025,689:162501.
- [15] Tao H, Wang Z, Wu X, Li L, Wang Y, Zhao C, et al. Effect of Al content on high-temperature oxidation behavior and mechanism of Al_xCoCrFeNi_{1.5}Ti_{0.1} high-entropy alloy coatings by laser cladding[J]. Surface and Coatings Technology, 2025,502:131961.
- [16] Bai L, Peng W, Zhu J, Wu X, Shi X, Xiang J, et al. High temperature chloride corrosion behavior of AlFe_{2.5}NiMoNbCr high-entropy alloy[J]. Corrosion Science, 2022,198:110139.
- [17] Chu X, Hu S, Zhang D. High temperature chlorine corrosion resistance of gradient high entropy alloy coatings prepared by high-velocity-oxygen-fuel spraying[J]. Journal of Physics: Conference Series, 2024,2713(1742-6588):12024.
- [18] Wang J, Jiang H, Xie W, Kong X, Qin S, Yao H, et al. Effect of Mo addition on microstructural evolution and corrosion behaviors of AlCrFeNi₃ eutectic high-entropy alloy[J]. Corrosion Science, 2024,229:111879.
- [19] Jordan P, Maharaj C. Asset management strategy for HAZ cracking caused by sigma-phase and creep embrittlement in 304H stainless steel piping[J]. Engineering Failure Analysis, 2020,110:104452.
- [20] Kishore K, Kushwaha S, Sai Pranay Teja K, Kumar Chandan A, Mukherjee M, Adhikary M, et al. Sigma phase embrittlement-induced failures of heat-resistant stainless steel traveling grate links[J]. Engineering Failure Analysis, 2023,144:106979.
- [21] Yuan Z, Yang Z, Lu Y, Yuan T, Tu Y, Ni Z, et al. Microstructure characterization and corrosion resistance of eutectic and near-eutectic AlCoCrFeNi HEAs[J]. Journal of Materials Research and Technology, 2025,36:8367-8379.
- [22] Inman S B, Sur D, Han J, Ogle K, Scully J R. Corrosion behavior of a compositionally complex alloy utilizing simultaneous Al, Cr, and Ti passivation[J]. Corrosion Science, 2023,217:111138.
- [23] Garg M, Grewal H S, Sharma R K, Gwalani B, Arora H S. High oxidation resistance of AlCoCrFeNi high entropy alloy through severe shear deformation processing[J]. Journal of Alloys and Compounds, 2022,917:165385.
- [24] Wang L, Zanna S, Mercier D, Maurice V, Marcus P. Early-stage surface oxidation of the equiatomic CoCrFeMnNi high entropy alloy studied in situ by XPS[J]. Corrosion Science, 2023,220:111310.
- [25] Korda A A, Akbar M A, Muhammad F, Achmad T L, Prawara B, Prajitno D H, et al. High-Temperature Oxidation and Microstructural Changes of Al_{0.75}CoCrFeNi High-Entropy Alloy at 900 and 1100 °C: Metals[Z]. 2024: 14, 33.
- [26] Xing Z, Pang J, Yuan K, Zhu G, Tan J, Wang A, et al. Effects of the B₂ phase on the corrosion behavior of Fe-Ni-Cr-Al medium-entropy alloys in lead-bismuth eutectic[J]. Journal of Alloys and Compounds, 2025,1035:181633.
- [27] Lu J, Zhang H, Chen Y, Xiao W, Ni N, Zhao X, et al. Y-doped AlCoCrFeNi_{2.1} eutectic high-entropy alloy with excellent oxidation resistance and structure stability at 1000°C and 1100°C[J]. Corrosion Science, 2021,180:109191.

- [28] Masahashi N, Kimura G, Oku M, Komatsu K, Watanabe S, Hanada S. Corrosion behavior of iron – aluminum alloys and its composite steel in sulfuric acid[J]. Corrosion Science, 2006,48(4):829-839.
- [29] Jin Y, Tian L, Huang Z, Wang F. Improving the electrochemical corrosion resistance of a high-Ca heat-resistant magnesium alloy by enhancing the barrier effect of the cathodic phase skeleton[J]. Journal of Alloys and Compounds, 2025,1010:177728.
- [30] Duan J, Jiang Z, Huang F, Zhang X, Zhang G. Mechanistic exploration of the exceptional corrosion resistance of the newly designed FeCoCrNiMoxNbx HEAs[J]. Journal of Materials Science & Technology, 2025,221:204-219.
- [31] Song G, Atrens A. Recently deepened insights regarding Mg corrosion and advanced engineering applications of Mg alloys[J]. Journal of Magnesium and Alloys, 2023,11(11):3948-3991.
- [32] W. C. Xiao, S F Liu Y, T. Yang. A novel single-crystal L12-strengthened Co-rich high-entropy alloy with excellent high-temperature strength and antioxidant property[J]. Journal of Materials Research and Technology, 2023,23:2343-2350.
- [33] Xu Y, Chirol M, Li C, Vardelle A. Formation of Al₂O₃ diffusion barrier in cold-sprayed NiCoCrAlY/Ni multi-layered coatings on 304SS substrate[J]. Surface and Coatings Technology, 2016,307:603-609.
- [34] Bai L, Peng W, Men D, Zhu J, Wu X, Shi X, et al. High Temperature Chloride Corrosion Behavior of 904L:AlFeNiMoNb High-Entropy Alloy[J]. Frontiers in Materials, 2021,Volume 8 - 2021.