



Plasma-sprayed Ni—Al coatings in contact with soda-lime glass at temperatures $>1000\text{ }^{\circ}\text{C}$

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ARTICLE INFO

Keywords:

Wettability

Glass

NiAl

Intermetallic phases

Thermal

Plasma spraying

Corrosion

ABSTRACT

This study investigates the interaction between atmospheric plasma sprayed Ni—Al intermetallic coatings and molten soda-lime silicate glass at temperatures $>1000\text{ }^{\circ}\text{C}$. Focusing on wetting behavior, alumina scale formation and interfacial chemical reactions. Cross-sectional analysis revealed the formation of a continuous Al_2O_3 scale on the surface of the coating, the thickness (2–12 μm) of which increased with thermal exposure. Elemental mapping confirmed the formation of an alumina-rich interface, and the presence of white streaks resulting from an enrichment of alumina within the glass. This indicated the scale's partial dissolution into the silicate melt. The wetting behavior of Ni—Al plasma-sprayed coatings is strongly influenced by heat treatment due to its impact on surface chemistry, energy and microstructure. It was observed that the contact angle increased up to 25° from the as-sprayed condition to the annealed coating. This indicates that the coatings become markedly more non-wetting and resistant to molten glass adhesion after high-temperature exposure. While the alumina layer enhances anti-wetting performance, it remains chemically active in contact with molten glass.

1. Introduction

Molten silicate glass interacts aggressively with metals during high-temperature processes, particularly in glass manufacturing. This can lead to chemical corrosion and physical adhesion or sticking at the glass-metal interface [1]. For example, in glass-forming operations, tools and dies are exposed to elevated temperatures ($>1000\text{ }^{\circ}\text{C}$) and the molten glass undergoes deformations under mechanical stress [2]. These severe conditions drastically reduce tool life and reliability. A significant practical problem is the adhesion of molten glass to surfaces, which can degrade product quality and lead to frequent tool maintenance. The adhesion of glass to mold materials not only compromises the surface finish and structural integrity of glass products but also significantly accelerates tooling wear and corrosion [3]. In high-temperature processes such as metallurgical operations or vitrification, similar phenomena are observed when molten glass or slags interact with structural alloys. This highlights the importance of understanding glass-metal

interactions in industrial contexts. To address these challenges, the development of advanced materials and coatings that can provide non-wetting, corrosion-resistant surfaces in contact with molten glass is being explored [4].

Molten silicate glass reacts aggressively with metals at high temperatures, resulting in chemical corrosion and physical adhesion at the interface. Young's equation fundamentally governs the tendency of a glass melt to wet and bond to a metal surface, relating the equilibrium contact angle (Θ_Y) to the balance of interfacial tensions. A low Θ indicates a high work of adhesion and strong wetting [5]. In practice, however, most metals oxidise under service conditions [6]. In this context, Roos et al. proposed that the interaction between glass and metal in forming processes should primarily be regarded as an interaction between glass and oxide. In this interaction, oxygen-dominated surfaces on both sides of the interface control wetting, adhesion and sticking behavior. The chemical nature of the underlying metal becomes secondary as long as oxidation is not suppressed [7]. An oxide, e.g.

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<https://doi.org/10.1016/j.surfcoat.2026.133451>

Received 9 December 2025; Received in revised form 30 March 2026; Accepted 2 April 2026

Available online 3 April 2026

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Al_2O_3 , will increase the contact angle, thereby promoting non-wetting. For instance, Al containing intermetallics such as NiAl swiftly form a Al_2O_3 layer when exposed to molten glass, raising the contact angle and hindering glass adhesion despite the partial dissolution of the oxide into the melt. Building on these insights, advanced high-temperature coatings have been developed to provide inert, non-wettable surfaces. A dense Al_2O_3 coating on glass-mold inserts was shown to resist glass sticking [8].

These approaches leverage oxide chemistry and wetting principles to minimize interfacial bonding in molten glass-metal systems. In this context, intermetallic Ni–Al phases, such as NiAl, have attracted attention due to their potential to fulfil these requirements. Fig. 1 shows the binary phase diagram of Ni–Al. Ni–Al-based coatings have been investigated as a potential ‘non-stick’ surface treatment for glass molding tools [3]. Such Ni–Al intermetallic exhibit high melting point, high hardness, good thermal conductivity, good resistance to oxidation and corrosion, as well as good wear resistance at high temperatures, making them attractive as durable die surfaces [9,10].

Over the past decades, a wide range of techniques has been developed to produce Ni–Al intermetallic coatings, including electron-beam physical vapor deposition [12] and plasma spraying [13]. Among these methods, plasma spraying stands out due to its versatility, cost-effectiveness, and relative ease of implementation. In addition, it enables the deposition of coatings with virtually any desired composition, making it well suited for manufacturing Ni–Al intermetallic layers that protect critical components against oxidation and corrosion under demanding service conditions.

The wetting behavior of glass on a metal surface is a critical factor governing adhesion and interfacial reactions. When molten glass strongly wets a metal surface i.e., when the contact angle is low, it spreads across the surface and adheres tightly. This typically exacerbates corrosion and makes detachment difficult [14]. Conversely, a non-wetting surface, characterized by a high contact angle, limits the contact area and mechanical adhesion of the glass, thereby mitigating material pickup and facilitating the separation of the glass from the metal [3]. Therefore, it is desirable to develop coatings or intermetallics that are resistant to chemical attack and non-wettable by the glass melt.

This study investigates the high-temperature corrosion and wetting

behavior of Ni–Al intermetallic phases in contact with soda-lime glass melts. The work is motivated by the need to clarify the performance of Ni–Al materials under conditions representative of industrial glass production. Sessile-drop contact angle measurements are employed to quantify the wettability of molten soda-lime glass on Ni–Al substrates, and complementary corrosion experiments are performed to examine chemical interactions at the interface. By coupling the contact angle results with microstructural and compositional analyses of the reaction layers, the mechanisms governing wetting and corrosion in these Ni–Al-glass systems were identified.

Previous studies have investigated high-temperature oxidation of Ni–Al and related aluminum containing coatings [15–17], the dissolution in silicate melts [18,19] and glass/metal wetting behavior [3,20–23]. However, these phenomena have largely been addressed in isolation. This study advances the current understanding by providing a time-dependent, combined analysis of wetting behavior and oxide scale evolution during direct contact between Ni–Al coatings and molten soda-lime glass under application-relevant conditions. This analysis distinguishes between the short-term anti-adhesion performance and the long-term corrosion limitations of Ni–Al coatings in glass-contact applications.

2. Materials and methods

2.1. Materials and coating process

In the atmospheric plasma spraying (APS) process, the feedstock materials were blended commercially available elemental powders of aluminum (> 99 wt% Al, particle size fraction: 20–53 μm) and nickel (> 99 wt% Ni, particle size fraction: 15–53 μm). The powders were mixed mechanically prior to spraying to achieve the desired stoichiometry for Ni–Al equiatomic. Pre-alloyed or clad powders were intentionally not used in this study to employ a cost-effective feedstock and to retain flexibility in adjusting the chemical composition of the coating. The coatings were deposited onto lamellar grey cast iron (EN GJL-250) substrates with dimensions of 50 mm $\times$ 5 mm $\times$ 5 mm. The substrates were sandblasted first with corundum particles to produce a surface roughness of $R_a = 3.5 \pm 0.3 \mu\text{m}$ to improve the mechanical anchoring

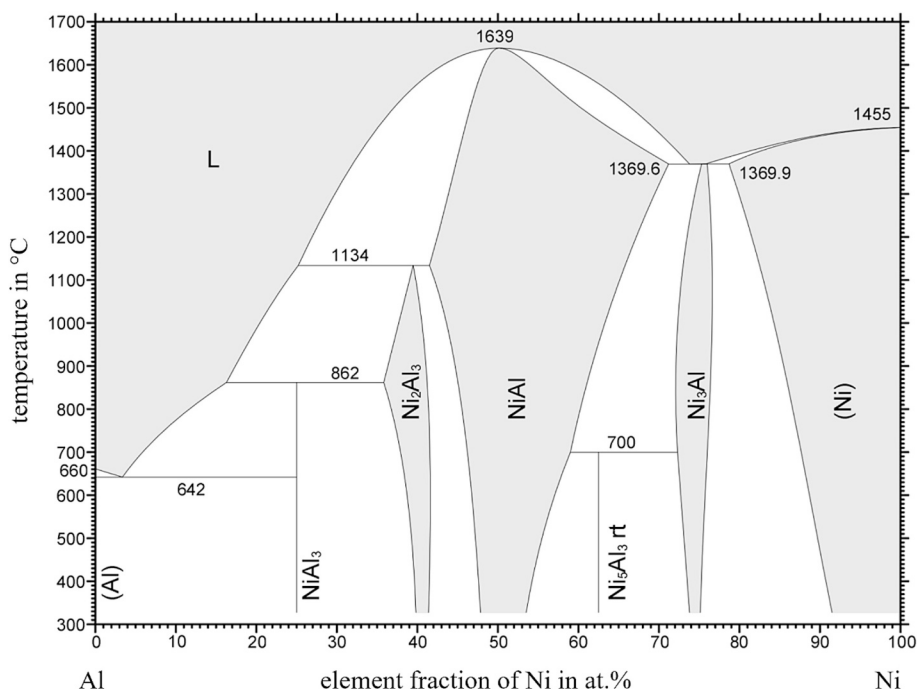


Fig. 1. Phase diagram of binary Ni–Al-system [11].

and adhesion of the coating. After sandblasting, the substrates were cleaned with ethanol to remove dust and residual contaminants.

Atmospheric plasma spraying was conducted using a GTV DELTA MFP 2000 plasma spray system at Neue Materialien Bayreuth GmbH. Fig. 2 shows the laboratory set-up of the atmospheric plasma spraying process. The APS system consisted of a plasma gun, a powder feeder, a gas supply, and a power supply on a computerized 6-axis robotic arm. The process parameters were as follows: plasma current 345 A, voltage 160 V, primary gas Argon (Ar) at $50 \text{ l} \cdot \text{min}^{-1}$, secondary gas hydrogen (H_2) at $10 \text{ l} \cdot \text{min}^{-1}$, spray distance 150 mm. The coating was deposited at a traverse speed of $750 \text{ mm} \cdot \text{s}^{-1}$ using six spray passes applied from left to right in adjacent, parallel tracks. The spraying process was carried out at room temperature.

2.2. Heat treatment of the as-sprayed coatings

The heat treatment was conducted at temperatures of 700°C for 64 h and 1000°C for 16 h to promote interdiffusion and microstructural homogenization. The samples were heat treated in an N_2 atmosphere and quenched in water to room temperature.

The specimen were pretreated in this way to determine their contact angle with the glass melt in Section 2.4.

2.3. Immersion experiments of coated specimen in lime-soda glass melt

Fig. 3 shows the set-up of the immersion test to investigate the interaction between coating and molten glass as a schematic drawing as well as the laboratory set-up before and after removal of the crucible. Coated specimens were partially immersed in a soda-lime glass melt. Milled glass shards of different compositions originating from the recycling process were used. Due to the use of recycled glass with varying composition, minor variations in the local chemical environment cannot be excluded. However, the observed corrosion behavior and general trends were consistent across all experiments, indicating that the influence on repeatability is limited. The resulting surface-area-to-glass-mass ratio was approximately $1.12 \text{ cm}^2 \cdot \text{g}^{-1}$. They were heated at $1 \text{ K} \cdot \text{min}^{-1}$ and then held at 1100°C between 2 and 48 h in air. The furnace cooling was with the same rate as heating. Afterwards, the cross-sectional microstructure was examined in three regions: the coating-glass interface, the portion of the coating immersed in the glass, and

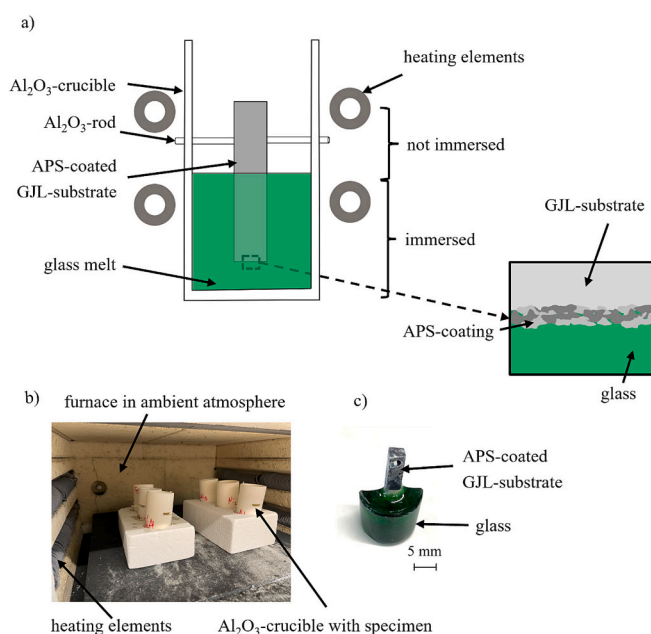


Fig. 3. Set-up of the immersion testing a) schematic, b) laboratory set up in furnace at ambient atmosphere, c) specimen in solidified glass after removal of crucible.

the portion exposed to air. Cross sections of the specimens were prepared using standard metallographic procedures, including cutting, mechanical grinding and polishing. The polished surfaces were examined using an optical microscope (Zeiss Axioplan 2, Carl Zeiss, Germany), and digital micrographs were acquired with an Olympus CCD camera. To conduct a detailed microstructural and compositional analysis, a Zeiss 1540 XB scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) was used to determine the chemical composition of the coatings and interfacial regions. This allows a systematic evaluation of corrosion, interfacial reactions and oxidation behavior under combined glass and high-temperature atmospheric exposure conditions. The thickness of the oxide layer was determined in SEM cross-sections using ImageJ software. Thirty measurements were taken of the oxide layer perpendicular to the interface between the coating and the glass across an area. The individual measurements were then averaged to obtain a characteristic thickness.

2.4. Contact angle measurements

Fig. 4 show the set-up for contact angle measurements (sessile drop method). The coated samples were placed horizontally in a high-temperature furnace with a cylindrical soda-lime glass specimen of 4

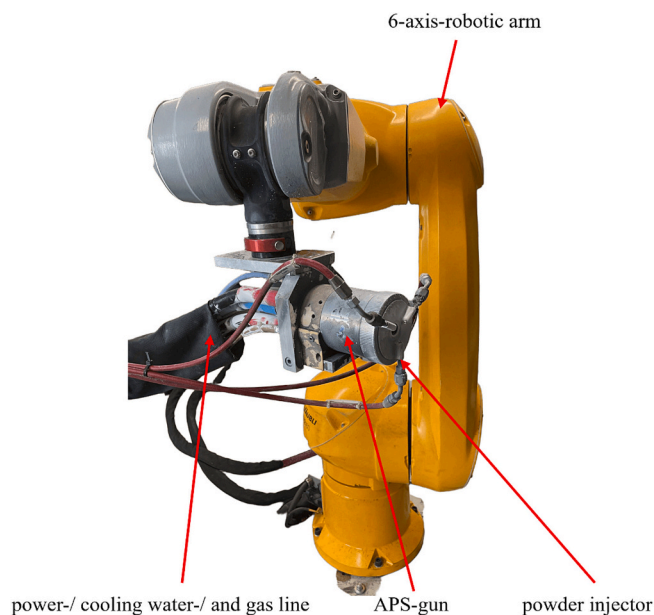


Fig. 2. Laboratory set-up of the atmospheric plasma spraying process, at Neue Materialien Bayreuth GmbH.

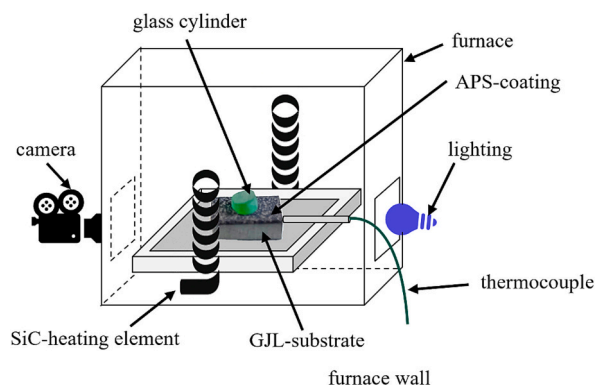


Fig. 4. Schematic set-up of contact angle measurement (sessile drop method).

mm diameter and 4 mm high positioned on the surface of the coating. Cut glass shards of different compositions originating from the recycling process were used. The system was then heated to 1100 °C at 5 K•min⁻¹ and held for 30 min in air with three repetitions. The contact angle between the molten glass and the coating was recorded continuously in situ during the entire heating ramp up to 1100 °C and the subsequent isothermal holding period using a blue-light illumination system in combination with an optical setup [24,25]. The captured images were optically analyzed to determine the change in contact angle Θ_Y as a function of time and temperature.

Fig. 5 shows the schematic and experimental setups used to determine the contact angle between molten soda-lime glass and Ni–Al coatings as a function of temperature.

3. Results

Fig. 6 shows cross-sectional SEM-micrographs of the Ni–Al coatings in as-sprayed and heat-treated conditions. The plasma-sprayed Ni–Al coatings were investigated in the as-sprayed condition and after heat treatment under nitrogen atmosphere. Heat treatments were performed at 700 °C for 64 h and at 1000 °C for 16 h. In the as-sprayed state, the coating exhibits pronounced compositional heterogeneity, with distinct Al- and Ni-rich regions. This heterogeneity originates from the rapid melting, flattening and solidification of individual powder particles during atmospheric plasma spraying (APS), which limits the interdiffusion of Ni and Al at the splat scale. Compositional inhomogeneities in thermal sprayed Ni–Al coatings, are attributed to short thermal interaction times and differing melting behaviors of Ni- and Al-containing phases [26–28]. Numerous pores and oxide inclusions are also visible, which are typical features resulting from the thermal spraying process [26]. After heat treatment, a significant microstructural transformation occurs. The previously distinct Al- and Ni-rich regions react to form Ni–Al intermetallic phases. This homogenization process is thermodynamically driven by the negative formation enthalpy of Ni–Al intermetallics, such as NiAl and Ni₃Al, and kinetically promoted by enhanced atomic mobility at elevated temperatures. As a result, APS microstructure becomes less chemically heterogeneous, and the contrast between individual splats is reduced. Thermal stresses arising from the mismatch in thermal expansion between the coating constituents and the substrate may further contribute to the formation or opening of cracks during high-temperature exposure [26,29]. A more detailed investigation of the microstructural evolution, heat treatment response, and intermetallic phase formation of these coatings is reported in our previous study [26].

Fig. 7 shows a low-magnification SEM micrograph of the interface between the as-sprayed Ni–Al coating and the soda-lime glass after exposure at 1100 °C. The underlying coating exhibits a microstructure comparable to that observed after heat treatment, indicating that diffusion processes occur during exposure. No significant penetration of molten glass into the coating porosity was observed.

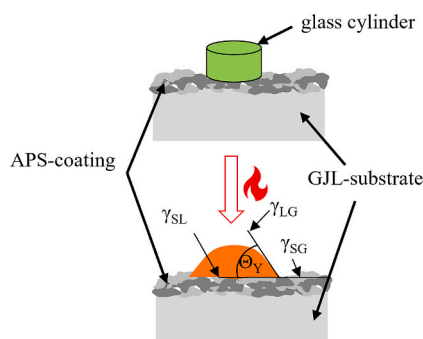


Fig. 5. Contact angle analysis schematic representation at room temperature and 1000 °C.

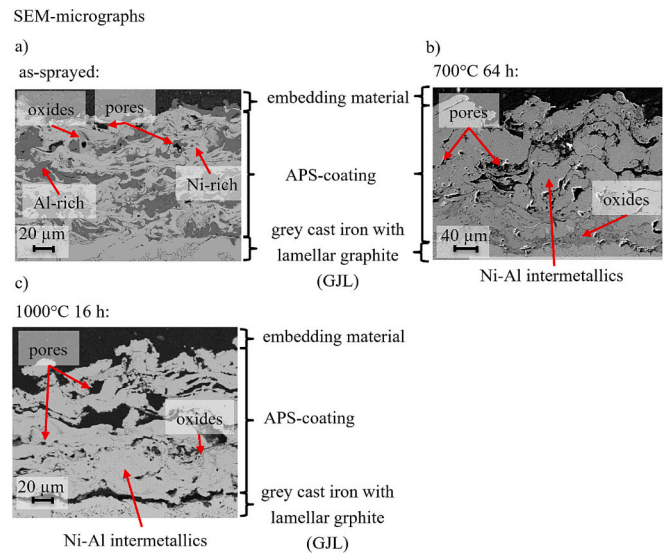


Fig. 6. Cross-sectional SEM micrographs of plasma-sprayed Ni–Al coatings. a) as-sprayed Ni–Al coating on GJL-substrate showing distinct Al-rich and Ni-rich regions and heat-treated coatings, where Ni–Al intermetallic phases are formed b) at 700 °C for 64 h in N₂ and c) at 1000 °C for 16 h in N₂.

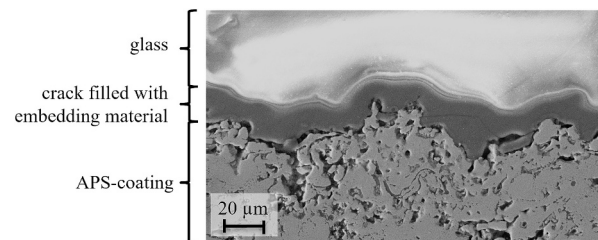


Fig. 7. Cross-sectional SEM micrograph of the interface between the as-sprayed Ni–Al coating and soda-lime glass after exposure at 1100 °C.

Fig. 8 shows a cross-sectional micrograph at a higher magnification of the as-sprayed Ni–Al coating after exposure to molten soda-lime glass at 1100 °C for 48 h. An oxide layer is visible at the interface between the

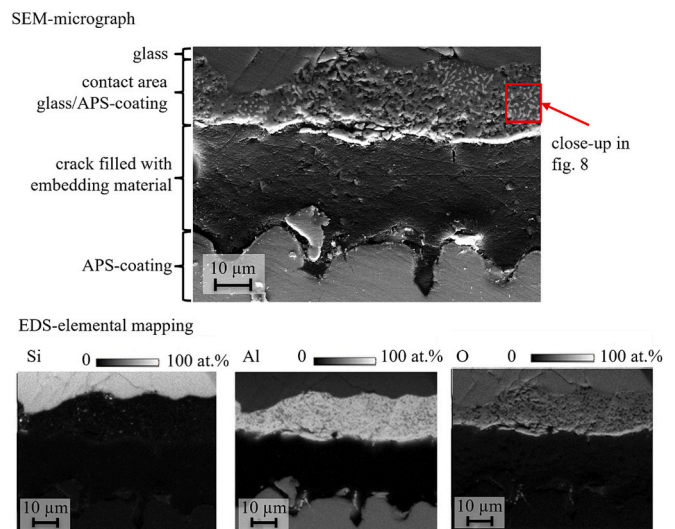


Fig. 8. Cross-section SEM-micrograph of the interface between the as-sprayed Ni–Al-coating and the soda-lime glass after immersion testing at 1100 °C for 48 h in air with EDS-elemental mapping of Si, Al and O.

coating and the glass. Table 1 shows the elemental mapping via energy-dispersive X-ray spectroscopy (EDS) that confirms this layer is rich in aluminum and oxygen, identifying it as an alumina (Al_2O_3) scale. The underlying Ni–Al coating has a uniform Ni and Al composition, while the glass above the oxide layer is rich in silicon (Si). It should be noted that the cracks observed at the interface are mainly artefacts of the preparation process. Due to the fragility of the Ni–Al/glass interface, cracks can easily form during sectioning. These were subsequently filled with embedding material during the mounting step. This not only stabilizes the fragile interface but also enables further metallographic preparation of the specimen. A more pronounced corrosive attack and thicker reaction layers were observed in the fully immersed region of the cylindrical samples. Within this region, corrosion behavior was comparable between the side surface and the flat base. Minor variations were observed at the edges around the base circumference, where a slight rounding of the reaction zone occurs.

Fig. 9 shows a higher magnification view of the interfacial region of the alumina scale morphology in more detail. EDS elemental mapping shows areas with presence of Ni. The Ni-rich areas are not oxidized.

Fig. 10 shows the thickness of the alumina scale formed on the as-sprayed coating in dependence of the square root of time. It varies depending on the duration of the contact with molten glass. After 2 h, the oxide layer was thin and discontinuous. Heating for 48 h results in a significantly increased thickness. The oxide growth kinetics were evaluated under parabolic growth behavior. The thickness of the oxide layer was determined from cross-sectional SEM micrographs, as described above, and plotted as a function of the square root of the exposure time. Eq. (1) shows the layer thickness-related parabolic oxidation constant determined as “ k_p ” [30]. Here, ‘ x ’ corresponds to the layer thickness and “ t ” to the time [30].

$$x \approx \sqrt{k_p' \cdot t} \quad (1)$$

Fig. 11 shows images of a glass cylinder placed on a plasma-sprayed Ni–Al coating at 900 °C and 1050 °C. The optical contact angles are marked on each image. The large contact angles at the lower temperature indicate that the glass does not wet the coating surface. As the temperature increases, the contact angle decreases. The droplet profile becomes flatter, reflecting enhanced wetting and increased interaction between the molten glass and the coating at the interface. These images demonstrate the strong temperature dependence of the wetting behavior of molten glass on the Ni–Al coating. There is a transition from non-wetting to wetting behavior as the temperature increases from 900 °C to 1050 °C.

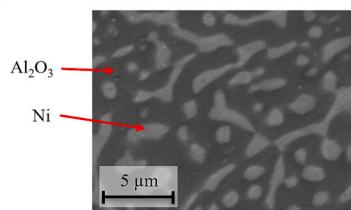
Fig. 12 shows the measured contact angles for the as-sprayed coating and after heat treatment at 700 °C for 64 h and at 1000 °C for 16 h. During the 30 min isothermal holding period, the contact angle continued to evolve and gradually approached a steady-state value. The values reported correspond to the contact angle after 30 min, at which no further significant changes were observed. Contact angle measurements reveal a correlation between thermal treatment and wetting behavior. As-sprayed coatings exhibit lower contact angles, indicating partial wetting and greater interaction with the glass. After heat treatment, the contact angle increases, reflecting significantly reduced wettability and enhanced non-stick properties. At lower temperatures, all samples exhibit contact indicating non-wetting behavior. As the

Table 1

Quantitative EDS analysis of the measured elemental fractions in the Al_2O_3 regions.

Element	Element fraction in at. %
O	59 ± 2
Al	36 ± 2
Si	1 ± 1
Ni	4 ± 1

SEM-micrograph



EDS-elemental mapping

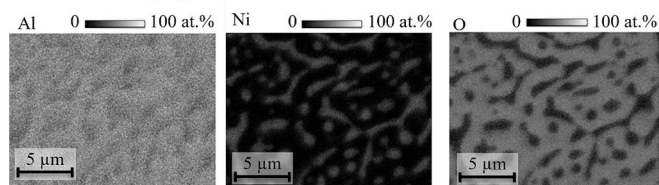


Fig. 9. Cross-section SEM-micrograph of highlighted area in Fig. 8 at a higher magnification after immersion testing at 1100 °C for 48 h in air with EDS-elemental mapping of the alumina scale and corresponding EDS-mappings of Al, Ni and O.

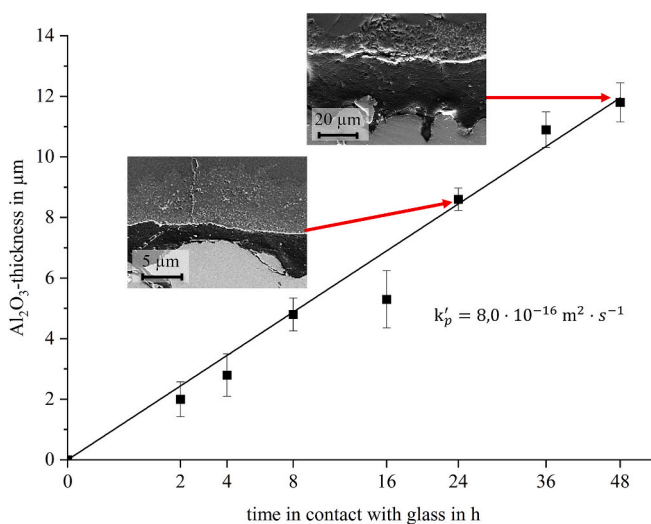


Fig. 10. Square root plot of thickness of Al_2O_3 scale in dependence of time in glass contact at 1100 °C with a heating and cooling rate of $1 \text{ K} \cdot \text{min}^{-1}$ in air.

temperature increases, the contact angle decreases systematically for all conditions.

4. Discussion

4.1. Interfacial reactions between Ni–Al intermetallic coatings and soda-lime glass

When Ni–Al intermetallic coatings are exposed to molten soda-lime glass, a continuous Al_2O_3 scale forms on their surface. The results suggest that this scale is not inert, but rather partially dissolves into the glass, as could be indicated by the presence of alumina-rich area near the interface to the coating [31]. This process is a competition between continuous oxide growth and dissolution [3]. In addition to these interfacial reactions, thermally activated diffusion processes occur within the coating due to the high-temperature exposure. The microstructural evolution observed during standalone heat treatment can be transferred to the present glass-contact conditions [26]. As soda-lime glass can dissolve up to $\sim 21 \text{ mol\%}$ Al_2O_3 at $\sim 1300 \text{ °C}$, which is about 30 times more than Cr_2O_3 , for example, the protective film is steadily

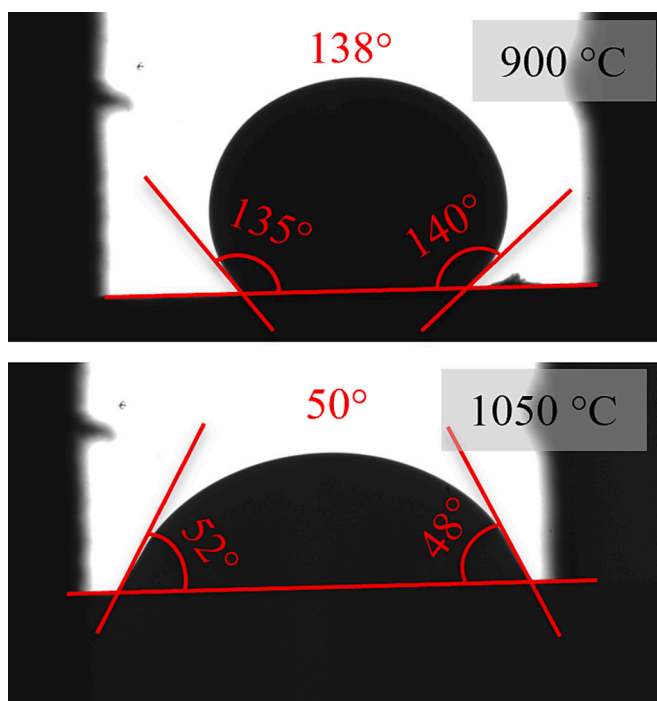


Fig. 11. Measured contact angle analysis representative images of the heat-treated coating (700 °C, 64 h, N₂) at 900 °C and 1050 °C in air.

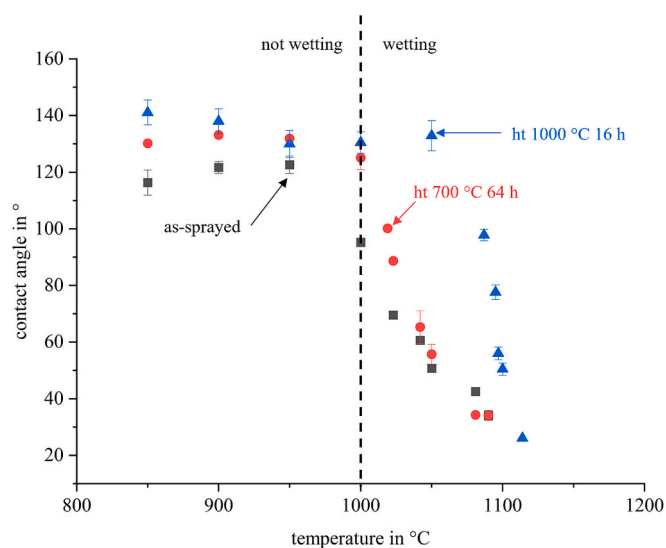


Fig. 12. Contact angle evolution of Ni–Al coatings during continuous heating (5 K·min^{−1}) up to 1100 °C with a holding time of 30 min in air for different initial coating conditions (as-sprayed and heat-treated).

consumed, releasing aluminum into the melt [19]. This explains the aluminum depletion observed in the coating and the appearance of alumina-enriched regions in the glass. In some cases, devitrification occurs, forming crystalline Ca–Al–silicate phases, such as anorthite, at the interface [32]. The instability of Al₂O₃ in glass has been confirmed by others. For example, Abdullah et al. demonstrated that an alumina-forming Ni–8Al–28Cr alloy degraded rapidly in soda-lime glass, losing aluminum within minutes. In contrast, a chromia-forming Ni–30Cr alloy exhibited much greater resistance [16]. Xu et al. reported that excessive aluminum in nickel-based alloys worsens corrosion resistance since repeated aluminum oxide formation and dissolution lead to selective aluminum leaching and exfoliation of the oxide [17]. Based on

the above observations and literature findings, the functional behavior of the Ni–Al coating in contact with molten soda-lime glass is better described by a time-dependent mechanism than by a static protective state. In the early stages of exposure, the selective oxidation of aluminum promotes the formation of an alumina-rich surface layer. This layer reduces the coating's chemical interaction with the glass melt, leading to decreased wetting and adhesion [8,33]. This effect is consistent with the reduced contact angles and pronounced short-term anti-adhesion behavior.

Fig. 13 shows the schematic of the reaction taking place between the Ni–Al coating and soda lime glass melt. For Ni–Al coatings with a high aluminum content, aluminum dissolution is the dominant corrosion mechanism when exposed to molten soda-lime glass. In the early stages, selective corrosion of the aluminum-rich regions results in localized corrosion and the formation of surface voids. At the same time, a non-protective Al₂O₃ scale forms. For typical high-temperature oxidation, such as in air, protective Al₂O₃ scales on Ni–Al alloys grow parabolically over time. This diffusion-controlled behavior means that the oxide thickness (or the rate of mass gain) increases proportionally over time as the diffusion of oxygen inward and aluminum outward slows with increasing scale thickness [34,35].

Following prolonged immersion, 48 h at 1100 °C, the initial NiAl phase is no longer detectable in certain areas, suggesting significant aluminum depletion due to rapid dissolution. As the Al₂O₃ scale is unstable in molten glass, the outer surface layer readily dissolves along the Al₂O₃ interface, enabling the glass to penetrate deeper into the coating microstructure. Subsequently, a new alumina layer forms. However, this secondary Al₂O₃ layer is progressively dissolve. The repeated formation and loss of oxide layers leads to the ongoing structural degradation of the coating during prolonged contact with molten glass. A dynamic equilibrium can be achieved when the oxide grows and dissolves at comparable rates. The dissolution rate of Al₂O₃ in silicate melts is temperature-dependent and changes as the glass approaches saturation. Not only do reaction rates increase, but solubility in the glass also rises [19]. The dissolution of Al₂O₃ into soda-lime glass at high temperatures is thermodynamically driven by a reduction in Gibbs free energy when alumina is incorporated into the silicate network [36]. Fluxing oxides, such as Na₂O and CaO, play a crucial role in depolymerizing the silica network and destabilizing the alumina scale [37]. This enables Al³⁺ to enter the melt as [AlO₄][−] tetrahedra. This results in the formation of calcium and sodium aluminosilicate species that can remain dissolved or temporarily precipitate as crystalline interfacial phases [38].

The strong driving force for the formation of Al₂O₃ ($\Delta G \approx -1248$ kJ/mol) compared with NiO ($\Delta G \approx -117$ kJ/mol) means that aluminum is preferentially oxidized in these alloys [39,40]. Consequently, nickel remains largely metallic, while aluminum is continuously consumed to

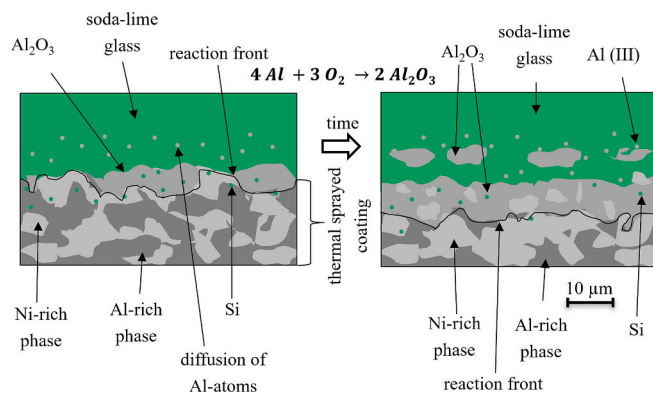


Fig. 13. Schematic summary of the mechanisms inferred from the experimental observations at the contact surface between the Ni–Al coating and the soda-lime glass melt.

form and lose alumina at the glass interface.

Eq. (2) shows due to the higher coefficient of thermal expansion, denoted as “ α ” of NiAl compared to Al_2O_3 , cooling from elevated temperature results in a pronounced mismatch strain “ ε ” [41].

$$\Delta\varepsilon \approx (\alpha_{\text{NiAl}} - \alpha_{\text{Al}_2\text{O}_3}) \cdot \Delta T \quad (2)$$

For NiAl, α can be quantified in the relevant temperature range using an established polynomial ($\alpha_{\text{NiAl}} \approx 12.7\text{--}15.6 \times 10^{-6} \text{ K}^{-1}$ for 300–1500 K [41]), while for Al_2O_3 , a mean value of $\alpha_{\text{Al}_2\text{O}_3} \approx 4\text{--}8 \times 10^{-6} \text{ K}^{-1}$ for 25–1000 °C follows from reference data [42].

Elastic constraint of the oxide layer and using a Young's modulus of $E \approx 211\text{--}390 \text{ GPa}$ [42,43] for Al_2O_3 , the corresponding thermally induced stress can be approximated in Eq. (3).

$$\sigma \approx E \cdot \Delta\varepsilon \approx 1.3\text{--}2.2 \text{ GPa} \quad (3)$$

The estimated stress values are an overestimation. At such stress levels, spallation of the oxide scale due to buckling instability would be expected. Creep and stress relaxation processes at elevated temperatures are expected to further reduce the effective stress. The actual stress level is likely lower, as the material does not behave as a fully elastic body with a constant modulus.

Thermomechanical stresses arising from thermal expansion mismatch represent an additional limiting factor for long-term coating durability, particularly under thermal cycling conditions.

4.2. Wetting behavior of Ni—Al coatings

Fig. 14 shows the wetting process of molten glass on APS-coatings. Before placing the specimen in the furnace, the glass is present as a solid cylindrical shard. In phase a), the glass rests on the coating surface. As the temperature increases, the glass softens and transitions to a semi-solid, semi-liquid state. In phase b), the droplet begins to expand, and the substrate surface is first wetted under the influence of gravity and hydrostatic pressure. The glass assumes a nearly spherical shape due to surface tension, while its high viscosity restricts flow. Initially, the melt forms a hemispherical droplet with a large contact angle, indicating poor wettability [44]. Further heating causes the glass to become fully liquid, adopting a flattened spherical shape in phase c). As the temperature rises, the viscosity decreases, allowing the melt to become more fluid and spread under the combined action of surface tension and gravity in phase d). Once the glass ceases to flow, equilibrium wetting is reached in phase e).

Wetting behavior is governed by viscous, capillary and gravitational forces. At $\sim 1000^\circ\text{C}$, viscosity decreases, while capillary and gravitational effects dominate, Bo increases, explaining the sharp drop in contact angle. As-sprayed coatings containing Ni- and Al-rich splats with thin native oxides present metallic sites that promote wetting. After heat treatment, the contact angle increases markedly, with the highest values observed after prior heat treatment at 1000°C . This reflects the formation of intermetallic phases (NiAl , Ni_3Al and Ni_2Al_3) and a stable Al_2O_3 surface film, both of which reduce the affinity for glass [45]. Table 2 lists current and previous measured contact angles. In a previous study XRD and SEM confirm the transformation from elemental Ni—Al splats to Ni—Al intermetallics [26]. Vattikuti et al. reported that Al_2O_3 -coated steel exhibited contact angles of $\sim 136^\circ$ at 800°C , compared to

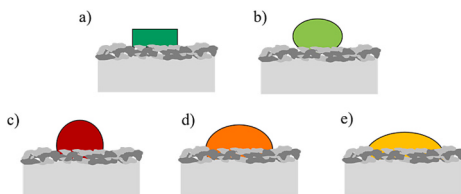


Fig. 14. Wetting process of glass on APS-coating a) pre-wetting phase, b) expansion phase, c) spherical phase, d) spreading phase, e) equilibrium state.

Table 2

Current and previous measured contact angles.

Glass	Substrate	Temperature in °C	Contact angle in °	Study
Ohara L-BAL 42	Al_2O_3 coated steel	800	136	Vattikuti et al. [23]
	SiO_2 coated steel	800	77	
	stainless-steel	800	29	Sui et al. [20]
	430 stainless-steel	500	4.7	
PbO-B ₂ O ₃ -Bi ₂ O ₃ -CuO K-PG325	CrAlSiN	500	150	Chang et al. [46]
		600	130	
		700	80	
		700	150	
	TiAlSiN	500	150	
		600	100	
		700	45	
		700	20	
	AlTiN	500	150	
		600	130	
Duran	Stainless-steel	1000	60–90	Zhong et al. [3]
		1100	30–40	
		1200	20–30	
		1200	105–118	
	NiAl-film	1000	60–75	
		1100	50–57	
		1200	93–103	
		1100	57–77	
	Ni-Al-N film	1200	45–60	
		1000	90–97	
		1100	43–54	
		1200	33–40	
	Ti-B-C film	1000	90–97	
		1100	37–51	
		1200	31–36	
	soda-lime	Ni-Al coating (as-sprayed)	121 ± 2	This study
			95 ± 1	
			34 ± 2	
		Ni-Al coating (ht 700 °C, 64 h, N ₂)	133 ± 1	
			125 ± 4	
			34 ± 4	
	Ni-Al coating (ht 1000 °C, 16 h, N ₂)	900	138 ± 5	
		1000	130 ± 4	
		1100	26 ± 2	

29° for bare steel and 77° for SiO_2 -coated steel [23]. Consistent with this, heat-treated Ni—Al coatings exhibited contact angles measured at 850°C similar to pure Al_2O_3 , whereas the as-sprayed state remained more wettable [23].

The contact angle behavior can be described using Young's equation [5,47]. Eq. (4) describes the contact angle as a thermodynamic equilibrium between the surface energy “ γ_{SG} ” (for solid-gas) of the surface of a wetted solid, the surface tension “ γ_{LG} ” (for liquid-gas) of the wetting liquid, and the interfacial energy “ γ_{SL} ” (for solid-liquid) between the wetted solid and the wetting liquid [5].

$$\cos\Theta_Y = \frac{\gamma_{\text{SG}} - \gamma_{\text{SL}}}{\gamma_{\text{LG}}} \quad (4)$$

Surface topography also plays a role when roughness increases from $R_a = 4.2 \pm 0.7 \mu\text{m}$ in the as-sprayed coating $R_a = 9.8 \pm 1.2 \mu\text{m}$ to following heat treatment at 1000°C for 16 h. According to the Cassie-Baxter model, roughening enhances the apparent contact angle by trapping air pockets under the droplet, which reduces the effective contact area [47,48]. A continuous oxide layer also acts as a barrier to spreading [8,49]. Zhong et al. found that NiAl films exhibited a good non-wettability, which they attributed to the stability of their intermetallic/oxide surfaces [3]. The results support this, showing that the combination of NiAl intermetallics and Al_2O_3 formation yields high contact angles and low glass adhesion. However as shown before, the protective Al_2O_3 film is not inert in molten soda-lime glass. During prolonged exposure at a high temperature, it gradually dissolves, which undermines the non-wetting behavior. Therefore, NiAl-based coatings perform well in the short term or at lower temperatures but degrade over

time as the alumina layer is consumed and the interface shifts from non-wetting to reactive.

5. Conclusion

The Ni–Al coating undergoes an oxidation–dissolution reaction when in contact with molten soda-lime glass. Al from the coating oxidizes to form Al_2O_3 , which then partially dissolves into the glass melt. As a result, the long-term corrosion resistance of such coatings is governed by continuous oxide loss, while the wettability and adhesion at the glass/coating interface evolve over time, potentially leading to sticking during prolonged exposure.

Our study shows that, while alumina-based protection is effective against oxidation in air, it is insufficient in the aggressive environment of molten soda-lime glass. The partial dissolution of the alumina layer accelerates coating degradation and can introduce defects into the glass, highlighting a critical trade-off between protecting the metal surface and contaminating the glass. The experimental results demonstrate that Ni–Al coatings provide temporary anti-adhesion properties when in contact with molten glass. Under the investigated conditions, this effect is maintained over short exposure times, making such coatings suitable for repeated short-cycle operations. However, gradual oxide dissolution and aluminum depletion limit their long-term durability during extended exposure. From an application perspective, e.g. in glass molding dies, Ni–Al coatings can effectively reduce adhesion in the initial stages, but their performance deteriorates with time.

The results show that Ni–Al coatings can provide non-wetting surfaces and minimize early-stage adhesion with appropriate heat treatment and microstructural tuning. These findings highlight the potential of Ni–Al coatings for short-duration applications involving molten glass contact, while also emphasizing the need for alternative materials or protective strategies, such as more chemically stable oxide formers or barrier layers, to achieve long-term stability.

CRediT authorship contribution statement

Michelle Hartbauer: Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. **Thomas Dörflinger:** Investigation. **Haneen Daoud:** Writing – review & editing, Resources, Project administration, Funding acquisition, Conceptualization. **Helge Schumann:** Writing – review & editing, Resources. **Gilvan Barroso:** Writing – review & editing. **Hubert Neubauer:** Writing – review & editing. **Florian Scherm:** Writing – review & editing, Supervision, Conceptualization. **Uwe Glatzel:** Writing – review & editing, Supervision, Resources, Conceptualization.

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.

Acknowledgements

We gratefully acknowledge financial support of the Bayerische Forschungsförderung under grant number AZ-1477-20. Their funding has been instrumental in advancing our work, and we deeply appreciate their commitment to fostering innovation and scientific progress.

Data availability

Data will be made available on request.

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